

# 徐匡迪文选

钢铁冶金卷(A)

**Selected Works of Xu Kuangdi  
on ferrous metallurgy (A)**

上海大学出版社

· 上海 ·

图书在版编目(CIP)数据

徐匡迪文选. 钢铁冶金卷/徐匡迪著. —上海: 上海  
大学出版社, 2005. 4

ISBN 7-81058-002-7

I. 徐... II. 徐... III. ①徐匡迪-文选②冶金-  
文选 IV. TF-53

中国版本图书馆 CIP 数据核字(2005)第 023943 号

责任编辑 汪元章 李顺祺

徐匡迪文选

钢铁冶金卷(A)

上海大学出版社出版发行

(上海市上大路99号 邮政编码200444)

(<http://www.shangdapress.com> 发行热线021-66135110)

出版人: 姚铁军

\*

上海出版印刷有限公司印刷 各地新华书店经销

开本: 787×960 1/16 印张: 34.5 字数: 千

2005年1月第1版 2005年4月第1次印刷

ISBN 7-81058-002-7/TF·001 二册总定价 180.00元

# 序

徐匡迪先生是中国当代科技界杰出的学科带头人和颇受欢迎的资深教育家,也是国际钢铁冶金学术活动中的知名学者。匡迪先生兼具深厚的专业学养和渊博的知识面,其成就涉及科学、教育、技术、工程、工业、经济、社会管理等方面,尤其难能可贵的是他崇尚务实,不断求真,往往以创新的思维、可行的途径去解决各类实际问题。汇集他长期以来在钢铁冶金方面的研究论文和有关钢铁工业发展的综述性文章,结集出版,无疑将对我国冶金界、科技界、教育界有所裨益和启示。

匡迪先生在20世纪50年代初期怀着报国之志选择了冶金专业并以优异成绩毕业于北京钢铁学院(现北京科技大学)冶金系,继而留校任教,20世纪60年代调到上海工作,长期以来,执教大学,辛勤耕耘浇灌,现已桃李天下。同时不断地致力于科研,并深入工厂进行开发、验证,在实践中,他才思敏捷,善于将观察到的现象转变成工艺成果,并上升到理论层次加以阐述,揭示其本质和规律,心得颇多,促进了冶金理论和工厂生产的发展,显示了他扎实的学科基础和联系生产实际的杰出能力,受到学术界、教育界与企业的尊重与欢迎。

改革开放初期,匡迪先生尚属年轻才俊,游学欧陆,头角渐露。以后在英国、法国、瑞典、日本、加拿大、美国、澳大利亚等国分别进行合作学术研究、技术开发、工程实施或是应邀在国际会议作主题讲演,每每受到关注与好评。他是当时我国大陆少数几位活跃在国际冶金学术论坛上的年轻学者之一。先后获得瑞典皇家工学院客座教授、美国加利福尼亚大学伯克利分校杰出贡献奖、香港理工大学名誉工学博士、香港大学名誉法学博士、英国土木工程师学会名誉外籍会员。

匡迪先生数十年来,在冶金学及其相关工程领域方面做了大量的科研、

开发工作,涉猎面颇广,诸如冶金物理化学、电冶金和炉外精炼、熔融还原、不锈钢精炼、喷射冶金等方面都有独到的研究成果和理论建树,其中有些还进一步开发成为工业装置用于工业生产。以徐匡迪院士为首的上海大学现代冶金与材料制备重点实验室学术梯队,近些年来,更以创新的精神,独具匠心地探索冶金科学的若干前沿领域,其中值得一提的有诸如强磁场下液态金属(合金)凝固行为的研究、用高温拉曼谱仪研究高温熔体的结构和性质等,不但难度很高,而且往往以学科交叉的新颖视角去研究冶金科学、材料科学中的若干难题,实属前沿性探索,其开拓创新精神难能可贵。此文集中也体现了这方面的进展和成果,相信对同行学者会有所启发、借鉴。由于他卓越的学术成就和杰出贡献,1995年当选为中国工程院院士,2003年当选为英国皇家工程院外籍院士、瑞典皇家工程院外籍院士。

自20世纪80年代后期以来,匡迪先生已不仅仅在冶金界、高教界工作,而且由于渊博的知识面和不断萌动于胸襟的改革精神使他逐步跻身于工业界、经济界直至管理决策层。据我所知,其间他在繁忙公务之余,利用各种时间,研读了国内、外经济学、管理学等方面的名著,而且能够结合中国的改革、发展的实际,提炼出自己的独特见解,进而与他坚实的理工科知识和工程经验相结合,使他在上海这一中国第一大城市的改革、发展、管理和决策过程中有了“用武之地”。十多年来在上海市工作过程中的诸多建树,证明了他是有真才实学的帅才,受到上海各界的好评与怀念。

我与匡迪先生相识较早,乃同一母校的先后校友,每每相叙交谈,往往为他的学识、见解所吸引、所打动,获益良多。新世纪伊始,匡迪先生卸任上海市长,当选为中国工程院院长,倾力于国家工程科学与技术进步这一崇高事业。到任后特别重视工程科学、工程技术与国民经济、社会发展相结合,拜访各方面的人士,组织启动了许多重大咨询课题,而且不少是由他亲自主持的,益现其务实精神和渊博的知识,诸多见解,往往获得高层领导和各界人士的共识或赞许,其间一些论述尚未完全包括在此文集内,相信今后还有机会进一步贡献于学界,贡献于社会。

中国工程院院士  
原冶金工业部副部长、殷瑞钰  
钢铁研究总院院长

2004年11月于北京

## 我的学术生涯

“八一三”日军侵占淞沪，父母亲携着2岁的姐姐以及腹中临产的我，匆匆逃离上海，随着难民潮艰难地向西南撤离。由于旅途颠簸劳顿，我于1937年底（12月11日）提早出生于浙赣交界处松岭的一座古庙中，没有医生和助产士，甚至没处去找农村的接生婆，只能由父亲在母亲的指挥下为我接生。当时，年轻父母既为家中新生的儿子高兴，又感忿于国家积贫、积弱，日寇烧杀抢掠和国民党军队溃不成军，致使老百姓处于如此浩劫之中，遂将我取名为“抗敌”，以铭记国恨家仇，寄望于子辈“男儿当自强，抗敌保家乡”。这个名字一直用到1944年我在昆明读小学二年级时，语文老师对我说：“日本侵略者失败已成定局，抗战胜利在即，我给你改个谐音的名字好吗？”随即用毛笔在毛边纸上写下“匡迪”，寓意“匡扶正义，迪吉平安”，我高高兴兴地捧回去呈给父母亲看，他们都说改得好，就改用此名至今。说了一段与学术生涯毫不相干的开场白，无非是两个目的：一是任何学术论文的作者都要署名，以示对论述及数据、结论负责，因此交待一下名字的来历，并非离题太远；二是我对祖国的热爱与赤子之心，始于童提启蒙学写名字之时，现在虽已过“天命”之年，每当提笔签名时，仍不敢忘双亲的期望与老师的教诲。

生于20世纪30年代的人，在中国近代史上亦算是经历丰富的一代。曾亲历过民族危亡的抗战时期；目睹了战后国民党的腐败和如火如荼的革命群众运动；参加过欢天喜地、敲锣打鼓欢迎解放军进城的行列，并为新中国的成立而热情欢呼，更难忘抗美援朝、保家卫国时唱着“共青团员之歌”争相报名参加“军干校”的高昂民族精神；当然也

受过知识分子思想改造、肃反、拔白旗、反右等政治运动折腾。直到“文革”时，少数人如我，被作为修正主义的“苗子”，一下子变为运动的“对象”，多数人则为没完没了的派性斗争感到迷惑，或因“亲朋好友”成为运动对象而退为观望（时称“逍遥派”）。十一届三中全会之后，拨乱反正，恢复实事求是的思想政治路线，我们恰值中年，挑起了教学、科研承前启后的担子，重新沐浴着科学春天的阳光。少数幸运者如我更享受到改革开放的成果，有幸出国进修、出国工作、出国讲学，使科研方法、学术水平有了极快的提高。

我之所以能做一点学术工作，其基础始于良好的教育。由于出身于知识分子家庭，父母对教育十分重视，回想起来，读过的小学（联大附小、杭州天长小学）、中学（杭州市立中学、省立杭州高级中学）都是当地最好的中、小学。除了师资一流、学风严谨，学校还有过许多名师（如杭高有过鲁迅、陈望道、陈建功、夏丏尊、李叔同、丰子恺、崔东伯等），亦出过不少名人。学校弘扬的是奋发、求实、俭朴的治学精神。1954年我报考北京钢铁学院，在江南水乡长大的我，其实并不知钢铁冶炼为何物，单凭着为祖国工业化奠定物质基础的理想，跨进了“钢铁摇篮”（首届校友赠礼刻成大理石碑，嵌在主楼大厅壁上）。五年（1954—1959）大学生活，尽管经历了肃反（1955年）、反右（1957年）、大炼钢铁（1958年），但整个教学过程还是完整和严谨的，特别是1954—1957年，教学秩序十分正常，肃反和反右仅利用了暑假2~3周，到1958年大炼钢铁时，由于我们是第一届四年制改五年制（1957年改），课程已基本上完，只占用了部分专业工艺课的教学时间。经过以后的工作检验，特别是80年代初去英国帝国工学院做短期访问学者和在瑞典皇家工学院任客座教授时，深感到自己在大学本科所学的基础，不仅不比这些世界名校差，有些方面，如普通基础课（特别是数学、力学、热力学等），由于做过很多题目、作业，学得比他们更扎实。我至今难忘卢兴阶老师讲高等数学时，在180人的阶梯教室中，他居然能从某个学生的游离目光中发现他未跟上教学进度，从而风趣委婉地重述要点，这种诲人不倦的精神真是令人敬仰，我亦清晰地记得，力学老师王显祖遒劲的板书和不用尺画的力的分解图（不但线条直，连角度都很准），特别是他言简语赅的讲课风格，使学生不用赶着记笔记，

而是在等着他的下一句话,课后再看课堂笔记,则是一篇精练的文章;物理化学是一门公认难学的课,特别是热力学部分,但高贻善老师把它讲活了,不但概念清晰严谨,例证与推演详实,而且每节课讲完,留下5~10分钟进行小结,有时他还让一位同学先小结一下,其他同学做补充,最后由他点评。我在“文革”后期(1974—1976年),因夫妻分居两地,住在集体宿舍,晚上闲时甚多,当拿出大学的基础课、专业基础课笔记复习时,惊喜地发现,一学期中高老师曾三次叫我起来小结,而是日晚我都在笔记本上专门作了回忆记录和老师的点评,可见高老师的教学在我心目中激起多大的回响和共鸣。

钢院教学的另一个显著的特点是注重实践。当时学校除了严格的课堂教学外,非常重视学生动手能力的培养,一年级时,每周半天金工实习,车、钳、刨、铣等各种床子都独立操作过。铸造更要从制泥芯、砂型、配箱,一直到化铁炉熔炼铁水和抬包浇注都要学生独立完成。专业方面的实习更加系统,二年级暑假的认识实习,要对从“原料—烧结—焦化—高炉—平炉—铸锭—开坯—初轧—精轧”的整个生产流程,到煤气厂、电厂、水厂,火车车辆调度场等辅助系统,都一一进行实地观察和记录主要参数。当时的青年学生“不知天高地厚”,人人都以“将来当总工程师时需要”为由拼命地问和记,结果实习结束后,工厂保密科把大家的笔记本都收了起来,说是其中涉及国家重大机密,不能留给学生自己。三年级生产实习是分专业进行的,我们冶金系是炉前工实习,从最粗重的渣坑清理、平台清扫、撬炉门、堵出钢孔,一直到炉前吹氧、取样、测温、扒渣、合金计算、补炉等都要学会操作。当时,炼钢的机械化、自动化程度很低,尤其是电炉,除了主要金属料由料篮从炉顶加入外,其余各种辅料(石灰、萤石、矿石),以及铁合金都要从炉门外3~4米处用铁锹扔入。每当炼不锈钢时,烤红的1~2吨微碳铬铁要从炉门扔进去,这可是一个考验操作工体力、技巧的“绝活”。看到炼钢工们龙腾虎跃的优美动作,使我们羡慕不已。由于当时铬铁是进口的,价格很贵(每一锹都超过学生一个月的伙食费),所以我们是没资格去扔的。为此,实习返校后,我们在学校宿舍外树了一个木制的“炉门框”,并从基建处要来两小车石块,炉门框两边4米外,一边站一人,开始了“扔锹练习”,有的同学还学着工人师傅的各种“花式动作”,引得

旁观者叫好、嬉笑。今天看来,当时的大学生似乎傻得可笑,或问为何不搞技术革新采用机械化投料?殊不知那是一个“劳动神圣”、“知识分子必须通过艰苦的体力劳动方能脱胎换骨、改造思想”的时代。四年级是炉长实习,除了跟班劳动外,主要是学习炉长如何全面掌握及判断炉况,指挥一炉钢的冶炼全过程,这里主要是如何和炉长交朋友,不然的话他会讨厌你老跟着他。同学们纷纷进行家访、谈心、拜师。那时的人都很真诚、率直,当工人师傅知道我们是决心学好本领、献身钢铁事业时,大家就掏心掏肺地结成对子,手把手地教起我们来。那一个月的时间真叫人终生难忘,我们这群只会纸上炼钢的大学生,在离厂前居然“独立自主”地炼出了两炉优质合金钢。那种喜悦和兴奋的心情,在以后的岁月中极少出现,因为那是付出了多少汗水和心血才学到的啊!五年级是毕业实习,做工厂设计的同学到工厂设计科或钢铁设计院,做科研论文的则到工厂的研究所或车间技术组,分别收集论文所需材料并进行现场试验或测试,两个月后,回校完成图纸或论文工作。我是带着深深的怀念和美好的感情来回忆20世纪50年代大学时所受的教育,诚然,岁月更替,科技飞速发展,现在的钢铁冶金已经完全机械化,并部分实现了信息化。在有的人看来,这些陈年旧事不值一提,甚至是幼稚可笑的。我亦时时警觉自己要与时俱进、不断创新,决不可固步自封,沉溺于传统的思维定式之中,但我还是认为实践环节教育最根本的教益,并非在学习操作(终究会用机械化、自动化代替),而是教会了我如何做人、怎样治学。我当然不主张今天学冶金的大学生再去花大量的时间学习现在已不需要的手工操作技艺,但我仍坚持我的研究生必须到现场去实习,不仅在炉前操作室摁按钮,而且要走出控制室到现场去感受生产过程,那里还有许多在电脑屏幕上、各种传感器显示不出来的东西。因为所有控制系统都是滞后响应的,即发现某参数偏离控制范围时,才做出调整,它们至今还不能完全代替人在实践经验中形成的预警判断,更何况探头(传感器)也有失误的时候。1984年5月我在瑞典Scan-Lancer公司工作时,曾在英国BSC的Recomby厂为北海油田生产抗硫化氢腐蚀的厚壁钢管,其硫含量应低于10 ppm( $\leq 0.001\%$ ),采用喷射冶金过程处理。按合同规定,出钢温度应 $\geq 1650$ ,但其中有一炉出钢时,我通过炼钢镜(国内带去)判断

温度只有 1 600 左右,甚至更低,于是提出停止钢包喷吹处理,否则可能冻包。英方炼钢分厂厂长察看了操控室自动测温记录后,用了一句英国式的幽默:“但愿这次是你的眼睛不准”,并要按原计划进行喷吹,我则坚持这一炉不列入“试验-供货”计划,他决心和我开个玩笑,在炉前记录上写下“徐教授认为这炉温度不够”并要我在下面签字,我毫不犹豫地签了,结果果然有近 200 吨钢水冻在包中,造成一次较大的事故。自此以后,每试验炉号出钢时,他们总要我用“中国眼镜”看一看温度如何,大学生生活中有许多值得回忆的内容,但作为对我专业培养影响最大的,我看就是基础课扎实和崇尚实践精神的养成。这方面除了教学计划安排以外,老师的言传身教亦是榜样和鞭策。朱觉教授当时是留美归国的名教授,但仍以近 60 岁的高龄带我们下厂实习,特别是他对新事物的敏感和孜孜以求的实干精神,成为我国电渣精炼技术的开拓者和奠基人。关玉龙教授当年风华正茂、才气横溢,听他讲课确实是一种享受,尽管他当时体力不如我们年轻的大学生,但他对炉前工艺的判断和感觉,使他在学生和现场工程技术人员以及工人中享有很高的声誉。

从 1959 年大学毕业,一直到 1976 年粉碎四人帮,我所从事的是专业教学工作,从带试验、带实习开始,一直到主讲专业课,指导毕业论文。教学工作对我思维逻辑性、表达条理化,以及不断查阅文献资料的习惯大有裨益。期间,亦参加过国家组织的航空用不锈钢管、军用轴承钢质量提高,以及薄壁氧气瓶钢的研制与生产,前两项还得了国家奖。但当时是三结合的联合攻关组(军队、工厂、院校),人人皆不署名,发表的文章亦自然是以攻关组名义,故不能收入论文集。

这里要提一下的是 1978 年,我和同事倪德麟在冶金部钢铁司的主持下,举办了为期一月的“超高功率电炉与炉外精炼”高级研修班。参加者都为各特钢厂的技术骨干,在这个研修班上所总结、介绍的是国外主要特钢厂采用这两项最新技术的情况,并编译了一百多篇国外文献的阅读材料,使当时久闭国门的钢厂技术人员耳目一新,约有一半参加者后来成为工厂的总工、技术副厂长及厂长。稍后,我又应上海金属学会之邀,在上海科技会堂举办钢铁冶金过程的物理化学系列讲座,每周半天。斯时,国外已有钢铁冶金过程的物理模型和数学模型以

适应计算机过程控制的建模需要,而“文革”前、“文革”中我国高校冶金教材中基础理论与工艺技术严重脱节,理论只能用来解释工艺的缘由而不能定量、定时的指导工艺。这一个系列讲座是以国外的理论模型成果为例,分析了整个冶金过程各种反应的热力学、动力学,并加以定量计算。结束时,要求一百多位参加者,结合本职工作撰写一篇运用理论解析冶金工艺过程的文章,由于参加讲座者多是各钢厂的技术骨干,写出的论文丰富多彩,不少还成了升高工时的代表作,论文绝大多数发表于国内和上海的钢铁冶金期刊。

1981年至1985年我先后到英国和瑞典从事喷射冶金的基础研究和工艺开发,由于所得成果与同事共同申请了英国、瑞典的专利,特别在瑞典SL公司任职期间,签有技术保密协议,故而此阶段鲜有文章发表。在此期间因工作之需,除瑞典外,还出差到过英、德、荷、芬、挪、俄、匈等七国,共计三十多家钢厂,并出席了多次国际冶金博览会、国际钢铁大会,广泛了解了世界钢铁工业的状况,亦结交不少钢铁界的著名学者、企业家和工程技术人员,从他们的研究工作中汲取了十分有益的营养。这里我要特别提到对我学术生涯影响最大的三位教授,首先是瑞典皇家工学院的埃克托普(Sven Ektorp)教授,他是一个充满各种创新思维的理想主义者,不但是喷射冶金、熔融还原的始作俑者,而且在20世纪80年代初就在实验室里建立了薄带连铸的试验装置,我从他身上学到的是对传统钢铁冶金技术不断创新的精神。埃克托普教授家住斯德哥尔摩郊外,他家的花园很大,在草地与花圃的一角,耸立着一座 $8\text{ m}^3$ 的小高炉,当有外国代表团来访时,他会请我们这些皇家工学院的教授、研究生帮他一起为高炉鼓风、上料、点火做好准备。待客人到达时则打开出铁口,放出炽热的铁水,铸出一块镌有他名字的铁块,作为纪念品,并为此十分自豪。当我告诉他1958年大炼钢铁时,我在甘肃永登山区建了60座几乎一模一样的“袖珍高炉”,并24小时不间断作业一个多月时,70多岁的他惊讶地张大了嘴巴说:“那我是用了中国人古老的炼铁技术啦!”第二位是我十分敬重的前日本东北大学冶金系主任不破祐先生(Fuwa),不破祐先生出生于日本名门望族、外交世家,辛亥革命前其祖父曾帮助过孙中山先生,上世纪50年代初先生毕业于东京大学,旋即赴美国MIT,在当时冶金学巨匠奇普曼(J.

Chipman)的指导下从事冶金物化研究,他与奇普曼教授共同完成的钢液中碳氧平衡曲线即 $[C][O]=0.0022(1600)$ ,是钢液精炼过程的经典之作,无论转炉炉内反应,真空处理中的沸腾脱碳、脱氧,都证明了这一研究的科学性、正确性。不破祐先生是位学识深渊、言谈儒雅的谦谦君子,我们第一次相逢于德国杜赛尔多夫的国际钢铁会议,他误认为我来自美国,连续问了我许多美籍华人教授的名字,当我说明我来自中国大陆时,他忙着鞠躬道歉,并详细地询问了我的工作经历,热诚邀请我去日本考察、讲学,因我当时在瑞典工作而未能成行。不破祐先生治学严谨,以他的地位、阅历来看,他发表的论文总量不多,但质量很高。他曾以“先辈”(日语中对长者的尊称)的口吻批评日本钢铁冶金界现在有一批“Paper Professor”和“Conference Professor”,光写文章应付各种会议。1988年我访日时,他早已从东北大学退休,转到新日铁公司任首席顾问、日本金属学会名誉会长。以他这样高的身分竟然亲自陪同我参观了东京大学、东京工业大学,我去仙台(东北大学)、名古屋(名古屋大学、新日铁名古屋制铁所)等地参观时,老先生一直送我到列车上,真使我这个无名后辈汗颜不已。第三位是欧特斯(Oeters)教授,他那时任教于柏林工业大学,我曾推荐过一位硕士到他门下攻读博士,故在欧洲工作时,常顺访他的实验室。欧特斯教授有着日尔曼民族特有的工作严谨、不苟言笑、诚实守信的特点,对我影响最大的是他对实验设备的设计十分重视和认真检查,因而保证了科研数据的准确性、可靠性。我三次去柏林,他的接待日程几乎是一样的参观实验室—由他的博士生报告各自的工作—工作午餐—请我作报告,他自己则总是静静地听,而在我报告后,他却第一个提问题。上世纪80年代中期,我回国后曾两次邀请他访问中国,他亦要求类似的日程安排,我当然是“主随客便”,遗憾的是当时中国博士生的英语水平较差,结结巴巴的讲述尚可事先背熟,等到他用德语口音浓重的英语提问时就“抓瞎”了,还得靠翻译帮助。顺便说一下,这三位我最尊敬的国外冶金专家学者竟然都是我母校的客座教授,所以无论从年龄、从学识乃至师生有序来讲,他们都当然是我的老师。

上世纪80年代中期我回国后,直到上世纪末的15年,是我学术工作的高潮期,在国外汲取的知识和受到的训练很快迸发出来,研究的重

点也从冶金工艺转向应用理论基础和某些创新性领域。当时我们上海工大的研究集体有两个共识：一是决不做“撒网捞鱼”式的研究，而是事先经过周密的热力学、动力学、热平衡计算，争取从实验室的条件试验后，一次进入工业规模试验。如在转炉中“熔融还原生产不锈钢母液”的工作，是从条件试验和理论计算后，建立试验吹炼的过程模型，在25吨氧气复吹转炉上一次试验成功的，其中母液中铬的增长、温度和渣中氧化铬含量的降低与计算机模拟曲线基本吻合，特别是吹炼终点更是完全一致；二是从学校和学科梯队的实际出发，只能找一些新的领域重点突破，而不可能“全面出击，配套成龙”。于是，先后选择了喷射冶金、熔融还原生产不锈钢母液、特殊物理场下的凝固和利用高温 Raman 谱仪及与相图计算方法相结合，来测定、推算高温熔渣中的结构和组元活度等。“强磁场下金属凝固行为”及“高温 Raman 谱技术”目前在国内外都有一定的影响。从2001年以来，我已有两位从事钢铁冶金学科领域研究的博士生的论文被评为全国百篇优秀博士论文（两年评一次）。

1995年我担任上海市市长以前，不管我在哪个岗位工作，每周仍回实验室半天，直接指导研究生的工作，即使1995年后，对于我名下的研究生，我还是要亲自面询研究进度、审查开题报告、批改博士论文，并对要求我署名的文章，一律亲自过目。凡不属于自己研究领域的，或未指导、参与过工作的文章，即使出自我的梯队的成员，也决不挂名。在这里我要特别感谢多年合作、肝胆相照的蒋国昌教授，从1995年起他在创建上海大学钢铁冶金实验室和指导科研集体的日常工作方面发挥了巨大的作用，他勤奋又锲而不舍的精神使高温 Raman 谱实验室从无到有，不断提高，现已可和国际同行对话、交流。在我们的梯队中还有一批年轻的博导教授，他们各有专长、思想活跃、勇于创新，在若干领域崭露头角：任忠鸣和邓康教授在强磁场下金属凝固的科学现象、丁伟中教授在金属氧化物的选择性还原、洪新教授在冶金过程节能和过程自动化、翟启杰教授在超细晶粒凝固控制等方面都进行着卓有成效的工作，其中任忠鸣教授还先后被评为国家自然科学基金杰出青年学者和长江学者计划的特聘教授。更值得高兴的是中科院院士、美国麻省理工学院客座教授周国治先生已于近期加盟这个集体，成为梯队的学术核心和领军人物。相信尽管我已离沪，但这个国家与上海市共建的重点实验室仍将奋

勇前进！

抚今追昔，感慨万千。中国已从什么钢材都要进口的农业国，发展成世界第一钢铁生产大国，这是几代钢铁工作者心血的结晶。我跨入钢铁冶金学科，今年是50周年（从1954年进大学算起），上海大学出版社从我已发表的钢铁冶金方面的论文中选出有代表性的论文编辑成册，我十分感谢出版社编辑和领导的关心与厚爱。“却顾所来径，苍苍横翠微”，这只能算是一个热爱和献身钢铁事业的中国科技工作者走过的足迹的记录吧！

徐匡迪

2004年11月

# 目 录

## 一、综 述

中国国民经济的发展与钢铁工业 .....	( 3 )
20 世纪——钢铁冶金从技艺走向工程科学 .....	( 16 )
从废钢冶炼纯净钢新流程的讨论 .....	( 34 )
21 世纪钢铁生产流程的理论解析 .....	( 44 )
中国钢铁工业的现状和发展 .....	( 59 )
中国钢铁工业近期发展对策的探讨 .....	( 76 )
钢液熔剂脱氮技术研究进展 .....	(106)
现代电炉炼钢的发展趋势 .....	(116)
熔融还原技术的发展 .....	(128)
不锈钢精炼技术的最新进展及其理论基础 .....	(141)
西欧钢铁工业的现状与发展趋势 .....	(155)
油、气管线用钢的性能要求与工艺技术进展 .....	(167)
不锈钢精炼技术的进步 .....	(185)
80 年代钢铁冶炼面临的技术问题 .....	(198)
喷吹冶金中的若干理论问题 .....	(211)

## 二、研究论文

微滴凝固的若干科学问题 .....	(227)
金属凝固细晶技术研究 .....	(248)
带电粒子流控制技术在冶金过程中的应用及前景 .....	(261)

铬铁矿在熔融滴下过程中的还原机理 .....	(269)
Behavior of Particles in Front of Metallic Solid/Liquid Interface in Electromagnetic Field .....	(278)
Temperature-Dependent Raman Spectra and Microstructure of Barium Metaborate Crystals and Its Melts .....	(297)
磁场中 Bi-Mn 合金中 MnBi 相定向排列组织的形成规律和机制 .....	(305)
Theoretical Investigation on By-only-current Electromagnetic Separation of Inclusion from Molten Metals .....	(314)
$x\text{CaSiO}_3 \cdot \text{LiBO}_2$ 固溶体中硅氧四面体微结构形态的拉曼光谱研究 .....	(326)
高阶亚正规熔体模型 .....	(332)
不锈钢高铬铁液的脱磷 .....	(352)
磁场对 Bi-Mn 合金两相区中 MnBi 相凝固组织的影响 .....	(359)
不锈钢母液制备工艺 .....	(369)
High Temperature Raman Spectra of Sodium Disilicate Crystal , Glass and its Liquid .....	(377)
Experimental Thermodynamic Research on the Equilibrium Between Silicon Alloy and $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ Melt .....	(390)
Research on Oxidation Refining of Ferrosilicon .....	(402)
Temperature Dependence of the Raman Spectra and Phase Transition of Zirconia .....	(413)
行波磁场连续净化铝合金液实验 .....	(420)
硅系合金氧化精炼过程的热力学分析 .....	(428)
交变磁场净化金属液时金属液紊流的形成及其控制 .....	(442)
Separation of Inclusions from Liquid Metal Contained in a Triangle/ Square Pipe by Travelling Magnetic Field .....	(452)
Investigation on Dephosphorization of Stainless Steel .....	(466)
冶金熔渣热力学性质的 SReS 模型 .....	(476)
High Temperature Raman Spectroscopy of Oxide Compounds in Crystal , Molten and Vitreous States .....	(485)
A Molecular Dynamics Simulation of $\text{CaSiO}_3$ Melt under an Electric Field .....	(488)
The Ionic Properties of $\text{CaSiO}_3$ Melt .....	(496)

Evaluation of Component Activity in Molten  $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$   
System with Model SELF-SReM4 ..... (509)

A Study on the Bonding Structure of  $\text{CaO-SiO}_2$  Slag by Means of  
Molecular Dynamics Simulation ..... (516)

CCSC System and Its Automatic Control Method ..... (525)

# SELF-SReM4 模型的新发展及其在 C-Mn-Fe-Si 四元系中的应用<sup>\*1</sup>

**摘要** 在亚正规熔体模型 SELF-SReM4.0 的基础上,提出了可解决碳化物析出问题的 SELF-SReM4.1 模型.并以 C-Mn-Fe-Si 四元系为例介绍了用上述两种模型计算组元活度的结果,分析了 Si-Mn, Mn-Fe 系中的若干平衡规律.

尽管在热力学意义上(不涉及物质结构)活度理论已很成熟,但活度的应用还不很普及.一方面,已掌握的热力学规律完全可用来为新技术的开发,或为实现过程优化及控制提供理论预测,另一方面,又往往由于缺乏相应的活度数据库而使定量的分析无从实施.依赖实验测试来建立活度数据库有较大难度,需要靠计算给出系统的数据,然后用实验对若干点进行校核.所以活度的计算已成为关键课题.

Wagner 的相互作用参数是迄今最流行的多元系活度计算方法.但溶液愈浓或组元愈多,用 Wagner 相互作用参数算出的活度误差愈大,为了开发高合金钢母液、铁合金的熔融还原技术和脱磷技术,改进铁合金的传统熔炼操作,建立 Ar-O<sub>2</sub> 混吹脱碳(AOD),真空吹 O<sub>2</sub> 脱碳(VOD)过程控制所需的数模,均迫切需把活度数据库扩展到高浓度合金的范畴,这就要求建立适当的熔体模型来进行计算.

SELF-SReM4 模型属于亚正规熔体理论的范畴,是上海市钢铁冶金新技术开发应用重点实验室(SELF)为描述四元系均相区而发展的模型,本文应用 SELF-SReM4.0<sup>[1]</sup>和最近提出的 SELF-SReM4.1 模型计算了有关C-Mn-Fe

\* 本文合作者:蒋国昌、张晓兵、唐恺、徐建伦、丁伟中.原发表于《金属学报》,34(5), 459~466(1998)

-Si 四元系的活度.

## 1 SELF-SReM4.0 模型的应用

### 1.1 C-Mn-Fe-Si 系组元活度的计算

直接用于四元均相区组元活度计算的 SELF-SReM4.0 模型具有如下形式：

$$G_C^{\text{ex}} = \sum_{j=2}^j \sum_{k=0}^{k'} \sum_{n=0}^{n'} A_{jkn} Y^j Z^k T^n \quad (1)$$

$$G_{\text{Mn}}^{\text{ex}} = \sum_{j=2}^j \frac{A_{j00}}{j-1} + \sum_{j=2}^j \sum_{k=0}^{k'} \sum_{n=0}^{n'} A_{jkn} Y^j Z^k T^n \left[ 1 - \frac{j-k}{Y(j-1)} \right] \quad (2)$$

$$G_{\text{Fe}}^{\text{ex}} = \sum_{j=2}^j \sum_{k=0}^{k'} \frac{A_{jk0}}{j-1} + \sum_{j=2}^j \sum_{k=0}^{k'} \sum_{n=0}^{n'} A_{jkn} Y^j Z^k T^n \left[ 1 - \frac{j-k}{Y(j-1)} - \frac{k-n}{YZ(j-1)} \right] \quad (3)$$

$$G_{\text{Si}}^{\text{ex}} = \sum_{j=2}^j \sum_{k=0}^{k'} \sum_{n=0}^{n'} \frac{A_{jkn}}{j-1} + \sum_{j=2}^j \sum_{k=0}^{k'} \sum_{n=0}^{n'} A_{jkn} Y^j Z^k T^n \left[ 1 - \frac{j-k}{Y(j-1)} - \frac{k-n}{YZ(j-1)} - \frac{n}{YZT(j-1)} \right] \quad (4)$$

$$G^{\text{ex}} = \sum_{j=2}^j \frac{A_{j00}}{j-1} Y + \sum_{j=2}^j \sum_{k=1}^{k'} \frac{A_{jk0}}{j-1} YZ + \sum_{j=2}^j \sum_{k=1}^{k'} \sum_{n=1}^{n'} \frac{A_{jkn}}{j-1} YZT + \sum_{j=2}^j \sum_{k=0}^{k'} \sum_{n=0}^{n'} \frac{A_{jkn}}{j-1} Y^j Z^k T^n \quad (5)$$

式中,  $G_i^{\text{ex}}$  ( $i = C, \text{Mn}, \text{Fe}, \text{Si}, \dots$ ) 为组元  $i$  的过剩偏摩尔自由能;  $G^{\text{ex}}$  是四元系的总过剩摩尔自由能; 模型所含的参数  $A_{jkn}$  需由已知的边界条件拟合定值;  $j' + k' + n'$  是模型的阶数, 令其均为小于 4 的整数;  $Y, Z$  和  $T$  是另一种浓度表示法, 定义为

$$Y = 1 - X_i \quad (6)$$

$$Z = 1 - \frac{X_2}{Y} \quad (7)$$

$$T = 1 - \frac{X_3}{YZ} \quad (8)$$

其中  $X_i (i = 1, 2, 3, \dots)$  为组元  $i$  的摩尔分数. 相应碳的活度计算公式是

$$\alpha_c = (1 - Y) \exp\left(\frac{G_c^{\text{ex}} - K}{RT}\right) \quad (9)$$

$K = 44\,650$ , 表示碳活度标准状态转换系数. 其他三个组元的  $G_i^{\text{ex}}$  均以纯物质为标准状态, 活度计算公式为

$$\alpha_i = X_i \exp\left(\frac{G_i^{\text{ex}}}{RT}\right) \quad (10)$$

在 C-Mn-Fe-Si 系中, 为拟合  $A_{jkn}$  参数而引用的已知边界条件示于表 1. 拟合所得的  $A_{jkn}$  参数数值示于表 2.

表 1 C-Mn-Fe-Si 系中用于拟合  $A_{jkn}$  参数的边界条件  
Table 1 The boundary conditions used in C-Mn-Fe-Si

Boundary	Information	Reference
C-Mn	The equilibrium with solid MnO under different $p_{\text{co}}$ and 1 628 K	[2]
C-Fe	$G_c^{\text{ex}}$ (1 873 K)	[3]
Mn-Fe	$G^{\text{ex}}$ (1 863 K)	[3]
Fe-Si	$G_{\text{Fe}}^{\text{ex}}$ (1 873 K)	[3]
Mn-Si	$\alpha_{\text{Mn}}$ (1 673 K)	[4]
Mn-Fe-Si	$\alpha_{\text{Mn}}$ (1 700 K)	[5]
C-Mn-Si	$[\% \text{C}]_{\text{sat}}$ (1 673 K)	[6]
C-Mn-Fe	$[\% \text{C}]_{\text{sat}}$ (1 873 K) iso - $\alpha_c = 0.25 (X_{\text{Mn}} \leq 0.2)$	[7][8]
C-Fe-Si	$[\% \text{C}]_{\text{sat}}$ (1 873, 1 823 K) iso - $\alpha_c = 0.25 (X_{\text{Si}} \leq 0.2)$	[7][9][8]
C-Mn-Fe-Si	$[\% \text{C}]_{\text{sat}}$ (1 903 K)	[10]

表 2 SELF-SReM4.0 给出的 C-Mn-Fe-Si 熔体  $A_{jkn}$  参数值  
 Table 2 The evaluated  $A_{jkn}$  for C-Mn-Fe-Si melt according to SELF-SReM4.0  
 (J/mol)

j	k	n = 0	n = 1	n = 2	n = 3	n = 4
2	0	- 99 631.98	0	0	0	0
	1	70 892.3	149 273.2	- 4 866 893	3 875 074	- 999 619.9
	2	11 188.69	- 6 476 583	10 451 850	- 624 549	629 122.3
	3	8 602.09	9 018 116	- 6 522 831	- 287 777	1 973 013
	4	- 5 964.38	- 4 449 743	1 619 816	2 243 857	- 1 210 548
3	0	- 24 960.3	0	0	0	0
	1	269 816.5	- 5 906 318	26 249 480	- 20 974 920	5 151 701
	2	- 101 181.5	30 216 970	- 49 750 090	22 538 070	- 2 791 611
	3	- 15 032.05	- 37 643 380	26 739 840	- 4 854 775	0
	4	26 173.44	17 491 260	- 5 845 056	0	0
4	0	79 471.32	0	0	0	0
	1	- 221 034.9	7 013 604	- 24 773 540	19 837 160	- 4 728 691
	2	121 382.5	- 25 283 520	40 333 950	- 15 442 520	0
	3	- 3 284.73	28 009 580	- 13 858 880	0	0
	4	- 21 359.98	- 12 086 190	0	0	0

## 1.2 Fe-Mn 及 Mn-Si 合金

熔

Fe-Mn 及 Mn-Si 合金是许多铁合金企业的主要产品。尽管这些合金的生产技术已经成熟,但尚未确切地掌握其熔炼反应热力学。这不仅影响现行技术的进一步优化,而且影响高硅 Mn-Si 合金及中、低碳 Fe-Mn 合金生产中某些重要

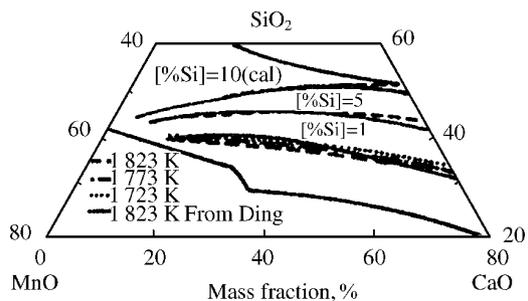


图 1 MnO-SiO<sub>2</sub>-CaO 渣与 C<sub>sat</sub>-Mn-Si 合金的平衡

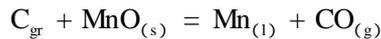
Fig. 1 The equilibrium between MnO-SiO<sub>2</sub>-CaO slag and C<sub>sat</sub>-Mn-Si alloy

因素的有效控制. 本节用 SELF-SREm4.0 模型对组元平衡关系进行预测并与实验对比.

(1) 熔炼 Mn-Si 时, 热力学上起决定性作用的是  $C_{\text{sat}}$ -Mn-Si 合金和  $MnO-SiO_2-CaO$  渣系之间的平衡. 图 1 按 SELF-SREm4.0 模型计算绘出了三组曲线, 分别对应于 1 823 K 下 [% Si] = 5%, 10% 及 1 723, 1 773, 1 823 K 下 [% Si] = 1%. 这些等 [% Si]、等温线上的各点代表着不同合金与该残渣组成的平衡关系. 它们是控制 Mn-Si 熔炼过程的重要依据.

丁伟中曾用实验测定了  $C_{\text{sat}}$ -Mn-Si 合金和  $MnO-SiO_2-CaO$  渣之间平衡<sup>[6]</sup> 图 1 中三条粗实线是其在 1 823 K 下测出的 [% Si] = 1%, 5%, 10.5% 的平衡曲线. 可见, 计算曲线与平衡实验所得基本吻合.

(2) 高碳 Fe-Mn 的吹  $O_2$  精炼称为 MOR 法. 此技术的核心是如何掌握 [C], [Mn] 的选择性氧化规律, 也即求解给定温度下可能得到的最低 [% C]. Mn-Fe 的脱碳反应如下:



$$\ln \frac{\alpha_{\text{Mn}} \cdot p_{\text{CO}}}{\alpha_{\text{C}} \cdot \alpha_{\text{MnO}}} = \frac{-25\,800}{T} + 16.28 \quad (11)$$

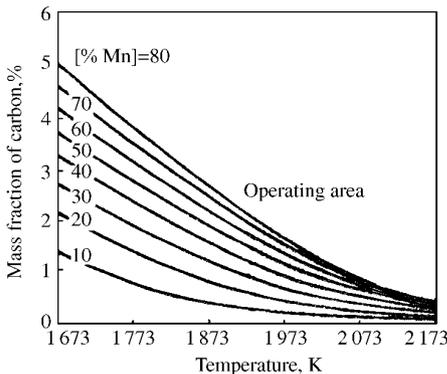


图 2 MOR 过程中温度对终点 [% Mn] 和 [% C] 的影响  
g.2 The effect of temperature on final [% Mn] and [% C] in MOR process

由于吹  $O_2$  的结果, 渣为 MnO 饱和,  $\alpha_{\text{MnO}} = 1$ . 假定气相中仅有 CO 和锰蒸汽. 而锰蒸汽分压  $p_{\text{Mn}}$  与  $\alpha_{\text{Mn}}$  的平衡关系为<sup>[11]</sup>

$$\ln p_{\text{Mn}} = \alpha_{\text{Mn}} \cdot \exp(37.67 - 3.02 \ln T - 33\,430/T) \quad (12)$$

因而

$$\begin{aligned} \alpha_{\text{C}} &= \alpha_{\text{Mn}} \cdot \exp(25\,800/T - 16.28) \\ &- \alpha_{\text{Mn}}^2 \cdot \exp(21.39 - 3.02 \ln T - 7\,630/T) \end{aligned} \quad (13)$$

图 2 给出的预测结果为在 2 023 K 的精炼温度下 ,产品为 50% [Mn] + 1% [C].

## 2 SELF-SReM4.1 模型及其应用

开发 SELF-SReM4 模型本意是要系统地给出整个四元均相区中的组元活度数据.但实际上,SELF-SReM4.0 模型在 C-Mn-Fe-Si 系中只能有效地用于 [% Si] < 20 左右的低 Si 区.为了描述高 Si 区,必须进一步考虑 SiC 析出的边界条件.此即 SELF-SReM4.1 模型的任务.

首先要说明 SELF-SReM4.1 与 SELF-SReM4.0 的一个重要区别.按 SELF-SReM4.1 模型,所有组元均以纯物质为标准状态,因此式(9)中的  $K = 0$ .  $A_{jkn}$  参数的拟合中也不再考虑其影响.

图 3 中,  $ab$  段是某一温度下 C-Mn-Si 系中的碳饱和线;  $bc$  段是 SiC( $\beta$ )析出线,而石墨-SiC( $\beta$ )-合金在  $b$  点三相共存.在  $ab$  段上,有

$$\frac{G_C^{ex}}{RT} = - \ln(1 - Y) \quad (14)$$

在  $bc$  段上,有

$$\frac{G_C^{ex} + G_{Si}^{ex}}{RT} = \ln K_{SiC} - \ln(1 - Y) - \ln YZ \quad (15)$$

令式(1)~(3)中的  $n = 0$ ,再将其代入式(14)和(15)即可得到  $abc$  线上的关系式,其中含有  $A_{jk0}^\#$  参数.  $A_{jk0}^\#$  参数只适用于计算  $abc$  线上的组元活度.为了同时也能描述整个液相区,还必须把其他边界条件也用于  $A_{jk0}$  的拟合.例如,可再增加以下两个边界条件:

$$(G_C^{ex})_{C-Mn} = \sum_{j=2}^j A_j Y^j \quad (16)$$

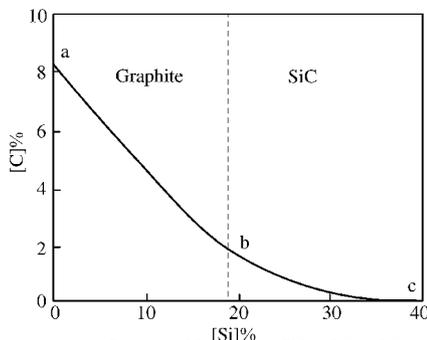


图 3 C-Mn-Si 系中的碳饱和线和 SiC( $\beta$ )析出线  
Fig. 3 The carbon saturated curve and SiC( $\beta$ ) separated curve of C-Mn-Si system at 1873 K

$$(G^{\text{ex}})_{\text{Mn-Si}} = - \sum_{k=1}^k \left\{ A_{2k} + \sum_{j=3}^j \frac{A_{jk}}{j-1} \right\} Z^k \quad (17)$$

$(G_C^{\text{ex}})_{\text{C-Mn}}$  是 C-Mn 二元系中 [C] 的过剩偏摩尔自由能;  $(G^{\text{ex}})_{\text{Mn-Si}}$  表示 Mn-Si 二元系的总过剩摩尔自由能. 由  $n = 0$  的式(1) ~ (3)和(14) ~ (17) 联立所得的关系式可用于拟合适应描述整个液相区, 且包括 *abc* 线上组元活度的  $A_{jko}$  参数. 实际上, 先由式(16)和(17)拟合得到  $A_{j00}$  和  $1 \leq k \leq 4$  的  $A_{2k0}$ ,  $A_{3k0}$ ,  $A_{4k0}$ . 其他的则利用图 3 中 *abc* 线的坐标来拟合. 表 3 是按 SELF-SReM4.1 模型推出的 C-Mn-Si 系中的  $A_{jko}$  参数.

表 3 SELF-SReM4.1 给出的 C-Mn-Si 熔体  $A_{jko}$  参数  
Table 3 The evaluated  $A_{jko}$  parameters of C-Mn-Si melt by SELF-SReM4.1  
(J/mol)

	k = 0	k = 1	k = 2	k = 3	k = 4
j = 2	515 766.7	- 43 590.46	- 179 439.6	- 1 126 557	1 168 272
j = 3	- 1 064 194	215 307.8	1 923 129	866 079.3	- 2 226 392
j = 4	549 825.9	215 307.8	- 2 722 537	1 953 612	0

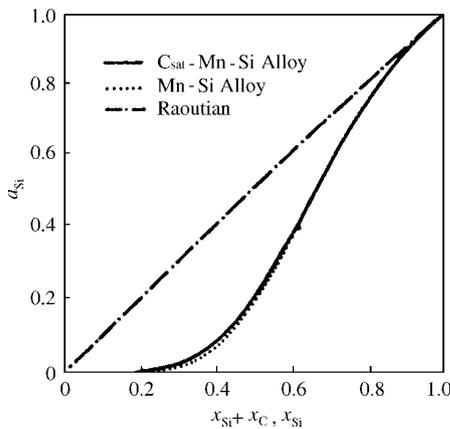


图 4 C-Mn-Si 合金和 Mn-Si 合金中组元 Si 的活度计算值的比较  
Fig. 4 Activity of Si in C-Mn-Si melt and Mn-Si melt at 1 873 K

丁伟中<sup>[6]</sup>发现 C-Mn-Si 合金熔体与 C-Fe-Si 合金有类似的关系. 即在高 Si 区内 C 和 Si 对  $\alpha_{\text{Si}}$  的影响相等. 图 4 是 C-Mn-Si 合金和 Mn-Si 合金中  $\alpha_{\text{Si}}$  计算值的比较, 两者吻合得很好. 由此证实了丁伟中的推断.

硅热还原法是生产中、低碳 Fe-Mn 的重要方法之一. 图 5 以 SELF-SReM4 模型为依据, 示出 1 773 ~ 1 873 K 下 C-Mn-Fe-Si 合金中, 与终点 [% Si] 相对应的  $\alpha_{\text{Mn}}^2 / \alpha_{\text{Si}}$  曲线. 由于

$$\frac{\alpha_{\text{Mn}}^2}{\alpha_{\text{Si}}} = K \frac{\alpha_{\text{MnO}}^2}{\alpha_{\text{SiO}_2}} \quad (18)$$

因此,利用 SELF-SReM4 模型由所需的产品成分 [% Mn] 及 [% Si] 计算  $\alpha_{\text{Mn}}^2/\alpha_{\text{Si}}$ ,再由所得的  $\alpha_{\text{MnO}}^2/\alpha_{\text{SiO}_2}$  通过 SELF-SReM4.0 模型计算 (MnO) 和 ( $\text{SiO}_2$ ),从而能有效地指导配料和预测收得率.

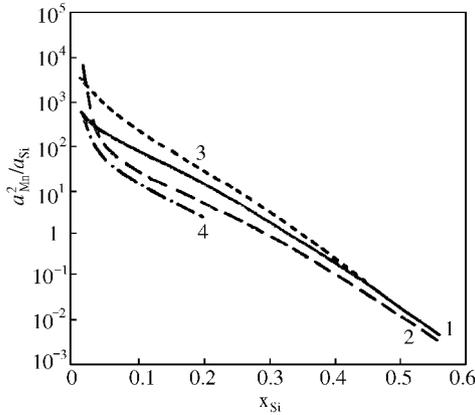


图5 C-Mn-Fe-Si 合金中 Si 含量对  $\alpha_{\text{Mn}}^2/\alpha_{\text{Si}}$  值的影响

Fig. 5 The  $\alpha_{\text{Mn}}^2/\alpha_{\text{Si}}$  values vs [% Si] in C-Mn-Fe-Si melt at 1 773 or 1 873 K

Curve	Alloy	$\alpha_{\text{C}}$	T, K	Calculation model
1	C-Mn-Si	1.0 or $K_{\text{SiC}}/\alpha_{\text{Si}}$	1 873	SELF-SReM3.1
2	C-Mn-Fe-Si (Mn/Fe = 4)	1.0 or $K_{\text{SiC}}/\alpha_{\text{Si}}$	1 873	SELF-SReM4.1
3	C-Mn-Si	0.5	1 873	SELF-SReM3.1
4	C-Mn-Fe-Si (Fe = 15%)	1.0	1 773	SELF-SReM4.0

### 3 讨论

SELF-SReM4 模型属高阶亚正规熔体模型范畴.模型所含  $A_{jkn}$  参数拟合是在各种边界条件通过 Gibbs-Duhem 公式构成的共同制约下实施的.若以  $\xi^{(m)}$  表示 m 阶 Wangner-Lupis 型活度相互作用系数,则  $A_{jkn}$  这一类参数就相当于  $j' + k' + n' = m$  条件下的  $RT\xi^{(m)}$ .由此可见,SELF-SReM4 模型将稀溶液中的活度计算和浓溶液中的活度计算完全统一起来;不仅给出了铁基熔体的“活度相互作用系数”,同时也给出了 Mn, Si 等其他元素为熔剂时的“活度相互作用系数”.

周国治最近将几何模型大大地向前推进了一步<sup>[12]</sup>.在热力学性质预测和相图计算方面几何模型是应用最广泛的方法.但是有两个问题,几何模型难以解决.实践中经常遇到不规则的均相区,其边界往往只含各二元子系的一部分,或由某种饱和析出线构成,即使是周国治最近推出的新几何模型也

不易处理此类均相区。另外,几何模型强调只利用二元子系作为已知值。对于三元系,新几何模型虽然考虑了各二元子系是否相似,三个组元的共同作用仍无法估计。但实际上,组元愈多则几个组元的共同作用也就愈不能忽略。以四元系为例,或许某些情况下,四元均相区本体内组元的总合贡献可不予考虑,四种三组元的共同作用却是举足轻重的,而其相似性的描述则比二元系复杂得多。相比之下,在这两方面,SELF-SReM4模型有优势。确切地说,新几何模型用于热力学性质预测和相图计算有其显著的优势,而SELF-SReM4模型着眼于四元均相区全域内组元活度的系统化,为工程问题的热力学预测提供足够可靠的组元活度数据库。

SELF-SReM4模型所给出的组元活度是否可靠在很大程度上取决于所用的“边界条件”,特别是二元子系的热力学性质。近年来,韩其勇和丁学勇等以Miedema生成热计算模型为基础,由微观着手进行了组元活度研究<sup>[13]</sup>。如果这一类研究能对已知二元系热力学性质的可靠性作出判断,并较确切地预报未知二元系的热力学性质,则依赖SELF-SReM4模型,不难进一步建立相应三元及四元均相区全域中的组元活度数据库。

## 4 结论

对C-Mn-Fe-Si四元系的均相区,SELF-SReM4.0适用于 $[\% \text{Si}] < 25\%$ 的范围,而SELF-SReM4.1不受Si含量限制。文中给出了该四元系的均相区内的组元活度系统数据,并进而分析了Si-Mn和Mn-Fe生产中的若干平衡问题。本文还讨论了SELF-SReM4模型的特点,指出了它与几何模型及Wagner相互作用参数法的区别和联系。

## 参 考 文 献

- [ 1 ] Zhang X B , Jiang G C , Tang K , Xu J J , Ding W Z , Xu K D. *Calphad* , 1997 ; 21(3)
- [ 2 ] Katsnelson A , Tsukihashi F , Sano N. *ISIJ Int* , 1993 ; 33 : 1045
- [ 3 ] Hultgren R. *Selected Values of Thermodynamic Properties of Metals and Alloys* , 1973 : 487
- [ 4 ] Tanaka A. *Trans Jpn Inst Met* , 1979 ; 20 : 516
- [ 5 ] Gee R , Rosenqvist T. *Scand J Metall* , 1978 ; 7 : 38
- [ 6 ] Ding W Z. PhD Dissertation , Trondheim University , Norway , 1993

- [ 7 ] Chipman J , Alfred R M , Gott L W , Small R B , Wilsong M D , Thomson C N , Guernsey D L , Fulton C J. *Trans AIME* , 1952 ; 44 : 1215
- [ 8 ] Darken L S. *Trans Metall Soc AIME* , 1967 ; 239 : 90
- [ 9 ] Schurmann E , Kramer D. *Giessereiforschung* , 1969 ; 21 : 29
- [ 10 ] Tuset J Kr , Sandvik J. *SINTEF Res Rep* 340358 , 1970
- [ 11 ] Kubaschewski O , Alcock C B. *Metall Thermochem.* 5th ed , Oxford : Pergamon Press , 1979 : 376
- [ 12 ] 周国治. 金属学报 , 1997 ; 33 : 126  
(Zhou Guozhi. *Acta Metall Sin* , 1997 ; 33 : 126)
- [ 13 ] 丁学勇 , 范鹏 , 韩其勇. 金属学报 , 1994 ; 30 : B49  
(Ding Xueyong , Fan Peng , Han Qiyong. *Acta Metall Sin* , 1994 ; 30 : B49)

## The New Development of the SELF-SReM4 Model and Its Application to the Quarternary System of C-Mn-Fe-Si

**Abstract** On the base of sub-regular melt model (SELF-SReM4.0 model) , a model SELF-SReM4.1 was designed to solve the precipitate of carbide. Taking C-Mn-Fe-Si quarternary system as an example , the calculated results of component activities by above mentioned two models are introduced and some equilibrium rules of Si-Mn and Mn-Fe systems are also analysed.

# 不锈钢母液铁浴熔融还原过程中的 铬回收率及母液的氧化脱磷<sup>\* 1</sup>

**摘要** 在 15 t 复吹转炉中进行了不锈钢母液的铁浴熔融还原工业试验,发现铬的收得率不高,且母液含磷过多. 不锈钢母液的铁浴熔融还原过程是某种二燃率条件下的 [C]-[Cr] 选择性氧化. 有高铬残渣伴随的母液宜于采取氧化脱磷,这种脱磷是 [C]-[Cr]-[P] 三元素之间的选择性氧化. 以 SELF-SReM4 模型为基础,定量地分析了有关问题.

## 1 铁浴熔融还原工业试验

不锈钢生产技术发展的一个重要问题是寻求降低生产成本,特别是降低金属原材料开支的途径. 喷吹 Ar-O<sub>2</sub> 混合气体的脱碳技术(AOD)过程直接使用高碳铬铁作为主要原材料,是不锈钢生产技术发展的一大进步. 近年发展起来的通过(CrO<sub>x</sub>)和(NiO)铁浴熔融还原生产不锈钢母液的技术也已逐渐成熟. 使用这项技术有可能在母液的生产中不用高碳铬铁和金属镍而降低成本. 本文报道进行工业试验的结果.

工业试验在 15 t 复吹转炉中进行<sup>[1]</sup>. 试验过程中,借助 YEWARK-II 系统控制供气参数,用上海市钢铁冶金新技术开发应用重点实验室(SELF)开发成功的“音平控渣系统”监察渣况并保证含碳铬矿团块的加入量合适. 新炉衬先经受两次洗炉,再进行熔池的脱磷,增碳至 4.5% (质量分数,下同)以上,并升温高于 1 873 K,然后即着手投加含碳铬矿冷团块(有时还需加入粒状 NiO)和焦炭,铁浴熔融还原过程开始进行.

\* 本文合作者:蒋国昌、张晓兵、徐建伦. 原发表于《金属学报》34(5) 467~472(1998)

试验中,顶枪供  $O_2$  速率是  $50 \sim 90 \text{ Nm}^3/\text{min}$ ;枪位按主氧流冲击强度等于  $4 \sim 5$  控制;底吹  $N_2$  的搅动功率低于  $5 \text{ kW/t}$ . 在此条件下,二燃率达  $24\% \sim 48\%$ ,加热效率近  $80\%$ .

图 1 是还原过程中熔池内主要元素浓度的典型变化规律. 如图 2 所示,由于平均加矿速率在  $7.6 \text{ kg}/(\text{t} \cdot \text{min})$  左右,铬的平均还原速率可高达  $0.16 [\% \text{ Cr}]/\text{min}$ . 其原因之一是试验中保持了  $\text{CaO}/\text{SiO}_2 = 0.8 \sim 2.0$  及  $(\% \text{ MgO}) + (\% \text{ Al}_2\text{O}_3) \leq 40$ . 最终可炼成含  $14.7\% [\text{Cr}]$  以及  $13\% [\text{Cr}] + 14.5\% [\text{Ni}]$  两种母液.

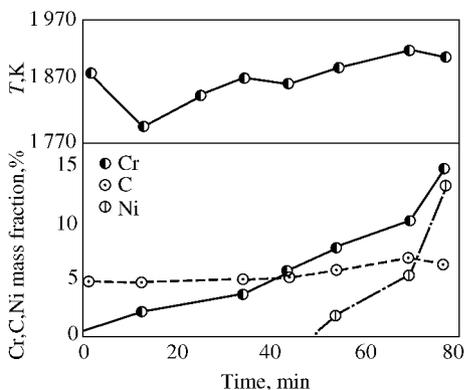


图 1 工业试验过程中熔池温度和组成的变化

Fig. 1 The variation of bath temperature and composition during the pilot test

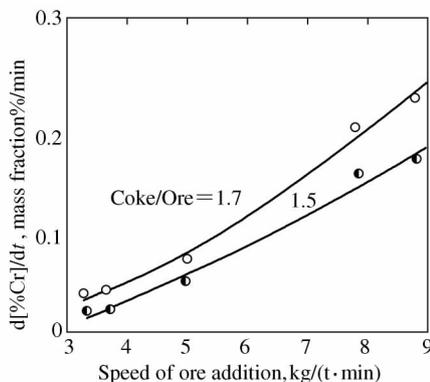


图 2 工业试验过程中加矿速率与还原速率的关系

Fig. 2 The relation of lump feeding rate vs reduction rate in the pilot test

试验发现了两个重要问题:(1) 本试验中熔池未作终脱氧,图 3 指出,高温还原时渣中残铬( $T \cdot \text{Cr}$ )平均可达  $6\%$ . 按物料平衡,铬的总收得率仅  $85\%$ . 文献[2]指出,如果在  $1850 \text{ K}$  和强  $\text{CO}$  气氛下用  $[\text{C}]$  还原 ( $\text{CrO}_x$ ),那么渣中残铬应低于  $0.5\%$ . 两者的差异需作进一步的定量讨论.(2) 即使未作终脱氧,母液最终的含磷量也有  $0.06\%$ . 这会限制母液的应用. 有必要定量地讨论如何优化其脱磷操作.

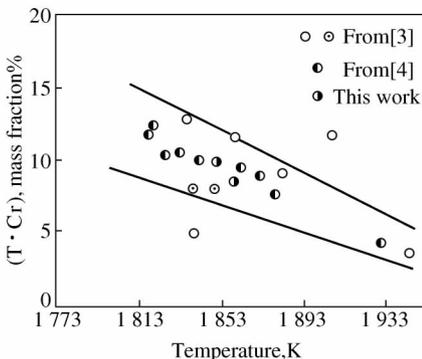


图 3 工业试验中熔池温度和渣中残铬量的关系

Fig. 3 The relation of the residual Cr content in slag vs bath temperature in the pilot test

## 2 C-Fe-Cr-Ni 和 C-Fe-Cr-P 系组元活度的计算

为了对上述问题进行定量分析, 必须知道母液组元活度的数据. 本文利用 SELF-SReM4 模型可给出可靠的活度数据. SELF-SReM4 模型为一种高阶亚正规熔体模型, 是专为计算 C-Cr-Fe-Ni 或 C-Cr-Fe-P 等四元系的均相区组元活度而开发的<sup>[5]</sup>. 图 4 与图 5 分别是 C-Cr-Fe-Ni 系与 C-Cr-Fe-P 系中各组元活度的计算结果.

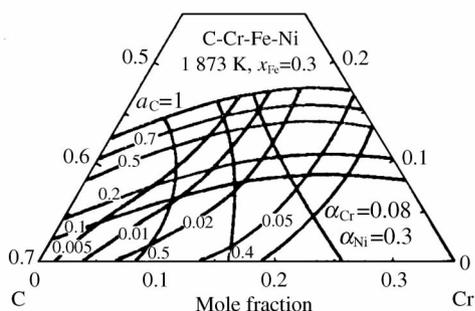


图 4 1 873 K 下 C-Cr-Fe-Ni 合金中各组元的活度计算值 ( $x_{\text{Fe}} = 0.3$  摩尔分数)

Fig. 4 The component activities of C-Cr-Fe-Ni alloys, calculated under the condition of 1 873 K and  $x_{\text{Fe}} = 0.3$  (mole fraction). The standard state for  $a_{\text{C}}$  is graphite and those for  $a_{\text{Cr}}$  and  $a_{\text{Ni}}$  are pure liquids

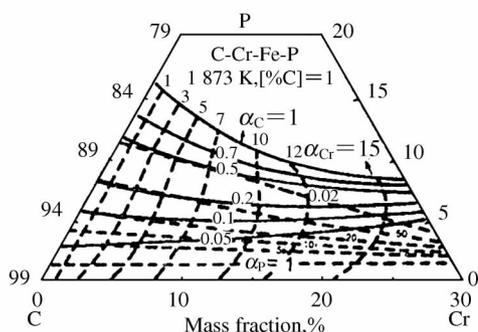


图 5 1 873 K 下 C-Cr-Fe-P 合金中各组元活度的计算值 ( $[\text{C}] = 1\%$ )

Fig. 5 The component activities of C-Cr-Fe-P alloys, calculated under the condition of 1 873 K and  $[\text{C}] = 1\%$ . The standard state for  $a_{\text{C}}$  is graphite and those for  $a_{\text{Cr}}$  and  $a_{\text{Ni}}$  are infinite dilute solution of 1% (mass fraction)

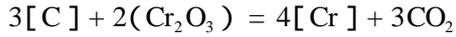
## 3 不锈钢母液铁浴熔融还原过程中铬的回收率

### 3.1 $[\text{C}]$ 和 $[\text{Cr}]$ 选择性氧化的转化温度

不锈钢母液铁浴熔融还原过程的实质可认为是 $[\text{C}]$ 和 $[\text{Cr}]$ 的选择性氧化. 为满足供能要求, 熔融还原过程中二燃率(PCR)通常可达到 50%, 但 $\text{CO}_2$ 对 $[\text{Cr}]$ 来说是强氧化剂, 所以在计算 $[\text{C}]$ 和 $[\text{Cr}]$ 选择性氧化的转化温度( $T_v$ )时必须考虑到二燃的影响.

事实上, 在还原过程中渣所含的是( $\text{CrO}_x$ ), 其  $x = 1 \sim 1.5$ . 由于无相应

的活度数据可利用,因此本文在  $x = 1.5$  的假设下进行预测.



$$\Delta G^\circ = 1\,052\,072 - 554.44T \quad (1)$$

$$T_v = -0.12\Delta G^\circ / \ln \left[ \alpha_{[\text{Cr}]}^4 \left( \frac{P_{\text{CO}_2}}{P^\circ} \right)^3 / (\alpha_{[\text{C}]}^3 \cdot \alpha_{\text{Cr}_2\text{O}_3}^2) \right] \quad (2)$$

图 6、7 中的  $\alpha_{[\text{Cr}]}$  及  $\alpha_{[\text{C}]}$  均用 SELF-SReM4 模型计算. 图 6 给出了 PCR = 40% 且 [% C] = 5 条件下 [% Cr] 和  $\alpha_{\text{Cr}_2\text{O}_3}$  对  $T_v$  的作用. 按此图,可为不锈钢母液铁浴熔融还原在不同条件下进行时预测合适的操作温度. 图 7 表明了 PCR 与过程温度对  $\alpha_{\text{Cr}_2\text{O}_3}$  有严重影响. 这里  $\alpha_{\text{Cr}_2\text{O}_3}$  的高低正是铬收得率的反映. 在 PCR = 25% 的前提下,曲线 3 和 4 以碳饱和的 Cr18 合金为例说明:若  $T_v$  从 1 773 K 提高到 1 823 K,则  $\alpha_{\text{Cr}_2\text{O}_3}$  将由 0.06 降至 0.023. 若熔池是碳饱和的 Cr18Ni8,且 PCR 不变,按曲线 5 和 6 的升温幅度可导致  $\alpha_{\text{Cr}_2\text{O}_3}$  由 0.02 降至 0.007 5.

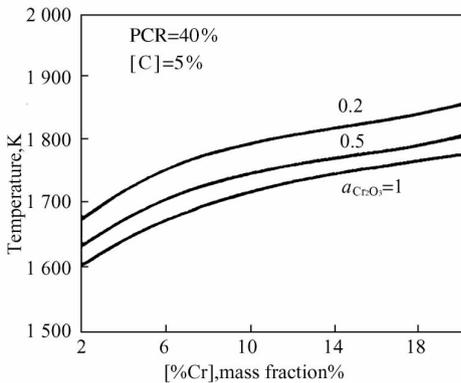


图 6 在给定 PCR 和 [% C] 的条件下按所需 [% Cr] 和  $\alpha_{\text{Cr}_2\text{O}_3}$  预测  $T_v$

Fig. 6 The prediction of  $T_v$  from [% Cr] and  $\alpha_{\text{Cr}_2\text{O}_3}$  under the given PCR and [% C]

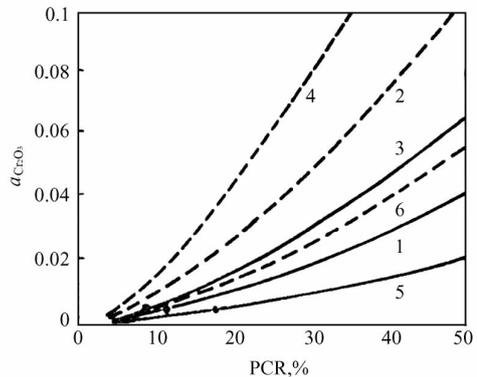


图 7 PCR 与过程温度对  $\alpha_{\text{Cr}_2\text{O}_3}$  的影响

Fig. 7 The effect of PCR and process temperature on  $\alpha_{\text{Cr}_2\text{O}_3}$

Curve	1	2	3	4	5	6
[% Cr]	13	13	18	18	18	18
[% Ni]	0	0	0	0	8	8
$T_v$ , K	1 823	1 773	1 823	1 773	1 823	1 773

因此图 6、7 说明:PCR 愈大,则 [C] 和 [Cr] 选择性氧化的转化温度 ( $T_v$ ) 就愈高. 所以必须在考虑 PCR 影响的前提下选择操作温度.

### 3.2 不锈钢母液铁浴熔融还原过程操作的改进

(1) 铁浴熔融还原过程中二燃的双重作用不可忽视. 它既为供能所必需, 亦有其副作用. 因此, 为了在终止加矿之后能有一个合适的铬收得率, 需采纳“许用二燃率”的概念. 由图 6 可知, 对碳饱和的 Cr18Ni8 合金, 1 823 K 下的许用二燃率约为 18%.

(2) 铁浴熔融还原过程中要注意保持合金的碳饱和度, 并在渣层中保存一个合适的碳块数量. 本试验发现: 底吹气即使含少量的  $O_2$  也可明显地导致还原速率降低.

(3) 不少研究者<sup>[5,6]</sup>认为, 渣层中的碳块是  $(CrO_x)$  的重要还原剂. 而本工业试验中渣内残铬 ( $\% CrO_x$ ) 不低, 表明该碳块的还原作用无法抵消  $CO_2$  的氧化作用. 实际上, 这些碳块的主要贡献在于使渣层的中、下部能保持强还原气氛.

(4) 为了协调二燃的双重作用, 顶枪主  $O_2$  流最好是近水平的, 且仅淹没在顶渣的表层内. 同时, 顶吹强度、底搅强度、渣层厚度和熔渣粘度这四个因素要匹配良好.

## 4 不锈钢母液的氧化脱磷

当母液由铁浴倾出时, 它处于接近碳饱和的状态, 且伴随母液流入脱磷反应器的渣把一些  $Cr_2O_3$  带进反应器内. 这正是采用 CaO 基熔剂进行氧化脱磷的最适条件. 作者曾提出“[Cr], [P], [C]三元素之间的选择性氧化”概念, 并借以阐述上述观点. 以 Cr18 为例, 其三元素之间选择性氧化的典型情况示于图 8 (图 8 ~ 10 中的  $p_{O_2}$  和  $a_{[O]}$  相应, 表示体系的氧位). 图中母液的组元活度是用 SELF-SReM4 模型计算的. 可以看到三条曲线和代表着临界 [% C] 的两个点. 第一个临界 [% C] 是热力学上为有效保 [% Cr] 所需的, 高于此临界值的 [C] 能还原  $(CrO_x)$ . 第二个临界 [% C] 表明平衡条件下母液能脱磷的限度, 高于此临界值的 [C] 能还原  $(P_2O_5)$ .

图 8b 所示是采用 CaO 基脱磷剂时的最佳脱磷条件. 由于操作温度仅 1 573 K, 磷酸根容量  $\lg(C_{PO_4^{3-}}) = 25.7$ , 所以 [P]-( $P_2O_5$ ) 曲线总在 [C]-CO 曲线下. 此状态下, 可用很高的操作氧位, 只要 [% C] 高于其第一个临界值就足以有效地保 [% Cr], 同时又不致干扰母液的脱磷.

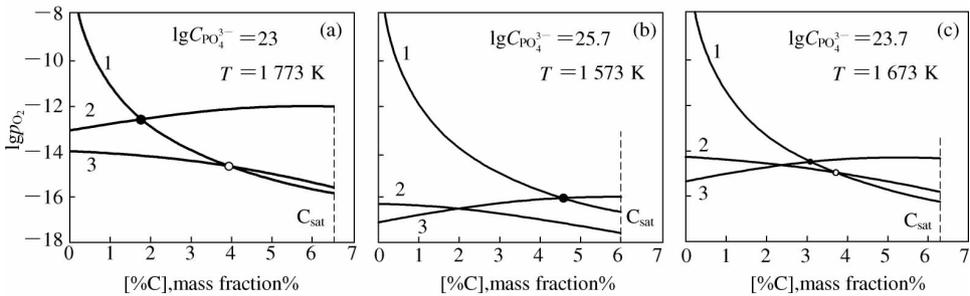


图8 不同条件下[Cr]-[P]-[C]之间的选择性氧化关系及临界 [% C]

Fig. 8 The selective oxidation among [Cr]-[P]-[C] and critical [% C] under different conditions [% Cr] = 18, [% P] = 0.02, (% P<sub>2</sub>O<sub>5</sub>) = 0.05 curve 1 : [C] + 0.5{O<sub>2</sub>} = {CO}  
 curve 2 : [P] + 2.5{O<sub>2</sub>} = (PO<sub>2.5</sub>) curve 3 : [Cr] + 1.5{O<sub>2</sub>} = (CrO<sub>1.5</sub>)

低温通常利于脱磷.事实上,随着操作温度的升高[C]的第一个临界点向低 [% C] 移动,但第二个临界点向低 [% C] 移动更快.图 8c 显示了一个极限状态,即两临界点几乎挤在一起.如此情况下母液的脱磷只能求助于用 O<sub>2</sub>,使操作处在非平衡态,在母液-熔剂界面上保持高的 α<sub>FeO</sub>.图 8a 是 1773 K 下用 BaO 基熔剂脱磷时的情况.可看到两个临界 [% C] 定义了一个碳含量范围,操作时若 [% C] 落在此域内,则脱磷效率最高.图 9 是系列工业试验的结果,其脱磷效率的峰值和本文的计算吻合.

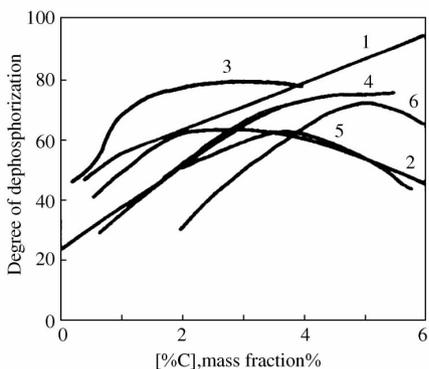


图9 不锈钢氧化脱磷试验中 [% C] 对脱磷率的影响  
 Fig. 9 The effect of carbon content on the dephosphorization degree in the oxidational dephosphorization pilot test of stainless steel

Curve	Agent	[% Cr]	T, K
1	BaO-based	15	1608
2	BaO-based	18	1813
3	BaO-based	15	1823
4	CaO-based	15	1573
5	Na <sub>2</sub> O-NaF	18	1673
6	Na <sub>2</sub> O-NaF	18	1773

图 10 给出了 [% P] 及 (% P<sub>2</sub>O<sub>5</sub>) 对临界 [% C] 的影响.如果要求 [% P] 脱得很低或恰恰起始的 (% P) 相当高,则第二个临界点也会明显地向低 [% C] 移动.

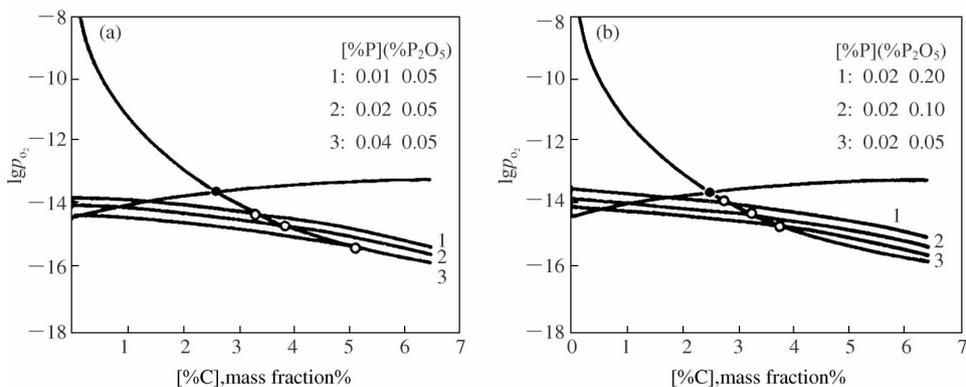


图 10 [%P]和(%P<sub>2</sub>O<sub>5</sub>)变化时临界[%C]的移动

Fig. 10 The effect of [%P] and (%P<sub>2</sub>O<sub>5</sub>) on the shift of critical [%C] under the condition of 1723 K, 18% [Cr] and lgC<sub>PO<sub>4</sub></sub> = 23.6

## 5 结论

完成了不锈钢母液铁浴熔融还原的工业试验. 平均还原速率为 0.16[%Cr]/min, 但铬收得率仅 85% 且 [%P] 超出标准. 为了获得适当的铬收得率, PCR 一定要低于其许用值. 该“许用二燃率”取决于当时的操作温度. 接近碳饱和的母液由含(CrO<sub>x</sub>)的渣伴随时, 是最适于进行氧化脱磷的条件.

## 参 考 文 献

- [ 1 ] 侯树庭 徐明华 张怀君 杨兴林 徐匡迪 蒋国昌 徐建伦 张晓兵. 钢铁, 1995 30(8): 16  
(Hou Shuting, Xu Minghua, Zhang Huaijun, Yang Xinglin, Xu Kuangdi, Jiang Guochang, Xu Jianlun, Zhang Xiaobing. *Iron and Steel*, 1995 30(8): 16)
- [ 2 ] Jiang G C, Pei W G, Borinder T, Gustafsson S. *Proceedings of Shenyang International Symp on Smelting Reduction*, Shenyang, 1986: 173
- [ 3 ] 竹内秀次 仲村秀夫 桒谷敏和 藤井澈也 野崎努. 铁と钢, 1990 76: 1847  
(Takeuchi Shuji, Nakamura Hideo, Sakuraya Toshikazu, Fuji Tetsuya, Nozaki Tsutomu. *Tetsu-to-Hagane*, 1990: 76: 1847)
- [ 4 ] Marukawa K, Anezaki S, Hirate Y, Ishikawa M. *Proceedings of Shenyang International*

*Symp on Smelting Reduction* , Shenyang , 1986 : 304

- [ 5 ] Zhang X B , Jiang G C , Tang K , Xu J L , Ding W Z , Xu K D. *Calphad* , 1997 ; 21 ( 3 )
- [ 6 ] 田冈启造 , 多田睦 , 山田纯夫 , 野村宽 , 大西正之 , 马田一 . 铁と钢 , 1990 ; 76 : 1863  
( Taoka Keizo , Tada Chikashi , Yamada Sumio , Nomura Hiroshi , Ohnishi Masayuki , Bada Hajime. *Tetsu-to-Hagane* , 1990 ; 76 : 1863 )

## Cr Yield and Oxidational Dephosphorization During the Bath Smelting Reduction Process

**Abstract** The pilot test of bath smelting reduction process producing stainless master alloy was carried out in a 15 t complex blowing converter. It was found that the yield of chromium is not high and the master alloy contains too much phosphorous. It indicates that the bath smelting reduction process producing stainless master alloy is indeed a process of [ C ]-[ Cr ] selective oxidational dephosphorization procedure. Essentially , it is a selective oxidation among [ C ]-[ Cr ]-[ P ] elements. Based on the model of SELF-SReM4 , these two problems were discussed quantitatively in this paper.

# CaO-SiO<sub>2</sub> 熔渣键合结构的 分子动力学研究<sup>\* 1</sup>

**摘要** 应用分子动力学计算机模拟方法研究了 CaO-SiO<sub>2</sub> 熔渣中的键合结构. 模拟结果表明偏径向分布函数  $g_{ij}(r)$  的特征与 X 射线衍射的结果相一致. SiO<sub>4</sub> 四面体中  $Q_n$  随组分变化的规律与 Raman 光谱测得结果相吻合. 分子动力学计算的振动态密度在  $636 \sim 737 \text{ cm}^{-1}$  和  $800 \sim 1200 \text{ cm}^{-1}$  处出现峰值, 与 Raman 光谱的结果相一致.

CaO-SiO<sub>2</sub> 是冶金、硅酸盐、地矿学等许多科技领域涉及的基本物质之一. 这些领域的研究者们用相似的方法, 从不同的角度对 CaO-SiO<sub>2</sub> 系进行了大量有成效的研究. 然而, 也遗留下一些迄今未能解决的难题<sup>[1]</sup>. 必须沟通微观键合结构与宏观物化性能间的渠道, 以能从根本上辨别是非, 建立正确的概念和理论. 用高温 Raman 光谱测定与 MC、MD 及 ab initio 计算相配合是作者借以沟通微观和宏观的方法. 本文即是用分子动力学 (MD) 计算机模拟方法研究 CaO-SiO<sub>2</sub> 熔渣键合结构的初步结果.

分子动力学的基点在于由微观粒子之间的相互作用来确定它们的构型. 该相互作用在分子动力学中用势函数来定量地描述. 当体系在给定的相互作用势下, 调整其构型而达到平衡时, 即能给出平衡热力学和动力学的各种性质. 但迄今为止, 即使是一个简单的熔渣体系也难于给出精确的相互作用势, 而是用简化了的各种经验势来讨论问题的. 例如, 对于 SiO<sub>2</sub> 熔体和玻璃的描述, 利用经验性的两体有效势 (包含有短程斥力与 Coulomb 静电作用) 已得到有说服力的结果<sup>[2]</sup>. Kieffer 和 Angell 在研究熔态二元硅酸盐中的液-液互不溶现象时引

\* 本文合作者: 蒋国昌、黄世萍、尤静林. 原发表于《中国科学》(E 辑) 28(6) 499~504(1998)

用了著名的 BMH(Born-Mayer-Huggins)势. 其结果表明:只有在  $0.5 < x_{\text{SiO}_2} < 1.0$  条件下才会出现液-液互不溶,并且发现 MnO-SiO<sub>2</sub> 在此浓度范围内的混合自由焓为正值<sup>[3]</sup>. 在模拟玻璃态的 CaSiO<sub>3</sub> 研究中也用了 BMH 势,并能定性地重现 Ca-Ca 偏结构因子的特征,并阐明结构的中程有序度<sup>[4]</sup>.

高温 Raman 光谱是熔体或高温固体中分子振动态的记录. 即在某一波段内,相应于不同波长的散射光强度<sup>[5]</sup>. 通常,高温 Raman 光谱的谱线是一条包络线. 必须首先确认该包络线下应有哪几个微结构单元的波峰. MD 计算可提供一种判断的依据. 这就是计算分子振动态密度. 即在所有可能的振动频率范围内某一振动频率出现的概率. 此态密度可由速度自相关函数引出<sup>[6]</sup>. 用分子动力学模拟熔态的 LiOH 及硅酸盐玻璃,其计算结果和 Raman 光谱的结果吻合很好<sup>[7,8]</sup>.

## 1 模拟计算

首先,假设在 CaO-SiO<sub>2</sub> 体系中粒子之间的相互作用服从上述的 BMH 势.

$$V_{ij} = A_{ij} \exp \left[ \frac{d_{ij} - r}{\rho} \right] + \frac{Z_i Z_j e^2}{r},$$

$$A_{ij} = B \left| 1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j} \right|,$$

$$d_{ij} = \sigma_i + \sigma_j,$$

BMH 势中的 B 是经验常数,  $\rho$  是硬度参数,表示粒子相互靠近时的变形程度.  $Z_i e$  是离子 i 的价数,  $n_i$  是表征其外壳电子特点的参数,  $\sigma_i$  表示粒子间的斥力参数. 表 1 是引自 Kieffer-Angell 的工作<sup>[3]</sup>.

表 1 本文所用参数

$\sigma_{\text{O}}$	0.142 nm	$n_{\text{O}}$	10	$Z_{\text{O}}$	- 2
$\sigma_{\text{Si}}$	0.131 nm	$n_{\text{Si}}$	7	$Z_{\text{Si}}$	+ 4
$\sigma_{\text{Ca}}$	0.158 nm	$n_{\text{Ca}}$	8	$Z_{\text{Ca}}$	+ 2
$\rho$	0.029 nm				
B	$0.19 \times 10^{-19} \text{J}$				
SiO <sub>2</sub>	42%	48%	50%	55%	60%
N <sub>tot</sub>	605	620	500	510	520
N <sub>O</sub>	355	370	300	310	320
N <sub>Si</sub>	105	120	100	110	120
N <sub>Ca</sub>	145	130	100	90	80

在给定的 SiO<sub>2</sub> 浓度条件(体系内粒子数不同)下,进行微正则系综(EVN)的分子动力学计算. 求解运动方程的时间步长为:  $t = 0.001$  ps. 其切断半径取  $L/2$  ( $L$  是体系所占体积的线尺寸),而该体系的体积又取决于 1 873 K 下的密度. 计算 Coulomb 相互作用势时采用 Ewald 求和方法. 体系的起始构型是随机的. 最初的 2 000 步相应于 4 000 K, 然后减至 1 873 K, 经 10 000 步以上而达成平衡, 其能量涨落  $< 0.2\%$ . 平衡后再运行 10 000 步, 计算体系的热力学和动力学性质. 计算中, 压力在 0.3 ~ 0.6 MPa 范围内.

## 2 结果与讨论

### 2.1 键合结构

为了描述 CaO-SiO<sub>2</sub> 熔渣的短程和中程结构, 通常是从分析偏径向分布函数(partial radial distribution function)  $g_{ij}(r)$  着手的. 模拟计算  $x_{\text{SiO}_2} = 0.42, 0.50, 0.60$  时的  $g_{ij}(r)$  示于图 1.  $x_{\text{SiO}_2} = 0.50$  时, 计算的  $g_{ij}(r)$  的主峰位置与 Waseda 等<sup>[9]</sup>用 X 射线衍射所得结果的比较见表 2.

表 2  $g_{ij}(r)$  的主峰位置与 Waseda 等用 X 射线衍射所得结果

	$r_{\text{Si-Si}}/\text{nm}$	$r_{\text{Si-O}}/\text{nm}$	$r_{\text{Ca-O}}/\text{nm}$	$r_{\text{O-O}}/\text{nm}$
MD	0.33	0.170	0.24	0.260
X 射线衍射	0.32	0.162	0.24	0.266

图 1 表明, 随着  $x_{\text{SiO}_2}$  的增大,  $g_{\text{Ca-Ca}}(r)$  的主峰减低, 其峰位向较大的  $r$  值方向移动, 这是体系中钙离子的数密度减小所致.  $g_{\text{Si-O}}(r)$  的主峰的位置几乎不变.  $g_{\text{O-O}}(r)$  在 0.26 nm 处主峰的位置相应于 SiO<sub>4</sub> 四面体的边长, 0.36 nm 处的次峰位置相应于 CaO<sub>6</sub> 中两个氧离子的间距<sup>[3]</sup>. 由此可见  $g_{\text{O-O}}(r)$  的主峰和次峰是 Si<sup>4+</sup> 和 Ca<sup>2+</sup> 离子周围 O<sup>2-</sup> 的配位数不同的反映.

另一方面, 计算了 SiO<sub>4</sub> 四面体中桥氧在不同的 CaO 浓度下的变化, 在  $r_{\text{Si-O-Si}}$  小于及等于 0.34 nm, 此距离内, 若 Si<sup>4+</sup> 出现两次, 则此 O<sup>2-</sup> 是桥氧 O<sub>b</sub>. 反之, 若 Si<sup>4+</sup> 出现一次, 则此 O<sup>2-</sup> 是非桥氧 O<sub>nb</sub>. 用这种方法即可判断系于每一个 Si<sup>4+</sup> 的四个 O<sup>2-</sup> 中, O<sub>b</sub> 和 O<sub>nb</sub> 分别占几个. 本文计算了 1 000 种构型, 其结

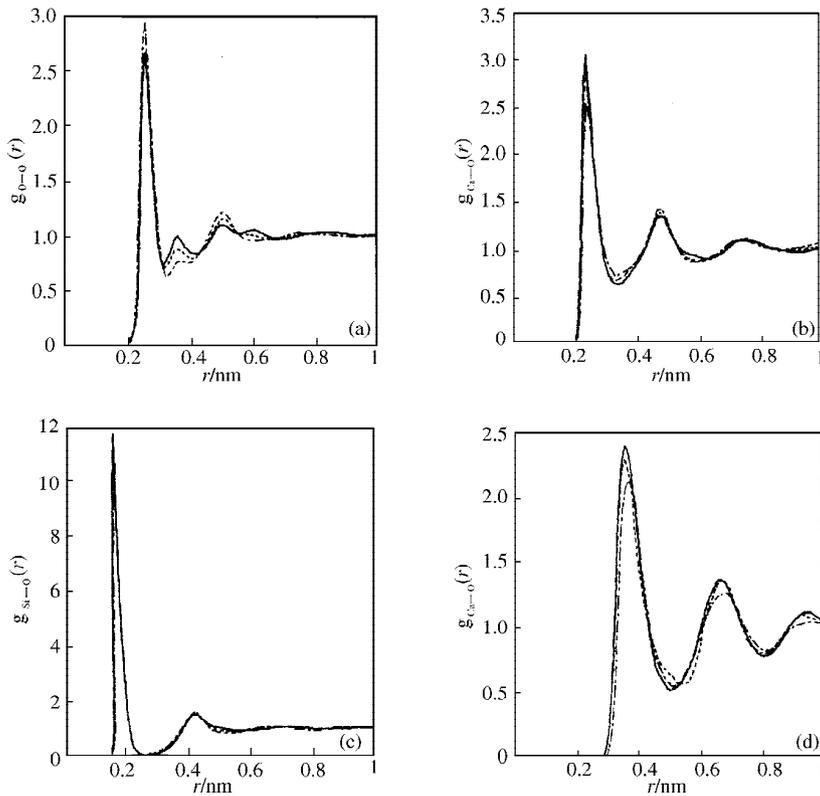


图1 径向分布函数

(a)  $g_{O-O}(r)$ , (b)  $g_{Ca-O}(r)$ , (c)  $g_{Si-O}(r)$ , (d)  $g_{Ca-Ca}(r)$   
 —示  $x_{SiO_2} = 42\%$ , ---示  $x_{SiO_2} = 50\%$ , - · -示  $x_{SiO_2} = 60\%$

果示于图 2(a). 这和由 Raman 光谱图解谱所得结果图 2(b)<sup>[10]</sup>吻合得很好. 图中的  $Q_n$  ( $n = 1, 2, 3, 4$ ) 表示  $SiO_n$ 四面体中有几个  $O_b$ .

## 2.2 振动态密度函数

一个体系 粒子位置与动量随时间的变化提供了其振动行为的全部信息. 因此可以通过粒子速度随时间变化的规律来取得这些信息. 在模拟体系中 离子的速度自相关函数(velocity autocorrelation function) $C_j(t)$ 可定义如下

$$C_j(t) = \frac{u_j(t)u_j(0)}{u_j(0)u_j(0)},$$

$u_j(t)$ 是粒子的速度,  $\bar{\quad}$ 表示系综平均. 假设在 MD 中经典动力学的规律仍然正确 并且能量完全均匀地分布于各振动态 则分子的振动态总密度 $\Gamma(\omega)$ 定

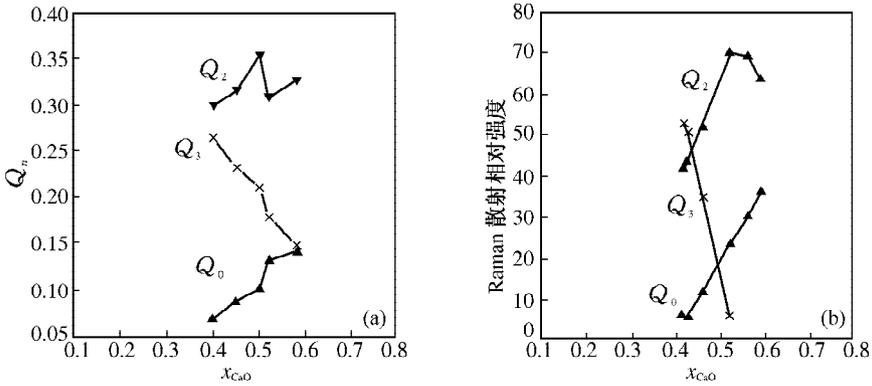


图2 分子动力学计算  $Q_n$  的结果(a)及 Raman 光谱实验所测得  $Q_n$  的结果(b)

义为

$$\Gamma(\omega) = \frac{C(\omega)}{n(\omega) + 1},$$

这里的  $C(\omega)$  是  $C_j(t)$  的 Fourier 变换，

$$C(\omega) = \int \sum_{j=1}^3 \exp(-i\omega t) \cdot C_j(t) \cdot dt$$

$j = 1, 2, 3$  表示 Ca、Si、O 等三种离子。 $n(\omega)$  称为 vibrational occupation number，是一种经典的分布，

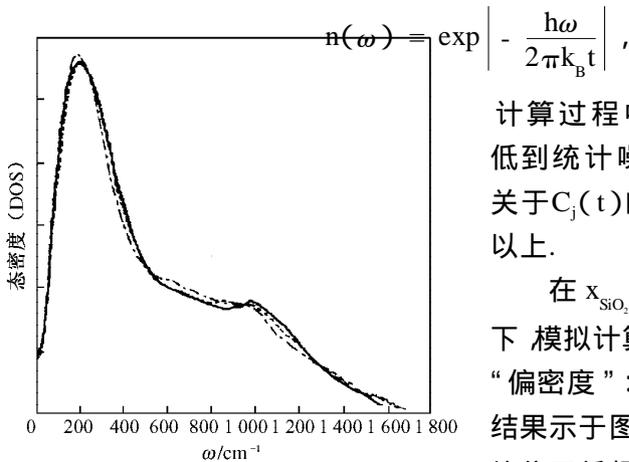


图3 振动态密度

— 示  $x_{\text{SiO}_2} = 42\%$ ，--- 示  $x_{\text{SiO}_2} = 50\%$ ，  
- · - 示  $x_{\text{SiO}_2} = 60\%$

计算过程中必须保证  $C_j(t)$  确实降低到统计噪声的水平下，所以本文关于  $C_j(t)$  的计算一直延伸到 0.6 ps 以上。

在  $x_{\text{SiO}_2} = 0.42, 0.50, 0.60$  条件下模拟计算出的  $\Gamma(\omega)$  示于图 3，而“偏密度”： $\Gamma_{\text{Si}}(\omega), \Gamma_{\text{Ca}}(\omega)$  的计算结果示于图 4。可以看到： $\Gamma_{\text{Ca}}(\omega)$  的峰位于低频区，与 IR 谱中  $260 \text{ cm}^{-1}$  处的  $\text{Ca}^{2+}-\text{O}^{2-}$  峰一致，这是由于 Ca—O 之间是离子键。CaO-SiO<sub>2</sub> 的 Raman

光谱图<sup>[5]</sup>中,在 $630\text{ cm}^{-1}$ 处的峰按群论分析认为是 Si—O—Si 键的弯曲振动与伸缩振动共同引起的.而 $800\sim 1\,200\text{ cm}^{-1}$ 处的峰是 Si—O 键伸缩振动的结果.图 4 示出  $\Gamma_{\text{Si}}(\omega)$  在  $636\sim 737\text{ cm}^{-1}$  和  $800\sim 1\,200\text{ cm}^{-1}$  处也有峰呈现,即和 Raman 光谱图也是吻合的.

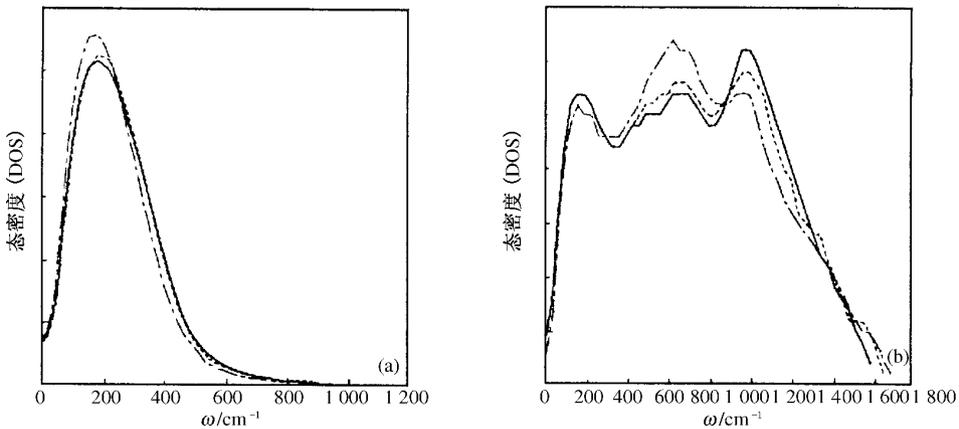


图 4 偏振态密度  $\Gamma_{\text{Ca}}(\omega)$ (a)及偏振态密度  $\Gamma_{\text{Si}}(\omega)$ (b)  
说明同图 3

为了分析 CaO-SiO<sub>2</sub> 熔渣中 Si—O 键的伸缩运动,需要考虑体系的内坐标.因此我们定义键伸缩坐标为  $\delta r_{\text{Si-O}} = r_{\text{Si-O}}(t) - r_0$ ,其中  $r_0$  是平衡的  $r_{\text{Si-O}}$ (t)值.其键伸缩坐标自相关函数可写成

$$C_{\delta r}(t) = \frac{\delta r(t)\delta r(0)}{\delta r(0)\delta r(0)},$$

这种伸缩坐标自相关函数可以反映出相应的键伸缩坐标的振动态密度.在  $x_{\text{SiO}_2} = 0.5$  时,计算了 Si—O 伸缩坐标的自相关函数,并用最大熵方法(MEM)<sup>[6]</sup>估算了键伸缩振动态密度,如图 5 所示.从图中可知,键伸缩振动态密度在  $940\text{ cm}^{-1}$  附近处出现峰值,这与基于速度自相关函数计算的振动态密度相一致.

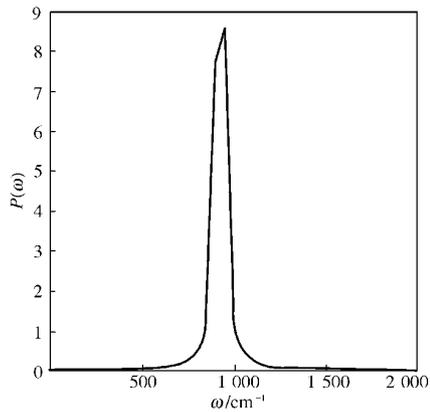


图 5 Si—O 键伸缩振动的自相关函数  $P(\omega)$

### 3 结论

本文表明：在分子动力学模拟计算中采用 BMH 势及表 1 所示的相互作用参数来描述 CaO-SiO<sub>2</sub> 二元系是成功的。在这个简化了离子模型的基础上，模拟计算偏径向分布函数的特征、振动态密度、SiO<sub>4</sub> 四面体中 Q<sub>n</sub> 随组成变化的规律等方面的结果与实测吻合良好。也就是说，在一些二元系中本文所用的 BMH 势及相互作用参数与键合结构相洽；因此进一步由它们算出的体系宏观性质，也就可以和微观结构相洽的了。

但 Si—O 键是极性共价键，预计在分子动力学模拟计算中采用三体势或包括电荷迁移相互作用势将能取得更好的模拟结果。

### 参 考 文 献

- [ 1 ] Chipman J. Physical Chemistry of Process Metallurgy. New York : P I ,1961
- [ 2 ] Woodcock L V , Angell C A , Cheese man C A. Molecular dynamics studies of the vitreous : simply ionic system and sillicate. J Chem Phys. 1976 ,65(4) :1565-1575
- [ 3 ] Kieffer J , Angell C A. Structural incompatibilities and liquid-liquid phase separation in molten binary silicate : a computer simulation. J Chem Phys ,1989 ,90(9) :4982-4991
- [ 4 ] Abramo M C , Caccamo C , Pizzimenti G. Structural properties and medium-rang order calcium-metasilicate ( CaSiO<sub>3</sub> ) glass : a molecular dynamics study. J Chem Phys ,1992 ,96(12) :9083-9091
- [ 5 ] Iguchi Y , Kashio S , Goto T , *et al.* Raman spectroscopy study on the structure of silicate slags. Canadian Metallurgical Quarterly ,1981 ,20(1) :51-56
- [ 6 ] Allen M P , Tildesley D J. Computer Simulation of Liquids. Oxford : Clarendon Press ,1987
- [ 7 ] Okazaki S , Okada I. A simulation approach to vibration dynamics of the OH<sup>-</sup>ion in molten LiOH. J Chem Phys ,1993 ,98(1) :607-615
- [ 8 ] Della Valle R G , Venuti E. A molecular dynamics study of the vibrational properties of silica glass. Chemical Physics ,1994 ,179 :411-419
- [ 9 ] Waseda Y , Toguri T M. Material Science of the Earths Interior. Tokyo : Sci Pub Company ,1989 ,Chapter 1
- [ 10 ] Matsumiya T , Nogami A , Fukuda Y. Applicability of molecular dynamics to analyses of

refining slags. In :4th International Conference on Molten Slags and Fluxes , Sendai Japan , ISIJ , 1992 , 115-120

# A Sub-regular Solution Model for MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO Molten Slag and Its Applications<sup>\* 1</sup>

**Abstract** A high order sub-regular solution model for predicting the component activities in a homogeneous region of a quaternary system was developed in the Shanghai Enhanced Lab of Ferrometallurgy, which is designated as SELF-SReM4.

SELF-SReM4 is composed of some polynomials of excess mole free energies vs content variable. A group of  $A_{jkl}$  parameters is included in the polynomials. Along with the reliable known thermodynamic properties associating the homogeneous region the  $A_{jkl}$  parameters can be evaluated. And then the component activities in that region are possible to be predicated.

This paper is devoted to illustrate the applications of SELF-SReM4 for molten slag of MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO. The results provide a basis for the optimization of the production of MnSi and the inclusion modification.

## 1 Introduction

It is emphasized that SELF-SReM4 is applicable to evaluate the thermodynamic properties of a homogeneous region of a random quaternary systems. As the matter of fact, in SELF, besides C-Fe based alloys an analysis of some Si alloys were involved<sup>[1]</sup>. The purpose of the present paper is to predict the component activities in the liquid region of the molten slag MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-

---

\* In collaboration with Zhang Xiao Bing, Jiang Guo Chang. Reprinted from 5th Int. Conf. on Molten Slags, Fluxes & Salts, Sydney, Australia, Jan. 5-8, 1997, pp. 259-262

CaO<sup>[2]</sup> , and then to optimize some associated processes.

Certainly , SELF-SReM4 should be attributed to the category of thermodynamics parameter model. It does not concern with the bond structure of the slag , does not intend to link up its macroscopic properties with the features of its micro-structure. So , SELF-SReM cannot be used to substitute for the bond structure model of molten slag being developed in SELF. On the contrary , it can provide series comparison to the later.

## 2 The prediction of component activities by means of SELF-SReM4

Take 1 , 2 , 3 , 4 to denote MnO , SiO<sub>2</sub> , Al<sub>2</sub>O<sub>3</sub> , CaO respectively. The final form of SELF-SReM4 is as follows :

$$f_1 = \sum_2^j \sum_0^k \sum_0^l A_{jkl} Y^j Z^k T^l \quad (1)$$

$$f_2 = - \sum_2^j A_{j00} / (1 - j) + \sum_2^j \sum_0^k \sum_0^l A_{jkl} Y^j Z^k T^l \{1 + [(j - k) / Y(1 - j)]\} \quad (2)$$

$$f_3 = - \sum_2^j \sum_0^k A_{jk0} / (1 - j) + \sum_2^j \sum_0^k \sum_0^l A_{jkl} Y^j Z^k T^l \{1 + [(j - k) / Y(1 - j)] + [(k - 1) / YZ(1 - j)]\} \quad (3)$$

$$f_4 = - \sum_2^j \sum_0^k \sum_0^l A_{jkl} Y / (1 - j) - \sum_2^j \sum_0^k \sum_0^l A_{jkl} Y^j Z^k T^l \{1 + [(j - k) / Y(1 - j)] + [(k - 1) / YZ(1 - j)] + [1 / YZT(1 - j)]\} \quad (4)$$

$$f = - \sum_2^j A_{j00} Y / (1 - j) - \sum_2^j \sum_1^k A_{jk0} YZ / (1 - j) - \sum_2^j \sum_1^k \sum_1^l A_{jkl} YZT / (1 - j) + \sum_2^j \sum_0^k \sum_0^l A_{jkl} Y^j Z^k T^l / (1 - j) \quad (5)$$

$f_i$  is the partial molar free energy of the component  $i$  , and is the integral molar

free energy of the quaternary system. The  $A_{jkl}$  involved in these equations are parameters which should be evaluated based on the known boundary conditions.  $j' + k' + l'$  is the order of the sub-regular solution. In this paper,  $j'$ ,  $k'$ ,  $l'$  all are taken to be 4.  $X_i$  is the molar fraction of the  $i$  component, and  $Y, Z, T$  are the variables of the molar fractions.

$$Y = 1 - X_1 \quad (6)$$

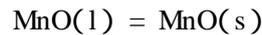
$$Z = 1 - (X_2/Y) \quad (7)$$

$$T = 1 - (X_3/YZ) \quad (8)$$

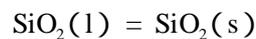
If the standard of the activity of the component  $i$  is taken as its pure solid state, then

$$\alpha_i = X_i \exp[(f_i - \Delta G_i^0)/RT] \quad (9)$$

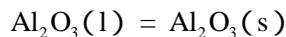
$X$  is the mole fraction.  $\Delta G_i^0$  is the free energy during the state transferring from liquid to solid. The values suggested by ISIJ<sup>[3]</sup> was adopted in this paper as follows.



$$\Delta G_1^0 = - 52\,752 + 25.67T \quad (\text{J}) \quad (10)$$



$$\Delta G_2^0 = - 10\,868 + 5.55T \quad (\text{J}) \quad (11)$$



$$\Delta G_3^0 = - 124\,882 + 53.63T \quad (\text{J}) \quad (12)$$



$$\Delta G_4^0 = - 99\,066 + 27.63T \quad (\text{J}) \quad (13)$$

Table 1 lists the adopted boundary properties for the evaluation in MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO.

**Table 1 The used boundary conditions in MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO**

Boundary	Information	Ref.
MnO-SiO <sub>2</sub>	$a_{(MnO)}(1\ 923\ K)$	4
MnO-Al <sub>2</sub> O <sub>3</sub>	$a_{(MnO)}(1\ 923\ K)$	5
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	$a_{(Al_2O_3)}(1\ 923\ K)$	6
SiO <sub>2</sub> -CaO	$a_{(SiO_2)}(1\ 873\ K)$	7
Al <sub>2</sub> O <sub>3</sub> -CaO	$a_{(CaO)}(1\ 773\ K)$	8
MnO-SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	$a_{(MnO)}(1\ 923\ K)$	6
MnO-SiO <sub>2</sub> -CaO	$a_{(MnO)}(1\ 923\ K)$	9
MnO-Al <sub>2</sub> O <sub>3</sub> -CaO	$a_{(MnO)}(1\ 923\ K)$	9
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -CaO	$a_{(SiO_2)}(1\ 873\ K)$	7
MnO-SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -CaO	$a_{(MnO)}(1\ 923\ K, 1\ 773\ K)$	9 10

The evaluated  $A_{jkl}$  parameters of the liquid region of MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO under 1 873 K in Table 2. The total of  $A_{jkl}$  parameters is 55.

**Table 2 The  $A_{jkl}$  parameters of MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO**

<i>j</i>	<i>k</i>	1 = 0	1 = 1	1 = 2	1 = 3	1 = 4
	0	20 364.18	0	0	0	0
	1	51 407.31	- 1 512 478	53 486.7	2 374 882	- 964 271.4
2	2	- 312 982.2	7 932 143	- 4 701 225	- 4 136 081	1 277 958
	3	604 647.7	- 12 416 530	10 802 550	- 498 074.1	1 137 433
	4	- 330 015.9	5 948 135	- 5 991 563	1 788 065	- 1 091 908
	0	- 155 654	0	0	0	0
	1	- 154 730	11 904 010	- 14 831 350	3 753 345	- 462 286
3	2	1 207 316	- 44 265 340	41 896 160	4 337 970	- 2 895 840
	3	- 2 297 821	61 696 790	- 56 723 820	- 2 520 007	0
	4	1 179 604	- 28 243 810	26 295 560	0	0

(cont d)

$j$	$k$	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$
	0	151 995.1	0	0	0	0
	1	96 188.2	- 13 304 270	22 119 150	- 12 790 780	3 601 156
4	2	- 894 208.3	42 869 880	- 48 971 320	6 432 668	0
	3	1 645 870	- 55 915 010	55 255 200	0	0
	4	- 775 411.4	24 992 650	- 24 240 480	0	0

Fig. 1 is the curves of  $a_1$ ,  $a_2$  and  $a_4$  under the restriction of 1 873 K and  $X_{Al_2O_3} = 0.1, 0.25$ .

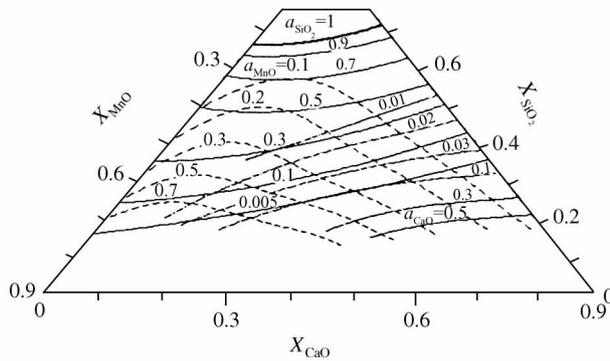


Fig. 1a Activities of components in MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO at 1 873 K and  $X_{Al_2O_3} = 0.1$

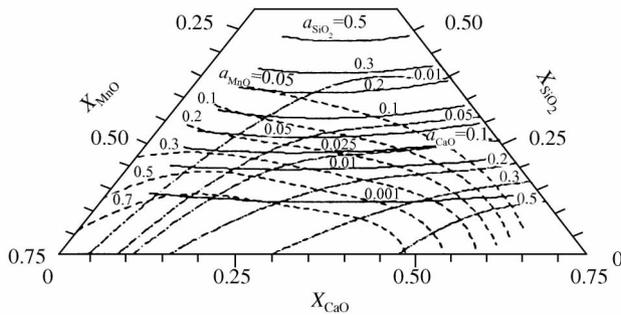


Fig. 1b Activities of components in MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO at 1 873 K and  $X_{Al_2O_3} = 0.25$

### 3 The comparison of the predicted equilibrium state with that of the experiment

The apparent equilibrium constant is

$$K_c = \frac{X_{MnO}^2 X_{Si}}{X_{SiO_2} X_{Mn}^2} \quad (14)$$

$$\ln(K_c \cdot \Gamma) = \exp(-\Delta G_{SiMn}^0 / RT) \quad (15)$$

$$\Gamma = \gamma_{MnO}^2 \gamma_{Si} / \gamma_{SiO_2} \gamma_{MnO}^2 \quad (16)$$

The  $\gamma_{Si}$  and  $\gamma_{Mn}$  were calculated based on SELF-SReM4<sup>[11]</sup>, the standard state of them was taken as the pure liquid. Here,  $\Delta G_{SiMn}^0$  denotes the standard free energy of the following reaction,

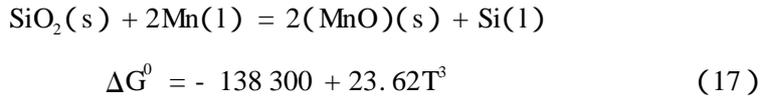


Fig. 2 indicates that  $K_c$  observed by Ding (1 823 K)<sup>[12]</sup> and Turkdogan (1 673 K)<sup>[13]</sup> is in a reasonable agreement with that calculated by this model. Moreover, Fig. 3 displays three groups of equilibrium curves, for a comparison under three different temperature of 1 723, 1 773, 1 823 K and three various [% Si] as 1, 3, 10. Every point on these curves represents the value of a [% Mn] for a given temperature and a given [% Si]. Especially, the case of 10% [Si] and 1 823 K leads to a clearly evident that the curve resulted from SELF-SReM4 and the experimental curve of Ding are almost overlap each other.

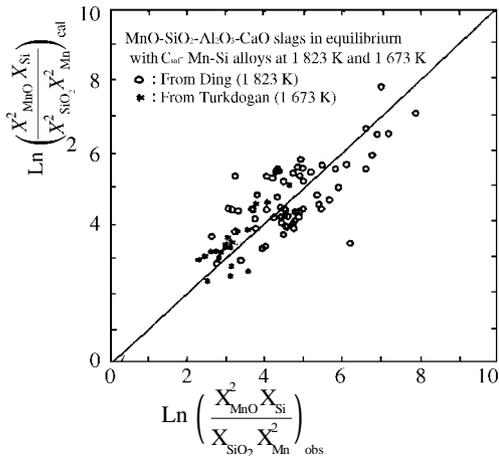


Fig. 2 Comparison of calculated and observed  $\frac{X_{MnO} X_{Si}}{X_{SiO_2} X_{Mn}^2}$  in equilibrium at 1 823 K

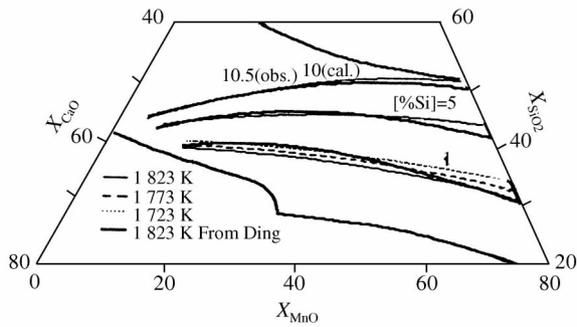


Fig. 3 Equilibrium relations in MnO-SiO<sub>2</sub>-CaO slags in contact with C<sub>Sat</sub>-Mn-Si alloys

#### 4 The prediction of inclusion modification by means of SELF-SReM4

The modification of inclusions is a key problem in the production of so called clean steel. An investigation on this kind of topic concerns with the variation of inclusions during steel solidification. Arising from the vital difficulty of sampling during steel solidification process, the estimation as shown by Key and Jiang<sup>[14]</sup>, Morales<sup>[15]</sup>, and this paper are quite significant for correct modification of inclusions.

Fig. 4 is an estimation for the deoxidization by means of Al-Si-Mn. It indi-

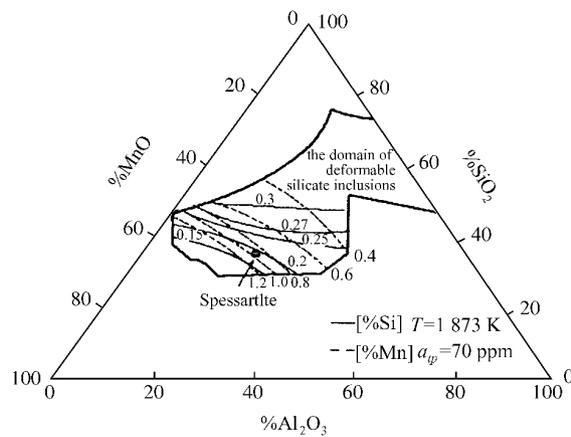


Fig. 4 Iso-content lines of silicon and manganese for MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> for Al-Si-Mn killed steel at a<sub>[O]</sub> = 70 ppm

cates the composition of deoxidization products for various [ % Si ] in the case of  $a_{\text{O}} = 70 \cdot 10^{-4} \%$  and under 1 873 K. The  $a_{\text{Al}}$ ,  $a_{\text{Si}}$ ,  $a_{\text{Mn}}$ ,  $a_{\text{O}}$  were calculated along with the frequently used method of interaction coefficient. The standard of them was taken as 1% dilute solution. The slag component activities were calculated based on SELF-SREm4.

Usually the compound of  $3 \text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  is thought to be the most suitable inclusion. Fig. 5 exhibits the region of [ % Mn ] / [ % Si ] corresponding to the formation of this kind compound under various temperatures and oxygen potentials.

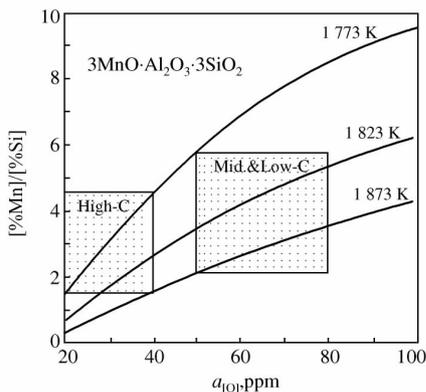


Fig. 5 Effect of  $a_{[\text{O}]}$  and temperature on the orital [ % Mn ] / [ % Si ] to spessartite

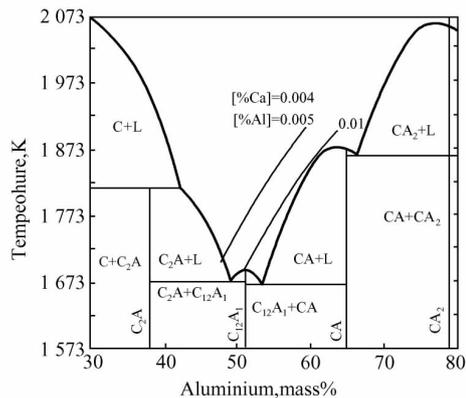


Fig. 6 Effect of temperature on the equilibria for  $\text{CaO}-\text{Al}_2\text{O}_3$  system with Fe-O-Ca-Al

The purpose of calcium treatment is to eliminate  $\text{Al}_2\text{O}_3$ . Fig. 6 resulted from the similar way as that used for Fig. 4 and 5 expresses the variation of the composition of the treated product vs. the temperature in the cases of different [ % Al ] and [ % Ca ]. If it is necessary to acquire a product of  $(12 \text{CaO}_7 \cdot \text{Al}_2\text{O}_3)$  under quite lower temperature, then the [ % Al ] and [ % Ca ] should be controlled according to the curve “4”.

For the service performance of bearing steel, the spherical inclusions mainly composed of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and CaO are most harmful. Fig. 7 indicates the steel composition associating the composition of the inclusion.

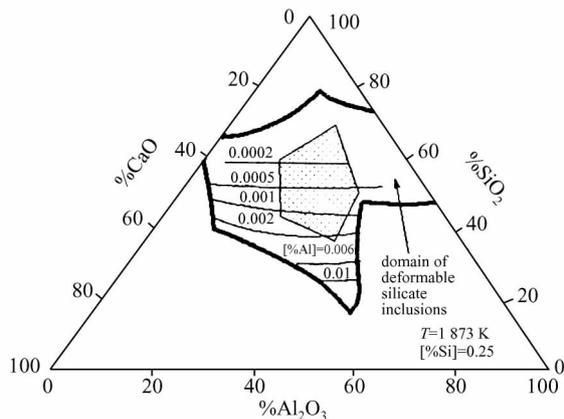


Fig. 7 Iso-activities of aluminium in the composition domains of "deformable" silicate inclusions for Si-Mn killed steels with aluminium at 1873 K

## 5 Discussion and conclusion

- (1) The application of SELF-SReM4 to the prediction of slag is possible. Comparing the use for alloy, the choose of boundary conditions are more difficult. On the other hand, inside the homogeneous space there are more available information, though the better to check their accuracy before use it.
- (2) Inside the polynary slag, where are the boundaries separating liquid and solid, this is a significant research task. By the application of SELF-SReM4 to the homogeneous liquid region and solid region respectively seems to be an interesting approach to solve the mentioned task.
- (3) The optimization of the production of MnSi and the modification of inclusions can be successful based on SELF-SReM4.

## References

- [ 1 ] Tang kai, Xu Jianlun, Jiang Guochang, Huan Heanyu, "Analytical Evaluation of Component Activities of Ca-Si-Al System", *Rare Metals*, 19 (1995) 137-143

- [ 2 ] Zhang Xiao Bing , Jiang Guo Chang , Tang Kai , Xu Jian Lun , Ding Wei Zhong , Xu Kuang Di , “ A Sub-Regular Solution Model Used to Predict the Component Activities of Quaternary Systems ” , to be published
- [ 3 ] S. Ban-Ya , M. Hino , “ Chemical Properties of Molten Slags ” , ISIJ , (1991 ) 17-21
- [ 4 ] K. P. Abraham , M. W. Davies , F. D. Richardson , “ Activities of Manganese Oxide in Silicate Melts ” , JISI , 9 (1960) 82-89
- [ 5 ] R. A. Sharma , F. D. Richardson , “ Activities of Manganese Oxide , Sulfide Capacities , and Activity Coefficients in Silicate Melts ” , Trans. AIME , August (1965) 586-1592
- [ 6 ] S. H. Risbud , J. A. Pask , “ Calculate Thermodynamics Data and Metastable Immiscibility in the System  $\text{SiO}_2\text{-Al}_2\text{O}_3$  ” , J. Am. Ceramic Society , 60 (1977) 418-424
- [ 7 ] R. H. Rein , J. Chipman , “ Activities in the Liquid Solution  $\text{SiO}_2\text{-CaO-MgO-Al}_2\text{O}_3$  at 1 , 600°C ” , Trans. AIME , February (1965) 415-425
- [ 8 ] R. A. Sharma , F. D. Richardson , “ Activities in Lime-Alumina Melts ” , JISI , August (1961) 386-390
- [ 9 ] S. R. Mehta , F. D. Richardson , “ Activities of Manganese Oxide and Mixing Relationships in Silicate and Aluminate Melts ” , JISI , May (1965) 524-528
- [10] G. F. Warren , P. R. Jochens , D. D. Howat , “ Liquidus Temperatures and the Activities of Manganese( II ) Oxide in Slags Associated with the Production of High-carbon Ferromanganese Alloys ” , INFACON , 1 (1974) 175-185
- [11] Zhang Xiao Bing , Jiang Guo Chang , Ding Wei Zhong , Xu Kuang Di , “ The Application of the Model named as SELF-SReM4 to the Optimization of the Production of FeMn and MnSi , II . The prediction of the component activities of  $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$  ” , to be published
- [12] Ding Wei Zhong , Ph. D Thesis , Trondheim University , Norway , 1993
- [13] E. T. Tuekdogan , R. A. Hancock , “ Equilibrium Measurement between Carbon-Saturated Mn-Fe-Si Melts and  $\text{CaO-Al}_2\text{O}_3\text{-MnO-SiO}_2$  Slags ” , Trans. Inst. Min. Met. , 67 (1957) 573-600
- [14] D. A. R. Key and Jiang Jumpu , “ Slag model and inclusion engineering in steelmaking ” , 3rd Int. Conf. on Molten Slag and Fluxes , University of Strathclyde , Glasgow , (1988) 263-269
- [15] R. D. Moeales & E. R. Martinez , “ Discussion on Formation of Non-Metallic Inclusions During Continuous Casting of High Carbon Billets ” , Proc. of the Sixth Int. Iron and Steel Congress , Nagoya , ISIJ. , (1990) 209-216

# In-Situ Composite Conductor of High Strength<sup>\* 1</sup>

**Abstract** The directional solidification of Cu-0.8 wt. % Cr alloy was investigated for high-strength conductors. An in-situ composite material was produced in which the matrix had a cellular morphology and well-distributed eutectic was formed around the cells in the directional solidification process. In such a microstructure, the cellular matrix is a conductor and the eutectics serve the function of reinforcement. As a result, the tensile strength of this in-situ composite is more than two times that of the ordinarily cast one. In this paper, the effects of various processing parameters on the primary arm spacing and the interface morphological instability were also discussed.

## 1 Introduction

Owing to its excellent conductivity, copper has been used widely in the production of varied electric conductors. Unfortunately, its low strength has limited its further uses in the fields that require not only high conductivity but also high strength, so, to improve both simultaneously is always of interest to researchers of this material. With respect to the strengthening mechanism, the researches may be divided into three groups: 1) Alloying<sup>[1]</sup>. The strengthening mechanism is either through solid-solution and/or aging. The alloying elements include Sn, Cd, Cr, Zr, etc. in small amounts in some combination; 2) Dis-

---

\* In collaboration with H. Q. Wen, X. M. Mao, Z. H. Pan, F. P. Qi and Q. Hua.  
Reprinted from Proc. 4th Decennial Int. Conf. on Solidification Processing, Sheffield, U.K. 7-10 July, 1997, pp. 657-659

person Strengthening<sup>[1]</sup>. The dispersed particles are high strength oxides such as  $ZrO_2$ ,  $Al_2O_3$ ,  $MgO$ ; 3) Synthetic Composite<sup>[2-4]</sup>. Here, the copper is reinforced effectively by bands or fibers of X (Ta, Nb, Cr). The strength of these synthetic composites may be up to 1 400 MPa, far beyond that of the first two methods. Research on Cu-X composites has focused on high strength conductors. However, the room temperature conductivity of these composites is often reduced greatly by a large number of deformation defects formed in their manufacture. In view of this, directional solidification may be the best way to utilize the strengthening effect of the second phase and so avoid these deformation defects in synthetic composites, since the strengthening phase is formed "automatically" or "in situ" during the directional solidification process. Moreover, other problems such as interface contamination and reactions in synthetic composites no longer exist in this directionally solidified material. This paper represents the feasibility of using directional solidification to produce an in-situ composite conductor of high strength.

## 2 Experimental Procedure

The binary Cu-Cr alloy containing 0.8 wt. % Cr was used in the experiments. This was melted from copper with a purity of 99.99 wt. % and chromium powder with a purity of 99.95 wt. % in a medium frequency induction furnace. The samples, 6 mm in diameter and 150 mm in length, were made by investment casting.

The experimental apparatus is shown schematically as Fig. 1. The radio-frequency

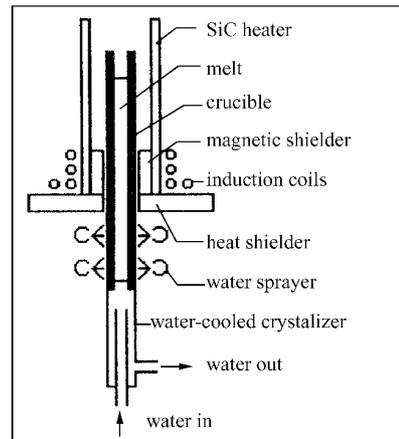


Fig. 1 Schematic diagram of the directional solidification apparatus

induction heating aims to increase the temperature of the high-temperature zone in the chamber so that the sample can be melted and superheated sufficiently before directionally solidifying. When operating, the sample in the crucible was situated on top of the water-cooled base. The furnace temperature was held at 1 250°C for 10 minutes before the water-cooled base was withdrawn and direc-

tional solidification was initiated. Solid/liquid morphologies were quenched by water within the water sprayer. The directionally-solidified specimens were etched by a solution of ferric nitrate in ethanol and photomicrographed in a Herlach microscope.

### 3 Results and Discussion

#### 3.1 Solidification Characteristics

For the eutectic or even off-eutectic alloys, as we know, the crystals of two phases can grow in a cooperative way in the coupled zone. Out of this zone, primary dendrites will appear in the microstructure<sup>[5]</sup>. When the temperature gradient in front of the S/L interface,  $G_L$ , is  $60^\circ\text{C}/\text{cm}$ , and the growth rate,  $V$ , is  $0.4\text{ mm}/\text{min}$ , the directionally-solidified microstructure of the Cu-0.8 wt. % Cr alloy is as in Fig. 2.

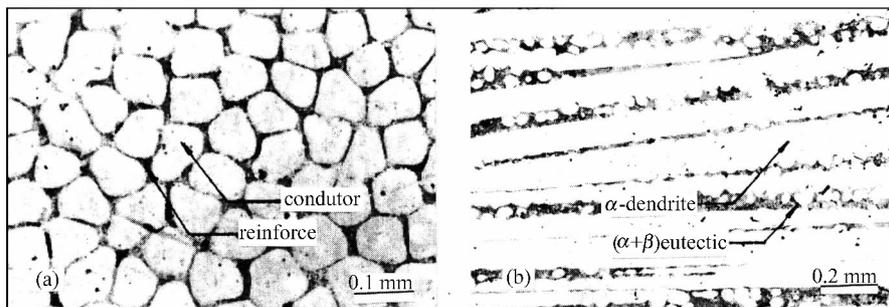


Fig. 2 Directionally solidified microstructure of the Cu-Cr Alloy ( $G_L = 60^\circ\text{C}/\text{cm}$ ,  $V = 4\text{ mm}/\text{min}$ ,  $C_0 = 0.8\text{ wt. \%}$ ): (a) longitudinal section, (b) transverse section

Fig. 2 shows that the microstructure presents a mixture of the  $\alpha(\text{Cu}) + \beta(\text{Cr})$  eutectic and primary, and that the latter may be cellular or dendritic in morphology. Of course, a primary cellular  $\alpha$  morphology is desired in terms of conductivity, since there are no electrical discontinuities as would be the case at dendritic branches. The material is also reinforced effectively by the high-strength eutectic containing a large amount of chromium. As shown in Fig. 2 (b), the eutectic is well distributed around the cells. This forms an in-situ composite material in which the cellular morphology acts as conductor and the well-

distributed eutectic around the cells serves as a reinforcement. In this sense , such a structure is similar to that of the copper-steel composite cable in railway transmission , where the steel core acts as the reinforcement and the copper coated outside as the main conductor.

### 3.2 Primary Arm Spacing

The primary arm spacing of dendritic or cellular crystals ,  $\lambda_1$  , has an important effect on the properties of directionally solidified material. Different models for the prediction of primary arm spacing are given by Hunt<sup>[6]</sup> and by Kurz and Fisher (K-F)<sup>[7]</sup> :

$$\text{Hunt : } \lambda_1 = 2\sqrt{2}(T_m \Gamma D_L)^{\frac{1}{2}} G_L^{-\frac{1}{2}} V^{-\frac{1}{2}} \left[ mC_0(k_0 - 1) - \frac{k_0 G_L D_L}{V} \right]^{\frac{1}{2}} \quad (V < 2V_{CS})$$

$$\text{K-F : } \lambda_1 = \left[ \frac{6\Delta T'}{G_L(1 - k_0)} \left( \frac{D_L}{V} - \frac{\Delta T_0 k_0}{G_L} \right) \right]^{\frac{1}{2}} \quad (V < V_{CS}/k_0)$$

Hunt's result shows that  $\lambda_1$  increases initially and then decreases with increase of  $V$  , with the critical point at  $V_{CS}$ . In contrast , the K-F relationship shows a monotonic decrease in  $\lambda_1$  with increase in  $V$ .

In the Cu-Cr alloy , the experimental results for  $\lambda_1$  versus  $V$  are shown in Fig. 3(a) and 3(b). When  $G_L = 30$  /cm and  $V = 0.2$  mm/min ,  $\lambda_1 \approx 0.1$  mm , and when  $G_L = 30$  /cm and  $V = 2$  mm/min ,  $\lambda_1 \approx 0.2$  mm. From these results , we can draw a conclusion that  $\lambda_1$  increases with increase of  $V$  , which is not consistent with the K-F model but is with the Hunt model. Therefore , a good microstructure with higher conductivity may be obtained with a high growth velocity. The higher velocity will result in cellular  $\alpha$  of increased  $\lambda_1$  which possesses the higher conductivity.

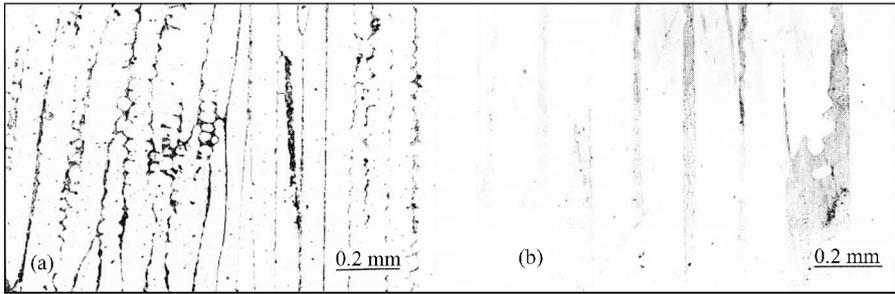


Fig. 3 Response of the primary arm spacing to velocity in a Cu-Cr alloy (  $G_L = 30$  /cm ,  $C_0 = 0.8$  wt% ) : (a)  $V = 0.2$  mm/min , (b)  $V = 2$  mm/min

### 3.3 Solid/Liquid Interface

The solid/liquid interface morphology plays an important role in the formation of the directionally solidified microstructure. Only when the interface is planar and stable can a lamellar or rod eutectic microstructure be formed during directional solidification. Otherwise , cellular or even dendritic crystals may occur. The stability criterion for a planar interface is<sup>[8]</sup> :

$$\frac{G_L}{V} \geq \frac{mC_0(k_0 - 1)}{k_0D_L} \quad (1)$$

i. e. , a planar interface is maintained when  $G_L/V$  is greater than or equal to that of the right-hand side in equation (1). In this paper , the S/L interface morphologies of the Cu-0.8 wt. % Cr alloy are shown in Fig. 4 , where  $G_L$  is equal to  $60^\circ\text{C}/\text{cm}$  , and  $V$  is equal to  $0.2$  mm/min. The coexistence of two interfaces under the same growth condition may result from disturbances in the directional solidification. Despite that , the effect of interface morphology on eutectic microstructure can be analysed. In Fig. 4(a) , the interface is cellular or near-planar , the primary crystals grow forward with a regularly cellular shape with the eutectic at their periphery. When the interface loses its stability and becomes a coarse one , the phases grow irregularly as shown in Fig. 4(b).

Therefore , as discussed in section 3.2 , maintenance of a cellular interface during directional solidification is essential for formation of an in-situ composite conductor of high strength. Theoretically , this cellular interface can be obtained by either increasing  $G_L$  at constant  $V$  or decreasing  $V$  at constant  $G_L$ . Of course ,

the latter is less useful in the production of the conductor.

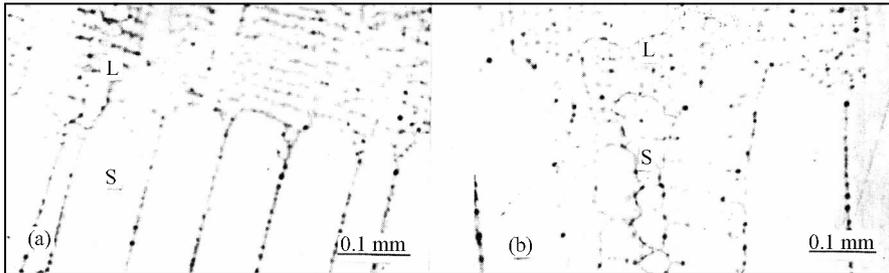


Fig. 4 S/L interface morphologies of the Cu-Cr alloy ( $G_L = 60 \text{ /cm}$ ,  $V = 0.2 \text{ mm/min}$ ,  $C_0 = 0.8 \text{ wt. \%}$ ): (a) cellular interface, (b) coarse interface

## 4 Conclusions

An in-situ composite of Cu-Cr alloy for use as a highstrength conductor was prepared by directional solidification. With  $G_L = 60 \text{ /cm}$ ,  $V = 4 \text{ mm/min}$ , and  $C_0 = 0.8 \text{ wt. \%}$ , the typical microstructure of this composite was a mixture of cellular primary  $\alpha$  with intercellular  $[\alpha(\text{Cu}) + \beta(\text{Cr})]$  eutectic. The former acts as a conductor and the latter serves the function of a reinforcement. The tensile strength of this in-situ composite is about 500 MPa, which is more than twice that of the ordinarily cast one. In this directionally-solidified microstructure, the primary arm spacing increases with increase of the growth rate, which is consistent with the Hunt model. Finally, it is also pointed out that the maintenance of a cellular interface during directional solidification is essential to the formation of an in-situ composite conductor of high strength.

## Acknowledgements

The authors wish to thank the Xiamen Institute of Railway Science and Technology, Xiamen, China, for financial support. Sincere thanks also go to researcher Wenbo Ye for useful discussion, Xiamen Institute of Railway Science and Technology, and to engineers Xieguo Mao and Ming Lei of Shibe and Shangdai Hi-Tech Park, Shanghai, for their help in the experiments.

## Appendix

- $\lambda_1$  primary dendrite/cell spacing  
 $T_m$  melting temperature  
 $\Gamma$  Gibbs-Thomson coefficient  
 $D_L$  solute diffusion coefficient in the liquid  
 $G_L$  temperature gradient  
 $V$  growth velocity  
 $m$  liquidus slope  
 $C_0$  composition  
 $k_0$  solute equilibrium distribution coefficient  
 $V_{CS}$  critical stability velocity  
 $\Delta T$  temperature difference in solid between the tip and the root of the dendrite  
 $\Delta T_0$  temperature range of equilibrium crystallization

## References

- [ 1 ] Z. D. Zhao ,L. G. Yao ,H. Y. Guo ,R. Q. Peng and G. Wu ,Copper and Its Alloys ,  
Material Handbook , Science Press , Beijing , 1993 , ch. 3  
[ 2 ] J. D. Verhoeven ,W. A. Spitzig ,L. L. Jones ,H. L. Downing ,C. L. Trybus ,E.  
D. Gibson ,L. S. Chumbley ,L. G. Fritzmeier and G. D. Schnittgrund ,J Mater Eng ,  
1990 , 2 , 127-139  
[ 3 ] D. A Hardwich ,R. G Phodes and L. G. Fritzmeier ,Metall Trans A ,1993 , 1 , 27-34  
[ 4 ] K. R. Anderson ,J. R. Groza ,R. L. Dreshfield and D. Ellis ,Metall and Mater Trans  
A ,1995 , 9 , 1197-2206  
[ 5 ] W. Kurz and D. J. Fisher ,Int Metals Rev ,1979 , 5-6 , 177-204  
[ 6 ] J. D. Hunt , in : The Solidification and Casting of Metals , The Metals Society , Book  
192 , London , 1979 , p. 3  
[ 7 ] W. Kurz and D. J. Fisher ,Acta Metall ,1981 , 29 , 11  
[ 8 ] W. Tiller ,K. A. Jackson ,J. W. Rutter and B. Chalmers ,Acta Metall ,1953 , 1 , 428

# Anisotropy of Electric Conductivity in Single Crystal<sup>\* 1</sup>

**Abstract** The electric conductivity in single crystal of the Cu-0.1 atm. % Cr alloy was investigated with the two probe spreading resistance method. An anisotropy contrary to that of the eutectic composites is shown in the conductivity, i. e., the conductivity along the growth direction is less than that in the transverse direction, while, the spreading resistance measured in the 45° orientation shows that the transition in conductivity from the longitudinal direction to the transverse direction is not linear. Moreover, the anisotropic degree is increased by the heat treatment at 350°C for 1 hour. All of these characteristics related closely to the solidification process of the single crystal were discussed in the paper.

## Introduction

As an effective method of the microstructure controlling for castings, the directional solidification technology has been used broadly in the production of anisotropic materials, such as the single crystal, columnar crystal and in-situ composite<sup>[1]</sup>. These materials are of great importance in manufacturing the high-temperature castings as well as many functional devices<sup>[2]</sup>. Therefore, concerns of a foundry-man should be paid not only to the mechanical properties but also to the physical properties. In this paper, the two-probe method, developed for

---

\* In collaboration with Wen Hongquan, Mao Xiemin. Reprinted from Proc. 5th Asian Foundry Congress Sep. 23-25, 1997, Nanjing, China (publ. by Southeast University Press, Changsha, Hunan), pp. 397-400

measuring the electric conductivity of semiconductor materials<sup>[3~5]</sup>, was employed to investigate the electrical property of conductive single crystal, which may help recognising the conduction characteristics of solid solution and using the spreading resistance method in the field of conductors.

## Principle and Method of Measurement

Two-probe method is a spreading resistivity measuring technology with high spatial resolution, which obtains the resistivity through characteristics at the original point of current-voltage curve in the contact area between probe and specimen. Since the effectively contact radius of the probe is of micron magnitude, this method can reflect the change of resistivity within a space of  $10^{-16} \text{ m}^3$ . The

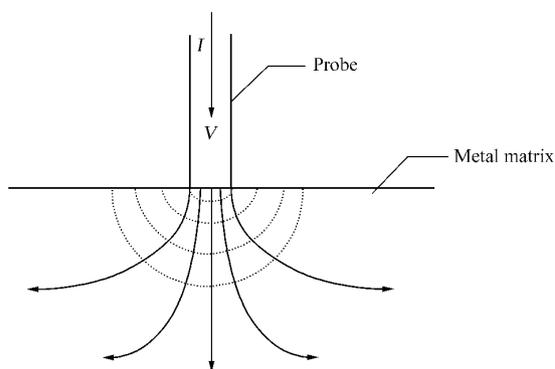


Fig. 1 Schematic representation of the spreading resistance method

scope of measured resistance covers five magnitudes and is not restricted by the structure of sample. The principle of the spreading resistance method is shown schematically in Fig. 1. The spreading resistance,  $R_s$ , is defined by the following equation<sup>[3]</sup>:

$$R_s = \frac{\rho}{4a} = \frac{V}{I} \quad (1)$$

where,  $\rho$  is the resistivity,  $a$  is the contact radius between probe and sample,  $V$  and  $I$  are respectively the voltage and density of the electric current used. In the case of two-probe spreading resistance method, equation (1) can be transformed into

$$R_s = \frac{\rho}{2a} \quad (2)$$

In consideration of the errors in practical measurement, a correction coefficient,  $C$ , is added to equation (2). Then,

$$R_s = C \frac{\rho}{2a} \quad (3)$$

In the experiment, the value of  $C$  was determined through dividing the measured resistivity of pure copper,  $2aR_s$ , by the resistivity of the International Annealed Copper Standard (IACS), i. e.,  $1.72 \times 10^8 \Omega \cdot m$ .  $a$  was treated approximately as to equate the probe radius. Then the resistivity of the Cu-Cr alloy could be calculated from equation (3), in which  $C$  was supposed to remain the same value of pure copper.

The single crystals of the Cu-0.1 atm. % Cr alloy were extracted from the directionally solidified Cu-0.1 atm. % Cr specimens prepared by the Bridgman method, where the temperature gradient is  $60^\circ\text{C}/\text{cm}$  and the growth velocity is  $3.2 \text{ mm}/\text{min}$ . Before measuring the resistance, the samples were annealed in the tube-type resistance furnace under the argon atmospheric protection at  $350^\circ\text{C}$  for 1 hour. The spreading resistance  $R_s$  was determined by the two-probe method respectively along the longitudinal, transverse and  $45^\circ$  orientations compared to the solidification direction, whose measuring distance is  $10 \mu\text{m}$ , and the probe pressure is 10 g. As a comparison, the resistance of non-annealed Cu-0.1 atm. % Cr single crystal was also determined. After all, the resistivities of these samples,  $\rho$ , were calculated from  $R_s$  with the method as indicated above.

## Results and Discussion

### Experimental Results

The electric resistivities of the single crystal of Cu-0.1 atm. % Cr alloy in the conditions of annealing and non-annealing are illustrated in Fig. 2 and Fig. 3. From Fig. 2, it can be seen that the resistivity along the solidification direction is greater than that perpendicular to this direction. In other words, the conductivity is of reversed anisotropy, which is contrary to that of the directionally solidified eutectic materials<sup>[6]</sup>. The resistivity measured in  $45^\circ$  direction suggested that the transition in resistivity from the longitudinal direction to the transverse direction is not linear. Moreover, the degree of the conductivity anisotropy is increased by the annealing treatment at  $350^\circ\text{C}$  for 1 hour when comparing Fig. 2 with Fig.

3.

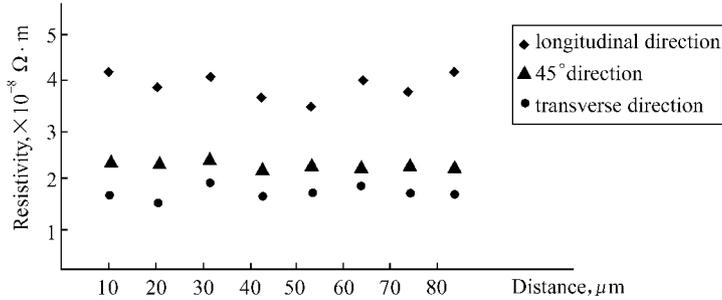


Fig. 2 Spreading resistivity of annealed Cu-0.1 atm. % Cr single crystal

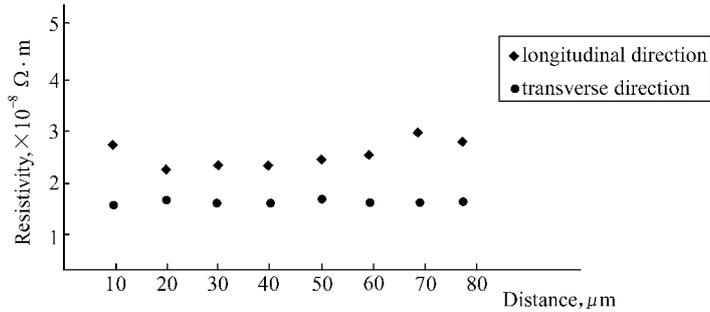


Fig. 3 Spreading resistivity of non-annealed Cu-0.1 atm. % Cr single crystal

## Discussion

From the Bloch model about the electron movement in solid , the conductivity can be represented as<sup>[7]</sup>

$$\sigma_{ij} = e^2 \int_{(\varepsilon_F)} (\tau v_i v_j \rho(\varepsilon))_{\varepsilon_F} ds \quad (4)$$

Here ,  $\sigma_{ij}$  is the conductivity tensor ,  $\varepsilon_F$  is the Fermi energy ,  $\tau$  is the relaxation time ,  $\rho(\varepsilon)$  is the density of electron energy distribution ,  $ds$  is the integral unit on Fermi face. Seen from equation (4) , it is the anisotropy of electron velocity at the Fermi face that causes the anisotropy of the resistivity. Of course , the velocity anisotropy does not imply a direction dependence of the resistivity in real space. This is because of the resistivity determined from an average over all scattering directions ,

which , for example , will thus be isotropic in a cubic system in real space. Despite that , the resistivity anisotropy in real space could be shown for the highly perfect and anisotropic crystal<sup>[7]</sup> , especially when measured by the spreading resistance method which has a high spatial resolution.

As we know , the copper crystal is a fcc structure. During the growth process of the single crystal , the crystal face near solidification interface should be close-packed so that the free energy is the lowest and the interface can be maintained stable. So the face perpendicular to the solidification direction is the close-packed face (111). Therefore , an anisotropic structure is formed with characteristic of that the crystal face perpendicular to the growth direction is close-packed. A few Cr atoms less than 1 atm. % are generally thought to form a dilute replacement solid solution so that the original anisotropic characteristic is remained. Because of the scattering effect of more ionic bodies of the copper and chromium atoms , the free electrons moving along the solidification direction will be scattered much more than that along other directions. So , it is not difficult to understand that the resistivity along the longitudinal direction is greater than that along the transverse direction , which is shown as Fig. 2. In addition , the anisotropy in crystal structure also causes the non-linear transition in conductivity from longitudinal direction to transverse direction.

On the other hand , the incorporation of Cr solute in Cu matrix will result in a large number of crystal defects. According to the maximum entropy principle , these defects caused by solute atoms tend to well-distribute in the copper matrix , which will conceal the anisotropy of electrical conductivity to a certain extent. In the case of annealing treatment , the crystal defects are deleted in some degree , and the original anisotropy of copper single crystal is revealed. So , the anisotropy of resistivity or conductivity is increased by the annealing treatment at 350°C for 1 hour.

## Conclusion

An anisotropy contrary to that of the eutectic composites by directional solidification is shown in the conductivity of single crystal the Cu-0.1 atm. % Cr alloy, i. e., the conductivity along the direction perpendicular to growth direction is greater than that along the parallel direction, and the spreading resistance measured in the 45° orientation suggested that the transition in conductivity from the longitudinal direction to the transverse direction is not linear. Moreover, the anisotropic degree is increased by the heat treatment at 350°C for 1 hour. These characteristics relate closely to the solidification process of the single crystal and thus to the crystal structure.

## Acknowledgements

The resistance measuring work was carried out in the Shanghai Institute of Metallurgy, and the authors would like to express their thanks to Ms Chen Lizhi, Operator in the institute.

## References

- [ 1 ] HU Hanqi, Solidification Principles of Metals, Mechanical Industry Press, Beijing, P. R. China, 1991
- [ 2 ] WEN Shusen, Introduction to Modern Functional Materials, Science Press, 1983
- [ 3 ] Mazur R G, Dickey D H, *J Electrochem Soc*, 1966, 113 :255
- [ 4 ] Schumann P A, Gardner E E, *J Electrochem Soc*, 1969, 116 :87
- [ 5 ] Mazur R G, Gruber G A, *Solid-State Technology*, 1981, 24 :64
- [ 6 ] WANG Yuanwei, XIAO Yirong, *Chin Functional Mater* 1995, 3 :220
- [ 7 ] CAI Boxun, Foundation of Solid Physics. High Education Press, Beijing, 1990

# 钢包精炼渣成分的最优化<sup>\* 1</sup>

**摘要** 本文用正交设计方法对用于钢包精炼的  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-CaF}_2$  渣系成分进行优化,试验表明影响炉渣泡沫稳定性能的因素依次为碱度,  $\text{CaF}_2$ ,  $\text{Al}_2\text{O}_3$  和  $\text{MgO}$  的含量,最佳的精炼渣组成为:  $\text{CaO}$  39.3%,  $\text{SiO}_2$  19.7%,  $\text{Al}_2\text{O}_3$  25%,  $\text{MgO}$  6%,  $\text{CaF}_2$  10% ( $B = 2$ )。

## 0 引言

随着连铸的发展和对高品质钢材需求的增加,二次精炼过程变得越来越重要,钢包炉作为一种重要的炉外精炼设备在生产中得到广泛的应用,使生产成本降低和钢水质量大幅度提高,但同时也有钢包炉耐火材料消耗量过高的问题,有时甚至可占总运行成本的一半以上<sup>[1]</sup>,如何提高炉寿命,成为生产中广为关注的问题。

以往在耐火材料成分优化和钢包炉结构设计上已取得了不少进展,但由于钢包炉耐火材料实际上在近极限状态下工作,故改善钢包炉运行条件的途径是提高耐火材料的使用寿命。

人们注意到电炉采用泡沫渣埋弧操作可使耐火材料损耗大大降低,于是试图在钢包炉中引入泡沫渣操作,但钢包炉采用还原性渣,不具备稳定的气源条件,要造泡沫渣则须引入气体源。德国 Krupp 公司采用在初炼时残留一部分碳,使之在钢包中生成  $\text{CO}$  气体,形成泡沫渣包裹电极<sup>[2]</sup>;德国 SKW 公司在 Trostberg 厂进行了用二酰氨石灰造泡沫渣的试验<sup>[3]</sup>;张鉴等人<sup>[4]</sup>将钢包渣分为精炼渣和发泡渣两部分,其中由氯化盐

\* 本文合作者:郑庆、张晓兵、蒋国昌.原发表于《上海大学学报》(自然科学报)3(增刊),161~164(1997)

和碳酸盐组成的发泡渣在精炼时分批加入,利用其分解所产生的气体形成泡沫渣.在钢包炉中实现泡沫渣埋弧操作后,渣线寿命有明显的提高<sup>[5]</sup>.

以上所列方法,均未在延长气体在渣中的停滞时间方面作研究.钢包炉要达到高效经济运行的目的,须了解渣-金-耐材三者的关系,尤其是精炼渣的成分对于钢水质量和耐材消耗有重要作用,为了形成稳定的泡沫渣,精炼渣除满足常见的冶金条件外,还应具备较好的储存气泡的能力,即气泡在渣中的稳定性高.本文正是从这一角度来进行研究的.

## 1 优化范围的确定

过去,对精炼渣所作的优化只考虑以下性能:(1)隔热;(2)防止钢水氧化;(3)吸附杂质;(4)脱硫;(5)对炉衬的侵蚀力较低.本研究将以此为边界条件对目前常用的CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO-CaF<sub>2</sub>系精炼渣的泡沫性能作优化.优化的边界条件如表1.

表1 优化的边界条件

序号	因素	范围	参考文献
1	$B = \text{CaO}/\text{SiO}_2$	$2.0 \leq B \leq 3.0$	[6, 7]
2	Al <sub>2</sub> O <sub>3</sub> wt %	Al <sub>2</sub> O <sub>3</sub> ≤ 10 或 20 ≤ Al <sub>2</sub> O <sub>3</sub> ≤ 30	[7, 8]
3	MgO wt %	6 ≤ MgO ≤ 12	[7, 9]
4	CaF <sub>2</sub> wt %	CaF <sub>2</sub> ≤ 10	[7, 10]

## 2 试验方法

有关熔渣泡沫性能的试验,以往采用向熔渣中吹气来模拟泡沫渣的形成<sup>[11]</sup>,用最大高度H和泡沫指数Σ衡量泡沫稳定性(后者表征气体在渣中的平均停留时间).本文采用向高温液态渣中喷吹CaCO<sub>3</sub>的方法,试验在管式钼硅炉中进行,X-TV在线观察并录像,试验装置如图1所

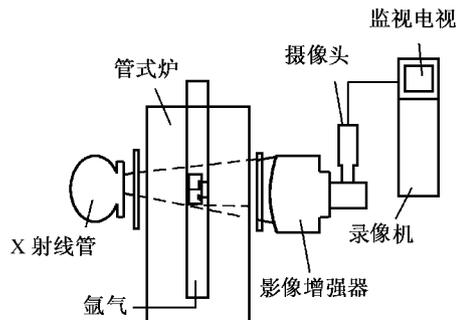


图1 试验装置示意图

法,试验在管式钼硅炉中进行,X-TV在线观察并录像,试验装置如图1所

示.  $\text{CaCO}_3$  由气动控制自动喷吹, 其粒度为 400 目, 质量为 1 g(化学纯), 石墨坩埚内径为 30 mm, 高 80 mm, 所有合成渣都经预熔, 单个渣样重 50 g, 试验温度为  $1550 \pm 2$ , 并采用氩气保护.

### 3 试验方案及优化结果

本试验采取正交试验的方法, 需要优化的参数为碱度  $B$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaF}_2$  共四个因素, 为了保证试验优化结果的可靠性, 各因素取四个水平, 不考虑因素之间的相互作用, 所以, 可用  $L_{16}(4^4)$  正交表, 测定的指标为  $H$  和  $\Sigma$ . 安排试验时作随机化处理以减少偶然误差. 试验的方案及结果如表 2. 为同其他结果(11)相比较, 取泡沫指数  $\Sigma$  作为主因素作分析, 表 3 为  $K_{ij}$ ,  $R_{sj}$  及有关数据, 其中  $K_{ij}$  为第  $j$  列中  $i$  水平的试验指标之和,  $R_{sj}$  为第  $j$  列中各  $k_i$  的极差.

表 2 试验方案及结果

试验号	B(CaO/SiO)	$\text{Al}_2\text{O}_3$	MgO	$\text{CaF}_2$	H(mm)	$\Sigma$ (s)
1	2.0	5	6	4	25	19.2
2	2.0	10	8	6	32	21.5
3	2.0	20	10	8	45	26.0
4	2.0	25	12	10	42	24.5
5	2.5	5	8	8	32	21.0
6	2.5	10	6	10	38	22.1
7	2.5	20	12	4	35	21.7
8	2.5	25	10	6	40	24.0
9	3.0	5	10	10	30	20.8
10	3.0	10	12	8	32	20.7
11	3.0	20	6	6	25	19.0
12	3.0	25	8	4	22	18.5
13	3.5	5	12	6	15	16.7
14	3.5	10	10	4	10	15.7
15	3.5	20	8	8	20	17.0
16	3.5	25	6	10	30	20.5

表 3 试验数据分析结果

$K_{1j}$	$K_{2j}$	$K_{3j}$	$K_{4j}$	$R_{sj}$	$K_{1j}^2$	$K_{2j}^2$	$K_{3j}^2$	$K_{4j}^2$	$\sum_{j=1}^4 K_{ij}^2$
91.2	88.8	79.0	69.9	21.3	8 317.44	7 885.44	6 241.00	4 886.01	27 329.88
77.7	80.0	83.7	87.5	9.8	6 037.29	6 400.00	7 005.69	7 656.25	27 099.23
80.8	78.0	86.5	83.6	8.5	6 528.64	6 084.00	7 482.25	6 988.96	27 083.85
75.1	81.2	84.7	87.9	12.8	5 640.01	6 593.44	7 174.09	7 726.41	27 133.95

离差平方总和  $Q_T = \sum_{j=1}^4 Q_j + Q_E$  ,其中  $Q_T, Q_j, Q_E$  可按下列各式计算:

$$Q_T = \sum_{k=1}^n (x_k - \bar{x})^2 = \sum_{k=1}^n x_k^2 - \frac{1}{n} \left| \sum_{k=1}^n x_k \right|^2 ,$$

$$Q_j = \frac{1}{4} \sum_{i=1}^4 K_{ij}^2 - \frac{1}{16} \left| \sum_{k=1}^{16} x_k \right|^2 \quad (j = 1, 2, 3, 4) ,$$

$$Q_E = Q_T - \sum_{j=1}^4 Q_j ,$$

$$\sum_{k=1}^{16} x_k = 328.9 , \left| \sum_{k=1}^{16} x_k \right|^2 = 108 175.21 ,$$

$$Q_T = 6 882.48 - 108 175.21/16 = 121.53 ,$$

$$Q_1 = 27 329.88/4 - 108 175.21/16 = 71.52 ,$$

$$Q_2 = 13.86 , Q_3 = 10.01 , Q_4 = 22.53 ,$$

$$Q_E = Q_T - Q_1 - Q_2 - Q_3 - Q_4 = 3.61 .$$

上述结果表明,影响泡沫指数的因素中,碱度最为显著,以下依次为  $\text{CaF}_2$  含量和  $\text{MgO}$  含量.从  $K_{ij}$  的排列来看,随着碱度的增大,  $K_{ij}$  减小,而  $\text{CaF}_2$  和  $\text{Al}_2\text{O}_3$  的影响则相反,其中  $\text{CaF}_2$  的影响较  $\text{Al}_2\text{O}_3$  要大,而  $\text{MgO}$  含量改变对  $\Sigma$  的影响不明显.

从以上分析可知,在所确定的优化范围内,为了获得最稳定的泡沫渣,碱度应取 2.0,并且渣的最佳成分为  $\text{CaO}$  39.3%,  $\text{SiO}_2$  19.7%,  $\text{Al}_2\text{O}_3$  25%,  $\text{CaF}_2$  10%,  $\text{MgO}$  6%.

## 4 结论

用于钢包精炼的  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-CaF}_2$  五元系熔渣的泡沫稳定性与其成分有关,其影响因素依次为碱度和  $\text{CaF}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  的含量,而最佳的精炼渣成分为:  $\text{CaO} 39.3\%$ ,  $\text{SiO}_2 19.7\%$ ,  $\text{Al}_2\text{O}_3 25\%$ ,  $\text{MgO} 6\%$ ,  $\text{CaF}_2 10\%$  ( $B = 2.0$ ).

## 参 考 文 献

- [ 1 ] 铃木信雄. 工业加热 LF 法について, (15) : 54
- [ 2 ] Litscher G W. Ladle Metallurgy of Steel for Continuous Casting and Ingot Casting. McMaster Symposium on Iron and Steelmaking, McMaster University, Hamilton, Canada, 1986 : 143
- [ 3 ] Slag Foaming with Diamide. Brief Report. Steel Times, 1988(11) : 55
- [ 4 ] 张鉴. 中国专利, No. 931065992
- [ 5 ] 任正德. 40 t 钢包炉泡沫渣埋弧作业. 特殊钢, 1995(4) : 41-45
- [ 6 ] Schrader D M, Rankovic L L. The Effect of Ladle Furnace Slags on Carbon-bonded Refractories. Iron and Steelmaking, 1988(6) : 23-25
- [ 7 ] Cramb A W, Byrne M. Chemical Interactions in Ladle : Tundish and Mold Slags. Iron and Steelmaking, 1986(5) : 257
- [ 8 ] 藤本英明. 取锅加热精炼法の開発. 铁と钢, 1988(10) : 1962
- [ 9 ] Kohler U, Taake. Int Conf on Sec Metallurgy. Archen, Germany, Sep., 1987 : 522-538
- [ 10 ] Turkdogan F T. Slags and Fluxes for Ferrous Metallurgy. Iron and Steelmaking, 1985 (2) : 64
- [ 11 ] Ito K. Study on the Foaming of  $\text{CaO-SiO}_2\text{-Fe}_2\text{O}_3$  Slag, Part I : Foaming Parameters and Experimental Results. Metall Trans, 1989(8) : 509

## Optimizing of the Composition of Refining Slags Used in Ladle

**Abstract** The optimum composition of  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-CaF}_2$  system which is widely used in ladle refining is determined by means of orthogonal

experiment and theoretical analysis. Factors influencing the stability of foamy slag have a descending order of the basicity , the composition of  $\text{CaF}_2$  ,  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  and the optimum composition is  $\text{CaO}$  39.3% ,  $\text{SiO}_2$  19.7% ,  $\text{Al}_2\text{O}_3$  25% ,  $\text{MgO}$  6% ,  $\text{CaF}_2$  10% (  $B = 2$  ).

# 高阶亚正规溶液模型及其在 $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ 炉渣中组元活度的计算<sup>\* 1</sup>

**摘要** 本文介绍了用于计算四元均相系中组元活度的 SELF-SReM4 高阶亚正规溶液模型. 模型由一组参数表示, 根据精选的“边界条件”, 可由二元系、三元系、四元系逐渐展开拟合出该组参数. 用该模型计算了  $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$  四元系, 包括四个三元子系中各组元的活度.  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$  三元系的  $\text{SiO}_2$  活度计算值与实验值和其他计算结果较一致,  $\text{MnO-SiO}_2\text{-CaO}$  三元系计算结果与渣金属平衡试验结果较一致.

## 1 前言

活度作为冶金熔体热力学研究的核心课题之一, 其重要性是显而易见的. 就热力学而言(不涉及物质结构), 活度理论已很成熟, 但活度的应用依然不很普及, 原因之一是缺少必要的活度数据库.  $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$  四元系是锰铁和硅锰铁合金的主要渣系, 也是常用脱氧产物的基本组成. 该渣系活度的研究对传统铁合金冶炼工艺的优化、脱氧夹杂物的控制有重要意义. 完成这些工作, 必须拥有组元活度以及它们随温度变化的系统的数据库. 遗憾的是现在还没有这样的数据库. 当然, 可通过实验的方法测定体系中各组元的活度以建立这样的活度数据库. 而要完成一个多元系中系统的活度数据测定, 要花费大量的时间和经费. 另外多元炉渣的实验误差也是相当大的. 更何况有些过程的热力学参数目前用实验无法测定. 因此, 用计算方法确定多元炉渣体系中组元的活度无疑

\* 本文合作者: 张晓兵、蒋国昌. 原发表于《金属学报》33(10), 1~10(1997)

是一比较现实的方法.

Masson 的聚合理论虽能较好地描述硅酸盐炉渣的结构<sup>[1]</sup>,但因其解析较困难,以致在冶金炉渣中无法使用. 万谷志郎用正规模型研究了一些炼钢炉渣<sup>[2]</sup>,利用大量试验数据拟合出许多阳离子间的相互作用能. Pellton 等在拟化学近似模型基础上<sup>[3,4]</sup>,引入温度和浓度对不同二原子间作用能的影响,计算了一些复杂渣系. Gaye 在统计热力学基础上,以(i-O-j)微结构元描述炉渣<sup>[5,6]</sup>,设两配位的氧离子和四配位的硅离子分别分布在两个互相交错的亚晶格上. 对有配位数变化的酸性氧化物,用“阳离子团”处理;而对有变价元素的氧化物,则引入离子分数与氧位的关系. Hillert 的双亚点阵模型用理想混合的阳离子亚点阵和阴离子亚点阵来描述硅酸盐炉渣<sup>[7]</sup>. 当 SiO<sub>2</sub> 浓度较高时,则用中性的 SiO<sub>2</sub> 分子作电荷平衡. 与金属熔体相比,炉渣中组元活度的计算要困难得多. 这不仅是由于对炉渣结构认识较浅,还在于高温炉渣的试验比较困难. 目前,热力学参数模型的研究比较活跃,其中 Pellton<sup>[4]</sup>和 Gaye<sup>[6]</sup>模型的应用比较成功. 但它们在计算多元系时,与正规溶液相同,只利用了二元系的参数. 虽然给多元系计算带来方便,但由于缺少多元系内部的信息,会造成一定误差.

本文作者曾介绍用解析法计算 C-Fe-X(X = Si, Mn, Cr, Ni) 三元金属熔体中组元活度的方法<sup>[8]</sup>,最近又建立了 SELF-SReM4 模型(SELF 是上海市钢铁冶金重点实验室的缩写;SReM4 表示用于四元系熔体的亚正规溶液模型),用它计算 C-Mn-Fe-Si, C-Fe-Cr-Ni 和 C-Fe-Cr-P 四元金属熔体组元活度<sup>[9]</sup>. 该模型在热力学基础上,导出用一组参数计算四元系液相区中各组元的活度的高阶亚正规溶液模型,并利用一些精选实验数据拟合出该组参数. 由于该模型对多元系各组元并未作溶剂或溶质的区分,所以它既可用于合金体系(包括非铁基多元高浓度合金),也能用于炉渣. 本文将介绍 SELF-SReM4 模型及其在 MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO 四元渣系中组元活度计算方面的应用.

## 2 SELF-SReM4 模型

SELF-SReM4 模型是一种高阶亚正规溶液模型,四元系中各组元的过剩偏摩尔自由能和体系的过剩自由能由下式计算<sup>[9]</sup>:

$$G_1^{\text{ex}} = \sum_2^j \sum_0^k \sum_0^l A_{jkl} Y^j Z^k T^l \quad (1)$$

$$G_2^{\text{ex}} = - \sum_2^j A_{j00} / (1 - j) + \sum_2^j \sum_0^k \sum_0^l A_{jkl} Y^j Z^k T^l \{1 + [(j - k) / Y(1 - j)]\} \quad (2)$$

$$G_3^{\text{ex}} = - \sum_2^j \sum_0^k A_{jk0} / (1 - j) + \sum_2^j \sum_0^k \sum_0^l A_{jkl} Y^j Z^k T^l \{1 + [(j - k) / Y(1 - j)] + [(k - 1) / YZ(1 - j)]\} \quad (3)$$

$$G_4^{\text{ex}} = - \sum_2^j \sum_0^k \sum_0^l A_{jkl} / (1 - j) - \sum_2^j \sum_0^k \sum_0^l A^{jkl} Y^j Z^k T^l \{1 + [(j - k) / Y(1 - j)] + [(k - 1) / YZ(1 - j)] + [1 / YZT(1 - j)]\} \quad (4)$$

$$G^{\text{ex}} = - \sum_2^j A_{j00} Y / (1 - j) - \sum_2^j \sum_1^k A_{jk0} YZ / (1 - j) - \sum_2^j \sum_0^k \sum_0^l A^{jkl} YZT / (1 - j) + \sum_2^j \sum_0^k \sum_0^l A_{jkl} Y^j Z^k T^l / (1 - j) \quad (5)$$

以上1、2、3、4分别表示四元系中各组元,其摩尔浓度  $X_i$  用  $Y$ 、 $Z$ 、 $T$  变量替代: $Y = 1 - X_1$ ,  $Z = 1 - (X_2 / Y)$  和  $T = 1 - (X_3 / YZ)$ 。

可见,四元系中各组元的过剩偏摩尔自由能和体系的过剩自由能由同一组  $A$  参数表示。由于四元系  $A$  参数与二元系  $\alpha$  参数及三元系  $\beta$  参数存在如下的关系,所以  $A$  参数可由边界条件自二元系→三元系→四元系逐步拟合得到。

$$(\alpha_j)_{12} = A_{j00} \quad (\alpha_k)_{23} = \sum_2^j A_{jk0} (1 - k) / (1 - j)$$

$$(\alpha_j)_{13} = \sum_0^k A_{jk0} \quad (\alpha_k)_{24} = \sum_2^j \sum_0^l A_{jkl} (1 - k) / (1 - j)$$

$$\begin{aligned}
 (\alpha_j)_{14} &= \sum_0^{k'} \sum_0^{l'} A_{jkl} & (\alpha_1)_{34} &= \sum_2^j \sum_1^{k'} A_{jkl} (1 - l)/(1 - j) \\
 (\beta_{jk})_{123} &= A_{jk0} & (\beta_{jk})_{124} &= \sum_0^{l'} A_{jkl} \\
 (\beta_{jl})_{134} &= \sum_0^{k'} A_{jkl} & (\beta_{kl})_{234} &= \sum_2^{k'} A_{jkl} (1 - k)/(1 - j)
 \end{aligned}$$

此外,三元系的各参数之间还存在以下制约关系,因此可以用这些关系作为精选和验证边界条件的依据.

$$\begin{aligned}
 (\beta_{j0})_{134} &= \sum_0^k (\beta_{jk})_{123} & (2 \leq j \leq j') \\
 \sum_1^{l'} (\beta_{jl})_{134} &= \sum_1^{k'} [(\beta_{jk})_{124} - (\beta_{jk})_{123}] & (2 \leq j \leq j') \\
 \sum_1^{l'} (\beta_{kl})_{234}/(1 - k) &= \sum_2^j [(\beta_{jk})_{124} - (\beta_{jk})_{123}]/(1 - j) & (2 \leq k \leq k') \\
 (\beta_{k0})_{234}/(1 - k) &= \sum_2^j (\beta_{jk})_{123}/(1 - j) & (2 \leq k \leq k')
 \end{aligned}$$

### 3 MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO 四元系的解析

本文  $j', k', l' \leq 4$ ;  $i = 1, 2, 3, 4$ , 分别代表组元 MnO、SiO<sub>2</sub>、Al<sub>2</sub>O<sub>3</sub>、CaO. 模型中其他组元活度的标准态取为纯液态. 各活度计算式为

$$\alpha_i = X_i \exp\{[G_i^{\text{ex}} - \Delta G_i^0]/RT\} \quad (6)$$

式中  $\Delta G_i^0$  是  $i$  组元液固态相变过程的自由能变化,由文献[10]给出.

SELF-SReM4 模型中的  $A$  参数应是温度的函数,在拟合该参数时,需要不同温度下的边界条件.但是,由于缺少这些数据,本文只得按正规溶液的方法对温度作近似处理.假定  $G_i^{\text{ex}}$  与温度无关,即  $RT_1 \ln \gamma_i' = RT_2 \ln \gamma_i'$ .

利用一些精选实验数据,  $A$  参数的拟合自二元系、三元系、四元系逐渐展开.表 1 为 MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO 系炉渣中拟合时所使用的边界条件及获得的各参数.可见大部分  $A$  参数已由二元系、三元系得到,其余的参数由四元系

本体的 MnO 的活度数据得到, 见式(7)~(10).

表1 MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO 系中边界条件和解析的参数

Table 1 The boundary conditions and evaluated parameters in MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO

Boundary	Information	Parameter	Ref.
MnO-SiO <sub>2</sub>	$\alpha_{\text{MnO}}(1\ 923\ \text{K})$	$(\alpha_j)_{12}$	[11]
MnO-Al <sub>2</sub> O <sub>3</sub>	$\alpha_{\text{MnO}}(1\ 923\ \text{K})$	$(\alpha_j)_{13}$	[12]
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	$\alpha_{\text{Al}_2\text{O}_3}(1\ 923\ \text{K})$	$(\alpha_k)_{23}$	[13]
SiO <sub>2</sub> -CaO	$\alpha_{\text{SiO}_2}(1\ 873\ \text{K})$	$(\alpha_k)_{24}$	[14]
Al <sub>2</sub> O <sub>3</sub> -CaO	$\alpha_{\text{CaO}}(1\ 773\ \text{K})$	$(\alpha_l)_{34}$	[15]
MnO-SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	$\alpha_{\text{MnO}}(1\ 923\ \text{K})$	$(\beta_{jk})_{123}$	[13]
MnO-SiO <sub>2</sub> -CaO	$\alpha_{\text{MnO}}(1\ 923\ \text{K})$	$(\beta_{jk})_{124}$	[16]
MnO-Al <sub>2</sub> O <sub>3</sub> -CaO	$\alpha_{\text{MnO}}(1\ 923\ \text{K})$	$(\beta_{jl})_{134}$	[16]
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -CaO	$\alpha_{\text{SiO}_2}(1\ 873\ \text{K})$	$(\beta_{kl})_{234}$	[14]
MnO-SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -CaO	$\alpha_{\text{MnO}}(1\ 923\ \text{K}, 1\ 773\ \text{K})$	$A_{jkl}$	[16, 17]

$$\begin{aligned}
 G_1^{\text{ex}} &= \sum_2^j \sum_0^k (\beta_{jk})_{123} Y^j Z^k - \sum_2^j \sum_1^k [(\beta_{jk})_{124} - (\beta_{jk})_{123}] Y^j Z^k T \\
 &\quad - \sum_2^j \sum_2^{l'} (\beta_{jl})_{134} Y^j Z(T^l - T) \\
 &\quad + \sum_2^k \sum_2^{l'} (\beta_{kl})_{234} Y^2 [1/(1-k)](Z^k - Z)(T^l - T) \\
 &= \sum_3^j \sum_2^k \sum_2^{l'} A_{jkl} [Y^j + Y^2/(1-j)] \\
 &\quad \times (Z^k - Z)(T^l - T) \tag{7}
 \end{aligned}$$

上式左端为已知值, 其中  $G_1^{\text{ex}}$  选用 Warren<sup>[16]</sup> 和 Abraham<sup>[17]</sup> 报道的实验数据. 忽略  $j' + k' + l' > 9$  的  $A_{jkl}$  后, 由(11)式可拟合出 10 个  $A_{jkl}$ . 而其余 30 个  $A_{jkl}$  按(8)~(10)式算出.

$$A_{2kl} = -(\beta_{kl})_{234}/(1-k) + \sum_3^j A_{jkl}/(1-j) \quad (2 \leq k \leq k', 2 \leq l \leq l') \tag{8}$$

$$A_{j11} = (\beta_{jl})_{134} - \sum_2^k A_{jkl} \quad (2 \leq j \leq j', 2 \leq l \leq l') \quad (9)$$

$$A_{jkl} = -(\beta_{jk})_{124} - (\beta_{jk})_{123} - \sum_2^{l'} A_{jkl} \quad (2 \leq j \leq j', 1 \leq k \leq k') \quad (10)$$

拟合得到的  $A_{jkl}$  参数值示于表 2.

表 2 MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO 系中  $A_{jkl}$  参数  
Table 2 The  $A_{jkl}$  parameters in MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO

j	k	l = 0	l = 1	l = 2	l = 3	l = 4
	0	20 364.18	0	0	0	0
	1	51 407.31	- 1 512 478	53 486.7	2 374 882	- 964 271.4
2	2	- 312 982.2	7 932 143	- 4 701 225	- 4 136 081	1 277 958
	3	604 647.7	- 12 416 530	10 802 550	- 498 074.1	1 137 433
	4	- 330 015.9	5 948 135	- 5 991 563	1 788 065	- 1 091 908
	0	- 155 654	0	0	0	0
	1	- 154 730	11 904 010	- 14 831 350	3 753 345	- 462 286
3	2	1 207 316	- 44 265 340	41 896 160	4 337 970	- 2 895 840
	3	- 2 297 821	61 696 790	- 56 723 820	- 2 520 007	0
	4	1 179 604	- 28 243 810	26 295 560	0	0
	0	151 995.1	0	0	0	0
	1	96 188.2	- 13 304 270	22 119 150	- 12 790 780	3 601 156
4	2	- 894 208.3	42 869 880	- 48 971 320	6 432 668	0
	3	1 645 870	- 55 915 010	55 255 200	0	0
	4	- 775 411.4	24 992 650	- 24 240 480	0	0

## 4 计算结果与讨论

图 1、2、3、4 是用表 1 给出的 A 参数值计算得到的 SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO、MnO-SiO<sub>2</sub>-CaO、MnO-Al<sub>2</sub>O<sub>3</sub>-CaO 和 MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> 四个三元系中各组元等活度曲线. 图 5 是 MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO 四元系中  $X_{Al_2O_3} = 0.1$  和 0.25 时各组元等活度曲线. 以上计算的活度均以纯固体为标准态.

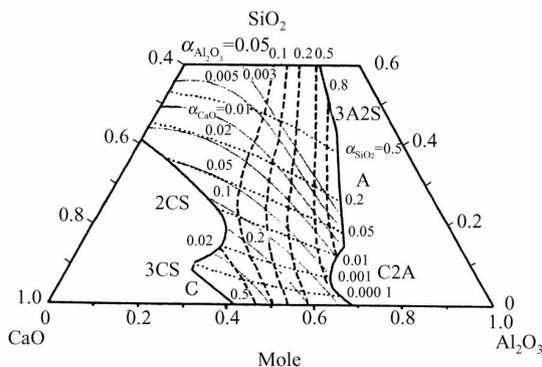


图 1 1873 K 下  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$  系炉渣中各组元活度的计算值  
 Fig. 1 Calculated activities of components in  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$  slag at 1873 K

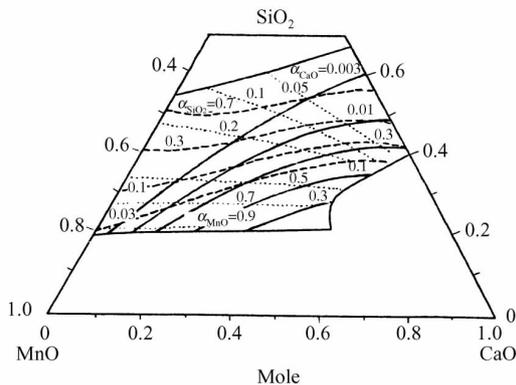


图 2 1923 K 下  $\text{MnO-SiO}_2\text{-CaO}$  系炉渣中各组元活度的计算值  
 Fig. 2 Calculated activities of components in  $\text{MnO-SiO}_2\text{-CaO}$  slag at 1923 K

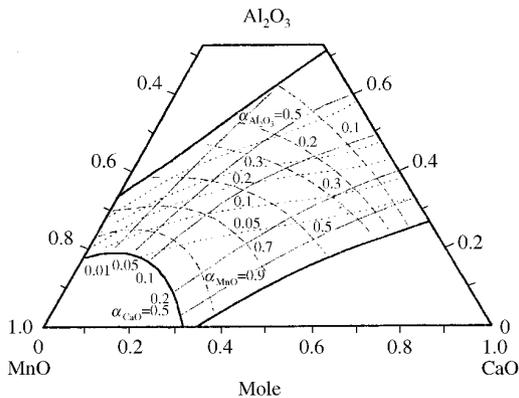


图 3 1923 K 下  $\text{MnO-Al}_2\text{O}_3\text{-CaO}$  系炉渣中各组元活度的计算值  
 Fig. 3 Calculated activities of components in  $\text{MnO-Al}_2\text{O}_3\text{-CaO}$  slag at 1923 K

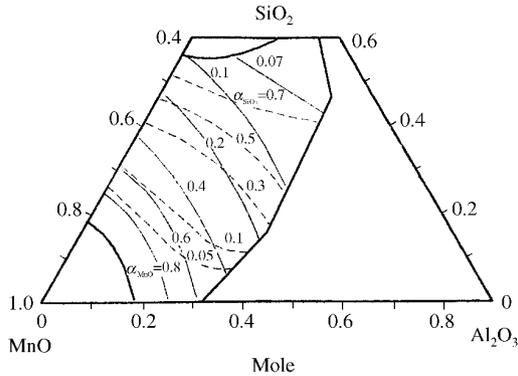


图 4 1923 K 下 MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> 系炉渣中 MnO 和 SiO<sub>2</sub> 活度的计算值

Fig. 4 Calculated activities of MnO and SiO<sub>2</sub> in MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag at 1923 K

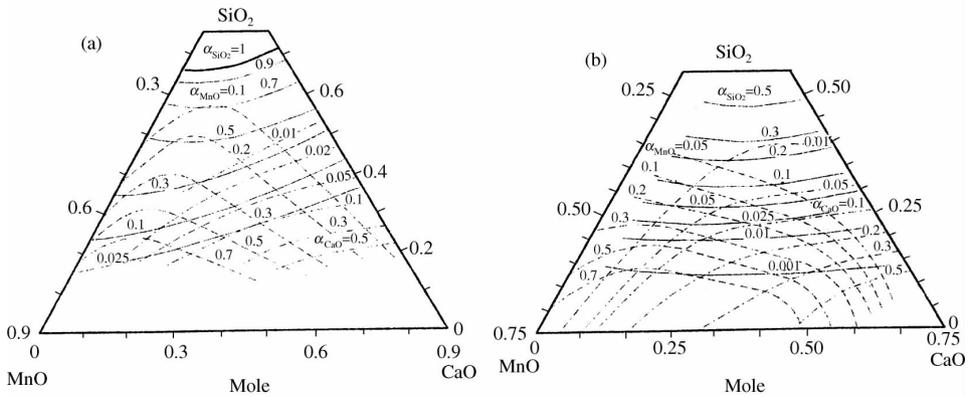


图 5 1873 下 MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO 系炉渣中各组元活度的计算值

Fig. 5 Calculated activities of components in MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO slag at 1873 K

(a)  $X_{Al_2O_3} = 0.1$

(b)  $X_{Al_2O_3} = 0.25$

SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO 系是钢铁冶炼的基本炉渣体系, Chipman 等曾测定了该炉渣中 SiO<sub>2</sub> 的活度<sup>[13]</sup>, Pelton 等也曾用拟化学近似模型计算了该炉渣中 SiO<sub>2</sub> 的活度<sup>[4]</sup>. 图 6 给出了用模型计算的 SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO 系中 SiO<sub>2</sub> 活度值与这些结果的比较, 可见互相间是比较一致的.

丁伟中曾实验测定了 C<sub>sat</sub>-Mn-Si 合金和 MnO-SiO<sub>2</sub>-CaO 渣之间的平衡<sup>[18]</sup>, 图 7 中三条粗实线是 1823 K 下 [% Si] = 1%, 5%, 10.5% 的渣-金属平衡曲线. 图中三条细实线是按 SELF-SReM4 模型计算得到的渣-金属平衡曲线, 分别对应于 1823 K 和 [% Si] = 1%, 5%, 10%. 虚线是 [% Si] = 1%

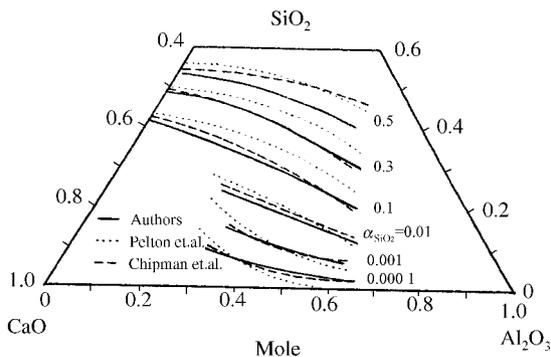


图6 SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO 系中 SiO<sub>2</sub> 活度计算值与其他研究结果的比较

Fig. 6 Comparison between the calculated activities of SiO<sub>2</sub> and other researched results in SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO slag

时不同温度(1 723 K , 1 773 K)的计算曲线. 其中合金中组元活度也由该模型计算<sup>[9]</sup>. 这些等 [% Si ] 等温线上的各点代表着不同合金与该残渣组成的平衡关系. 当然, 这些曲线可作为 MnSi 熔炼过程控制的重要依据. 由图 7 可见, 计算曲线与平衡实验所得的曲线是基本一致的.

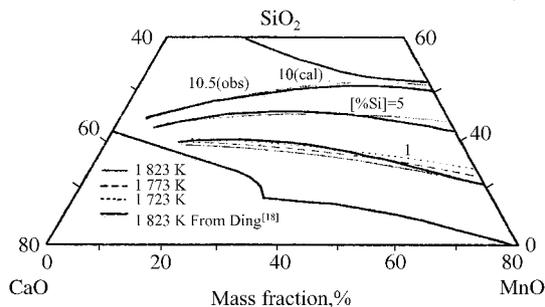


图7 MnO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> 系炉渣与 C<sub>sat</sub>-Mn-Si 合金平衡的计算结果与试验值的比较

Fig. 7 Comparison of calculated results and experiments in the equilibrium between MnO -SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag and C<sub>sat</sub>-Mn-Si alloy

SELF-SReM4 模型的关键是 A 参数的拟合. 拟合出该组参数后, 在计算机上计算体系中各组元的活度非常简单. 和其他溶液模型一样, “边界条件”对其结果的影响举足轻重. “边界条件”的可靠性决定了模型的精

度. 由于四元系拟合从二元系、三元系逐渐展开, 而二、三元系实验值比四元系多且可靠, 特别是二元系的“边界条件”的应用是使模型具有较高精度的基本保证. 另一方面, 由于利用了三元系和四元系本体的信息, 即考虑了多元系中各组元之间的相互作用, 进一步提高了计算精度. 拟合模型的多项式只是对体系中某一热力学性质逼近. 就拟合而言,  $j'$ 、 $k'$ 、 $l'$  值的大小只影响拟合精度. 但按热力学关系, 用该多项式(经变化后)表示其他组元的性质时, 可能会产生较大误差. 因此选取合适的  $j'$ 、 $k'$ 、 $l'$  参数可使该多项式既较真实地逼近这一组元的热力学性质, 又较精确地转换得到其他组元的性质. 所以  $j'$ 、 $k'$ 、 $l'$  的定值相当重要. 合理地选择“第一组元”可提高整个体系的解析精度.  $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$  系中, 可利用的  $\text{MnO}$  的精选数据比较多, 故选  $\text{MnO}$  为“第一组元”. 此外, 在使用“边界条件”时, 须注意不同标准状态的转换.

与合金相比, 将 SELF-SReM4 模型用于熔渣难度大得多. 其原因在于有关熔渣的实测难度很大, 已积累的数据相对少得多, 相互间的偏差却常常很可观. 因此“边界条件”的鉴别更显得重要.

## 5 结论

(1) 模型的导出、A 参数的拟合受热力学规律严格控制, 该模型属热力学参数模型范畴. 模型应用的关键在于边界条件的可靠性.

(2) 根据精选的“边界条件”, 可使用相应的拟合公式. 参数的拟合由二元系、三元系逐渐展开. 由于二元系、三元系的实验值多且可靠, 保证了模型的精度. 另一方面, 由于利用了多元系本体的信息, 提高了计算精度.

(3) 对多元系各组元既未作溶剂或溶质的区分, 也没有炉渣和金属熔体的限制, 使该模型具有较大的应用范围. 在整个均相区中, 用同一组参数表示体系和各组元的性质, 应用比较方便.

(4) 模型中各三元系参数之间存在着制约关系, 故该模型可作为验证和精选“边界条件”的工具.

(5) 用 SELF-SReM4 模型计算了  $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$  四元系, 包括四个三元子系中各组元的活度.  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$  三元系的  $\text{SiO}_2$  活度计算值与实验值及其他计算结果较一致,  $\text{MnO-SiO}_2\text{-CaO}$  三元系计算结果与渣-金属平衡试验结果较一致.

## 参 考 文 献

- [ 1 ] Masson V R. *2nd Int Conf on Molten Fluxes and Slags* , Lake Tahoe , 1984 :3
- [ 2 ] 万谷之郎 ,日野光兀. 铁と钢 ,1988 ,74 :1701
- [ 3 ] Pelton A D , Blander M. *2nd Int Conf on Molten Fluxes and Slags* , Lake Tahoe , 1984 : 281
- [ 4 ] Kriksson G , Pelton A D. *Metall Trans.* 1993 ;24B :795
- [ 5 ] Gaye H , Welfringer J. *2nd Int Conf on Molten Fluxes and Slags* , Lake Tahoe , 1984 :357
- [ 6 ] Gaye H , Riboud P V , Welfringer J. *5th Int. Iron Steel Congr* , Washington D. C. , 1996 :631
- [ 7 ] Hillert M , Jansson B , Sundman B , J Agren. *Metall Trans* , 1985 ;16A :261
- [ 8 ] Jiang Guo Chang , Zhang Xiao Bing , Xu Kuang Di. *Acta Metall Sin* , 1992 ;5B :476
- [ 9 ] Zhang Xiao Bing. Ph. D. Thesis , Shanghai University , 1996 :24
- [ 10 ] S. Ban-Ya , M. Hino. *Chemical Properties of Molten Slags* , ISIJ , 1991 :17
- [ 11 ] Abraham K P , Davies M W , Richardson F D. *J Iron Steel Inst* , 1960 ;196 :82
- [ 12 ] Sharma R A , Richardson F D. *Trans Metall Soc AIME* , 1965 ;233 :1586
- [ 13 ] Rein R H , Chipman J. *Trans Metall Soc AIME* , 1965 ;233 :415
- [ 14 ] Sharma R A , Richardson F D. *J Iron Steel Inst* , 1961 ;198 :386
- [ 15 ] Risbud S H , Pask J A. *J. Am Ceramic Society* , 1977 ;60 :418
- [ 16 ] Mehta S R , Richardson F D. *J Iron Steel Inst* , 1965 ;203 :524
- [ 17 ] Warren G F , Jochens P R , Howat D D. *INFACON* , 1974 :175
- [ 18 ] Ding W , Olsen S E. *Metall Trans* , 1996 ;27B :5

### High Order Sub-Regular Solution Model and Its Applications in the Calculation of Component Activities of $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ Molten Slag

**Abstract** A high order sub-regular solution model for predicting the component activities in a homogeneous region of a quaternary system was developed in the Shanghai Enhanced Lab of Ferrometallurgy , which is designated as SELF-SREm4. It is composed of some polynomials of excess mole free energies versus content variable. A group of parameters is included in the polynomials. Along

with the reliable known thermodynamic properties associating the homogeneous region the parameters can be evaluated. And then the component activities in that region are possible to be predicated. This paper is devoted to illustrate the applications of SELF-SReM4 for molten slag of  $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$  and its sub-ternary systems. The evaluated results were very close to those of slag-metal equilibrium experiments and the Chipman's and Pelton's results.

## Mn-Si-C<sub>Sat</sub> 合金熔体活度的计算<sup>\* 1</sup>

**摘要** 由 SELF-SReM3 模型导出了与碳化物平衡区域内的碳饱和合金体系组元活度的计算方法,并用之于对 Mn-Si-C<sub>Sat</sub> 合金熔体的计算和预测,计算结果与实验值吻合较好.在引入炉渣活度数据后,对不同温度下的渣金平衡反应结果进行了计算和预测.

碳热还原法生产铁合金的过程是在富碳条件下合金熔体、炉渣及碳相互间反应的过程,因而合金熔体往往呈碳饱和状态.为了研究铁合金冶炼过程中热力学平衡关系并进而指导这类合金的生产,碳饱和合金熔体的活度是必要的基础数据.在许多碳饱和合金体系中,当合金某元素含量超过某一临界值时,碳饱和合金与碳化物间达到平衡.例如在 Fe-Si-C<sub>Sat</sub>、Mn-Si-S<sub>Sat</sub> 和 Cr-Si-C<sub>Sat</sub> 等合金中,当合金的含 Si 量超过一临界值后,碳饱和合金与碳化硅间建立起平衡.而在该区域内的合金组元活度值由于实验测定上有许多困难迄今为止鲜见报道.因此,研究碳饱和合金熔体在与碳化物平衡区域内的活度是相当有意义的工作.

文献[1,2]报道了由基于亚正规溶液模型的解析算法为基础发展起来的 SELF-SReM3 模型计算得到的 C-Fe-x (x = Mn, Si, Cr, Ni) 合金体系及 C-Si-Al 合金体系的系统活度数据.本文介绍了在该模型基础上,利用优选的碳饱和数据作为边界条件直接计算和预测在与碳化物平衡的碳饱和合金体系组元活度的工作.

\* 本文合作者:唐恺、徐建伦、丁伟中、张晓兵、蒋国昌.原发表于《中国有色金属学报》7 (增1) 43~46(1997)

## 1 计算方法

如图 1 所示,在某一温度下 Mn-Si-C<sub>Sat</sub> 合金熔体中,在 ab 线上合金 L 与固体石墨碳平衡,而在 bc 线上合金 L 与固体碳化物 SiC<sub>β</sub> 相平衡.因此,ab 线和 bc 线分别是与石墨和 SiC<sub>β</sub> 平衡的碳饱和合金(严格地说,bc 线是液态合金碳化物析出线,但为了叙述简洁起见,在此仍沿用碳饱和合金这一术语).

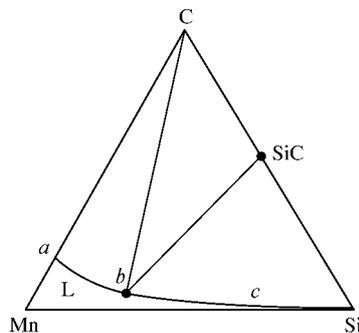


图 1 某一温度下 Mn-Si-C<sub>Sat</sub> 合金熔体的碳饱和线

在 ab 线上合金与石墨碳平衡,故

$$\ln \gamma_C = - \ln x_C \quad (1)$$

而在 bc 线上,显然有下列关系式成立:

$$\alpha_C \cdot \alpha_{Si} = k \quad (2)$$

式(2)中,k 是下列反应的平衡常数:



将式(2)取对数并展开,得

$$\ln \gamma_C + \ln \gamma_{Si} = \ln k - \ln x_C - \ln x_{Si} \quad (4)$$

在 Mn-Si-C<sub>Sat</sub> 三元合金熔体中,不论在合金与石墨碳平衡区域内还是在合金与 SiC<sub>β</sub> 平衡区域范围内,其热力学特性均可用液态合金均相区的计算公式来描述.根据基于亚正规溶液模型的解析算法,将组元 C、Mn、Si 的活度系数表达成如下包含其浓度变量的多项式形式:

$$\ln \gamma_C = \sum_2^j \sum_\theta^k A_{jk} Y^j Z^k \quad (5)$$

$$\ln \gamma_{Mn} = \sum_2^j \frac{A_{j0}}{j-1} + \sum_2^j \sum_\theta^k A_{jk} Y^j Z^k \left[ 1 + \frac{j-k}{Y(1-j)} \right] \quad (6)$$

$$\ln \gamma_{Si} = \sum_2^j \sum_\theta^k \frac{A_{jk}}{j-1} + \sum_2^j \sum_\theta^k A_{jk} Y^j Z^k$$

$$\left[ 1 + \frac{j - k}{Y(1 - j)} + \frac{k}{YZ(1 - j)} \right] \quad (7)$$

式(5)~式(7)中,  $A_{jk}$  是多项式中的参数, 需由所选体系的碳饱和数据来计算定值; 而浓度变量  $Y$ 、 $Z$  与组元  $C$ 、 $Mn$ 、 $Si$  的摩尔分数之间的关系是

$$Y = 1 - x_C \quad (8)$$

$$Z = x_{Si} / Y \quad (9)$$

将式(5)和式(7)代入式(1)和式(4)中, 整理得

$$\sum_2^j \sum_{\theta}^k A_{jk} Y^j Z^k = -\ln(1 - Y) \quad (10)$$

$$\sum_2^j \sum_{\theta}^k \frac{A_{j0}}{j - 1} + \sum_2^j \sum_{\theta}^k A_{jk} Y^j Z^k$$

$$\left[ 2 + \frac{j - k}{Y(1 - j)} + \frac{k}{YZ(1 - j)} \right] = \ln k - \ln(1 - Y) - \ln YZ \quad (11)$$

式(10)和式(11)分别是用于由合金的碳饱和数据计算与石墨碳和  $SiC_{\beta}$  平衡区域内各组元活度的计算式。若已知图 1 中  $ab$  线和  $bc$  线的具体位置(即浓度变量  $Y$ 、 $Z$  值), 则由(10)和(11)两式可直接拟合求得表达碳饱和线上合金中各组元活度系数表达式中的  $A_{jk}$  参数值, 然后经由式(4)~式(7)可计算得到组元  $C$ 、 $Mn$ 、 $Si$  的活度系数。进而, 对  $Mn-Si-C_{Sat}$  三元系中各组元的活度可由下列诸式计算之:

$$\alpha_C = \exp[\ln \gamma_C](1 - Y) \quad (12)$$

$$\alpha_{Mn} = \exp[\ln \gamma_{Mn}][Y(1 - Z)] \quad (13)$$

$$\alpha_{Si} = \exp[\ln \gamma_{Si}]YZ \quad (14)$$

## 2 计算结果与讨论

$Mn-Si-C_{Sat}$  合金的碳饱和溶解度有多篇文献报道<sup>[3-9]</sup>, 在 1 873 K 时合金中的碳饱和溶解度如图 2 所示。在合金  $Si$  含量  $\leq 19.1\%$  时,  $Mn-Si-C_{Sat}$  合金与石墨碳平衡, 在碳饱和线上组元  $C$  的活度为 1(以纯石墨为标准态); 当  $Si$

含量高于此值时, Mn-Si-C<sub>Sat</sub>合金与 SiC<sub>β</sub> 建立平衡<sup>[10]</sup>, 而在 Si 含量为 19.1% 时是 Mn-Si-C<sub>Sat</sub>合金、石墨、SiC<sub>β</sub> 三相平衡点, 由反应式(3)的平衡常数计算得到 C 和 Si 在三相平衡点的活度分别是 1 和 0.033<sup>[11]</sup>.

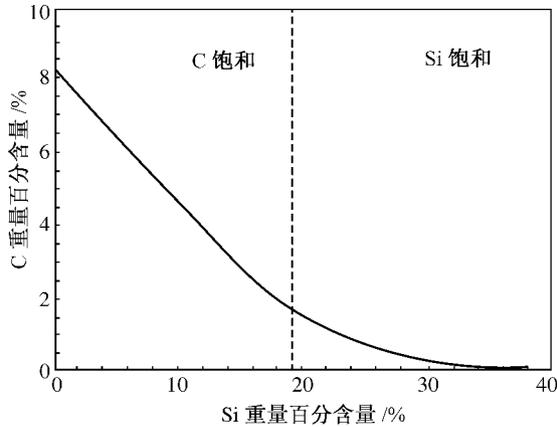


图2 1873 K 温度下 Mn-Si-C<sub>Sat</sub>合金碳饱和溶解度与含 Si 量的关系

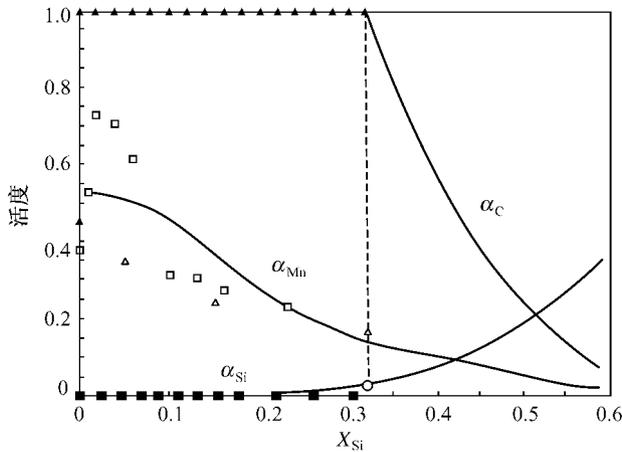


图3 计算得到的 Mn-Si-C<sub>Sat</sub>合金中各组元的活度值(1873 K)

△— $\alpha_{Mn}$  Gee et al. ; □— $\alpha_{Mn}$  Tanaka ; ■— $\alpha_{Si}$  Ding ;  
▲— $\alpha_C$  Ding ; ○— $\alpha_{Si}$  Ding

对式(10)和(11)中的  $A_{jk}$  参数取:  $j \leq 4, k \leq 4, (j+k) \leq 7$ , 按前述方法由图2提供的信息计算得到的  $A_{jk}$  参数值列入表1中, Mn-Si-C<sub>Sat</sub>合金中组元 C、Mn、Si 的活度如图3所示. 图3中还列出了几个作者的实验结果. 采用

本文推导的计算方法,由合金碳饱和数据直接计算得到的合金各组元活度值与实验结果吻合较好.

表1 组元 C, Si, Mn 活度系数表达式中的  $A_{jk}$  参数值

	k = 0	k = 1	k = 2	k = 3	k = 4
j = 2	33.121 16	- 93.595 25	- 40.389 85	- 445.674 3	514.058 4
j = 3	- 68.339 67	259.043 20	358.642 30	742.125 3	- 1 021.043 0
j = 4	35.308 35	- 161.428 70	- 440.950 0	215.683 2	0

本文采用一组  $A_{jk}$  参数来描述三元系中三个组元的活度系数的计算式. 因此,只要计算得到一组  $A_{jk}$  参数值,就能由式(5)~式(7)方便地计算出各组元的活度系数. 这显然较之 Pelton 等<sup>[8]</sup>用三组不同的参数分别计算三个组元活度系数更合理. 同时在一组  $A_{jk}$  描述各组元的活度系数的基础上,还便于计算公式的推导和计算机编程计算.

碳饱和合金熔体的碳饱和数据的正确与否直接影响到计算结果的准确性,对于含 Si 量较高区域内的活度,受碳饱和数据的影响尤为显著,因此正确的活度数据是建立在精确的碳饱和数据基础上的.

研究渣金反应的平衡结果是揭示硅锰合金生产过程中内在规律的重要内容之一,也是验证本文计算得到的 Mn-Si-C<sub>Sat</sub> 合金组元活度值准确性的另一途径. 在硅锰合金生产过程中,合金中的 Si 含量取决于下列渣金反应的平衡结果:



对于任意给定成分的碳饱和硅锰合金,合金与炉渣之间反应的平衡关系可由下式表示:

$$\frac{\alpha_{\text{MnO}}^2}{\alpha_{\text{SiO}_2}} = k_{15} \cdot \frac{\alpha_{\text{Mn}}^2}{\alpha_{\text{Si}}} \quad (16)$$

其中,  $k_{15}$  是反应(15)的平衡常数,由 Rao 等<sup>[11]</sup>报道的 MnO-SiO<sub>2</sub> 二元炉渣体系 1 823 K 的组元活度值,结合本文计算得到的 Mn-Si-C<sub>Sat</sub> 合金在 1 873 K 的温度下的合金活度值,计算得到渣金平衡结果如图 4 所示. 图中还给出了 1 873 K 时的渣金平衡实验结果,图 4 从另一侧面印证了本文计算得到的合金活度数据的准确性.

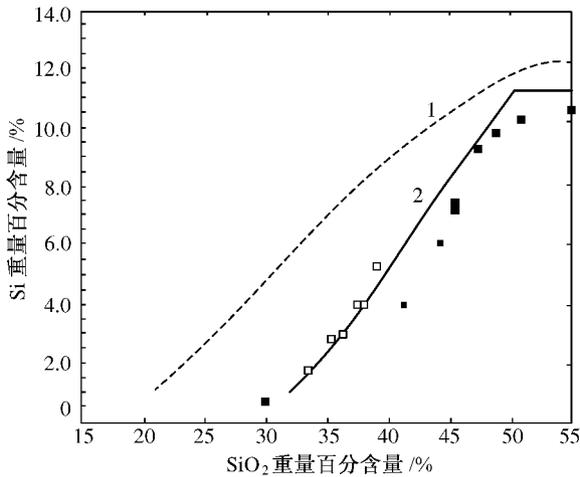


图4 Mn-Si-C<sub>sat</sub>合金与SiO<sub>2</sub>-MnO二元炉渣  
反应平衡计算结果

■—Ding's 1823 K ; □—Tanaka's 1873 K ;  
1—1823 K 计算值 2—1873 K 计算值

### 3 结论

本文报道了在 SELF-SReM3 模型基础上推导的由优选的合金碳饱和数据作为边界条件,直接计算和预测与碳化物平衡的碳饱和合金组元活度的计算新方法,并将之用于 Mn-Si-C<sub>sat</sub> 系的计算,计算结果与实验值吻合较好.应用本文推导的新方法,由合金体系的碳饱和数据即可直接对碳饱和合金的组元活度进行预测.

### 参 考 文 献

- [ 1 ] 蒋国昌, 张晓兵, 徐匡迪等. 金属学报, 1992, 28 : B240
- [ 2 ] Tang K, Xu J L, Jiang G C *et al.* Rare Metals, 1995, 14 : 137
- [ 3 ] Chipman J *et al.* Trans ASM, 1952, 44 : 1215
- [ 4 ] Esin O A, Vatolin N A. Russ Zhur Appl Chem. 1954, 27 : 1252
- [ 5 ] Turkdogan E T, Hancock R A, Herlize S I. JISI, 1956, 182 : 274
- [ 6 ] Peturshevskii MS and Gel'd P V. J. Prikladnoi Khemi, 1959, 32 : 86
- [ 7 ] Schenck H, Forhberg M G, Steinmetz E. Arch Eisenhüttenwes, 1963, 34 : 37

- [ 8 ] Tanaka A. Trans JIM ,1980 ,21 :28
- [ 9 ] Ni R M , Ma Z T , Wei S K. Steel Research ,1990 ,61 :113
- [ 10 ] Ding W Z. PhD Thesis , NIT , Norway ,1993 ,1
- [ 11 ] Rao B K , Gaskell D R. Metall Trans ,1981 ,12B :207

## Calculation of Activities in Mn-Si-C<sub>Sat</sub> Ternary Alloy

**Abstract** SELF-SReM3 model has been extended to evaluate and predict the component activities of carbon saturated ternary alloy in the composition region of equilibrated with carbides. Activities of Mn ,Si and C in Mn-Si-C<sub>Sat</sub> ternary alloy has been evaluated by the new proposed calculation procedure. The calculation results show a good agreement with the experimental values. The slag/metal equilibrium relation between Mn-Si-C<sub>Sat</sub> alloy and MnO-SiO<sub>2</sub> binary slag at various temperature were predicted.

# SELF-SReM4 模型在 C-Cr-Fe-P 四元系组元活度解析中的应用<sup>\*1</sup>

**摘要** 介绍了用 SELF-SReM4 模型解析 C-Cr-Fe-P 四元系(包括相应的二元、三元子系 C-Fe, Cr-Fe, Fe-P, C-Cr-Fe, C-Fe-P, Cr-Fe-P)中组元活度的方法和结果.

众所周知,生产高合金钢时最经济的原材料就是该钢种的返回钢,提高返回比是降低生产成本的重要手段.由于此冶炼过程中无法像生产低合金钢那样进行脱磷(以免铬的大量烧损),钢多次返回后,其中的磷日积月累地逼近钢的成分规格,以致无法使用.随着经济的发展,不锈钢的市场需求将迅速增大,也就更迫切地需要大量低磷返回钢作为原材料.另一方面,一些用于苛刻环境下的钢只能允许很低的磷含量.例如,尿素级和硝酸级不锈钢要求  $C(P) \leq 0.015\% \sim 0.020\%$  (质量分数).为了抑制腐蚀疲劳及焊接开裂,  $C(P)$  应降至  $50 \times 10^{-6} \sim 100 \times 10^{-6}$  以下.预计 20 世纪内会提出脱磷至  $14 \times 10^{-6}$  的要求.因此,不锈钢脱磷将是 21 世纪特殊钢精炼方面的重大课题之一.不锈钢和铬铁脱磷的研究是一个可望产生巨大经济价值的重大课题,也是钢铁冶金界迫切需要解决而实际上至今尚无成熟解决办法的一个难题.不锈钢和铬铁脱磷有两条不同的技术路线,氧化脱磷和还原脱磷.但无论是哪条路线,其核心问题都是如何做到脱磷保铬.关于这一点,目前尚未有一项较成熟的技术.面对如此窘境,有必要依靠理论预测来分析脱磷技术. C-Cr-Fe-P 四元系中的组元活度是进行这种理论预测必需的基本数据.当然,可通过实验的方法测定体系中各组元的活度以建立这样的活度数据库,但要完成

\* 本文合作者:张晓兵、蒋国昌.原发表于《中国有色金属学报》7(增1) 21~27(1997)

一个多元系统的活度数据测定,则要花费大量的时间和金钱,有时这些花费是难以承受的,并且,多元高合金或复杂渣系的实验误差也是相当大的.另一种方法是利用某种用于多元高合金金属熔液组元活度计算的模型得到C-Cr-Fe-P四元系中各组元活度.前文已介绍了四元冶金熔体活度计算的SELF-SReM4模型<sup>[1]</sup>.该模型在热力学基础上,利用一些精选实验数据作为“边界条件”拟合出 $A_{jkl}$ 参数,从而用一组参数就能计算四元系液相区中各组元的活度,并有较高的正确性.

## 1 SELF-SReM4 模型

在一个均相的四元系中,以Y、Z、T作为浓度变量.

$$Y = 1 - X_1 \quad (1)$$

$$Z = 1 - (X_2/Y) \quad (2)$$

$$T = 1 - (X_3/YZ) \quad (3)$$

$X_1, X_2, X_3, X_4$  是四个组元的摩尔分数.文中1、2、3、4分别表示C、Cr、Fe、P.

以 $f_i (i = 1, 2, 3, 4)$ 表示组元*i*的过剩偏摩尔自由能, $f$ 表示四元系的偏摩尔自由能总量.按SELF-SReM4模型,有

$$f_1 = \sum_2^j \sum_0^k \sum_0^l A_{jkl} Y^j Z^k T^l \quad (4)$$

$$f_2 = - \sum_2^j A_{j00} / (1 - j) + \sum_2^j \sum_0^k \sum_0^l A_{jkl} Y^j Z^k T^l \cdot [1 + [(j - k)/Y(1 - j)]] \quad (5)$$

$$f_3 = - \sum_2^j \sum_0^k A_{jk0} / (1 - j) + \sum_2^j \sum_0^k \sum_0^l A_{jkl} Y^j Z^k T^l \cdot [1 + [(j - k)/Y(1 - j)] + [(k - 1)/YZ(1 - j)]] \quad (6)$$

$$f_4 = - \sum_2^j \sum_0^k \sum_0^l A_{jkl} / (1 - j) + \sum_2^j \sum_0^k \sum_0^l A_{jkl} Y^j Z^k T^l \cdot [1 + \{(j - k)/Y(1 - j)\} + [(k - 1)/YZ(1 - j)] + [1/YZT(1 - j)]] \quad (7)$$

$$f = - \sum_2^j A_{j00} Y / (1 - j) - \sum_2^j \sum_1^k A_{jk0} YZ / (1 - j)$$

$$\begin{aligned}
& - \sum_2^j \sum_1^k \sum_1^l [A_{jkl} YZT / (1 - j)] \\
& + \sum_2^j \sum_0^k \sum_0^l [A_{jkl} / (1 - j)] Y^j Z^k T^l \quad (8)
\end{aligned}$$

由此可见,SELF-SReM4 模型中只需要一组  $A_{jkl}$  参数,就能用式(4)~(8)求解 C-Cr-Fe-P 四元合金液相区中的  $f_1$ 、 $f_2$ 、 $f_3$ 、 $f_4$  和  $f$ 。模型将这些热力学量表示成高次多项式,各组元活度之关系又严格服从 Gibbs-Duhem 定理,故本计算结果有较高精度。

## 2 C-Cr-Fe-P 四元系组元活度的解析

### 2.1 二元系

表 1 给出 C-Fe、Cr-Fe 和 Fe-P 三个二元系中  $\alpha$  参数的拟合式及所选用的边界条件。 $\alpha$  参数与 A 参数的关系见式(9)~(11)。C-Fe 二元系可以用由 Hultgren 精选的碳饱和实验数据<sup>[2]</sup>。Cr-Fe 二元系可以用由 Ranyor 精选的碳饱和实验数据<sup>[3]</sup>。Fe-P 二元系中磷的活度系数,已有一些实测结果见报道<sup>[4~8]</sup>。本文用 Froberg 等的实验结果<sup>[5]</sup>作为“边界条件”。

$$(\alpha_j)_{13} = \sum_0^k A_{jk0} \quad (9)$$

$$(\alpha_k)_{23} = \sum_2^j A_{jk0} (1 - k) / (1 - j) \quad (10)$$

$$(\alpha_1)_{34} = \sum_2^j \sum_1^k A_{jkl} [(1 - l) / (1 - j)] \quad (11)$$

表 1 二元系参数的拟合式及边界条件

体 系	拟 合 式	边 界 条 件	参 考 文 献
C-Fe(1-3) Z = 1T = 0	$(f_1)_{13} = \sum_2^j (\alpha_j)_{13} Y^j$	$\Delta H - T\Delta S^E$	Hultgren <sup>[2]</sup>
Cr-Fe(2-3) Y = 1T = 0	$f_{23} = \sum_2^k (\alpha_k)_{23} Z [1 / (1 - k)] (Z^{k-1} - 1)$	$\Delta H - T\Delta S^E$	Raynor <sup>[3]</sup>
Fe-P(3-4) Y = 1Z = 1	$(f_4)_{34} = \sum_2^l \alpha_l \{ T^l [1 + 1/T(1 - l) - 1/(1 - l)] \}$	$RT \ln \gamma_P(\text{Fe})$	Froberg <sup>[5]</sup>

## 2.2 三元系

三元系可以解析的体系有 C-Cr-Fe、C-Fe-Cr 和 Cr-Fe-P,集中各参数的拟合式和边界条件见表 2. 三元系参数与四元系参数的关系见式(12)~(13). 可见,拟合三元系参数时可以利用已拟合出的二元系参数. C-Cr-Fe 系可利用 Healy(1 873 K)的碳饱和数据<sup>[9]</sup>和 SchÜmann(1 823 K)精选的该值<sup>[10]</sup>. C-Fe-P系,Healy<sup>[11]</sup>、Schenck<sup>[12]</sup>和 Elliott<sup>[13]</sup>等均测定过此系中的碳饱和和 [C%]<sub>Sat</sub> 曲线. 本文利用 Elliott 等的实验结果作为边界条件. 而对 Cr-Fe-P 系,本文所用的边界条件是 Froberg<sup>[6]</sup>Ag 浴试验的结果.

$$(\beta_{jl})_{134} = \sum_0^k A_{jkl} \quad (12)$$

$$(\beta_{kl})_{234} = \sum_2^{l'} A_{jkl}(1-k)/(1-j) \quad (13)$$

表 2 三元系参数的拟合式及边界条件

体系	拟合式	边界条件	参考文献
C-Fe-Cr (1-2-3) T = 0	$(f_1)_{123} - \sum_2^j (\alpha_j)_{13} Y^j + Y^2 \sum_2^k (\alpha_k)_{23} (Z^k - 1)/(1-k)$ $= \sum_2^j A_{j0} Y^j (Z-1) + \sum_3^j \sum_2^k A_{j0} (Z^k - 1) [Y^j + Y^2/(1-j)]$	碳饱和数据	[9] [10]
C-Fe-P (1-3-4) Z = 0	$(f_1)_{134} - \sum_2^j (\alpha_j)_{13} Y^j + Y^2 \sum_2^{l'} (\alpha_k)_{34} T^k/(1-1)$ $= \sum_2^j (\beta_{jl})_{134} Y^j T + \sum_3^j \sum_2^{l'} (B_{jl})_{134} T^l [Y^j + Y^2/(1-j)]$	碳饱和数据	[11]
Cr-Fe-P (2-3-4) Y = 1	$(f_2)_{234} - \sum_2^k (\alpha_k)_{23} Z^k + Z^2 \sum_2^{l'} (\alpha_k)_{34} T^k/(1-1)$ $= \sum_3^k \sum_2^{l'} (\beta_{kl})_{234} T^l + [Z^k + Z^2/(1-k)] + \sum_2^k (\beta_{kl})_{234} Z^k T$	RTln $\gamma_{Cr}$	[6]

## 2.3 C-Cr-Fe-P(1-2-3-4)四元系

按 SELF-SReM4 模型

$$\begin{aligned}
 (f_1) - \sum_2^j \sum_0^k A_{j0} Y^j Z^k + \sum_2^j \sum_1^{l'} (B_{jl})_{134} Y^j Z T^l \\
 + \sum_2^k \sum_1^{l'} (\beta_{kl})_{234} Y^2 (Z^k - Z) T^l \\
 = \sum_3^j \sum_2^k \sum_1^{l'} A_{jkl} (Y^j - Y^2(1-j)^{-1})(Z^k - Z) T^l \quad (14)
 \end{aligned}$$

式中的  $A_{jk0}$ 、 $(B_{jl})_{134}$ 、 $(\beta_{kl})_{234}$  为已知, 而四元系本体中若干浓度坐标点 YZT 的  $f_i$  本文取 Froberg 等<sup>[5]</sup>所测 1 873 K 下该四元系中的碳饱和曲线。

$$A_{2kl} = -(\beta_{kl})_{234}/(1-k) + \sum_2^{l'} A_{jkl}/(1-j) \quad (2 \leq k \leq 4, 2 \leq l \leq 4) \quad (15)$$

$$A_{jkl} = (\beta_{jl})_{134} - \sum_2^k A_{jkl} \quad (2 \leq j \leq 4, 1 \leq l \leq 4) \quad (16)$$

令  $(j' + k' + l') > 9$ ,  $A_{jkl} = 0$ , 且  $A_{333}$  也为 0, 则由可拟合得到 45 个  $A_{jkl}$  参数, 见表 3。

表 3 C-Cr-Fe-P 四元系中  $A_{jkl}$  参数

j	k	l = 0	l = 1	l = 2	l = 3	l = 4
2	0	- 1 710 787	0	0	0	0
	1	1 508 703	- 5 525 639	- 23 090 020	47 703 860	23 918 480
	2	415 291.8	- 15 133 950	66 441 360	- 13 475 330	7 386 632
	3	- 538 413.7	14 074 920	- 37 012 910	80 146 550	- 19 919 180
	4	168 470.8	- 4 129 383	1 774 527	- 8 481 713	12 528 430
3	0	4 207 629	0	0	0	0
	1	- 4 281 143	14 987 180	26 901 660	- 58 348 340	- 99 621 780
	2	- 719 525.7	30 406 250	- 131 259 600	260 055 500	0
	3	1 281 418	- 28 078 100	68 826 120	- 133 900 800	0
	4	- 333 506.4	8 107 141	0	0	0
4	0	- 2 687 695	0	0	0	0
	1	3 122 090	- 14 868 330	28 917 550	- 55 589 060	77 677 260
	2	- 164 707.4	0	0	0	0
	3	- 314 537.2	0	0	0	0
	4	0	0	0	0	0

### 3 计算结果

至此, 已获得了 C-Cr-Fe-P 四元系  $A_{jkl}$  全部非零值, 用 SELF-SReM4 模型

中的式(4)~(7)就可计算该体系中各组元的活度值.

$$\alpha_C = (1 - Y) \cdot \exp[(f_1 + K)/RT] \quad (17)$$

$$\alpha_{Cr} = Y(1 - Z) \cdot \exp(f_2/RT) \quad (18)$$

$$\alpha_{Fe} = YZ(1 - T) \cdot \exp(f_3/RT) \quad (19)$$

$$\alpha_P = YZT \cdot \exp(f_4/RT) \quad (20)$$

以上各活度除碳取纯石墨为标准态外,其他都取纯液态为标准态.(12)式中的K值是纯石墨碳与假想标准态之间的转换系数,  $K = 44\ 650$ .

图1,2分别是1873 K下C-Fe和Cr-Fe二元系各组元的活度曲线.图3是1873 K下Fe-P二元系中磷活度系数.以上图中还给出其他研究结果.

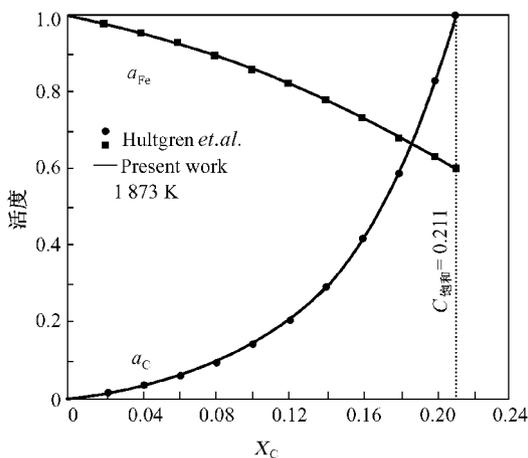


图1 C-Fe二元系中1873 K下的C、Fe活度( $\alpha_C$ 、 $\alpha_{Fe}$ )

图4是计算的1873 K下C-Cr-Fe三元系中 $\alpha_C$ 和 $\alpha_{Cr}$ 的等值线.与Healy的结果一致.

图5是计算的1873 K下 $\alpha_C$ 和 $\alpha_P$ 曲线.图中碳活度取纯石墨为标准态,磷活度取1% (质量分数)溶液为标准态.与Frohberg等1873 K下等 $a_P$ 线也是比较一致的.

图6是计算的1873 K下Cr-Fe-P三元系中 $\alpha_{Cr}$ 和 $\alpha_P$ 的等值线.

图7、8是计算的C-Cr-Fe-P四元系中 $\alpha_C$ 、 $\alpha_{Cr}$ 和 $\alpha_P$ 的等值线.

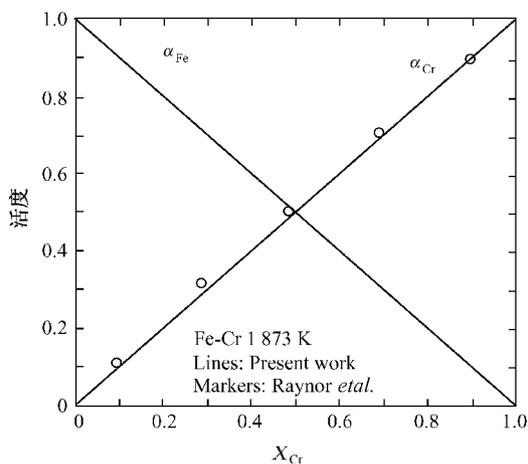


图2 Fe-Cr 二元系中 1873 K 下的 Cr, Fe 活度( $\alpha_{Fe}$ ,  $\alpha_{Cr}$ )

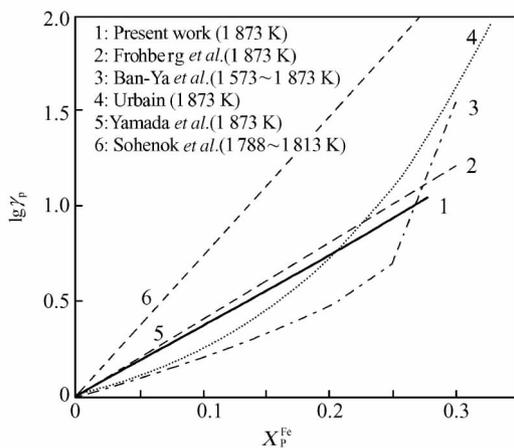


图3 Fe-P 二元系中 1873 K 下 P 的活度( $\alpha_P$ )

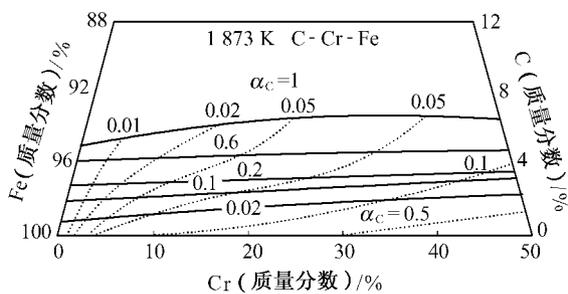


图4 C-Cr-Fe 三元系中 1873 K 下  $\alpha_C$ ,  $\alpha_{Cr}$  的等值线

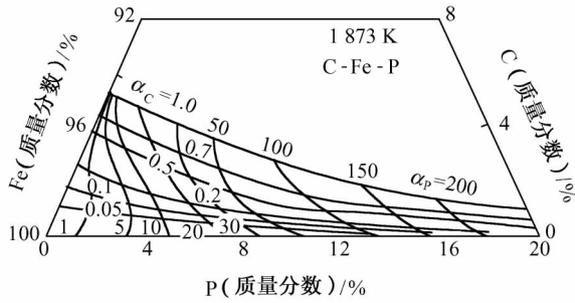


图5 1873 K下 C-Fe-P 三元系中  $\alpha_C$   $\alpha_P$  的等值线

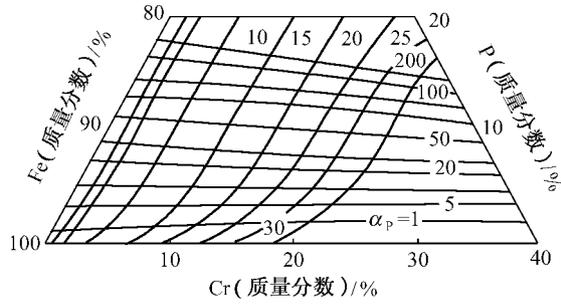


图6 1873 K下 C-Fe-P 三元系中  $\alpha_{Cr}$   $\alpha_P$  的等值线

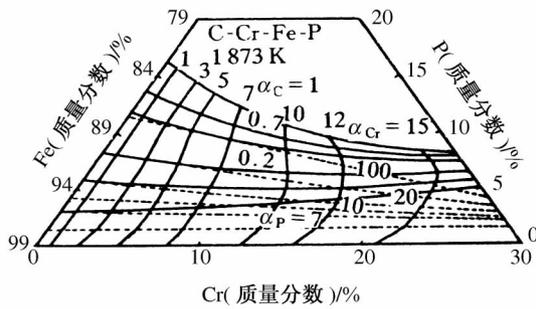


图7 1873 K下 C-Cr-Fe-P 四元系中  
 $\alpha_C$   $\alpha_{Cr}$  和  $\alpha_P$  的等值线  
C(C) = 1% (质量分数)

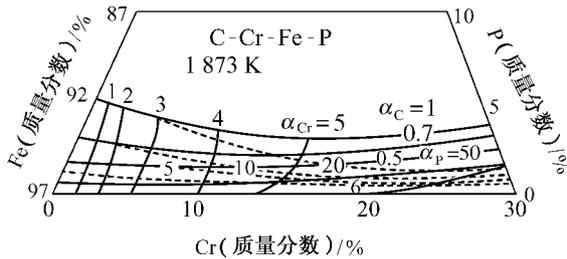


图8 1873 K下 C-Cr-Fe-P 四元系中  
 $\alpha_C$ ,  $\alpha_P$  和  $\alpha_{Cr}$  的等值线  
 $C(C) = 3\%$  (质量分数)

## 4 结论

(1) SELF-SReM4 模型属热力学参数模型,各拟合方程的导出基于热力学规律. 体系中各活度值由同一组  $A_{jkl}$  参数表示.

(2)  $A_{jkl}$  参数拟合中可以利用不同的“边界条件”根据不同的已知条件,有相应的  $A_{jkl}$  参数拟合方法. 这使 SELF-SReM4 模型具有适应不同体系的能力. 和其他溶液模型一样,“边界条件”对其结果的影响举足轻重.“边界条件”的正确性决定了模型的精度. 四元系参数  $A_{jkl}$  与二元子系参数  $a_j$  和三元子系参数  $\beta_{jk}$  参数有关.  $A_{jkl}$  拟合从二元系、三元系逐渐展开,而二、三元系实验值比四元系多且可靠,特别是二元系的“边界条件”的应用使模型具有较高精度的基本保证.

(3) 一般,某组元的热力学性质是未知的,也可能是相当复杂的函数,需通过逐步回归找到一多项式表示该函数. 但是利用这一多项式函数(经变化后)表示其他组元的性质时,可能会产生较大误差. 所以,  $j$ 、 $k$ 、 $l$  的定值相当重要. 组元数越多,这些参数定值越困难.

(4) 不同的已知条件可能是相对于不同的标准状态,在 SELF-SReM4 模型中必须将它们转换成纯物质标准状态.

(5) 由于一个  $A_{jkl}$  参数可和若干个二元、三元子系有关,它可在几个不同的  $\alpha$  参数或  $\beta$  参数和  $A_{jkl}$  参数的关系式中出现. 这些关系式可用来校核拟合结果,或反过来校核某个已知条件的可靠性. 另外,若 SELF-SReM4 模型充分逼近真实,一个多元系的液相区的各个“边界条件”就不是独立的,而是通过方程组相互牵制. 因此,若是多数“边界条件”有精选值,按照 SELF-SReM4 模型,利用它们去检验精度有疑问的“边界条件”不失为一条有根据的蹊径.

(6) 本文用 SELF-SReM4 模型解析了 C-Fe ,Cr-Fe ,Fe-P ,C-Cr-Fe ,C-Fe-P ,Cr-Fe-P 及 C-Cr-Fe-P 四元系中组元的活度. 计算结果与其他研究结果比较一致.

## 参 考 文 献

- [ 1 ] Zhang Xiaobing , Jiang Guochang , Tang Kai , Xu Jianlun , Ding Weizhong & Xu Kuangdi. A Sub-Regular Solution Model Used to Predict the Component Activities of Quarternary System , to be published
- [ 2 ] Hultgren R H. Selected Values of the Thermodynamic Properties of Binary Alloys. New York : Wiley , 1973
- [ 3 ] Kubaschewski O *et al.* Metallurgical Thermochemistry , 5th ed. Oxford : Pergamon , 1979
- [ 4 ] Urbain G. Mem Sci Rev Metall , 1959 , 56 : 529
- [ 5 ] Froberg M G *et al.* , Arch Eisen huettenwes , 1968 , 39 : 587
- [ 6 ] Schenck H , Steinmetz E , Gohlke R. Arch Eisen huettenwes , 1966 , 37 : 775
- [ 7 ] 万谷志郎 鈴木乾雄. 铁と钢 , 1975 61 : 2933
- [ 8 ] 山田启作 加藤荣一. 铁と钢 , 1979 65 : 264
- [ 9 ] Healy G W. Trans ISS , 1987 , Dec : 51
- [ 10 ] Schürmann E , Kramer D. Giessereiforschung , 1969 , 21 : 29
- [ 11 ] Griffing N R , Frogeng W D , Healy G W. Trans TMS-AIME , 1962 , 224 : 148
- [ 12 ] Schenck H & Feldman U. thesis 1956 Technisch Hochschule , Aachen
- [ 13 ] Hadrys H G , Froberg M G , Elliott J F. Metall Trans , 1970 , 1 : 1867

## Self-SReM4 Model and Its Application in Evaluating the Component Activities of C-Cr-Fe-P System

**Abstract** The sub-regular solution model , SELF-SReM4 , developed in Shanghai Lab of Ferrometallurgy was introduced. By means of this model the component activities of C-Cr-Fe-P quarternary alloy and its sub-systems (C-Fe , Cr-Fe , Fe-P , C-Cr-Fe , C-Fe-P and Cr-Fe-P) were evaluated.

# 铁基合金组元活度的计算<sup>\* 1</sup>

**摘要** 活度数据库是实施热力学预测必不可少的前提条件,而活度的解析计算成了研究建立该数据库的核心课题。现已公布的各种方法都有其不同的特点和适用范围,这是在应用它们之前务必了解的。就稀溶液而言,瓦格纳、卢皮斯的“相互作用参数法”是最实用的。而对多元系高合金多元系来说,SELF-SReMB模型能成为建立活度数据库的可靠基础。

## 1 引言

金属熔体组元活度的研究历来是冶金热力学的核心课题。瓦格纳、奇普曼、埃利奥特、卢皮斯等著名学者都曾在此领域里辛勤耕耘<sup>[1~4]</sup>。我国冶金界的一代宗师魏寿昆院士也在活度的理论和应用方面作出了重要贡献<sup>[5]</sup>。近年,他又十分精辟地阐述了多元系相互作用参数的实验测定方法及数据处理等问题,澄清了几个容易混淆的重要概念。

尽管在热力学意义上(不涉及物质结构)活度理论已很成熟,活度的应用依然不很普及。冶金研究者常会面临这样一种窘境。一方面,已掌握的热力学规律完全可用来为新技术的开发,或为实现过程优化及控制提供理论预测;另一方面,又往往由于缺乏相应的活度数据库而使定量的分析无从实施。活度数据库的重要性现在是一致公认的,但仅仅依赖实验测试来建立活度数据库则远远满足不了需要,比较现实的方针只能是靠计算给出系统的数据,然后用实验对若干点进行校核。所以活度的计算已成为关键课题。

瓦格纳的相互作用参数是迄今最流行的多元系活度计算方法,它是在无

\* 本文合作者:张晓兵、蒋国昌。原发表于《庆祝林宗彩教授八十寿辰论文集》,北京:冶金工业出版社,1996:118~126

限稀溶液的前提下,按泰勒级数展开而得.在无限稀范畴里它是有效的,但将其用于稀溶液则出现热力学上的不一致性问题.溶液愈浓,用瓦格纳相互作用参数算出的活度误差愈大.而为了开发高合金钢母液、铁合金的熔融还原技术和脱磷技术,为了改进铁合金的传统熔炼操作,为了建立 AOD、VOD 过程控制所须的数模,为了指导夹杂物的变性处理,把活度数据库扩展到高浓度合金的范畴已属当务之急,寻求新的计算方法也就更加迫切.

所有这些计算方法大体上可分为三类:

- (1) 相互作用参数法及其修正;
- (2) 溶液模型法、几何模型法、经验模型法;
- (3) 基于相图的算法.

关于这些计算方法很难严格地分类,因为一些方法既可属于这一类,又可属于另一类.本文主要讨论前两种计算方法,因为基于相图的算法目前还无法直接用以描述钢铁冶金中常见的多元系.

## 2 相互作用参数法及其修正

相互作用参数概念是瓦格纳提出的.借助于泰勒级数,他给出了用  $\varepsilon$  参数计算  $\ln \gamma_i$  的公式.而后卢皮斯等又对相互作用参数法理论的深化作出了重要贡献,并进一步发展了  $\rho$  参数<sup>[4]</sup>.多年来相互作用参数法至少在碳钢和低合金钢领域里是已得到公认的活度计算方法.但实际上,它的应用仍然存在着一些问题.其中的一部分要归因于文献报道的相互作用参数数值有分歧;另一部分可以说起源于该方法的本质,本文即意在讨论这方面的问题.

按泰勒级数,卢皮斯指出,一个多元系(1, 2, ..., m 个组元)中有

$$\ln \gamma_i = \ln(\gamma_i)^0 + \sum_{j=2}^m (\varepsilon_i^j x_j) + \sum_{j=2}^m (\rho_i^j x_j^2) + \sum_{j=2}^m \sum_{k>j}^m (\rho_i^{jk} x_j x_k) \quad (1)$$

在数学上,式(1)还有一个余项  $R_3$ , 即

$$R_3 = \frac{1}{3} \left[ \sum_{j=2}^m x_j (\partial \ln \gamma_i / \partial x_j)_{\zeta x} \right]^3 \quad (2)$$

从计算精度考虑,  $R_3$  应小于  $\gamma_i$  的测定误差.式2中的下标  $\zeta x$  表示在  $m$  维空间的“点”  $\zeta x_2, \dots, \zeta x_m$  上求偏导,并且  $0 \leq \zeta \leq 1$ .所以  $R_3$  是该多元系整体的参数.

众所周知,式(1)所含的  $\varepsilon, \rho$  参数在无限稀条件下定义,但实际上多数是

在不同的有限稀二元系或三元系中测定,且几乎全在有限稀的多元系中应用。以*i-j-k-l*四元系为例,*j,k*和*l*对 $\ln \gamma_i$ 的共同作用在式(1)中是被忽略的。这种矛盾所造成的误差实际上包含于 $R_3$ 内。因此,将式(1)用于有限稀多元合金时,随着*m*的增加其影响就会显著变大。只有当多元系为无限稀时, $R_3$ 才可能趋于零。

在此观点的基础上还要再提及的是,将来自不同二元系或三元系的(忽略了该多元系整体影响的) $\varepsilon$ 、 $\rho$ 参数用于式(1),就很难保证各 $\gamma_i$ 满足吉布斯-杜亥姆方程。瓦格纳、卢皮斯为 $\varepsilon$ 、 $\rho$ 参数导出了倒易关系,如 $\varepsilon_i^j = \varepsilon_j^i$ 就是其中之一。这些关系是式(1)能否成立的基础。若 $\varepsilon_i^j \neq \varepsilon_j^i$ ,则式(1)不能保证体系的自由能为状态函数。佩尔顿等<sup>[6]</sup>指出:

$$\varepsilon_i^j - \varepsilon_j^i = \ln [\gamma_i / (\gamma_i)^0] / [\gamma_j / (\gamma_j)^0] \quad (3)$$

显而易见,仅仅在无限稀条件下 $\varepsilon_i^j = \varepsilon_j^i$ 才能成立。这就是有限稀条件下,式(1)使用了不含该多元系整体影响的 $\varepsilon$ 、 $\rho$ 参数而造成的热力学不一致性。

怎样解决上述的矛盾?众多学者的成果大体上可归纳为两种方法。

(1) 将式(1)看作是经验规律,通过试验测定数据的拟合或计算给出式(1)中的若干参数。现在这已是相当普遍的方法。例如,草川等<sup>[7]</sup>用渣金平衡数据研究 $\varepsilon_i^k$ ,*i*表示[P],*k*表示[Ca]。计算中利用了已知的 $\varepsilon_i^j$ (*j*表示[O],[S],[N],[Si],也可表示[P])以及实测的[%*j*]和[%Ca]。若把这些 $\varepsilon_i^j$ 看作是泛用性的参数,那么草川所得的 $\varepsilon_i^k$ 则包含了该七元系的特征信息,不宜用于其他体系。关于[Ca],还有一个不能不注意的特殊问题。众所周知,Ca在钢水中的溶解度极小。因此对[Ca]来说,它的“稀溶液”范围更是十分狭小的,不能按瓦格纳、卢皮斯的原意来确定该 $\varepsilon_i^k$ 。德雷斯勒在研究高碳锰铁、硅铁、铬铁中的相互作用参数时也采取类似方法。他所报道的参数 $\rho_i^j$ 和 $\rho_i^{jk}$ (*i,k*表示[C],*j*表示[Mn],[Si])就是按不同温度下的测定值同时拟合的<sup>[8,9]</sup>。由黑利测得的 $\rho_i^j$ (*j*表示[Cr])<sup>[10]</sup>也不是符合瓦格纳、卢皮斯原意的参数,它们和低浓度区域中的相应参数有不同的数值。董元麓等<sup>[11]</sup>和冀春霖等<sup>[12]</sup>都研究了C-Fe-V三元系中的相互作用参数。他们所用方法并无显著不同,只是试验的浓度区域有所差别,但给出了不一致的结果。这证明两者的 $\rho$

参数含有不同浓度区域的不同信息.

以上三例说明如果要求相互作用参数能覆盖较大的浓度区域,那么拟合法是可用的,但是不能不看到如此所得的参数不再是泛用性的.另外,可以只用  $\varepsilon$  参数进行拟合(称瓦格纳式);也可按式(1)的  $\varepsilon$ 、 $\rho$  参数进行拟合(称卢皮斯式).这两种拟合所得的两个  $\varepsilon_i^j$  并不相等,而且两种方法还会带来不同的系统误差.式(2)表明  $R_3$  随着  $m$  的增加而变大.因此,  $m$  较大的多元系即使其浓度很低,以采用式(1)拟合为好.

(2) 佩尔顿等的修正法.如前述,在有限稀条件下使用式(1),则应有一余项.佩尔顿等注意到在有限稀条件下使用式(1)会带来热力学上的不一致问题,而从解决这个不一致问题出发提出该余项就是无限稀条件下基体 Fe 本身的活度系数<sup>[13]</sup>,即

$$\ln \gamma_{Fe} = -0.5 \sum_{j=2}^m \sum_{k=2}^m \varepsilon_j^k X_j X_k \quad (4)$$

式中的  $i$  表示 Fe.应该指出,卢皮斯比佩尔顿等更早就推导了式(4),而佩尔顿等还推导了含有  $\rho$  参数的  $\ln \gamma_{Fe}$ .他们将式(4)叠加于式(1),得

$$\begin{aligned} \ln \gamma_i = & \ln(\gamma_i)^0 + \ln \gamma_{Fe} + \sum_{j=2}^m (\varepsilon_i^j X_j) + \sum_{j=2}^m (\rho_i^j X_j)^2 \\ & + \sum_{j=2}^m \sum_{k>j}^m (\rho_i^{jk} X_j X_k) \end{aligned} \quad (5)$$

式(5)和式(1)比,可以在相当宽广的浓度区域里应用.或者说,此修正方法使许多学者长年积累下来的  $\varepsilon$ 、 $\rho$ (保持瓦格纳、卢皮斯原意的)参数在相当宽广的浓度区域里保持有效.但在进入非 Fe 基的浓度范围后,此法的应用就成了问题.如在 Mn、Cr、Si 等变为合金基体时,必须有该基体中的  $\varepsilon$ 、 $\rho$  参数,而这几乎是尚未研究的处女地.另一方面,式(5)的基础和达肯二次式<sup>[14]</sup>一致,它们都属于正规溶液模型.所以佩尔顿等推荐的相互作用系数修正方法难以覆盖整个液相区.由于该法和达肯二次式一致,因此它同时又属于溶液模型法.

### 3 溶液模型法

#### 3.1 正规溶液模型法

正规溶液模型是关于实际溶液的理论模型中问世较早者之一.文献上,

正规溶液的定义或特点有三种提法：其一，若组元混合（混合是文献上延续使用着的术语，更确切的术语可能应是溶合或熔合）时的熵变与体积变化近乎理想溶液，而焓变不为零，则该溶液是正规的；其二，统计热力学认为，若组元混合时原子间只有最近邻的相互作用，且所有原子呈无规则排列，则该溶液是正规的；其三，若溶液中组元活度系数和浓度呈二次方关系，则该溶液是

正规的。这三者是完全一致的。实际上，前者是唯象的定义，第二种提法是实质，后者是数学上的表现形式。所以，对二元正规溶液，有

$$RT \ln \gamma_1 = \alpha x_2^2 = \Delta(G_1)^{\text{ex}} \quad (6)$$

$$RT \ln \gamma_2 = \alpha x_1^2 = \Delta(G_2)^{\text{ex}} \quad (7)$$

式中  $\alpha$  是常数。对三元正规溶液，里查逊用图 1 表明<sup>[15]</sup>，其中：

$$x_2' = x_3' = (x_2 + x_3) = (1 - x_1) \quad (8)$$

$$(x_2/x_2') = (x_3/x_3') = (1 - x_1) \quad (9)$$

因而

$$\begin{aligned} \Delta(G_1^{123})^{\text{ex}} &= \Delta(G_1^{12'})^{\text{ex}} [x_2/x_2'] + \Delta(G_1^{13'})^{\text{ex}} [x_3/x_3'] \\ &\quad + (1 - x_1)^2 \Delta(G_{2'3''})^{\text{ex}} \end{aligned} \quad (10)$$

$\Delta(G_1^{12'})^{\text{ex}}$  表示 1-2 二元系中，在点  $(x_1, x_2)$  上组元 1 的过剩自由能变化。相应的  $\Delta(G_1^{13'})^{\text{ex}}$  表示 1-3 二元系中，在点  $(x_1, x_3)$  上组元 1 的过剩自由能变化。而  $\Delta(G_{2'3''})^{\text{ex}}$  表示 2-3 二元系在点  $(x_2, x_3)$  上的过剩自由能总量。从而有

$$\begin{aligned} \Delta(G_{2'3''})^{\text{ex}} &= [x_2 \Delta(G_2^{2'3''})^{\text{ex}} \\ &\quad + x_3 \Delta(G_3^{2'3''})^{\text{ex}}] / (1 - x_1) \end{aligned} \quad (11)$$

$\Delta(G_2^{2'3''})^{\text{ex}}, \Delta(G_3^{2'3''})^{\text{ex}}$  表示 2-3 二元

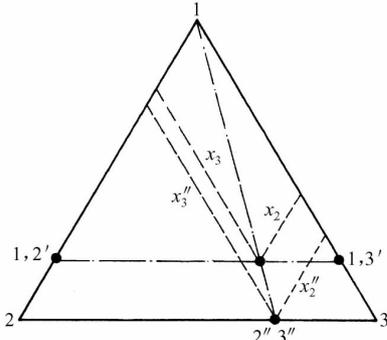


图 1 三元正规溶液

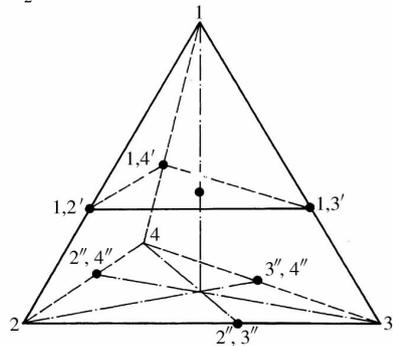


图 2 四元正规溶液

系中,在点 $(x_{2''}, x_{3''})$ 上组元 2、3 的过剩自由能变化. 对于四元正规溶液 (见图 2)有

$$\begin{aligned} \Delta(G_1^{1234})^{\text{ex}} = & [x_2 \Delta(G_1^{12'})^{\text{ex}} + x_3 \Delta(G_1^{13'})^{\text{ex}} + x_4 \Delta(G_1^{14'})^{\text{ex}}] / (1 - x_1) \\ & - (1 - x_1)^2 [\Delta(G_{2'3''})^{\text{ex}} + \Delta(G_{2'4''})^{\text{ex}} \\ & + \Delta(G_{3'4''})^{\text{ex}}] \end{aligned} \quad (12)$$

由式(10)及式(12)可以看到,按正规溶液模型,多元系组元的活度系数能只用所属二元系的参数叠加而得.反过来,若一个多元系,其组元的活度系数能只用所属二元系的参数叠加而得,则该多元系是一个正规溶液.

### 3.2 Darken 二次式

达肯二次式和里查逊的式(10)及式(12)有所不同.前者并不是由正规溶液模型导出的,而是达肯从归纳活度系数随组元浓度变化的规律得到的经验公式.对许多二元系,他发现在组元1为溶剂的端区有

$$\begin{aligned} \lg \gamma_1 = & \alpha_{12} x_2^2 \\ \lg[\gamma_2 / (\gamma_2)^0] = & \alpha_{12} [(x_1)^2 - 1] \end{aligned} \quad (13)$$

$\alpha_{12}$ 表示组元1为溶剂的端区中之比例常数.式(13)显然不同于式(6).可以认为式(13)是准化学近似模型的结果.或者改变一下其中组元2的标准态,则两式就一致了.所以,达肯二次式实质上证明了许多二元系的两个端区都符合正规溶液模型.他还指出,各种二元系的端区宽度不等,同一体系的两个端区也不等宽.一般它们在  $x_2 \leq 0.15 \sim 0.50$  的范围内.此外,各种二元系的  $\alpha_{12}$  不等,且同一体系的  $\alpha_{12}$  并不等于  $\alpha_{21}$ .

达肯将他的二次式用于三元系,得到

$$\begin{aligned} \lg \gamma_1 = & \alpha_{12} x_2^2 + \alpha_{13} x_3^2 + (\alpha_{12} + \alpha_{13} - \alpha_{23}) x_2 x_3 \\ \lg[\gamma_2 / (\gamma_2)^0] = & -2\alpha_{12} x_2 - (\alpha_{12} + \alpha_{13} - \alpha_{23}) x_3 + \lg \gamma_1 \\ \lg[\gamma_3 / (\gamma_3)^0] = & -2\alpha_{13} x_3 - (\alpha_{12} + \alpha_{13} - \alpha_{23}) x_2 + \lg \gamma_1 \end{aligned} \quad (14)$$

式(14)来源于该三元系的  $\Delta(G_{123})^{\text{ex}}$ , 有

$$\begin{aligned} \Delta(G_{123})^{\text{ex}} / RT = & x_2 \ln(\gamma_2)^0 + x_3 \ln(\gamma_3)^0 - \alpha_{12} x_2^2 \\ & - \alpha_{13} x_3^2 - (\alpha_{12} + \alpha_{13} - \alpha_{23}) x_2 x_3 \end{aligned} \quad (15)$$

若  $\ln(\gamma_2)^0 = \alpha_{12}$ ,  $\ln(\gamma_3)^0 = \alpha_{13}$ , 则式(15)演变成为正规溶液的特征,即

$$\Delta(G_{123})^{\text{ex}} / RT = \alpha_{12} x_1 x_2 + \alpha_{23} x_2 x_3 + \alpha_{13} x_1 x_3 \quad (16)$$

因此,达肯的式(14)是一个变态的正规溶液模型,即相当于不再取纯溶质作为其标准态的经验规律.它只能用于溶质摩尔浓度在 0.20 ~ 0.30 以下的三个角区.此幅度比二元系的端区更小.

达肯规定  $\alpha_{ij}$  均为恒量,还规定  $\alpha_{12}$  和  $\alpha_{13}$  分别是 1-2 和 1-3 两个二元系的参数,由式(13)定值.而  $\alpha_{23}$  则利用二元系及三元系中 [C] 的等活度数据算出,且认为  $\alpha_{23}$  是 2-3 二元系的参数.事实上,  $\ln \gamma_i$  可用 Darken 二次式求值,也可用上述的  $\varepsilon, \rho$  方程表示.无疑,这里的  $\alpha_{ij}$  参数与上述的  $\varepsilon, \rho$  参数之间应有确定的换算关系.而上述已说明,在有限稀三元溶液条件下,  $\varepsilon, \rho$  参数应含有三元系整体的信息,所以不难推理这里的  $\alpha_{ij}$  参数全应是三元系的参数.冀春霖等用他们自己的实验数据并借助文献资料验证了达肯二次式<sup>[16]</sup>.他们证明即使在 C-Fe-Si、C-Fe-S 的 Fe 角中  $\alpha_{23}$  (2 表示 Si 或 S, 3 表示 C) 均明显随合金组成而变,但 C-Fe-Co、C-Fe-Ni 的 Fe 角中  $\alpha_{23}$  (2 表示 Co 或 Ni) 变化较小.应该说明的是,冀春霖等的计算已把其他  $\alpha_{ij}$  参数随合金组成的变化一起归并在  $\alpha_{23}$  的变化之中.

### 3.3 亚正规溶液模型

如上所述,正规溶液模型的适用范围是有限的.另一方面,它又有相当简洁的优点.因此在其基础进行修正的研究层出不穷.这些修正大体上可分为两类,一是从溶液结构出发的修正,一是经验性的修正.亚正规溶液模型和准正规溶液模型就是第一类修正.

正规溶液模型假设最近邻的离子成对地相互作用,所以其标志是二次式.亚正规溶液模型实质上是中心原子模型的一个特例.它考虑了次近邻离子间的作用,所以其标志是组元浓度的指数大于 2.可以认为三个离子间的相互作用对应于 3 次方,其余类推.指数大于 3 的关系式,称为高阶的亚正规溶液模型.此时,离子间的相互作用能不仅是温度的函数,而且随组元浓度改变,过剩熵变不再为零.按亚正规溶液模型写出二元系的过剩自由能总量可有很多形式,例如:

$$\Delta(G_{12})^{\text{ex}} = A_{12} x_1 x_2 + A_{112} x_1 x_2^2 + A_{1122} (x_1 x_2)^2 \quad (17)$$

其中,  $A_{12}$ 、 $A_{112}$ 、 $A_{1122}$  分别是描述离子对 1-2、三离子团 1-1-2、四离子团 1-1-2-2 的参数.

本文作者采用 SELF-SReM3 模型成功地给出了 C-Fe-x(x = Si, Mn, Cr, Ni) 三元系中, 1 873 K 或 1 823 K 下整个液相区内的  $\alpha_C$ , 再用“ I-D ”法计算  $\alpha_{Fe}$  和  $\alpha_x$ . 以 C-Fe-Si 合金为例, SELF-SReM3 模型如式(18) ~ 式(21)所示:

$$f_C = \sum_{j=2}^5 \sum_{k=0}^3 A_{jk} Y^j Z^k + \sum_{j=2}^4 A_{j4} Y^j Z^4 + \sum_{j=2}^5 A_{j5} Y^j Z^5 \quad (18)$$

$$\Delta(G_C)^{ex} = K + f_C \quad (19)$$

$$\begin{aligned} \Delta(G_{Fe})^{ex} = & \Delta(G_{Fe}^{y=1})^{ex} + f_C(1 - Y^1) + \sum_{j=2}^5 \sum_{k=0}^3 (1 - k) \cdot \\ & A_{jk} Z^k (1 - Y^{j-1}) / (j - 1) - \sum_{j=2}^4 3A_{j4} Z^4 (1 - Y^{j-1}) / \\ & (j - 1) - \sum_{j=2}^3 4A_{j5} Z^5 (1 - Y^{j-1}) / (j - 1) \end{aligned} \quad (20)$$

$$\begin{aligned} \Delta(G_{Si})^{ex} = & \Delta(G_{Si}^{y=1})^{ex} + f_C(1 - Y^1) + \sum_{j=2}^5 \sum_{k=0}^3 A_{jk} Z^k (1 - Y^{j-1}) / (j - 1) \\ & + \sum_{j=2}^4 A_{j4} Z^4 (1 - Y^{j-1}) / (j - 1) + \sum_{j=2}^3 A_{j5} Z^5 (1 - Y^{j-1}) / (j - 1) \\ & + \sum_{j=2}^5 \sum_{k=0}^3 k(1 - Z) A_{jk} Z^{k-1} (1 - Y^{j-1}) / (j - 1) \\ & + \sum_{j=2}^4 4(1 - Z) A_{j4} Z^3 (1 - Y^{j-1}) / (j - 1) \\ & + \sum_{j=2}^3 5(1 - Z) A_{j5} Z^4 (1 - Y^{j-1}) / (j - 1) \end{aligned} \quad (21)$$

其中,  $Y = 1 - x_C$ ,  $x_{Si} = YZ$ ; 上称  $Y = i$  表示 Fe-Si 二元系.

### 3.4 SELF-SReM3 模型的特色

#### 基本思路

多元系组元活度解析的核心问题是算出“第一组元”在整个液相区内的活度值. 这一方面是因为用实验通常只能得到若干“点”上该组元的活度值; 另一方面, 则因为其他组元的活度不难利用吉布斯-杜亥姆公式求解. 显然, 选择溶剂作为“第一组元”是不明智的. 对 C-Fe-x 三元系, SELF-SReM3 模型选择 C 作为“第一组元”, 因为在铁基合金中 C 的热力学性能数据很丰富, 且

经过众多冶金学者的考察已归结出精选值。

SELF-SReM3 模型在所研究的“空间”内,包括其边界上,按高阶亚正规溶液模型和吉布斯-杜亥姆公式,建立组元偏摩尔自由能及体系偏摩尔自由能总量和合金浓度的“关系式组”。然后,为其液相区给出充分的“边界条件”,通过该关系式组拟合出模型所含的待定的  $A_{jk}$  参数。在  $A_{jk}$  确定之后,用该关系式组计算组元活度,即相当于数学上的方程组求解。

#### 亚正规溶液模型的阶数

用高阶的亚正规溶液模型建立的该关系式组并不是描述所研究体系的精确方程,而是一种逼近性的方程。一般情况下,究竟要用几阶的亚正规溶液模型能充分逼近所研究体系的真实行为是并不清楚的。但是若不考虑数学处理上的难度,亚正规溶液模型的阶数的增加会提高逼近程度。这是 SELF-SReM3 模型可信度的一个基础。

#### 边界条件

按正规溶液模型,三元系中组元的活度完全由其“二元子系”的热力学性质决定。按照几何模型,对一个三元系来说,在其三个“二元子系”中各取一特定点,则三元系某一点上的性质就取决于三个特定点上该二元子系的性质。因为几何模型均以正规溶液模型为基,所以两者的结果相仿是不难理解的。对 C-Fe-Si 等显然不是正规溶液,并且 C-Si 不构成溶液的体系,SELF-SReM3 模型所用的边界条件包括:

- (1) C-Fe 二元系中 C 的偏摩尔自由能精选值;
- (2) 不含 C 的 Fe-Si 二元系之偏摩尔自由能总量精选值;
- (3) C-Fe-Si 中的 C 饱和线;
- (4) C-Fe-Si 中公认的  $\alpha_c = 0.025$  等活度线。

因此,SELF-SReM3 模型中利用了该三元系的整体信息,而不是仅仅依靠液相区边界上三个特定点上的信息来拟合上述的  $A_{jk}$  参数。在数学上,这不是一个简单的内插定值的问题,而是在多因素通过上述的“关系式组”相互制约条件下进行内插定值的问题。这就是 SELF-SReM3 模型能以更高的可信度,由边界条件出发,提供该三元系整个液相区内组元活度值的另一个原因。

#### 误差来源

原则上 SELF-SReM3 模型的结果有两个误差来源:其一,高阶亚正规溶液模型逼近所研究体系真实行为的程度;其二,SELF-SReM3 模型中所含  $A_{jk}$  参数的拟合精度。这两者,在某种程度上是有矛盾的,因为所取阶数愈高, $A_{jk}$  参数愈多,拟合本身的难度愈大。

SELF-SReMB 模型从三方面改进了佩尔顿等<sup>[18]</sup>和王之昌<sup>[19]</sup>的方法. 其一, 式(19)中的 K 是王之昌法的特点, 而 SELF-SReMB 模型修正了 K 的定值手续<sup>[20]</sup>. 其二佩尔顿等和王之昌的方法用于 C-Fe-Mn 系是成功的. 对其他合金, SELF-SReMB 模型指出, 三元系性质只有碳饱和曲线是不足的,  $\alpha_c = 0.025$  的等活度曲线也必须用作边界条件. 其三, 放弃了用  $C_{jk}$  参数计算  $\alpha_x$  的方法, 而改用“I-D”法进行计算. 这三方面的改进保证了不同的三元合金可用统一的解析方法计算组元活度.

尽管如此, SELF-SReMB 模型还需要在以下几方面取得进一步的完善.

(1) 含碳化物形成元素时的固态析出相之变化. 以液态 C-Fe-Si 三元系为例, 低 [% Si] 区的一个边界是 [C] 的饱和线. 此线是 SELF-SReMB 模型必需的边界条件之一. 在此线上,  $\alpha_c = 1$ . 但高 [% Si] 区中, 该边界上的固态析出相已非 C, 而变为 SiC 了. 在此线上,  $\alpha_c \neq 1$ , 而是  $\alpha_{Si}$  的函数, 即

$$\alpha_c \alpha_{Si} = \exp(\Delta G_{13}^{\theta} / RT) \quad (22)$$

这里的  $\Delta G_{13}^{\theta}$  表示 SiC 的标准生成自由能. 若要用 SELF-SReMB 模型更精确地描述高 [% Si] 区, 则必须测出 SiC 的析出线, 并在此线上, 用式(22)取代  $\alpha_c = 1$  作为边界条件. 这样一来,  $A_{jk}$  参数的拟合就得引入迭代法. C-Fe-Cr 也有类似的问题. 在这里还要顺便提请注意, 高 [% Si] 区中的 [% C] 很小, 但此种合金并非 C 的稀溶液.

(2) C-Fe- $x_1$ - $x_2$ - $y_1$ - $y_n$  系合金的组元活度 ( $x$  表示高浓度组元,  $y$  表示微量组元). SELF-SReMB 模型不难推广到 C-Fe- $x_1$ - $x_2$  或 C-Fe- $x$ - $y$  四元素. 原则上, 对多元系也可推出类似乎式(18)~式(21)的公式. 但是五元系以上的  $A_{jk}$  参数拟合工作量太大, 不易推行. 另一方面, 由于  $y_i$  组元均是微量的, 因此有可能引入瓦格纳、卢皮斯的  $\varepsilon$ 、 $\rho$  参数. 对 C-Fe- $x_1$ - $x_2$ - $y$  的  $\ln \gamma_y$ , 以 1~5 分别表示五个组元, 有

$$\ln \gamma_y = \ln(\gamma_5)_{1235} + \ln(\gamma_5)_{1245} - \ln(\gamma_5)_{125} - \rho_5^{34}(x_4 x_3) \quad (23)$$

$$\rho_5^{34}(x_3 x_4) = \ln(\gamma_5)_{2345} - \ln(\gamma_5)_{235} - \ln(\gamma_5)_{245} + \ln(\gamma_5)_{25} \quad (24)$$

式(22)中的  $\ln(\gamma_5)_{1235}$ 、 $\ln(\gamma_5)_{1245}$ 、 $\ln(\gamma_5)_{125}$  可用 SELF-CFeX 模型解出, 以适应高浓度.  $\rho_5^{34}(x_3 x_4)$  当  $x_3 x_4$  不太大时可忽略不计, 否则就要用式 24 进行解析. 其中所含各个  $\ln(\gamma_5)$  都可用 SELF-CFeX 模型解出.

## 4 几何模型和经验模型

### 4.1 几何模型

几何模型的出现很早,比较知名的有库勒模型、柯里奈模型、穆基雅努模型、图普模型、希尔特模型、周国治模型等。多年来此领域的研究很活跃。周国治最近推出一个新的几何模型,使各家的方法得以概括并更为合理<sup>[21]</sup>。几何模型的意图是用二元系的热力学性质测算三元系的热力学性质(以及从三元系测算四元系)。另外,还要求多元系退化为其子系时仍能保留正规溶液或亚正规溶液的特色。因此,几何模型和正规溶液有千丝万缕的联系。

几何模型目前主要用于有色合金和熔盐体系的相图预报。

### 4.2 经验模型

经验模型常作为整理实验数据的方法出现,以高克森等提出的模型<sup>[22]</sup>为例。他们研究的是 S-Fe-Co-Ni 合金,分别以 1、2、3、4 代表四个组元。(123)系的过剩自由能总量用马尔古利斯式表示:

$$\begin{aligned} \Delta G^{\text{ex}}/RT = & A_{12}x_1x_2(x_1 + x_2) + A_{13}x_1x_3(x_1 + x_3) + A_{23}x_2x_3(x_2 + x_3) \\ & + x_1x_2x_3(A_{12} + A_{13} + A_{23} + C_1x_1 + C_2x_2 + C_3x_3) \end{aligned} \quad (25)$$

其中 A 和 C 均是待定参数,且  $A_{ij} = A_{ji}$ 。此式的前三项是典型的亚正规溶液模型,它们分别表示三个二元子系的性质。当仅用三个二元子系模拟而和多元系不一致时,经验模型往往采取增加一直接由多元系实测确定的项。上式的第四项表示该三元系整体的特征,就是一例。(124)和(134)的描述与式(24)可以不完全一致,可以为了方便参数的拟合而人为地取某个或某些参数等于零。这正是经验模型和上述溶液模型不同之处。而且,若说式 24 是完整的,那么经验模型还允许采用不完整的公式。如高克森等仅用 Fe-Co 和 Fe-Ni 两个二元子系描述 Fe-Co-Ni 三元系,且取  $A_{24} \neq A_{42}$  和  $A_{34} = A_{43} = 0$ 。因此,经验模型所得的参数不是泛用性的,模型本身也可以是非泛用性的。

## 5 结论

建立活度数据库是实施热力学预测所必不可少的前提条件,因此活度的

解析计算成了研究的核心课题. 现已公布的各种方法都有其不同的特点和适用范围. 这是在应用它们之前务必了解的.

就稀溶液而言, 无疑瓦格纳、卢皮斯的“相互作用参数法”是最实用的. 人们作了很多努力, 试图拓宽相互作用参数法的应用. 但是对于多元系, 特别是高合金来说, SELF-SReMB 模型能成为建立活度数据库的可靠基础. 因为一方面, 它依赖该合金的整体信息给出活度数值, 各组元的活度通过吉布斯-杜亥姆公式而相互制约; 另一方面, 它为不同的三元合金, 除 C-Fe-x 系外也包括 C-Mn-x 等体系, 给出了统一的关系式和统一的待定参数拟合法.

## 参 考 文 献

- [ 1 ] Wagner C. , Thermodynamics of Alloys , Addison-Wesley , Reading , Massachusetts , 1952
- [ 2 ] Chipman J. , *Metall Trans.* , 3 ( 1972 ) , 4 , 879-885
- [ 3 ] Sigworth G. K. , Elliott J. F. , *Metal Science* , 8 ( 1994 ) , 298-310
- [ 4 ] Lupis C H P. Chemical Thermodynamics of Materials , Elsevier Science Publishing Co. Inc. , N. Y. , 1983
- [ 5 ] 魏寿昆. 活度在冶金物理化学中的应用, 中国工业出版社, 1964
- [ 6 ] Pelton A. D. , Bale C. W. , *Metall Trans.* , 17A ( 1986 ) , 6 , 1211-1215
- [ 7 ] 草川隆次, 大堀学, 近藤広一, 吉岗敬二. 鉄と钢, 68 ( 1982 ) , 14 , 1905-1914
- [ 8 ] Dresler W. , *Can. Metall. Q.* 28 ( 1989 ) , 2 , 109-115
- [ 9 ] Dresler W. , *I & SM* , ( 1990 ) , 3 , 95-100
- [ 10 ] Healy G. W. , *I & SM* ( 1989 ) , 12 , 51-59
- [ 11 ] 郭上型, 董元箴, 朱本立, 李大经. 钢铁研究总院学报, 4 ( 1989 ) , 1 , 19-24
- [ 12 ] 车荫昌, 冀春霖, 齐国均. 钢铁研究总院学报, 3 ( 1988 ) , 8 , 7-15
- [ 13 ] Bale C. W. , Pelton A. D. , *Metall Trans.* 21A ( 1990 ) , 7 , 1997-2001
- [ 14 ] Darkon L. S. , *Trans Met Soc. AIME* , 239 ( 1967 ) , 90-96
- [ 15 ] Richardson F. D. , *Physical Chemistry of Melts in Metallurgy* , 1974
- [ 16 ] 齐国均, 冀春霖, 1984 , 227-236
- [ 17 ] 蒋国昌, 张晓兵, 徐匡迪. 金属学报, 6B ( 1992 ) , 6 , 240-246
- [ 18 ] Pelton A. D. , Flengas S. N. , *Canadian J. Chemistry* , 47 ( 1969 ) , 2283-2292
- [ 19 ] 王之昌. 中国科学(A) , ( 1986 ) , 8 , 862-873
- [ 20 ] 张晓兵, 蒋国昌, 王之昌. 上海工业大学学报, 11 ( 1990 ) , 10 , 490-496
- [ 21 ] Chou K. C. , CALPHADD X X III Meeting , Wisconsin , USA , 1994
- [ 22 ] Gokcen N. A. , Baren M. R. , *Metall Trans.* , 16A ( 1985 ) , 5 , 907-911

# 氮气加压熔炼高氮钢 若干理论问题探讨<sup>\* 1</sup>

**摘要** 导出了氮在铁合金溶液中的溶解度模型,探讨了表面活性元素对吸氮过程的影响,且对含氮铁合金溶液的凝固过程、氮的偏析及保持氮在熔体中的最小压力进行了精确解析。

## 符号说明

- |  |  |
|--|--|
| <p><math>a</math>——气-液两相的比表面积 <math>m^{-1}</math> ;</p> <p><math>\alpha_i</math>——表面活性元素 <math>i</math> 的活度 ;</p> <p><math>\alpha_N</math>——熔体中氮的活度 ;</p> <p><math>C_S^i, C_L^i</math>——溶质元素在固-液界面两侧的百分浓度 ;</p> <p><math>C_0</math>——熔体的原始成分 ;</p> <p><math>C_L</math>——固-液界面前沿液体内部成分 ;</p> <p><math>D_S, D_L</math>——溶质在固相和液相中的扩散系数 <math>m^2/s</math> ;</p> <p><math>D_p</math>——溶质元素偏析度, % ;</p> <p><math>e_N^i</math>——以无限稀溶液为标准态的一次相互作用系数 ;</p> <p><math>E_N^i</math>——压力作用系数 ;</p> | <p><math>f_S</math>——固相率, % ;</p> <p><math>f_N</math>——氮的活度系数 ;</p> <p><math>F_N</math>——考虑压力后的氮活度函数 ;</p> <p><math>k_s, k_{t0}</math>——式(8),(10)反应速度常数 <math>m/s</math> ;</p> <p><math>k_N</math>——吸氮速度常数 <math>m/s</math> ;</p> <p><math>K_i^{ad}</math>——组元 <math>i</math> 在钢水内部和外表面的分配常数 ;</p> <p><math>K_N</math>——吸氮反应平衡常数 ;</p> <p><math>L</math>——试样长度 <math>m</math> ;</p> <p><math>m</math>——溶质元素的分配系数 ;</p> <p><math>[N]_0</math>——熔体的初始氮含量 ;</p> |
|--|--|

\* 本文合作者:陆利明、李宏、壮云乾、蒋国昌. 原发表于《钢铁研究学报》8(1) 6~10 (1996)

% ;	$\alpha$ ——表征溶质在固相中扩散程度的物理量 ;
$P_{N_2}$ ——气相氮分压 ,MPa ;	$\gamma_N^i$ ——二次相互作用系数 ;
$P_N$ ——固-液界面前沿氮的平衡压力 ,MPa ;	$\delta_s$ ——扩散边界层厚度 ,m ;
$P_{N_{max}}$ ——固-液界面前沿氮的最大平衡压力 ,MPa ;	$\Delta H_i$ ——摩尔组元 $i$ 由表面进入体内的焓变 ,J/mol ;
$r$ ——吸氮速度 ,l/s ;	$\rho_N^{i,j}$ ——二次相互作用系数 ;
$r_8, r_{10}$ ——式(8) ,(10)的反应速率 ,l/s ;	$\theta_i$ ——组元 $i$ 的表面覆盖率 ;
$t_f$ ——完全凝固所需时间 ,s ;	$\theta_T$ ——总表面覆盖率.
$T$ ——温度 ,K ;	上 标
$v_a$ ——气-液界面可吸附氮的位置 ;	$i$ ——组元或固-液界面 ;
$v$ ——固-液界面的推进速度 ,m/s ;	ad——吸附态.
$X_i$ ——组元 $i$ 的摩尔分数 ;	下 标
$Y_i$ ——沿凝固方向固-液界面的位置 ,m ;	eq——平衡态 ;
	$i$ ——组元或固-液界面 ;
	L——液相 ;
	S——固相.

## 1 前言

氮和碳一样 ,在钢中以间隙原子的形式存在 ,且具有较强的强化能力和耐蚀性能.所以 ,以氮部分或全部代替碳的高氮钢在国外已被广泛用作工具、模具、结构材料.然而 ,氮在钢中的溶解度很小 ,因此提高钢中氮的溶解度 ,抑制氮在凝固过程中的析出是制备高氮钢的关键.目前 ,国外用于制备高氮钢的方法有氮气加压法、粉末冶金法和表面渗氮法<sup>[1]</sup>.其中氮气加压法的应用最有前途 ,其最高运行压力已达 4.2 MPa<sup>[2]</sup>.但是 ,在氮气加压法渗氮过程中 ,还有许多理论问题 ,如氮在铁合金溶液中的溶解度、氮在凝固过程中的偏析等尚需完善.本文在这些方面作了探索.

## 2 氮在铁合金溶液中的溶解度

众所周知,氮在纯铁中的溶解度可由 Sievert 定律来预测,而氮在铁合金溶液中的溶解度受其合金成分影响很大,要是能对这种影响进行定量的描述,这对高氮合金钢溶氮量及其性能预测、计算是很有意义的。

在 Fe-N-2-3-...-i-...-n 多元系中,氮的溶解反应为



由质量作用定律可得:  $K_N = a_N / (P_{N_2})^{1/2} = f_N [\% N] / (P_{N_2})^{1/2}$  则

$$f_N [\% N] = K_N \sqrt{P_{N_2}} \quad (2)$$

整理后得

$$\ln [\% N] = \ln K_N + \ln \sqrt{P_{N_2}} - \ln F_N \quad (3)$$

由式(3)可知,只要求出  $f_N$  值,  $[\% N]$  也就迎刃而解。众所周知,  $f_N$  应是组元 N, 2, ..., n 组成的函数,而氮含量又是温度、压力和组元 2, ..., n 组成 ( $x_2, \dots, x_n$ ) 的函数。因此,当 T,  $P_{N_2}$  为常数时

$$\ln f_N = f(x_2, \dots, x_n) = \sum_{i=2}^n e_N^i [\% i] \quad (4)$$

将式(4)代入式(3),虽然能较好地反映常压下稀铁合金溶液的吸氮规律,但当压力大于 0.1 MPa 或合金含量较高时,发生明显的误差。这可能是由于在推导式(4)时忽略了压力影响以及套用稀溶液相互作用系数所致。

考虑到压力的影响,用  $F_N$  代替  $f_N$  则

$$\ln F_N = f(x_2, \dots, x_n) \ln \sqrt{P_{N_2}} \quad (5)$$

将式(5)进行泰勒展开(包括二次项),可得

$$\ln F_N = \sum_{i=2}^n e_N^i [\% i] + \sum_{i=2}^n \gamma_N^i [\% i] [\% i]$$

$$+ \sum_{i,j=2}^n \rho_N^{i,j} [\% i][\% j] + \sum_{i=2}^n E_N^i [\% i] \ln \sqrt{P_{N_2}} \quad (6)$$

将式(3)中的  $f_N$  换成  $F_N$ , 便可得氮在铁合金溶液中的溶解度模型

$$\ln[\% N] = \ln(K_N \sqrt{P_{N_2}}) - \ln F_N \quad (7)$$

由式(7)可知,当温度一定时,只要知道合金成分和氮分压,便可对氮的溶解度进行预测.由此作者计算了纯铁和几种常用钢种在1873 K下氮的溶解度(见图1曲线).由图1可知,根据式(7)的计算值和文献[2]在3种  $P_{N_2}$  时实验结果相当吻合.在此,为了避免套用稀溶液相互作用系数而带来的误差,式(7)中的系数均采用 Rawers 的研究结果(见表1)<sup>[2]</sup>.

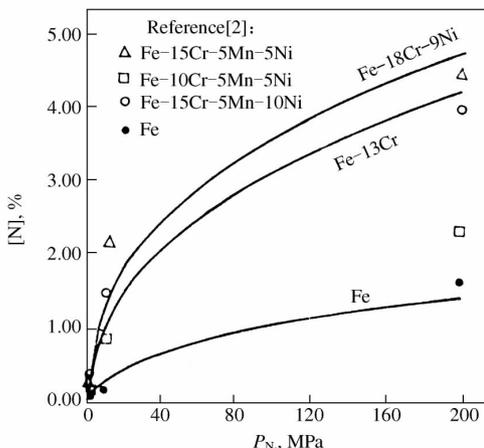


图1 1873 K下不同材料的氮溶解度  
Fig. 1 Nitrogen solubility in several materials at 1873 K

表1 计算中所用的相互作用系数

Table 1 Evaluation of interaction coefficient for Fe-Cr-Mn-Ni system

$e_N^i$			$\gamma_N^i \times 10^3$			$\rho_N^{i,j} \times 10^3$			$E_N^i \times 10^3$		
Cr	Mn	Ni	Cr-Cr	Mn-Mn	Ni-Ni	Cr-Mn	Cr-Ni	Mn-Ni	Cr	Mn	Ni
-0.13	-0.087	0.017	2.3	0.13	0.8	0.9	-1.5	0.2	7.3	11.0	4.8

### 3 钢水吸氮过程动力学

本文试图从微观动力学角度来解释表面活性元素对吸氮过程的影响.不妨假设吸氮过程分三步进行:



$$[N]_i = [N] \quad (10)$$

在低氧位或硫位下,液体表面可供氮吸附的位置很多,所以式(8), (9)很快达到平衡,即  $[N]_i = [N]_{eq}$ . 此时反映液相传质的基元反应式(10)起限速作用,其速率方程为:  $r = r_{10} = a k_{10} ([\% N]_i - [\% N]) = a k_{10} \times ([\% N]_{eq} - [\% N])$ ,为一级反应.

在高氧位或硫位,液体表面大部分位置被表面活性元素(O, S)所占据,此时可供氮吸附的位置减少,于是式(8)的吸附过程变为限速环节,其速率方程为:  $r = r_s = a [k_s (1 - \Sigma \theta_i)^2 / K_N^2] \times ([N]_{eq}^2 - [N]^2)$ ,为二级反应. 式中  $(1 - \Sigma \theta_i)$  为空位率.

根据上述的微观动力学推导,可以定性地说明表面活性元素对吸氮反应的影响. 然而,吸氮反应速度常数  $k_N$  和  $\theta_i$  间定量关系需由宏观动力学知识导出. 假定表面活性元素  $i$  在钢水内部和外表面的分配常数  $K_i^{ad}$  为

$$K_i^{ad} = \theta_i / [(1 - \Sigma \theta_i) \alpha_i] \quad (11)$$

即总表面覆盖率  $\theta_T = \Sigma \theta_i = \Sigma K_i^{ad} \times \alpha_i / (1 + \Sigma K_i^{ad} \times \alpha_i)$ . 引用 Hua<sup>[3]</sup> 等推荐的经验关系可得

$$k_N = 1.19 \sqrt{1 - \theta_T} - 0.19 \quad (12)$$

式(12)给出了反应速度常数  $k_N$  和  $\theta_T$  的定量关系. 德田昌则<sup>[4]</sup>在研究 S、O 等表面活性元素对  $k_N$  影响时,也发现了类似现象. 而且式(11)中  $K_i^{ad}$  为温度的函数,即  $\ln K_i^{ad} = \Delta H_i / (RT) + C_i$  (式中  $C_i$  为常数). 在 1 873 K 时,  $C_s = -4.46$ ,  $C_o = -5.65$ ;  $\Delta H_i$  为 1 mol 组元  $i$  由表面进入体内的焓变,  $\Delta H_s = -146.3$  kJ/mol,  $\Delta H_o = -167.2$  kJ/mol. 代入式(12),从而也反映了温度对  $k_N$  的影响.

#### 4 高氮钢凝固过程及偏析解析

发生于凝固期间的溶质再分配会影响凝固后的组织、性能的均匀性,应予以重视. 关于凝固期间固相充分扩散和无扩散两种情况下的溶质再分配, Flemings 等<sup>[5]</sup>早已建立了相应的数学模型.

其实,固相扩散是很困难的,所以固相充分扩散的情况很少发生. 对于置

换型原子,其固相扩散系数  $D_s$  约为液相扩散系数  $D_L$  的千分之一,可视作固相无扩散处理.但是,对于诸如 C, N 等间隙原子,其固相扩散不能忽略,所以有必要寻求一种新的溶质再分配模型.

假设:1) Fe-N 相图的液相线和固相线是直线;2) 液相完全扩散,固相不完全扩散;3) 固-液界面的推进速度  $v$  随时间  $t$  按抛物线规律减小,则  $v = (L/2t_f)t^{-1/2}$ ,  $Y_i = (L/2t_f)t^{1/2}$ ;4) 溶质元素在固相中的扩散边界层厚  $\delta_s$  (见图2)为  $\delta_s = 2D_s/v$ ;5) 溶质横向分布均匀,故取单位横截面.如图2所示,试样自左向右逐渐凝固,在这时刻,对体积元  $dV$  ( $dV = dY$ ) 应用质量守恒定律

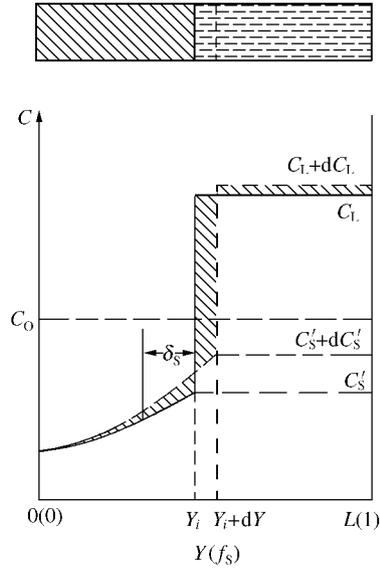


图2 氮在凝固过程中的再分配固相有限扩散,液相充分扩散  
Fig. 2 Nitrogen redistribution during solidification

$$(C_L - C_s^i)Ldf_s = L(1 - f_s)dC_L + 1/2(\delta_s \times dC_s^i) \quad (13)$$

整理且两边积分,可得

$$C_s^i = mC_0[1 - (1 - 2\alpha m)f_s]^{(m-1)/(1-2\alpha m)} \quad (14)$$

这就是固相不完全扩散、液相充分扩散条件下的溶质再分配模型.式中  $\alpha = D_s t_f / L^2$  是表征固相扩散程度的物理量, $\alpha$  越大,固相扩散越完全.但是在式(14)的推导过程中,用边界层近似代替了实际固相扩散过程,Cynle<sup>[6]</sup>曾推算,当  $\alpha > 0.1$  时,由此而带来的误差  $\Sigma$  不可忽视.这可能是为什么  $\lim_{\alpha \rightarrow \infty} C_s^i$  无法还原到固相充分扩散式的缘故.因此,引进  $\alpha$  修正式  $\alpha' = \alpha[1 - \exp(-1/\alpha)] - \exp(-1/2\alpha)$  代替  $\alpha$ ,结果令人满意.由式(14)即可对 Fe-N 熔体凝固过程进行解析,图3是 Fe-1% N 在各种  $\alpha$  下的  $T-f_s$  曲线.

凝固终了  $f_s = 1$ , 此时固相成分  $C_s^E$  为  $C_s^E = C_s^i \Big|_{f_s=1} = mC_0\{2\alpha'm\}^{(m-1)/(1-2\alpha'm)}$ , 则熔体凝固后溶质元素的偏析程度  $D_p$  为

$$D_p = (C_S^E - C_0)/C_0 = m\{2\alpha' m\}^{(m-1)/(1-2\alpha'm)} - 1 \quad (15)$$

$D_p$  越接近 0 ,偏析就越小. 图 4 为 Fe-N 熔体的  $D_p$ - $\alpha$  曲线. 由图 4 可知 ,随  $\alpha$  值的减小 ,即固相扩散越慢 ,枝晶臂间距越大 ,材料的微观偏析也越显著 ,严重时会影响材料的性能 ,特别是耐蚀性和耐磨性. 对于高氮钢 , $\alpha$  在 2 ~ 3 之间(图 4 中阴影部分) , $D_p$  可达 5% ,所以在高氮钢熔炼时应考虑避免偏析. 同时 , $\alpha$  值减小 ,也会导致固-液界面前沿氮量积累增加 ,氮气泡析出的危险增加. 所有这些均不利于高氮钢的生产 ,应尽力避免.

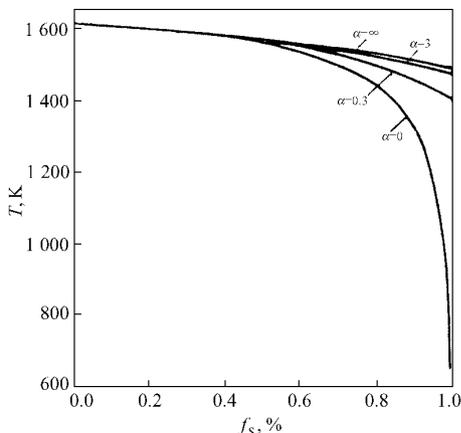


图 3 Fe-1% N 熔体凝固解析

Fig. 3 Evaluation of solidification of Fe-1% N melt

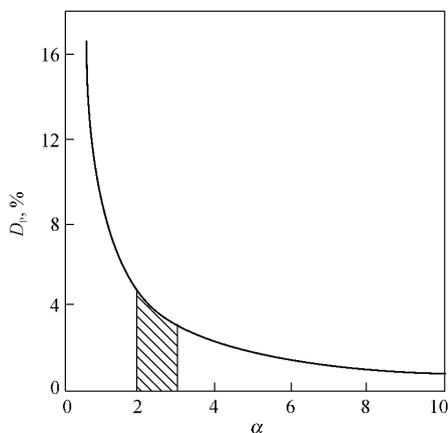


图 4 固相扩散对 Fe-N 熔体氮偏析度的影响

ig. 4 Influence of solid diffusion on segregation of nitrogen in Fe-N melt

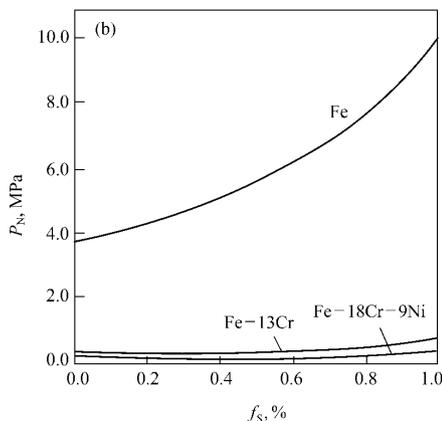
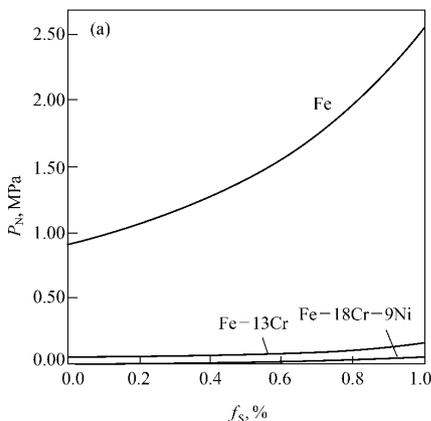


图 5 不同材料凝固过程中氮的平衡压力曲线 ( $\alpha = 3$ )

(a)  $[N]_0 = 0.1\%$  ; (b)  $[N]_0 = 0.2\%$

Fig. 5 Relations between equilibrium pressure of nitrogen at solid-liquid interface and solid phase ratio

## 5 高氮钢凝固过程气泡生成反应

根据上节讨论可知 随着凝固过程的进行 固-液界面处液相中氮浓度变化为  $C_L^i = C_S^i/m = C_0 \times \{1 - (1 - 2\alpha' m)f_s\}^{(m-1)/(1-2\alpha' m)}$ . 所以 凝固过程中氮的平衡压力变化为  $P_N = (F_N C_L^i / K_N)^2$ . 随着凝固过程的进行 残留熔体的 [N]量不断增加  $P_N$  也随之增加(见图 5). 当  $f_s = 1$  时 氮的平衡压力达最大  $P_{Nmax} = (F_N C_L^E / K_N)^2$ . 由图 5(b)可知 对于 Fe-0.2% N 合金 当  $\alpha = 3$  时,  $P_{Nmax} = 10.23$  MPa. 如果有氮气泡形核条件 那么完全有可能克服表面张力 ( $2\sigma/r$ )、静压力( $P_M$ )而析出. 为此 高氮钢需要加压凝固 且为了避免氮析出所需施加的最小压力为  $P_{min} = P_{Nmax} - P_M - 2\sigma/r$ . 当然 实际在高氮钢凝固过程中 由于含较高的合金元素 增加了氮的溶解度 所以为避免氮气泡析出的压力可能较上述计算值小得多. 由图 5 可知 在同样的氮量 (0.2%) 下 Fe-13Cr 的  $P_{Nmax} = 0.74$  MPa, 而 Fe-18Cr-9Ni 的  $P_{Nmax} = 0.33$  MPa, 但其值都高于大气压 故需加压凝固.

在我国 由于市场需求、高氮钢冶炼困难等因素 高氮钢的研究和应用明显落后于发达国家. 可以相信 随着对材料性能要求的提高 相应买方市场的出现 氮在代替合金元素、强化和改善材料性能等方面的优越性必将得到应有的重视 高氮钢的应用也会日趋普遍.

## 参 考 文 献

- [ 1 ] Bern H. Steel Research ,1992 ,63(8) :343
- [ 2 ] Rawers J C , Gocken N. Steel Research ,1993 ,64(2) :110
- [ 3 ] 蒋国昌. 纯净钢及二次精炼. 上海:上海科技出版社,1995. 3
- [ 4 ] 德田昌则. 搅拌下の精炼反应. 见:日本钢铁协会第 100 回西山纪念技术讲座. 神户,东京:1984. 29
- [ 5 ] Brody H D , Flemings M C. Trans. TMS-AIME ,1966 ,236 :615
- [ 6 ] Cynle T W , Kurz W. Metall. Trans. A ,1981 ,12A(6) :965

## Several Theoretical Problems in N<sub>2</sub> -Pressurized Melting of High Nitrogen Steel

**Abstract** The solubility of nitrogen in Fe-Cr-Mn-Ni system is modelled , and the influence of surface active elements on the absorption of nitrogen is discussed. The segregation of nitrogen , the minimum pressure to keep nitrogen in melt , and the solidification process of nitrogen-containing melt are precisely calculated.

# 15 吨铁浴熔融还原工业性试验<sup>\* 1</sup>

**摘要** 上海市于 1992 ~ 1993 年在上钢五厂的 15 吨复吹转炉上完成了铬矿、氧化镍、铁矿的熔融还原工业性试验,炼成了 Cr13、Cr18Ni8 两种不锈钢母液和铁液. 不锈钢母液的熔融还原以含碳铬矿团块、氧化镍矿冷料入炉,过程速率平均为 0.16 ~ 0.25 [% Cr]/min; 铁矿的熔融还原以巴西铁矿氧化球团为原料,冷态入炉,反应速率常数约为 0.1 kmol(O<sub>2</sub>)/[(% TFe) · m<sup>2</sup> · min]. 试验中,二次燃烧率达 24% ~ 48%,二次燃烧热能利用率为 80%. 通过试验,建立了监察渣况的有效手段,掌握了各种参数的合理匹配关系.

## 1 前言

铁浴式熔融还原是现在冶金界普遍倾向的方法. 日、美都在政府参预下进行了全面的中间试验. 在铬矿的熔融还原方面,日本完成了 150 t 级规模的试验,实现了不锈钢的双联(铁浴式熔融还原-脱碳保铬吹炼)生产.

在上海市科委领导下,上海第五钢铁厂、上海市钢铁冶金新技术开发应用重点实验室、上海钢铁工艺技术研究所合作,于 1992 年开始进行了 15 t 级 Cr-Ni 系和 Cr 系两种不锈钢母液的熔融还原工业试验以及铁矿石的熔融还原. 这对国产不锈钢保持市场竞争力以及上海地区转炉炼钢改进等问题都有重大意义.

---

\* 本文合作者:侯树庭、徐明华、张怀琨、杨兴林、蒋国昌、徐建伦、张晓兵. 原发表于《钢铁》30(8), 1~8(1995)

## 2 试验条件和方法

15 t 顶底复吹转炉配有 YEWPARK I 型控制系统和音平 (dB) 监控系统. 冷炉衬经 2 h 洗炉和升温后, 兑入低磷铁水, 加热增碳至 4.5% 以上. 铁水温度高于 1 873 K, 开始投料进行熔融还原.

铬矿以预制的含碳冷固团块形式入炉, 所用铁矿石是巴西氧化性球团; NiO 以小于 5 mm 的小颗粒状态直接加入.

采用单通道双流氧枪供氧, 顶枪供氧强度 50 ~ 90 m<sup>3</sup>/min. 底吹氮的搅拌强度在 5.0 kW/t 以下. 试验熔渣组成为 (% CaO) / (% SiO<sub>2</sub>) = 0.8 ~ 1.2, 而且 (% MgO) + (% Al<sub>2</sub>O<sub>3</sub>) < 40.

试验过程中, 炉气的温度、流量、成分和含尘量均在烟道中测定. 温度和成分连续检测, 流量和含尘量间断测定.

## 3 结果与讨论

熔池内主要元素的典型变化规律示于图 1, 成品的典型成分为 14.7 [% Cr] 的母液、13 [% Cr] ~ 14.5 [% Ni] 的母液和 4.5 [% C] 的铁液.

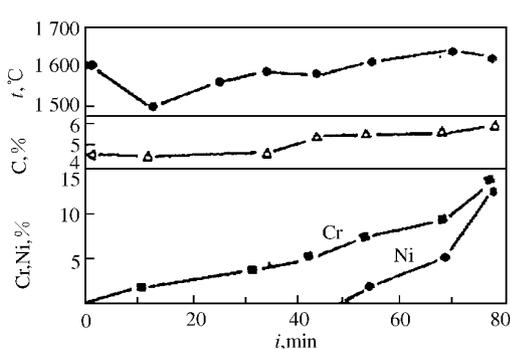


图 1 试验熔池内主要成分和温度的变化  
 Fig. 1 The variation of bath temperature and composition in this pilot test

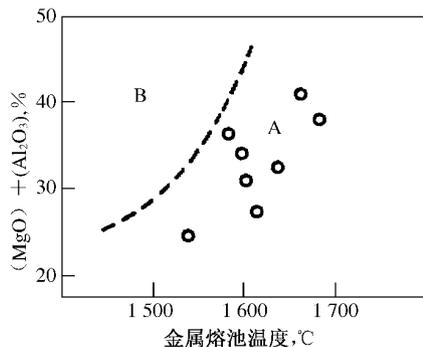


图 2 铬矿熔融还原试验时渣成分、温度在还原区的分布  
 Fig. 2 The influence of the slag composition and temperature on the process during Cr-ore smelting reduction  
 ○—试验结果 ;A—只有硅酸盐的快速还原区 ;  
 B—硅酸盐 + 尖晶石快速还原区

### 3.1 氧化铬的还原

本试验重点考察了加矿速率、加焦速率及熔池温度对铬矿还原速率(用  $d[\% \text{Cr}]/dt$  表示)的影响。

不同渣系和不同熔池温度条件下,铬矿的还原有两个反应速率不同的区域(图2的A区和B区)。两区的划分主要是因为B区内尖晶石的形成能阻碍氧化铬的还原。本试验所取试样基本上都落在图2的A区中,这是由于对 $(\% \text{MgO}) + (\% \text{Al}_2\text{O}_3)$ 和熔池温度进行了动态控制之故。

本试验结果与日本几家公司的试验数据基本吻合,见表1。冷固团块的还原速率大致高于氧化性球团,而预还原度高者优于预还原度低者,预热者更好。图3表明还原速率都随着加矿速率的增加而增加;并且提高焦矿比有重要作用。事实上,只有在焦矿比大于理论预测所得的当量值(本试验中为1.5)时,加入的矿才可能即时被还原。

表1 试验主要结果及5 t以上规模工业试验文献数据  
Table 1 The main results and some literature data which size is over 5 tons

熔融还原方法	供 矿		供氧强度 $\text{m}^3/(\text{t} \cdot \text{min})$	熔池温度	还原速率 $\% \text{Cr}/\text{min}$	
	状 态	强度 $\text{kg}/(\text{t} \cdot \text{min})$			平 均	最 大
复吹、顶喷煤粉	氧化性球团	3.5		1 660	0.06	
顶底侧吹、投矿	矿粉	7.7		1 660	0.14	
复吹、投矿	球团(预还原60%)	<3	3.18	1 570	0.147	
复吹、投矿	球团(预还原66%)	6.7		1 615	0.22	0.29
复吹、投矿	球团(预还原80%)	~30	4.8	1 605	0.70	0.97
复吹、投矿(本试验)	冷固含碳团矿	7.42	4.5	1 595	0.16	0.25

图4是加矿速率、温度与 $(\% \text{TCr})$ 的关系。在给定的温度下,加矿速率的增加使 $(\% \text{TCr})$ 呈积累势。如果试验温度升高,还原就会加快,则 $(\% \text{TCr})$ 呈减少势。在加矿终止后,氧化铬的还原也具有同样规律。这反映加矿速率的

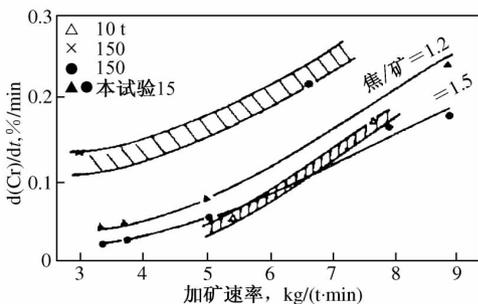


图3 铬矿熔融还原过程中加矿速率和还原速率的关系

Fig. 3 The relation between lump feeding rate and reduction rate in the Cr-ore smelting reduction process

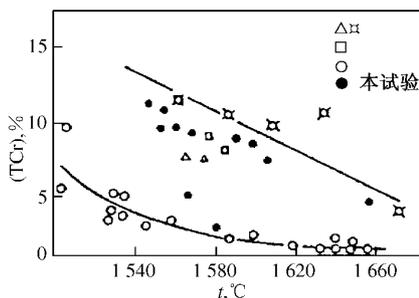


图4 不同铬矿熔融还原试验中熔池温度与熔渣含铬量的关系

Fig. 4 The relation between the Cr content in metal and slag in various processes of Cr-ore smelting reduction

增加受供能速率的制约. 温度给定时, 有一个许可的最大加矿速率, 或许可得最高 (% TCr). 实际的 (% TCr) 愈接近这个最高的 (% TCr), 对加快还原愈有利.

日本的经验反复说明, 铁浴式熔融还原有一条基本原则: 必须依托厚渣层将转炉上部顶吹氧造成的高氧化性气氛和下部三相(渣、金、碳)充分混合的强还原区“隔绝”开. 若一旦将厚渣层击穿, 就会使已还原的铬发生重氧化. 另一方面, 厚渣层中顶枪氧流冲击坑近旁的铁珠极大多数难逃重氧化. 本试验也证实了这个规律.

重氧化不仅降低了还原速率, 而且严重时会造成难以承受的烟尘率. 据新日铁报道, 在正常操作条件下, 铁矿熔融还原的烟尘率也有 5% ~ 10%, 可见铁浴式熔融还原中重氧化的控制是核心技术. 本试验中, 还原铬矿时, 铬的烟尘率为铬投入量的 4.3%, 或母液总重量的 0.5%, 铁的烟尘率是母液总重量的 5.4%; 还原铁矿时, 铁的烟尘率是母液总重量的 5.7%. 这大体上与新日铁的结果吻合.

### 3.2 铁氧化性球团的还原

相对于铬矿而言, 铁氧化性球团的还原反应快得多. 随着加矿速率的增加, (% TFe) 的累积显著慢于 (% TCr). 由此可见, 氧化性球团的熔融还原过程中还可增加投料强度, 既快又不导致喷溅的投料强度. 在本试验中靠采用音平(dB)控渣系统而成功地实现.

若渣量不变, (% TFe) 愈高, 则还原反应驱动力愈大; 若 (% TFe) 不变, 渣量愈大, 还原也愈快, 见图 5. 这一方面是由于三相(渣、金、碳)充分混合的反应区得以扩大, 更重要的是减小了重氧化的几率. 新日铁<sup>[7]</sup>的看法也如此.

另一个影响还原速率的关键因素是温度. 随着温度升高速率常数增加. 同时, 随着炉容量和渣量的增加, 发现表现活化能下降.

### 3.3 NiO 的利用

NiO 极易还原. 本试验发现, 加料期间积累的(NiO)仅 1%. 随着 (% TCr) 的下降, (% NiO) 可低至 0.2%, 即渣中残镍只占镍加入量的 0.5%. 但实际上 Ni 的收得率不超过 95%.

通常, 氧化镍含硫甚高. 而本试验的加料期间, 若焦矿比大于当量值, [% S] 稳定在 0.14% 水平上; 反之则为 0.1% 左右. 这可能是气化脱硫程度不同而造成的差异.

### 3.4 燃烧与热传输

熔融还原的冶炼周期主要为熔融还原反应器中的能量输入速率所左右. 从上钢五厂目前的条件出发, 由于没有预还原设施联动, 该能量输入只有依靠二次燃烧率(PC)及其热能利用系数( $\eta_{PC}$ )来解决. 本试验中, PC 为 24% ~ 48%, 与国外提出的  $\geq 40\%$  的指标接近.

底吹搅拌强度( $\varepsilon$ )对二次燃烧及其热能利用系数有影响, 表明增强搅拌有利于增加  $\eta_{PC}$ , 但会降低 PC, 见图 6.

另一个影响  $\eta_{PC}$  的因素是枪位(本文用顶枪氧流的冲击强度指数  $\psi$  表示)随着  $\psi$  的增加  $\eta_{PC}$  升高. 这说明“火点”应在厚渣层的顶部之中.

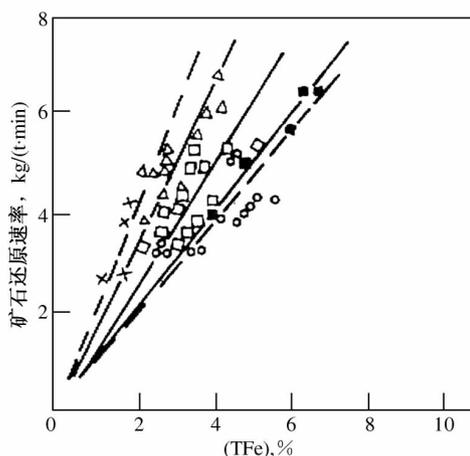


图 5 铁矿石熔融还原时不同条件下 (TFe)% 与还原速率的关系

Fig. 5 The relation between reduction rate and (% TFe) in various processes of Fe-ore smelting reduction

符号	渣量等试验条件	试验者
○	0% ~ 10%	
□	10% ~ 20%	
■	平均 40%	本试验
△	50% ~ 60%	
×	喷砂粉	

总之,操作的关键在于顶枪氧流、底吹搅拌强度和渣层特征这些因素之间要有恰如其分的匹配.对有效的能量输入来说是这样,对抑制重氧化来说也是这样.

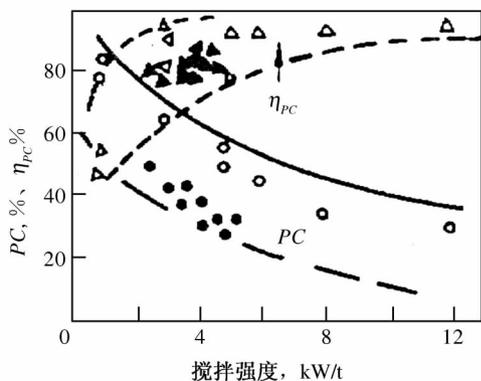


图 6 底搅拌强度对二次燃烧率 PC 及其利用率  $\eta_{PC}$  的影响

Fig. 6 The effect of stirring intensity on the post combustion ratio and its efficiency

○、△—5 t ;▲、●—本试验

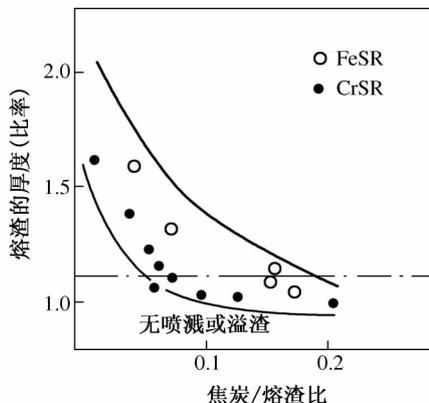


图 7 焦炭/熔渣比对熔渣喷溢的影响

Fig. 7 The effect of coke/slag ratio on possibility of slag slopping

### 3.5 熔渣的泡沫化和喷溅

铁和铬、镍氧化物的还原过程都存在熔渣的泡沫化问题.本试验发现,熔渣的喷溅和溢出在很大程度上取决于渣中碳含量,见图 7.

### 3.6 物料渣耗和金属收得率

本试验中的典型物料平衡示于表 2,而表 3 是相应的消耗量.

表 2 投入产出一览表  
Table 2 The material balance

投 入				产 出					
原铬矿 t	焦炭 t	氧气 m <sup>3</sup>	石灰 t	母 液			烟尘 t	废气 m <sup>3</sup>	熔渣 t
				% Cr	% C	重量 t			
9.7	13.8	8 100	2.7	14.7	5.7	17.7	3.2	897	8.1

表3 冶炼 Cr13 母液时的消耗及铬收得率

Table 3 The material consumption and the yield of Cr in the smelting reduction process for stainless steel master material Cr13

含碳团块, kg	炉衬, kg	石灰, kg	O <sub>2</sub> , m <sup>3</sup>	N <sub>2</sub> , m <sup>3</sup>	焦炭, kg	金属烟尘, %	铬收得率, %
548	11.5	152.5	456.2	37	780	5.9	85.36

注：根据炉底蚀损速率推算。

影响收得率的因素有二：① 渣中残余量。加矿结束后的终还原必须改进；② 金属的烟尘损失。应大大加速反应过程，缩短生产周期。

在进行不锈钢母液的试验时，MgO-C 质炉衬的损耗比炼钢时还小，能适应工业化要求。

### 3.7 两个有关试验顺行和安全的问题

#### (1) 炉容比和供氧强度

铁浴熔融还原的渣量是转炉炼钢(非少渣)的 2~5 倍，相当于炉容比减小，一般只在 1.17~1.58，煤气发生量则是后者的 1.5 倍，因而易喷溅。本试验的炉容比为 1.02~1.10，供氧强度曾高达 4.3 m<sup>3</sup>/(t·min)，而吹炼平稳，这和使用音平控渣仪实施在线监察不无关系。

#### (2) 煤气中的氧含量

铁浴熔融还原要求 PC 高，还原过程比转炉炼钢的枪位易出现偏高。同时，氧流对熔池面冲击不强，但只要渣中有足够的碳量，该含氧量可落在安全范围内。

## 4 结论

上海市于 1992~1993 年在上钢五厂 15 t 复吹转炉进行了铬矿、氧化镍、铁矿的熔融还原工业试验，炼成了 Cr13 和 Cr18Ni8 两种不锈钢母液以及铁液。

试验用原料为含碳铬团块、氧化镍原矿、氧化性铁球团，入炉时未经预热预还原。不锈钢母液试验中，铬的熔融还原速率平均达 0.16[% Cr]/min，最高为 0.25。渣中残镍仅 0.2%。铁矿的还原速率常数约为 0.1 kmol(O<sub>2</sub>)/[(% TFe)·m<sup>2</sup>·min]。这些都和国际上目前报道的同吨位规模试验的先进水平一致。

铁浴熔融还原的关键在于顶吹氧流、厚渣层及底搅拌强度三者之间的合理匹配,以求解决高强度供能与重氧化的矛盾,而且加矿速率必须和供能强度适应.本试验依靠供气的计算机控制系统、音平控渣系统等手段以及恰当地选择各种工艺参数的工艺方案较好掌握了熔融还原过程,使之能在设定温度下顺利地进行,取得 $PC=24\% \sim 48\%$   $\eta_{PC}$ 最高达到80%等成果.

在上钢五厂实现铁浴式熔融还原的中试生产已具备良好的基础.

## Pilot Test of Bath Smelting Reduction in 15 t Converter

**Abstract** During 1992–1993, a 15 t combined blown converter was used to run the pilot test of smelting reduction of Cr-ore, Ni-oxide and iron ore at Shanghai Steel Works No. 5. Two kinds of stainless steel master material, Cr13, Cr18Ni8 and hot metal were obtained. The process for stainless steel was adopted the carbon bearing Cr-ore lump and Ni-oxide. The resulting rate in average was found to be 0.16%–0.25% /min. For the process of hot metal, the iron-ore pellets produced by Brazil as raw material were added in the converter in cold state. The average reaction rate was shown to be about 0.1 kmol (O<sub>2</sub>) / [(% TFe) · m<sup>2</sup> · min]. During this pilot test, the post combustion ratio reached 24%–48%, and its heating efficiency was 80%. Through this pilot test, the effective mean to monitor slag behaviour was established and an operating procedure to match all the parameters was reasonably optimized.

# 金属中氧化物及氮化物分量的测定<sup>\* 1</sup>

**摘要** 介绍 Leco TC-436 氧氮测定仪同时测定金属中的氧化物及氮化物分量的惰性气体脉冲加热法,即调节升温速度使各种氧化物和氮化物在不同的温度下分解出来,同时分析了升温速率对检测结果的影响。

## 1 前言

金属中的氧含量和氮含量对金属的质量是一个很重要的指标。关于金属中的氧、氮的测定,目前主要有以下方法:(1)真空熔融微压法;(2)化学蒸馏-容量法,即 Kjehldal 法;(3)惰性气体脉冲(或高频)-库仑法定氧等。但这些方法通常只能测定试样中的总氧量或总氮量。随着人们对金属产品质量要求的提高,往往需要知道金属中的氧化物和氮化物的分量,而目前的分析方法不能满足以上要求。

美国 LECO 公司生产的 TC-436 氧氮测定仪,既可采用恒温测定氮氧总量,又可采用逐步升温法或台阶式升温法进行测定,这样为分析试样中的不同氧化物、氮化物提供了可能性,但 LECO 公司并没有成熟的分量分析技术。作者利用 TC-436 氮氧测定仪摸索了金属中氮化物和氧化物分量的测定方法。方法保持了快速、准确、操作方便的特点,试样准备也简单。

## 2 仪器的原理和分析方法

TC-436 氧氮分析仪采用脉冲加热方式,即将装于石墨坩埚内的试样放

\* 本文合作者:陈启文、马金昌、郭曙强、徐建伦、蒋国昌。原发表于《上海金属》,17(4), 52~55(1995)

入脉冲炉中,在惰性气氛(氦气)下熔融.试样中的氢、氧、氮分别以  $H_2$ 、 $CO$  和  $N_2$  的形式释放出来,随同氦气流通过温度为  $400^\circ C$  的稀土氧化铜,使  $CO$  变成  $CO_2$ ,氢氧化成水,混合气流进入红外线室.从  $CO_2$  的含量测得氧量,然后再通过碱石棉和无水过氯酸镁吸收管,除去  $CO_2$  和  $H_2O$ ,氦携带  $N_2$  进入热导池检测氮.然后将红外池和热导池所得电信号经微机处理,直接以氮和氧的重量百分数显示.流程图如图 1 所示.

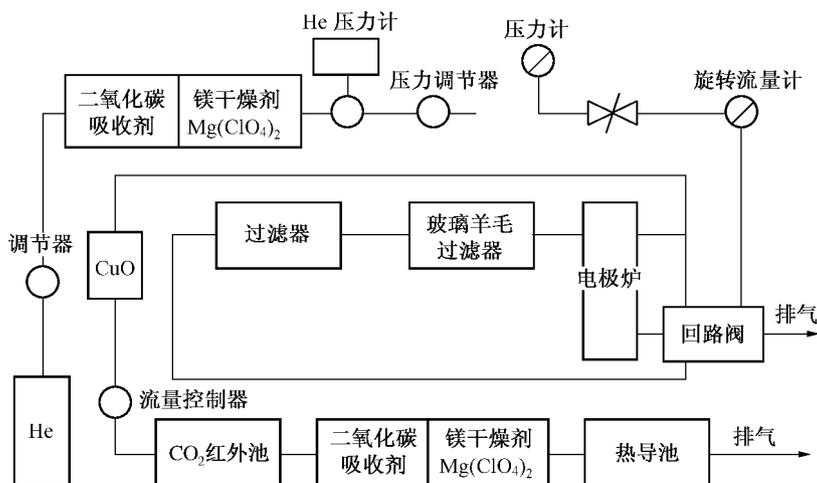


图 1 LECO TC-436 氧氮分析仪主气路示意图

TC-436 型氧氮检测仪和它的前身 TC-136 在功能上有所不同. TC-436 可以在计算机的控制下,使加热炉逐步升温或台阶式升温.在装有炉内测温装置的情况下,还可显示加热炉的温度.以前的 TC-136 一般不具备此种功能,只能通过所提供的功率显示估计炉内温度. TC-436 可根据试样中的氧化物、氮化物种类,即它们的分解温度差异,确定升温速率和台阶的大小.

先准备含某单一氧化物、氮化物的金属试样,根据其中氧化物、氮化物的分解温度,摸索其分解功率供给速率,得到一系列单一氧化物、氮化物中氧氮释放曲线.在分析含多种氧化物、氮化物的金属试样时,可根据所得到的这一系列曲线,结合它们的分解温度来判断金属中氧化物、氮化物的种类,然后换算得到它们各自的含量.

### 3 试样的制备

使用还原铁粉加 0.1% 重量的石墨,在  $1550^\circ C$  的刚玉坩埚中熔化,至熔

清时,加入适量的  $\text{Fe}_2\text{O}_3$ ,并吹入一定量的  $\text{N}_2$ ,然后加入适量的 Si, Al, Mn, Ti, B 制成 Fe-Si, Fe-Al, Fe-Mn, Fe-Ti, Fe-B 合金,用石英管搅拌,快速抽取直径 5 mm 的棒状试样.冷却后,在钻床上用粗砂纸打磨表面,细砂纸抛光.然后切成 10 mm 左右的小段,用丙酮处理表面.分析前取出,用滤纸擦干,称重,分析.

多组元合金试样的制备采用同样方法.加入第一组元后取样,再加入第二组元取样.根据金属的性质,一般先加入 Mn,然后依次是 Si、Al、Ti、B 等.

## 4 分析条件控制技术

分析过程中,对每一种试样,须确定特定的加热炉常数.以下几种方法可以使炉子的控制更加简单些.

(1) 对具有未知分析总时间的混合物试样,将分析时间按最大分析时间考虑,以便在整个分析过程中没有任何峰值“丢失”,并且控温程序有充分的时间完成.

(2) 温度变化速率决定了定量测定分量的可能性.对加热功率的考虑,一般是终点功率低于脱气功率(outgas high)(一般低 500 W).不使坩埚中的污染物和试样一起放出气体.设置起始功率要远低于氮化物、氧化物分解所需的最低功率.

(3) 将自动分离键设置在 ON 位,以便每个峰值的含量百分比及峰值的数目都将打印出来.

## 5 试验结果及讨论

图 2,图 3 是 Fe + Al 金属样中  $\text{Al}_2\text{O}_3$  和 AlN 含量的分析曲线.类似 Fe + Al 试样,可以做出 Fe + Si, Fe + Mn, Fe + Ti, Fe + B 以及含其他合金元素的金属样的分析曲线(略).从这些曲线可以看出,在一定的起始功率下  $\text{Al}_2\text{O}_3$ 、AlN 的分解起始功率,即起始温度,以便分析含多种合金元素的试样时,进行对照.图 4,图 5 是含两种合金元素 Al, B 的试样的分解曲线.

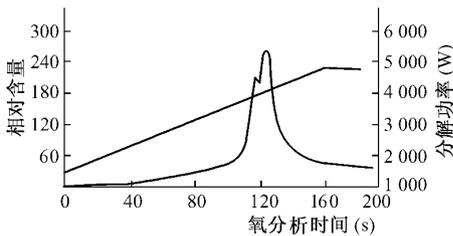


图2 氧化铝的分解曲线

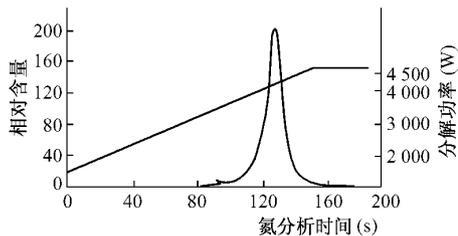


图3 氮化铝的分解曲线

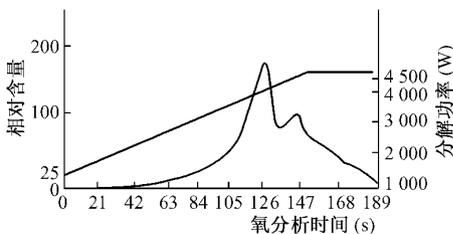


图4 氧化铝,氧化硼的分解曲线

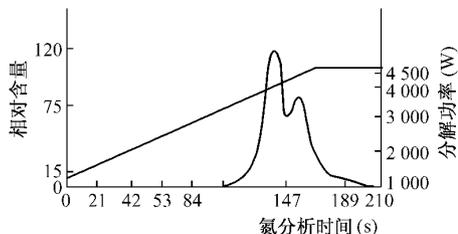


图5 AlN, BN的分解曲线

从图2,3和图4,5两组图形的对照来看,  $Al_2O_3$  的分解高峰功率在4 000 W左右,说明有较好的比照一致性。

在得到一系列Fe加单合金元素的试样的分解曲线以后,我们可以结合计算氧化物、氮化物的分量。在分析过程中,氧化物的分解顺序一般是:  $FeO/Fe_2O_3-MnO-SiO_2-Al_2O_3/CaO-TiO_2$ , 氮化物的分解顺序是:  $Si_3N_4-AlN-TiN(ZrN)$ 。

图6,7是某管线钢的分析曲线。管线钢的成分是: 0.05% C, 0.195% Si, 0.765% Mn, 0.02% Ti, 0.019% Zr。熔炼条件是: 中频感应炉返回料熔炼, Al脱氧。分析条件是: 最低功率1 500 W, 最高功率3 500 W, 功率递增速度25 W/s。

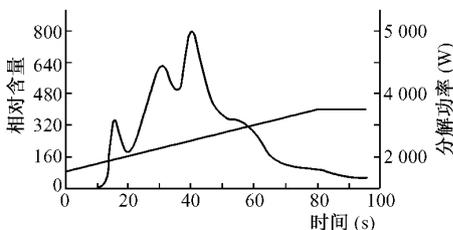


图6 管线钢中氧化物的分解曲线

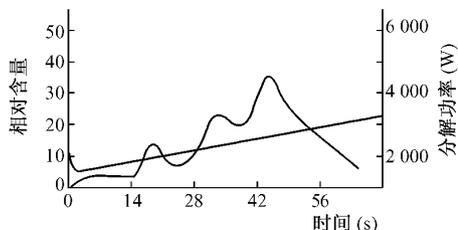


图7 管线钢中氮化物的分解曲线

分析过程中发现,最低功率为2 500 W时,无明显分开的峰。所以,确定合

理的最低功率和合理的升温速度对区分各种氮化物、氧化物有较大的影响.

从分析结果看,试样中存在以下氧化物和氮化物:  $\text{MnO}$ 、 $\text{SiO}_2$ 、 $\text{Al}_2\text{O}_3$ 、 $\text{TiO}_2$  ( $\text{ZrO}_2$ );  $\text{Si}_3\text{N}_4$ 、 $\text{AlN}$ 、 $\text{TiN}$ . 通过换算可得到各自的含量,氧化物含量为

$$\text{MnO} = 0.017\%、\text{SiO}_2 = 0.031\%、\text{Al}_2\text{O}_3 = 0.045\% .$$

由于合金中  $\text{Ti}$ 、 $\text{Zr}$  的含量很低,在所提供的分析条件下, $\text{TiO}_2$ 、 $\text{ZrO}_2$  的分解峰值来不及区分,氧就释放完全. 所以认为  $\text{TiO}_2$ 、 $\text{ZrO}_2$  共同占有的氧量为 0.0153% .

氮化物含量为

$$\text{Si}_3\text{N}_4 = 0.002\%、\text{AlN} = 0.006\%、\text{TiN}(\text{ZrN}) = 0.02\% .$$

## 6 结论

(1) 利用 Leco TC-436 氮、氧分析仪测定金属中的氮化物、氧化物分量是可行的,而这种分量的测定对系统了解金属中氮化物、氧化物夹杂具有重要意义.

(2) 使用逐步升温法分离氮化物、氧化物时,升温速度对氮化物、氧化物的分离具有较大的影响. 由于缺乏直接的温度测量,这里升温速度是由加热功率来显示的.

## Measurement of Oxide and Nitride Component in Metal

**Abstract** The simultaneous measurement of oxide and nitride component in metal by inert gas pulse heating in Leco TC-436 oxygen/nitrogen determination Instrument was introduced. The oxide and nitride can be decomposed at different temperature through adjusting heating rate. The influence of heating rate on test results was also analyzed.

# 含碳团块-铁浴第二步法熔融还原 冶炼碳素铬铁和不锈钢母液<sup>\* 1</sup>

**摘要** 含碳团块-铁浴第二步法熔融还原,选用环型还原焙烧炉预还原含碳铬矿团块、转炉铁浴终还原第二步流程冶炼碳素铬铁和不锈钢母液。该流程被设计成一个封闭系统,以使能量得到反馈利用,且以煤代焦;铁浴中余渣残铬由低浓度铁液吸收,以提高铬的回收率。在物料平衡和热平衡基础上对该法冶炼碳素铬铁和不锈钢母液进行了计算机模拟,结果表明,用本设计流程生产碳素铬铁的总能耗低于埋弧电炉的相应指标约122 kg/t标煤,铬回收率提高约3.4%。

## 1 前言

第二步法熔融还原作为生铁、铁合金及高合金钢母液的新冶炼技术已得到国内外冶金界的高度重视。尽管开发此项新技术的最终目标是以生铁为其主要产品,但首先进入工业规模试验的则是铁合金或高合金钢母液的熔融还原,这是因为后者可在相当小的生产规模下显示出经济上的竞争力。一般这种竞争力应是以下几项技术经济指标的综合结果,即:1)生产率,2)能源结构及能耗,3)临界生产规模和生产成本,4)设备投资,5)公害处理设施的投资及运行费用,6)过程可控性。其中最关键的是能耗。本文借助于计算机模拟计算结果,讨论铬熔融还原技术的能耗问题,以及介绍在转炉铁浴终还原器中用低浓度铁液回收余渣残铬等问题。

\* 本文合作者:张晓兵、蒋国昌、徐建伦。原发表于《化工冶金》,14(3),199~206(1993)

## 2 工艺流程选择

二步法熔融还原技术有许多工艺流程. 前文中作者已指出, 选用复吹转炉作为终还原器是最有吸引力的方案<sup>[1]</sup>. 就预还原而言, 铬和锰一样都必须采用含碳团块. 这是与铁不同之处. 作为含碳铬矿团块的预还原反应器, 回转窑是比较成熟的, 而最近旋转反应器(环型还原焙烧炉)已在铬矿的固态还原中显示出某些优于回转窑的特点.

本文按含碳团块-铁浴的工艺流程(图1)进行铬熔融还原的模拟计算. 此设计具有如下特点.

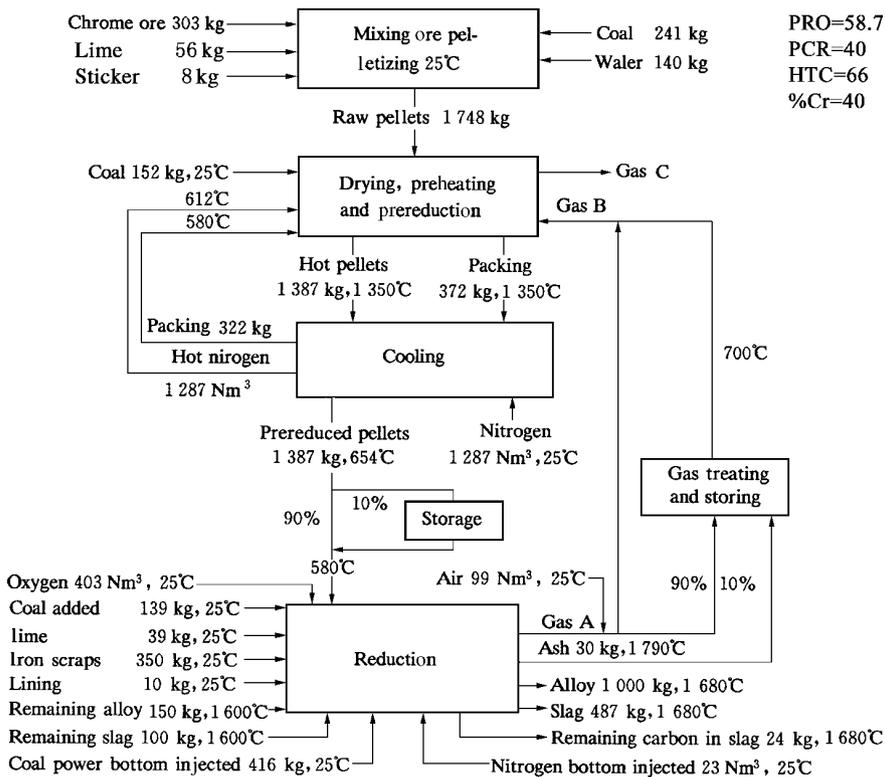


图1 工艺流程和物料平衡图

Fig.1 The chart of the process and the material balance

(1) 转炉为间断操作, 每炉结束时不带渣出铁, 将渣及少量残余合金液留在炉内, 然后一次加入下炉所需之全部铁料, 使其与剩余合金液之总量能满足开吹之需. 开吹后, 利用余渣中的残碳作为部分燃料使加入的铁料熔化、

升温,并利用低浓度合金液吸收余渣中的残铬,然后再出渣.这样余渣中铬得到充分回收,渣中  $\text{Cr}_2\text{O}_3$  含量可小于 1%,而现用埋弧电炉生产碳素铬铁余渣中  $\text{Cr}_2\text{O}_3$  含量为 3% ~ 5%.出渣后,在连续加团块及渣料等条件下进行熔融还原吹炼.

(2) 充分考虑了能量在本系统内的反馈利用.采取两条措施:① 将转炉废气直接热送旋转床反应器作为预还原和预热的主要能源;② 为避免经预还原后的高温团块在冷却过程中再氧化和燃烧,采用氮气冷却.预还原团块冷却至 650 左右,而鼓入氮气得到加热,用于预热和干燥团块,另外全过程以煤代焦.

(3) 设置缓冲容器,以解决转炉(间断操作)和旋转床反应器(连续运行)之间的衔接.即在输送转炉废气的途中并联贮气罐,作为转炉出铁和出渣时调节环型还原焙烧炉输气之用.预还原团块经适当冷却后直接喂入转炉或暂存于料仓内,不采用高温热装.

### 3 物料平衡和热平衡及模拟计算结果

本文以含 20% ~ 60% Cr 和 7.15% ~ 8.17% C 的高碳铬铁及不锈钢母液为对象,其假设成分如表 1.计算中涉及到的各种物料的组成见表 2.系统内各阶段气相组成变化由表 3 给出,各热力学参数示于表 4.

表 1 合金成分  
Table 1 The component of alloy

	% Cr	% Fe	% Si	% C	% S(<)	% P(<)
1	20	72.26	0.5	7.15	0.030	0.025
2	40	51.75	0.5	7.66	0.032	0.030
3	60	31.24	0.5	8.17	0.040	0.035

表 2 各物料的成分  
Table 2 The component of materials

	$T_{\text{Cr}}$	$T_{\text{Fe}}$	$M_{\text{Cr}}$	$M_{\text{Fe}}$	C	P	S	H	N	CaO	$\text{SiO}_2$	MgO	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$
Ore	31.64	14.12								0.39	3.62	9.92	13.21	
Coal					79.45	0.01	0.66	4.38	0.82	0.35	2.24	0.14	1.03	1.37
Lime							0.015			93.0	3.9	2.7	0.25	

(续 表)

	T <sub>Cr</sub>	T <sub>Fe</sub>	M <sub>Cr</sub>	M <sub>Fe</sub>	C	P	S	H	N	CaO	SiO <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
Liner					5.0		0.01			54.0	2.55	41.94	1.50	
Ash	24.43	11.11								1.73	13.02	19.96	15.28	
Dry pellets	25.62	11.44			11.92	0.009	0.10			3.63	3.74	8.14	10.79	
Pre-reduced pellets	29.70	13.27	14.85	11.94	7.37	0.011	0.115			4.21	4.34	9.44	12.52	
Slag	1.0	0.10					0.48			20.46	12.83	29.64	34.98	

表 3 物料平衡图中气体成分

Table 3 The component of gases in the process

	V(Nm <sup>3</sup> /t)	T( )	% CO	% CO <sub>2</sub>	% H <sub>2</sub>	% H <sub>2</sub> O	% N <sub>2</sub>
Gas A	985	1 790	55.19	29.04	3.28	9.94	2.39
Gas B	1 062	1 828	48.59	29.47	1.70	10.54	9.53
Gas C	2 703	165	24.20	16.60	3.53	11.09	44.58

表 4 热平衡计算中的有关参数

Table 4 The coefficients related to the calculation

	C* →CO	CO→ CO <sub>2</sub> *	H <sub>2</sub> → H <sub>2</sub> O*	Cr <sub>2</sub> O <sub>3</sub> → Cr*	Cr*→ Cr <sub>2</sub> O <sub>3</sub>	FeO→ Fe*	Fe*→ Fe <sub>3</sub> C	SiO <sub>2</sub> → Si*	C <sub>lime</sub> * → [C]	SiO <sub>2</sub> * → CaOSiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub> ,FeO→ Cr <sub>2</sub> O <sub>3</sub>
ΔH <sub>298</sub>	- 9 201	- 6 413	- 13 678	10 851	- 489	4 644	142	32 087	1 881	- 1 518	2 526

	Pellets	Slag	Ash	Coal	Iron	Alloy	Gas	Air
C <sub>p</sub>	0.877 8	1.254	0.994 8	1.212	0.836	∑ C <sub>p</sub> <sup>i</sup> · i%	∑ C <sup>j</sup> · j%	0.233C <sub>p</sub> <sup>O<sub>2</sub></sup> + 0.767C <sub>p</sub> <sup>N<sub>2</sub></sup>

\* The unit of ΔH is kJ/kg. The unit of slag formation heat is kJ/kg SiO<sub>2</sub>.\*\* All C<sub>p</sub> values are from Ref. [3]. Its unit is kJ/kg · °C. The i% and the j% are represented as the weight concentration in alloy and in gas respectively.

该冶炼过程可分为团块的干燥、预热、预还原、冷却和转炉终还原几个阶段. 对各阶段, 在物料平衡和热平衡分析基础上建立方程, 由计算机对各工艺条件进行模拟计算. 具体方程或计算步骤见文献[2].

假设二次燃烧率为 40%, 热利用率为 66%, 团块的预还原率为 58.7%, 在此条件下进行冶炼 Cr = 40% 的不锈钢母液的模拟计算, 结果见图 1. 图 2, 3

分别列出了相应的预还原和终还原过程的热平衡计算结果. 图 4 5 6 分别表示团块预还原率、热利用率、二次燃烧率的影响.

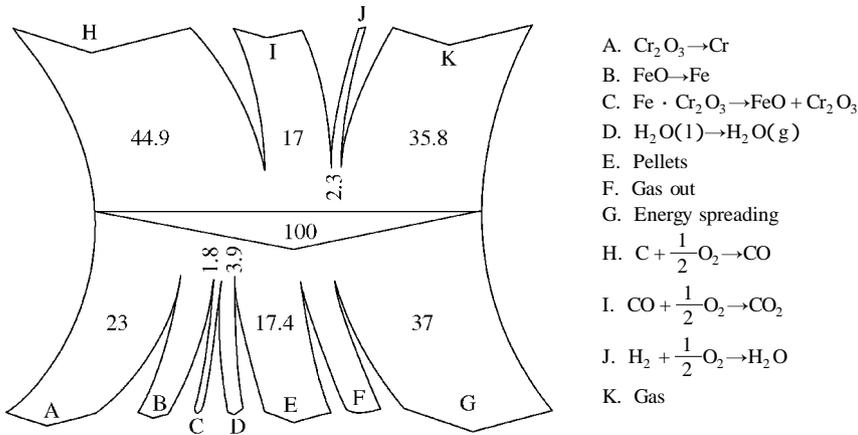


图 2 预还原热平衡图

Fig. 2 Chart of the thermal balance in the process of pre-reduction  
(PRD = 58.7, PCR = 40, HTC = 66, Cr = 40%, Q = 9 293 MJ/t)

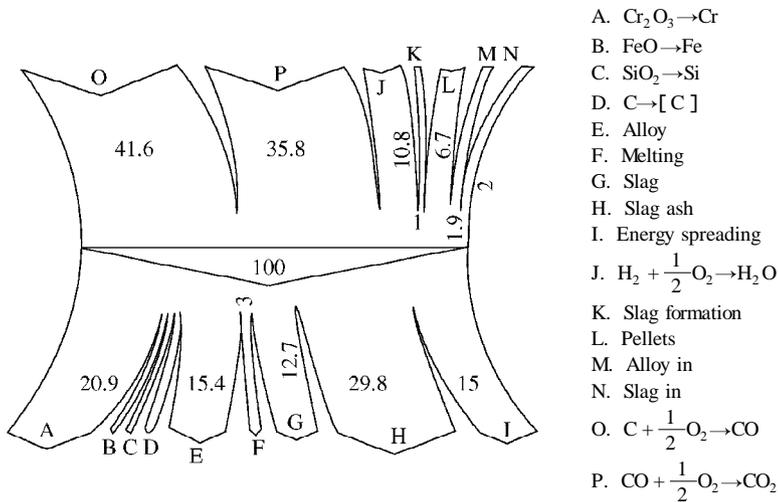


图 3 终还原热平衡图

Fig. 3 Chart of the thermal balance in the process of reduction  
(PRD = 58.7, PCR = 40, HTC = 66, Cr = 40%, Q = 10 068 MJ/t)

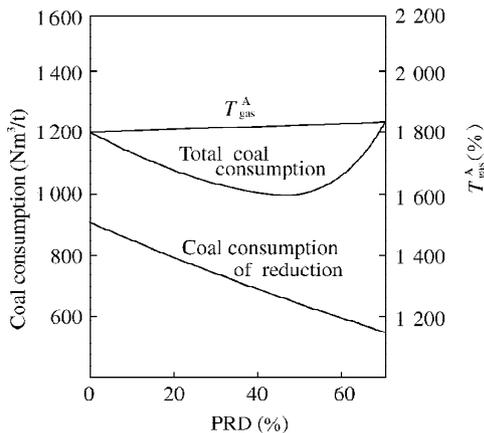


图4 预还原率对能耗的影响

Fig.4 The influence of the pre-reducibility on energy consumption

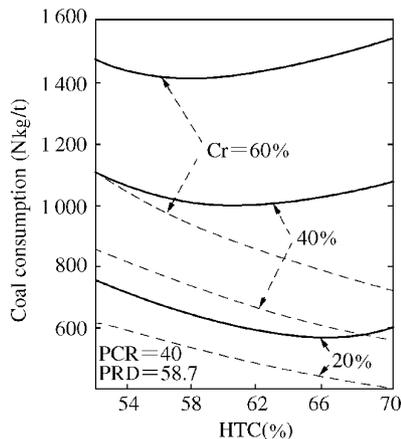


图5 热效率对能耗的影响

Fig.5 The influence of the calorific efficiency on energy consumption

(Solid lines : Total coal consumption ;  
Dashed lines : Coal consumption of the reduction)

## 4 分析与讨论

### 4.1 总能耗预测

在预还原率为 58.7% ,二燃率为 40% ,热利用率为 66% 的条件下 ,用本文设计的流程冶炼碳素铬铁 (Cr = 60% ~ 65% ) 时的能耗为 1 566 kg/t 标煤. 若把氧耗也折成能耗 ,按每标准立方氧耗 0.6 度电 ,每度电耗 0.4 kg 标准煤计算 ,上述产品的总能耗为 1 692 kg/t 标煤. 而用传统的埋弧电炉生产碳素铬铁 ,国内 1990 年平均电耗为 3 260 kWh/t 或 1 304 kg/t 标煤<sup>[4]</sup>. 除电能外 ,埋弧电炉还需消耗焦炭约 425 kg/t<sup>[5]</sup> ,相当于耗约 510 kg/t 标煤 (此值考虑了须 1.3 ~ 1.4 吨精煤炼 1 吨焦炭)<sup>[6]</sup> ,因此其总能耗为 1 814 kg/t 标煤 ,即采用本文设计工艺冶炼碳素铬铁能耗可降低约 1 22 kg/t 标煤.

在所设条件下 ,用本文设计的流程冶炼 Cr = 20% 和 40% 的合金时 ,总能耗计算值分别是 652 和 1 134 kg/t 标煤.

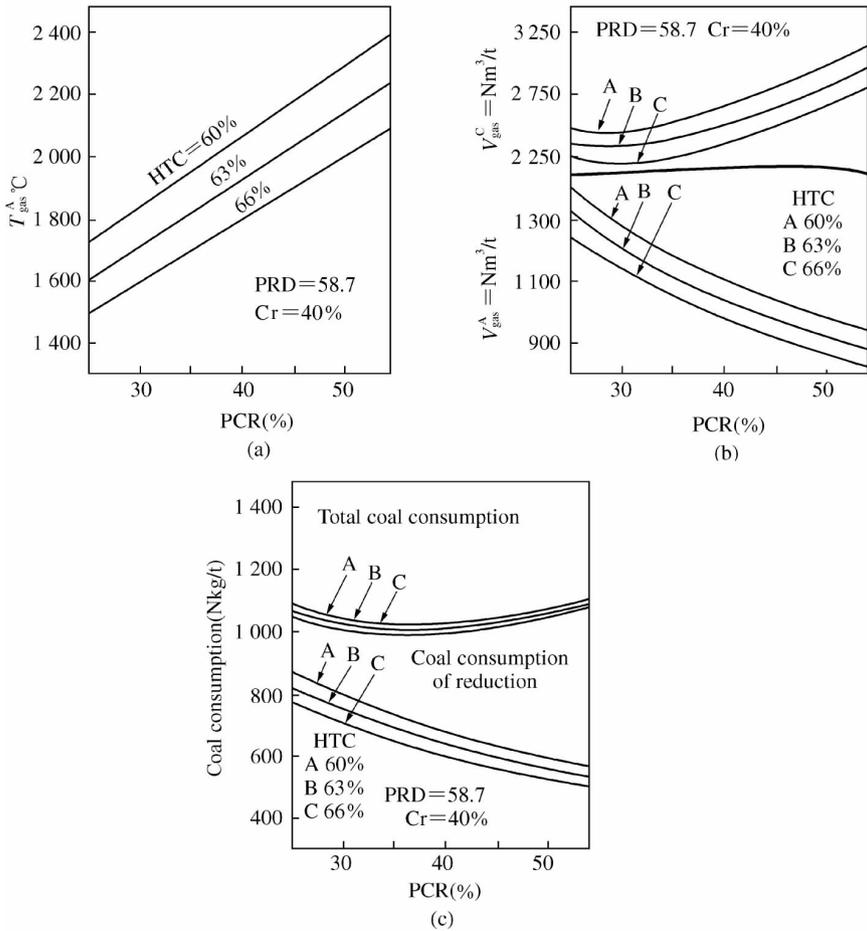


图 6 二次燃烧率对能耗的影响

Fig. 6 The influence of the post combustion rate on energy consumption

#### 4.2 预还原率的影响

图 4 表明终还原耗煤与预还原率成反比, 预还原率每提高 10%, 终还原耗煤降低 6% ~ 7%。过程总耗煤与预还原率的关系存在着最低点, 预还原率低于 43% 时, 提高预还原率使总耗煤降低; 预还原率高于 43% 时, 提高预还原率反而提高总耗煤, 特别是大于 55% 后, 预还原率的增加将大大增大过程总耗煤。关于后者的起因, 可作如下讨论。按所设计流程, 预还原反应器输入热能中的热量中有 50% 左右依赖于转炉炉气的物理热和化学热(见图 2)。若预还原率超过 55%, 则终还原煤耗很低, 提供给预还原的转炉炉气量也将很

少,预还原反应器中的加煤量就得增加,而预还原的能量利用率较低,故总耗煤将增加。

可见,选择合理的预还原率是保证全流程总能耗指标降低的关键因素之一。

#### 4.3 复吹转炉中二燃率及其热利用率的影响

图6(c)表明二燃率增加则终还原耗煤明显下降。二燃率为30%~40%时,过程的总耗煤最低。其原因与上述相类似,即过高的二燃率导致转炉废气量和化学能降低。

图5表明二燃生成热的利用率对终还原过程的煤耗有很大影响。事实上,二燃产生的热若不能有效地向下传给铁浴,则必然导致转炉炉气温度剧增(见图6(a))。这既不利于节能,也不利于转炉炉衬寿命提高。过高的热利用率将导致预还原耗煤增加。图6(b)为二燃率和热利用率时转炉炉气和环型还原焙烧炉废气量影响。按本文计算,若二燃率为40%,其热利用率按成品含铬量选择,  $Cr = 20\%$  为65%;  $Cr = 40\%$  为60%;  $Cr = 60\%$  为57%。

#### 4.4 关于不锈钢母液的计算

按理  $Cr$  增大时,能耗呈指数曲线上升,但本文关于  $Cr = 20\%$  或  $Cr = 40\%$  的能耗计算值不合此规律,其原因在于:理论上, $Cr$  增大时反应温度必须提高,但本文是在相同温度条件下进行模拟计算的。另外,本文所取预还原反应器热损较大(为18%),并认为与  $Cr$  变化无关。所以,本文关于不锈钢母液的能耗计算值较高。

#### 4.5 铬的回收率

本法冶炼碳素铬铁和不锈钢不用硅石,而用石灰造渣,渣量比埋弧电炉减少约185 kg/t,为815 kg/t左右,并采用留渣(100 kg/t)操作。出铁后,加铁料,利用渣中残碳升温;熔化后的铁液进一步吸收了渣中残铬,使渣中( $Cr_2O_3$ )降至1%以下,并为下炉开吹创造条件。用埋弧电炉生产碳素铬铁渣量一般为1000 kg/t,渣中( $Cr_2O_3$ )为3%~5%。这样用本法生产碳素铬铁在理论上可提高铬的回收率为3.4%左右。

## 5 结束语

以环型还原焙烧炉预还原含碳铬矿团块和转炉铁浴终还原二步法流程

为基础,进行物料平衡和热平衡计算。结果表明,用本流程生产碳素铬铁时总能耗为1 692 kg/t标煤,此值比用埋弧电炉的能耗水平降低122 kg/t标煤,铬回收率提高约3.4%。按我国1990年碳素铬铁产量18万吨计算,可节约标准煤约2.2万吨,多产碳素铬铁6 120吨。

本文还对预还原率、二次燃烧率及其热利用率的选择进行了讨论。

## 参 考 文 献

- [ 1 ] 蒋国昌,徐匡迪.上海金属,1988,10(2) 3-12
- [ 2 ] 徐匡迪,蒋国昌,张晓兵等.第五届冶金过程动力学和反应工程学术会议论文集,济南:1991,10:162-181
- [ 3 ] 费因,H. A. 冶金过程物料与能量平衡计算手册.冶金工业出版社

## Two-steps Production of Chromite and Pregnant Solution of Chromium Alloy

**Abstract** The two steps process was selected to produce chromite or pregnant solution of chromium alloy, in which the pellets containing carbon were prereduced in a turning furnace, then they were reduced in a converter bath. The process was used as a close system to calculate mass and heat, and the gas from the converter was used as main fuels to prereduce pellets so that the energy can be fed back. According to the calculated results it was indicated that the total energy consumption was only 1 692 kg standard coal per ton of high carbon chromite.

# Some Advances on the Theoretical Research of Slag<sup>\* 1</sup>

**Abstract** This paper is a review and a comment regarding slag models and optical basicity. It was thought to be better to establish slag model and basicity concept based on the cell structure of slag.

## 1 Introduction

It has been long, that the development of metallurgical technology relied upon a lot of experiment-sieving procedures. The development of materials was in a similar situation. During many years it always originated from a “flavouring” experiment in a laboratory small furnace. Nevertheless, in recent years the invention of new materials changes its way to rely on the so called composition design. Certainly, the principle of theoretical estimation in advance should be also abided for the creation of a new metallurgical technology.

To perform such a theoretical estimation the support of a thermodynamic data base, particularly the systematical activity data of melt components in various cases is needed first of all. Based on the now available activity data of metal for ironmaking and steelmaking, it is, at least, possible to carry out many estimations, even if some interesting problems as component activity in concentrated alloys and the relationship between activity and microstructure of liquid metal are waiting to be studied. However, this is not the case for slag. There are man-

---

\* In collaboration with Jiang Guo-chang and Wei Shou-kun. Reprinted from *ISIJ, Int.*, Vol. 33, No.1, pp. 20-25(1993)

y instances , that many reliable estimations are failure due to lack of slag data. Perhaps , this is why many metallurgists nowadays focus their attention on the research regarding slag.

The International Conferences on Molten Slags and Fluxes held in 1980 , 1984 and 1988 collected and exhibited the results of this field. Moreover , as glass and magma are silicate similar to molten slag , a number of glass-chemists and geochemists run some corresponding studies with almost the same approaches. It is doubtlessly worthwhile for a metallurgist to know something about their contributions. This paper intends to give a brief review concerning some results of these three fields.

## 2 A Review on Slag Modelling

The process of gradually understanding slag is just the process of developing of various slag models. Based on Mysen's opinion <sup>[1]</sup> it is reasonable to divide the slag models into three categories :

### (1) The Physical Parameter Model

The essence of this kind of slag model is an inference on microstructure of slag from the measured physical properties. For example , the bonding energy of Si-O bond is estimated according to the activation energy of viscous flow and based on the presumed relationship between microstructure and the physical properties.

### (2) The Thermodynamic Parameter Model

The ultimate aim of these models is to deduce an equation group from the available thermodynamic experimental data , and by means of this equation group to evaluate interpolatingly and/or extrapolatingly. The foundation of these models is a set of presumed microstructural units. And the relationship between these units and experimental data is stipulated to follow the basic principle of thermodynamics.

### (3) The Structural Model

According to this approach the properties are related to the microstructure which is either measured by some of advanced instruments or determined along the theoretical approach of chemical bonding.

In ferro-metallurgy, the well known molecular theory, the complete ion theory, the molecular-ion coexisted theory and the regular solution theory, all are thermodynamic parameter model. Apart from these, the sub-regular solution model which is recently used in slag research as well as the latest developed models of Gaye and Pelton also belong in this category. Among the mentioned three categories, the progression of this category is the fastest. The following is a brief comment on the models involving in this category.

#### Regular Solution Model

Since Lumsden adopted regular solution model in his slag investigation 30 years ago, this model has been used quite well in equilibrium calculation for oxidation slag. Particularly, for the redox equilibrium of iron in slag and the partition of O, Mn, P between slag and metal. The calculated results were found in harmony with measurements in a comparatively large composition region.<sup>[2~4]</sup>

Nowadays, the most contributions to the use of regular solution model in slag are given by Ban-ya. As he indicated, the basic point of this model is that  $O^=$  anions compose of the main microscopic lattice in slag. Various cations distribute in the gaps among them to form different kinds of cells (i-O-j). Here, i and j denote cations. The equation for the calculation of activity coefficients, in fact, is an extension of the quadratic form from Darken. However, many  $\alpha_{ij}$  parameters including in this equation were evaluated by Ban-ya.<sup>[2]</sup> Further-more, an assumed pure liquid is taken as the standard in regular solution model. Ban-ya pointed out a conversion of standard must be included in the equation.<sup>[2]</sup>

On the other hand, so far the following weak points still limit the use of this model in slag.

(1) Generally the deviation of calculation from measurement is in a degree of 10%.<sup>[3]</sup> Eventhough the error of this kind of experiment perhaps arrives 10% ~ 30%,<sup>[2]</sup> it seems that some effects arise from the model. The Darken's quadratic form modified by Ban-ya for activity coefficient evaluation is

$$\begin{aligned}
 RT \ln \gamma_i = & \sum_j \alpha_{ij} X_j^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} + \alpha_{jk}) X_j X_k \\
 & + \Delta G \quad i \neq j \neq k
 \end{aligned} \tag{1}$$

According to the theory of regular solution,  ${}^{[5]} \alpha_{ij} = \frac{1}{2} Z N_0 (2U_{ij} - U_{ii} - U_{jj})$ .

Here, bonding energy of cells  $U_{ij}$ ,  $U_{ii}$ ,  $U_{jj}$  all are assumed to be independent on slag composition. So as the approach of Darken and Ban-ya, some  $\alpha_{ij}$  could be evaluated pursuant to the data of binary and ternary systems. Considering that actually there are interaction between different kinds of cells, the bonding energy in binary or ternary systems should be not the same of that in multiple component system. Thereby it is difficult to keep the evaluated  $\alpha_{ij}$  in constant. Moreover, Ji pointed out that, at least, in some cases  $\alpha_{jk} \neq \alpha_{kj}$ .<sup>[6]</sup>

(2) As Ban-ya's idea, one of the premises of regular solution model is an assumption that the coordination number of cations is constant. In contrast, this is possible only if it is referred to an intermediate concentration region. Hence the component which content is lower than 5% is neglected by Bab-ya in his evaluation of  $\gamma_i$  for multipul component systems.<sup>[2]</sup> Perhaps, this is just the reason to explain why regular solution model is not so suitable in simulation the behaviour of reduction slag.

(3) Till now based on regular solution model it is impossible to treat the behaviour of slag containing  $S^{=}$ ,  $F^-$ ,  $Cl^-$ , which are used more and more in ironmaking and steelmaking.

#### Sub-regular Solution Model

By means of sub-regular solution model, Shim published his results concerning  $\alpha_{FeO}$  of steelmaking slag<sup>[7]</sup> and  $Fe_7O-Na_2O-SiO_2$  slag.<sup>[8]</sup> The following is the basic equation of this model.

$$\begin{aligned}
 RT \ln \gamma_i = & \sum_j \{ \varepsilon_{ij} X_j^3 + (\vartheta_{ij} + \zeta_{ij} T) X_j^2 \} + \sum_j \sum_{k>j} \left\{ (\varepsilon_{ij} + \varepsilon_{ik}) X_j X_k \right. \\
 & (X_j + X_k + 0.25) + \left( \vartheta_{ij} + \vartheta_{ik} - \frac{1}{2} \vartheta_{jk} - \frac{1}{2} \vartheta_{kj} \right) X_j X_k + \\
 & \left. \left( \zeta_{ij} + \zeta_{ik} - \frac{1}{2} \zeta_{jk} - \frac{1}{2} \zeta_{kj} \right) T X_j X_k \right\}
 \end{aligned}$$

$$+ \sum_j \sum_{k>j} \sum_{l>k} (\varepsilon_{ij} + \varepsilon_{ik} + \varepsilon_{il}) X_j X_k X_l \quad (2)$$

The approach of evaluation  $\varepsilon$ ,  $\vartheta$  and  $\zeta$  parameters is quite similar to that used in regular solution model. The merit of this model essentially superior than regular solution model is that the bonding energy is assumed to be changeable in some degree to follow the variation of composition. The  $\alpha_{\text{FeO}}$  of Shim<sup>[7]</sup> is obviously closed to the experiment than that given by regular solution model.

The following equation was used by Jiang to calculate the component activities of molten C-Fe-X (X = Cr, Ni, Si, Mn) alloy<sup>[9]</sup>

$$RT \ln \gamma_i = \sum_j \sum_k A_{jk} Y^j Z^k \quad (3)$$

Here, Y and Z are variables of composition. The evaluation of  $A_{jk}$  parameters through value fitting is based on the thermodynamic data of the boundary of liquid region. It is thought, that this approach should also be possibly useful for slag simulation. The problem is that some of the data is either in shortage or no generally accepted value. Thereby, the process to evaluate  $A_{jk}$  parameters is just the process to distinguish and judge which are the reliable boundary data.

#### Molecular-Ion Coexisted Model

In China, the leading exponent of molecular-ion coexisted model is Zhang Jian. Based on the concept of "effective concentration", the basic assumption of this model, the activity of  $\text{Al}_2\text{O}_3$  in basic slag used for steel refining was evaluated.<sup>[10]</sup> In contrast, regular solution model has not given the value of  $\alpha_{\text{Ca}^{2+}\text{-Al}^{3+}}$  and  $\alpha_{\text{Mg}^{2+}\text{-Al}^{3+}}$ . So far the molecular-ion coexisted model was also claimed to be useful for the description of the oxidational ability of  $\text{CaO-MgO-Fe}_2\text{O}_3\text{-SiO}_2$  melted slag<sup>[11]</sup> as well as the partition of sulphur between this slag and molten steel.<sup>[12]</sup>

The so called associated solution model<sup>[13]</sup> or two-sublattice model with hypothetical vacancies<sup>[14]</sup> are based on the similar assumption as the approach of Zhang. However, this category does not to be widely accepted in metallurgical field. On the other hand, several researchers belonging to other specialities work with the similar approach. For instance, Hastie *et al.*<sup>[15]</sup> and Bottinga *et al.*<sup>[16]</sup> all take the idea that it is not necessary to declare whether the presumed microstructural units are ion or molecular. And they all choose some of the intermedi-

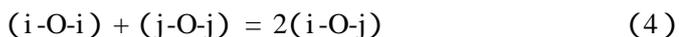
ate compounds of the concerned systems as microstructural unit. In addition, it is thought by Hastie that various microstructural units mix together ideally, so component activity equivalent to the concerned unit content which is namely the "effective concentration" defined by Zhang. Hastie's approach has been applied to simulate a system of 8 components including elements such as Na, Al, B, Cl, Br. The difference between them is: Zhang aims at the behaviour under steelmaking temperature and so calculates directly based on equilibrium constant under 1 873 K. On the contrary, minimizing free energy of the system is the way of other two research groups. This makes an important achievement in description of phase diagram.

#### Pelton's Model

This is a modified quasi-chemical approximation model based on Yokokawa-Niwa's model<sup>[17]</sup> which is one of the classical and standard ways in lattice-like modelling of slag. So far it was used in simulation the equilibrium between SiO-CaO-MgO-MnO-FeO-Na<sub>2</sub>O slag vs. solid oxide or molten metal or gaseous phase.<sup>[18]</sup> Its feature is as follows:

(1) Take various i-O-j cells including the cells of i = j as microstructural units.

(2) During mixing the following reaction happens



The relative amount of cells is determined by the variation of free energy of the mentioned reaction. Namely,

$$\frac{Y_{(i-O-i)}^2}{Y_{(i-O-i)} Y_{(j-O-j)}} = 4 \exp(-2W_{ij}/ZRT) = K \quad (5)$$

Y denotes mole fraction of cells. Z denotes coordination number.  $W_{ij} = (\omega_{ij} - \eta_{ij}T)$ ,  $\omega_{ij}$  denotes the variation of mole enthalpy,  $\eta_{ij}$  denotes the variation of mole non-configurational entropy. Both of them are related to slag composition in a polynomial form. The parameters involved in these polynomials are evaluated through value fitting with the published thermodynamic data. Thereby, the equilibrium constant of the mentioned cell reaction is changeable to follow the variation of slag composition.

In fact, the equation used to determine the mole fraction of cells is just the

characteristics of quasichemical approximation model. The Pelton's modification is that to involve the variation of non-configurational entropy.

(3) Through the so called asymmetrical approximation the  $W_{ij}$  deduced from various MO-SiO<sub>2</sub> and Na<sub>2</sub>O-SiO<sub>2</sub> was used to describe M<sup>\*</sup>O-M<sup>\*\*</sup>O-SiO<sub>2</sub> ternary system. An additional item taken from ternary data is needed only in several cases. [19]

#### Gaye's Model

As the further development of Kapoor-Frohberg's Model, [20] Gaye's Model has been widely adopted, at least, in Europe. Provided, at present, this is the most successful thermodynamic parameter model. According to the paper published in 1984, a slag containing 6 oxides can be treated. [21] Moreover, in 1990, the result of the cooperation of IRSID with NSC was published. [22] It extends the application to the slags in which multi-anions as O<sup>=</sup>, S<sup>=</sup>, F<sup>=</sup> are coexisted, and to the slag containing P<sub>2</sub>O<sub>5</sub>.

This is also a modified quasi-chemical approximation model. Similar to Pelton's approach, it just uses binary system parameters to simulate multiple component systems. The difference from Pelton's Model is that not only the formation energy  $W_{ij}^A$  of i-A-j cell but also the interaction energy  $E_{ij}^A$  and  $E_i^{AB}$  between various cells, A and B denote O<sup>=</sup> or S<sup>=</sup> or (2F)<sup>=</sup>, are taken into account. The binary parameters involved in this model were suggested to be a linear function of slag composition and to be independent on temperature. In slag two kinds of sub-lattices were assumed. One is composed of anions, the another is composed of cations. Various cation entities distribute on the cation sub-lattice. This is an assumption to deal with P<sub>2</sub>O<sub>5</sub> and Al<sub>2</sub>O<sub>3</sub>. For example, it is presumed that the cation entities of P<sub>2</sub>O<sub>5</sub> are PO<sup>3+</sup> and P<sup>5+</sup>. But, as pointed out by Gaye himself, dealing with Al<sub>2</sub>O<sub>3</sub> with this approach needs further improvement.

It is worthwhile to note, that dealing with  $C_s$  data of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-FeO-MnO-MgO-CaO slag by means of Gaye's model is much superior than the treatment based on optical basicity. [23] Moreover, a number of researchers use Gaye's Model to estimate  $C_s$ , [23] melting point [24] of some slags and the modification of non-metallic inclusions. [25]

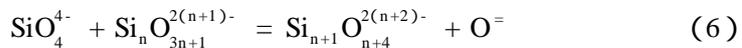
#### Polymer Model

Masson is known widely due to his great contribution<sup>[26]</sup> to polymer model. In metallurgical field this model has been highlighted. A plenty of metallurgists study slag behaviour along this model. As they trust that the slag microstructure should be a polymer. And anyhow, in description of polymerization of some binary silicate in part of their liquid region the adoption of polymer model is successful. On the contrary, this model was criticized a lot by geochemists. As Mysen<sup>[1]</sup> and Bottinga<sup>[16]</sup> indicated :

(1) The experiment, polymer model depends on the results of which as evident is not reliable.

(2) Generally, it is just possible to deal with binary silicate of either chain-like or branched-chain-like microstructure. Namely, it is limited in the region of mole fraction of SiO<sub>2</sub> is lower than 0.5. It seems to be difficult to deal with the slag containing some elements the valency as well as the coordination number of which is changeable.

(3) The following polymerization reaction is assumed as the foundation of polymer model



This reaction claims that the mole fraction of O<sup>-</sup> should be larger if the polymerization degree becomes larger. Nevertheless, the real mole fraction of O<sup>-</sup> is always a small quantity. And, the equilibrium constant of this polymerization reaction becomes larger to follow the increase of temperature. This claims that an increase of polymerization degree results from an elevation of temperature. Obviously this could not be in reality.

Magma which is the objective of geochemists is a silicate based material as slag. So it should be a polymer. The microstructural unit of magma is considered as a ring which is composed of 3 to 6 monomers,<sup>[1]</sup> by geochemists. At present, it seems no theoretical model is available to describe this kind of ring-microstructure.

### 3 A Review on Slag Basicity

In spite of that basicity is a concept frequently used in metallurgy, it en-

tered into the hall of modern theory just after the appearance of optical basicity. It was first suggested by Duffy and Ingram in their research on glass-chemistry.<sup>[27]</sup> Together with them, Sommerville made efforts to introduce this concept to metallurgists.<sup>[28]</sup> Later on, Nakamura *et al.* suggested a new optical basicity theory based on photoacoustic spectroscopy and average electron density.<sup>[29]</sup> In 1987, Jiang introduced the concept of optical basicity in a national seminar.<sup>[30]</sup>

Nowadays optical basicity has been utilized by a number of metallurgists to sum up various capacity data of many slags as well as the solubility of (MgO) and redox equilibrium of (Fe<sub>2</sub>O).<sup>[31]</sup> Intrinsically, the reason is that the chemical characteristics of slag has to be concerned if one refers to slag-metal reaction. However, basicity is just the brief and practical index reflecting chemical characteristics of slag. This function is not replaceable with slag modelling.

On the other hand, some weak points were found during utilizing optical basicity:

(1) Various cells as i-O-j and i-O-i are taken essentially to be microstructural units in optical basicity. But for calculating optical basicity of a practical slag, the basicity characteristics of oxide molecular instead of that of cells is utilized.

(2) Neither Duffy's approach nor Nakamura's approach is ideal in elucidation completely the influence of "environment" on anion activity. The comparison of bonding energy of Al-O in variant MO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> systems (MO = Na<sub>2</sub>O, CaO, MgO) is a typical example. Appen<sup>[32]</sup> and Varshal<sup>[33]</sup> indicated that of Al-O in Na<sub>2</sub>O system is the strongest one, and that in MgO is the weakest one. This is, however, in contrast to optical basicity. Yokokawa also doubted the basicity characteristics of Al<sub>2</sub>O<sub>3</sub> given by the theory.<sup>[34]</sup> The characteristics of Na<sub>2</sub>O needs to be improved further yet.<sup>[31]</sup>

(3) For transition metal oxides, the characteristics given by Duffy *et al.* is successful in description of phosphorus capacity only. On the contrary, that given by Nakamura *et al.* is successful just in simulation of sulphur capacity. It seems that a transition metal oxide should have a variable characteristics.

## 4 Discussion

(1) In history, molecular theory, ionic theory and molecular-ion coexisted

model were used to describe slags. The later does not get wide support in metallurgists. One of the possible reason is that some molecules used as microstructural unit in this model could not be detected with experiment. On the other hand , it was understood earlier that the ions in slag are far from the completely independent state. Experiments indicated all the ions are involved in this or that kind of cells. As already mentioned , many modern slag modelling take various cells as the microstructural units. Hence , it is reasonable to say this is the Cell Theory era.

(2) In reality , slag should be a polymer made up of many cells. Unfortunately , even the real polymerization feature of  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  slag so far does not be understood thoroughly. Nevertheless , the polymerization degree might effect directly on physical properties , such as viscosity. For simulating chemical activation of slag it seems fairly to undertake study based on cell characteristics. This is also the view point of Bottinga.<sup>[16]</sup>

The so called cell characteristics is essentially two items. Namely , the relative amount of cells and the bonding energy of them. In Gaye's Model and Pelton's Model , these two items determine the mixing free energy of the slag exactly. In fact , in a slag system the variation of composition is just the variation of the amount of cells with different bonding energy. One of the contributions of molecular-ion coexisted model is : it indicates that the thermodynamic activity of component does not have a meaningful relationship with the apparent concentration , it is a function of the relative amount of concerned microstructural unit supposed to be mixing together with others ideally. According to optical basicity , the basicity characteristics (B) given for compounds is intrinsically just an extent of bonding intensity of some cells. Thereby , its stipulation of taking oxide compound as calculation unit is a weak point which must neglect or screen the influence of other cells. The "bonding basicity" concept suggested by Jiang is a step aiming at modify on this weak point.<sup>[35]</sup> It is thought that the bonding basicity ( $B_{ij}Y_{ij}$ ) of cell (i -O- j) should have essentially a relationship with the thermodynamic activity of related component.

(3) Even it is limited in the term of cell characteristics , several topics need to be talked over further.

(a) The existing state of sulphur is changeable to follow the variation of

oxygen pressure. <sup>[5]</sup> If sulphur in oxidational slag is contained in cell (Ca-O-S), in reductional slag it may become to (Ca-S-Ca) or (Ca-S-Si). Similarly, during dephosphorization with reduction slag, phosphorus might also be involved in cell (Ca-P-Ca) and so on. Provided, from this point it is able to sum up the capacity data of both of oxidational and reductional slags.

(b) Alumina is a typical amphoteric oxide, the coordination number of it is variable. And through the formation of complex, cell (i-O-j) becomes to (i-O <sub>j</sub><sup>k</sup>). <sup>[27]</sup> In addition, different cations could have different effect on this triple-bonded oxygen anion. Perhaps, these are the grasps to understand the behaviour of alumina and so on.

(c) As a typical transition metal oxide, the behaviour of Fe<sub>2</sub>O is difficult to be described satisfactorily, at present, with optical basicity. The complexity of this description concerns the redox equilibrium together with the amphoteric feature of Fe<sub>2</sub>O<sub>3</sub>. Recently, it has been found that some kinds of metallic bonds might affect this oxide also. <sup>[36]</sup>

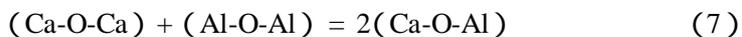
(4) The research on cell structure depends upon the progression of modern detection instruments. Meanwhile, it cannot help paying special attention to the improvement of preparation technology for slag samples. A typical instance is that, the experiments regarding activity of iron oxide are always performed under a lower temperature due to the strong corrosivity of the slags.

Considering that the experiments so far are not so reliable, it is essential to approach the reality from both sides: theoretical way and experimental way, and to rely upon the agreement of them. Nowadays some estimations about the energy characteristics of cells by means of quantum chemistry and so on seems to be noticeable.

(5) For metallurgists it is too early to develop an actual structural model. The thermodynamic parameter models are more practical. Whether these models are successful or not, it all depends on whether they are able to sum up reasonably the known thermodynamic data. And it does not concern the assumed microstructural units whether they are of reality or not. From this point, the molecular-ion coexisted model should have its suitable status. But, in every sense, it is not to say the assumed microstructural units are proved to be of actuality, pursuing to that the model can describe the concerned activity. If a thermodynamic

parameter model is used widely and its microstructural units for various slag systems are assumed not to follow the desire of getting agreement with experimental results , but in accordance with a seriously universal stipulation , then the assumption of this model might close to reality in a closer degree. From this point , the molecular-ion coexisted model is not so satisfied.

The molecular-ion coexisted model usually takes some unstable compounds as microstructural units , and then subjects criticism. From the view point of cell theory , these molecularly factually hint the clusters of some cells , and different molecular relates to different cell cluster. Eventhough , the existence of unstable compounds under high temperature is not easy to acquire evidence , the existence of many cells is now proved. In the liquid region of  $\text{CaO-Al}_2\text{O}_3$  (1 873 K) , the cell reaction which governing the thermodynamics of this system is



The formation free energy of unstable compound  $3\text{CaO-Al}_2\text{O}_3$  , but not of other stable compound , was chosen by Jiang to calculate equilibrium constant of the cell reaction.<sup>[35]</sup> This is a reasonable selection , because only  $3\text{CaO-Al}_2\text{O}_3$  contains just cell of (Ca-O-Al). This unstable compound was also taken as microstructural unit in molecular-ion coexisted model , but this was only for getting agreement with experimental results.<sup>[10]</sup>

After all , a thermodynamic parameter model may acquire more reliability if its microstructural units are more closer to reality. Perhaps , from this view point to undertake the next improvement of Gaye's model is beneficial. The amphoteric behaviour of alumina and the variation of environment of S = have not been dealt with quantitatively in Gaye's model. And , provided , for  $\text{P}_2\text{O}_5$  and so on one have to take double bonding into account.

(6) To compare the approaches of Pelton , Gaye and the author , Eq. (5) can be useful in binary system. According to either Pelton or Gaye , the energy parameters for calculation of  $K$  are evaluated through value fitting of thermodynamic data. As the idea of the author , however ,

$$K = f(B_{ij} , G^m) \quad (8)$$

and then the data of microstructure as bonding energy can be adopted. For lime-alumina-silica ternary system , the governing equation suggested by the author

is<sup>[37]</sup>

$$Y_{12}^{\alpha} Y_{13}^{\beta} Y_{14}^{\delta} Y_{24}^{\nu} / Y_{44}^{\sigma} Y_{11}^{\tau} Y_{22}^{\nu} Y_{33}^{\epsilon} = f^* (B_{ij}, G^m) \quad (9)$$

Here,  $\alpha, \beta, \delta, \nu, \sigma, \tau, \nu, \epsilon$  all are stoichiometric parameters in cell mixing reaction. Subscripts 1, 2, 3, 4 denotes Si, Al<sub>a</sub> (acid Al<sup>3+</sup>), Al<sub>b</sub> (basic Al<sup>3+</sup>), Ca respectively, 12 denotes Si-O-Al cell and so on.

## 5 Conclusion Remarks

This paper is a review and a comment regarding slag models and optical basicity. It is possible to say, undertaking the research from the following two aspects might be beneficial. One is to elucidate the cell structure depending on both experiment and theory. Based on this, the precise evaluation of basicity characteristics in various cases can be given. The another is establishment of a model to calculate the relative amount of various cells, taking the influence of the variation of coordination number and chemical valency into account. And finally to correct the research by experiment.

### Acknowledgements

This research is supported by The National Natural Science Foundation of China.

The authors are very grateful to Professor Zhang Jian for his systematical introduction of the Molecular — Ion Coexisted Model.

## References

- [ 1 ] B. O. Mysen : Structure and Properties of Silicate Melts , Elsevier Sci. Publishers B. V. , (1988) , 48 , 79 , 116
- [ 2 ] S. Ban-ya and M. Hino : *Tetsu-to-Hagané* , 74 (1988) , No. 9 , 1701
- [ 3 ] M. Hino , I. Kikuchi , A. Fujisawa and S. Ban-ya : Proc. of 6th IISC , Vol. 1 , ISIJ , Tokyo , (1990) , 264
- [ 4 ] R. Nagabayashi , M. Hino and S. Ban-ya : Proc. of 3rd Int. Conf. on Molten Slags and Fluxes , Glasgow , U. K. , June , (1988) , 24

- [ 5 ] F. D. Richardson : Physico-Chemistry of Melts in Metallurgy , Academic Press Inc. , London , (1974) , 116
- [ 6 ] Qi Guojun and Ji Chunlin : Proc. of 5th National Conf. on Metallurgical Physico-Chemistry , China , (1984) , 227
- [ 7 ] Dow-Bin Hyun and Jae-Dong Shim : *Trans. Iron Steel Inst. Jpn.* , 28 (1988) , 736
- [ 8 ] Dow-Bin Hyun and Jae-Dong Shim : Proc. of 6th IISC , Vol. 1 , ISIJ , Tokyo , (1990) , 177
- [ 9 ] Jiang Guochang , Zhang Xiaobing and Xu Kuangdi : *Acta Metall. Sin.* , 28B (1992) , 240
- [ 10 ] Zhang Jian and Wang Chao : Proc. of National Academic Symp. on Special Steel Melting , China , (1986) , 1
- [ 11 ] Zhang Jian , Wang Chao and Tong Fusheng : A Calculation Model on the Oxidational Power of a Multi-Component Molten Slag , private communication
- [ 12 ] Zhang Jian , Wang Chao and Tong Fusheng : Proc. of the Wei Shoukun Symp. , China , (1990) , 57
- [ 13 ] R. C. Sharma and Y. A. Chang : *Metall. Trans.* , 10B (1979) , 103
- [ 14 ] M. Hillert , B. Sundman and X. Z. Wang : *Metall. Trans.* , 21B (1990) , 303
- [ 15 ] J. W. Hastie , D. W. Bonnell and E. R. Plant : Proc. of 3rd Int. Conf. on Molten Slags and Fluxes , Glasgow , U. K. June , (1988) , 254
- [ 16 ] Y. Bottinga , D. F. Weill and P. Richet : Thermodynamics of Minerals and Melts , ed. by R. C. Newton , Springer-Verlag , N. Y. , Heidelberg , Berlin , (1981) , 207
- [ 17 ] T. Yokokawa and K. Niwa : *Trans. Jpn. Inst. Met.* , 10 (1969) , 3 , 81
- [ 18 ] A. D. Pelton , G. Eriksson and M. Blander : Proc. of 3rd Int. Conf. on Molten Slags and Fluxes , Glasgow , U. K. , June , (1988) , 66
- [ 19 ] A. D. Pelton and M. Blander : *Metall. Trans.* , 17B (1986) , 805
- [ 20 ] M. L. Kapoor and M. G. Froberg : Proc. of Symp. on Chemical Metallurgy of Iron and Steel , Sheffield , U. K. , (1971) , 17
- [ 21 ] H. Gaye and J. Welfringer : Proc. of 2nd Intern. Symp. on Metallurgical Slags and Fluxes , Lake Tahoe , Nevada , Nov. , (1984) , 257
- [ 22 ] J. Lehmann , H. Gaye , W. Yamada and T. Matsumiya : Proc. of 6th IISC , Vol. 1 , ISIJ , Tokyo , (1990) , 256
- [ 23 ] C. Saint-Jours and M. Allibert : Proc. of 3rd Int. Conf. on Molten Slags and Fluxes , Glasgow , U. K. , June , (1988) , 65
- [ 24 ] R. Boom , B. Deo , W. Van Der Knoop , F. Mensonides and G. Van Unen : Proc. of 3rd Int. Conf. on Molten Slags and Fluxes , Glasgow , U. K. , June , (1988) , 273
- [ 25 ] D. A. R. Kay and Jiang Junpu : Proc. of 3rd Int. Conf. on Molten Slags and Fluxes , Glasgow , U. K. , June , (1988) , 263
- [ 26 ] C. R. Masson : Proceedings of Symp. on Chemical Metallurgy of Iron & Steel , London ,

- U. K. , (1971) , 3
- [27] J. A. Duffy and M. D. Ingram : *J. Non-Cryst. Solids* , 21 (1976) , 373
- [28] J. Sosinsky and I. D. Sommerville : *Metall. Trnas.* , 17B (1986) , 331
- [29] T. Nakamura , Y. Ueda and J. M. Toguri : *J. of JIM* , 50 (1986) , 456
- [30] Jiang Guochang : *J. of Shanghai University of Technology* , 10 (1989) , No. 3 , 257
- [31] I. D. Sommerville : *Proc. of Technological Advances in Metallurgy* , Lulea , Sweden , Sept. , (1986) , Paper 13
- [32] A. A. Appen : *Glass Chemistry (Chinese Version)* , Publisher of Civil Eng. of China , (1974) , 268
- [33] V. G. Varshal : *Izv. A. N. SSSR Inorg. Mater.* , (1972) , No. 5 , 934
- [34] T. Yokokawa , T. Maekawa and N. Uchida : *Bull. JIM* , 25 (1986) , 3
- [35] Jiang Guochang and Xu Kuangdi : *Proc. of 6th IISC* , Vol. 1 , ISIJ , Tokyo , (1990) , 240
- [36] M. D. Ingram : *Proc. of 3rd Int. Conf. on Molten Slags and Fluxes* , Glasgow , U. K. , June , (1988) , 166
- [37] Jiang Guochang and Zhang Xiaoping : *Proc. of 4th Int. Conf. on Molten Slag and Fluxes* , ISIJ , Tokyo , (1992)

# The Kinetics of Reduction of MnO in Molten Slag with Carbon Saturated Liquid Iron<sup>\* 1</sup>

**Abstract** This investigation devotes to the kinetics of the reduction of (MnO) with carbon-saturated liquid iron. The experiment condition involves high content realm of both (% MnO) and % Mn. It was found that the reduction is limited by the interfacial reaction. By means of a X-TV dynamic metallurgical phenomena displaying device, the slag-iron interface was proved to be the essential site for evolving the reduction product CO. The content variation of surface active agent S affects obviously on the reduction rate. If no carbon is added in slag, then a hump emerges on the curve of (% FeO) vs. reaction time. In this case, the apparent reaction order is 2. If there is a carbon addition in slag, the process is of apparent first order. Based on the three step model of reactions in series, the aforementioned phenomena and regularities were elucidated unitedly.

## 1 Introduction

The production of HC-FeMn through smelting reduction process gained high light of metallurgists. As the basic reaction in ironmaking and steelmaking, the regularity of oxidation and reduction of manganese has been discussed in a lot of text books. These, however, limited themselves in the lower region

---

\* In collaboration with JIANG Guochang, DING Weizhong, GU Liping, GUO Shuqiang and ZHAO Baixiong. Reprinted from *ISIJ International*, Vol. 33, No. 1, pp. 104-108 (1993)

of (% MnO) and % Mn. To grasp the process technology of smelting reduction of HC-FeMn, this investigation is devoted to the discussion of the kinetics under the condition involving much higher content realm of both % Mn and (% MnO).

## 2 The Experiment

Some of the experiments were carried out in a resistance furnace. Fig. 1 is the installation system. The metal in predetermined composition was composed of chemical pure iron and electrolytic Mn metal. After the graphitecrucible containing metal addition was put into the furnace and an Ar flow of 1 NI/min was input, the heating started. The premelted slag was spreaded on the surface of molten metal several minutes after the temperature had reached the settled goal with an accuracy of  $\pm 5$  K. The premelted slag was composed of pure chemical agents according to the given composition shown in Table 1. In few experiments, the slag included some coke slices. Slag sampling of 6–100 mg started from the moment of slag addition and performed according to the given time interval. After separating from metal the slag samples were analysed by means of atomic absorption spectrophotometer.

**Table 1 The condition of experiment in resistance furnace**

Run	Slag						Metal		Temp. (K)
	(% MnO) <sub>i</sub>	(% FeO) <sub>i</sub>	(% MgO) <sub>i</sub>	<i>B</i>	wt(g)	C-add.	Content	wt(g)	
021	52.85	7.0	$\frac{1}{5}$ (% CaO)	0.9*	20	0	Mn base, % S <sub>i</sub> = 0.027	80	1 823
022	51.74	7.0	$\frac{1}{5}$ (% CaO)	0.9*	20	0	Mn base, % S <sub>i</sub> = 0.048	80	1 823
023	50.67	7.0	$\frac{1}{5}$ (% CaO)	0.9*	20	0	Mn base, % S <sub>i</sub> = 0.079	80	1 823
111	40.00	0	5	1.1	200	0	% Mn <sub>i</sub> = 0	600	1 823
112	40.00	0	5	1.1	200	0	% Mn <sub>i</sub> = 10	600	1 823
113	40.00	0	5	1.1	200	0	% Mn <sub>i</sub> = 30	600	1 823
213	42.78	5	6	1.3	20	5	% Mn <sub>i</sub> = 0	80	1 853
214	42.78	5	6	1.3	20	5	% Mn <sub>i</sub> = 30	80	1 853
217	42.78	5	6	1.3	20	0	% Mn <sub>i</sub> = 0	80	1 853

$B^* = (\text{CaO} + \text{MgO})/\text{SiO}_2$ ,  $B = \text{CaO}/\text{SiO}_2$ , “*i*” denotes initial moment.

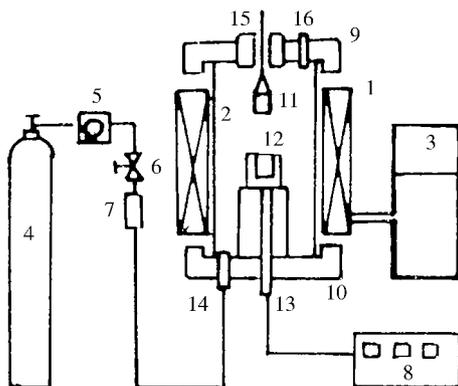


Fig. 1 The experiment set in resistance furnace

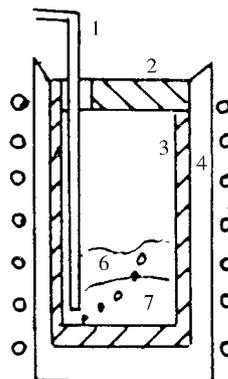


Fig. 2 The experiment set in induction furnace

The other experiments were performed in an induction furnace, as shown in Fig. 2. After melting down the metal, premelted slag was added. In some heats, some coke was added together with the slag addition. And then, started carbon injection for keeping % C through a graphite torch. Temperature fluctuation was up to  $\pm 25$  K. The experiment scheme is shown in Table 2.

**Table 2 The condition of experiment in induction furnace**

Run No.	Metal		Slag			Temp. (K)
	Base	% Mn <sub>i</sub>	(% MnO) <sub>i</sub>	B	C-add. (g)	
301	Fe	0	42.78	1.3	80	1 893
311	Fe	0	42.78	1.3	0	1 893

B = (CaO)/(SiO<sub>2</sub>), "i" denotes initial moment.

### 3 The Reaction Mechanism

It was found that if the initial slag contains no (FeO), an increase of (% FeO) then emerges in the initial stage of (MnO) reduction. And the curve of (% FeO) vs. reaction time frequently exhibits a hump as shown in Fig. 3. It is indicated in this figure, the higher the % Mn, the lower the hump and the slower the reduction rate of (MnO). Pomfret, <sup>[1]</sup> Plashevsky<sup>[2]</sup> and Shinoza-

ki<sup>[3]</sup> studied this behaviour under different conditions. Pomfret's investigation centred on the influence of changing CO pressure and Plashevsky's research concerned the effect of temperature and initial (% MnO). Their results are similar to Fig. 3 , especially to the curve of Run 111.

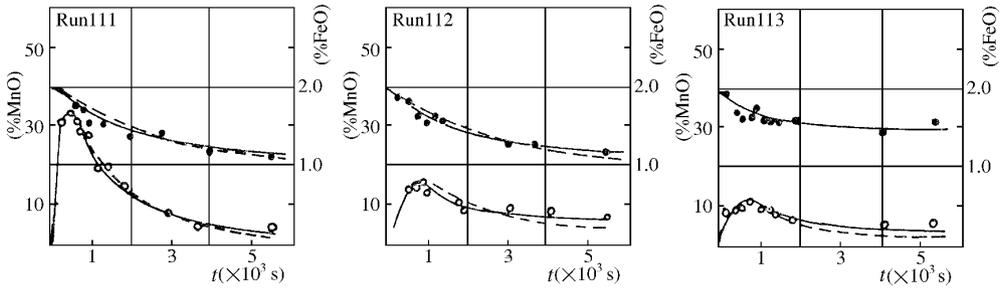


Fig. 3 The Reduction ratio of (MnO) and the behaviour of (FeO)

Fig. 3 points out that the reduction of (% MnO) in this experiment progresses following a model involving three sub-reactions in series.



The suggestion of reaction (3) will be illustrated in next section. Under 1 823 K , assuming reaction (1) is in equilibrium

$$N_{\text{FeO}} = 0.26 \frac{\gamma_{\text{MnO}} N_{\text{MnO}} \alpha_{\text{Fe}}}{\gamma_{\text{FeO}} \alpha_{\text{Mn}}} \quad (4)$$

Here ,0.26 comes from

$$\log K_1 = - \frac{6\,640.0}{T} + 2.95 \quad (5)$$

Table 3 is the calculation result corresponding to Fig. 3. The equilibrium (% FeO) is larger than the (% FeO)<sub>max</sub> shown in Fig. 3. This makes sense that reaction (1) is possibly in thermodynamics.

Table 3 The possibility of reaction (1) in thermodynamics

Run No.	Parameters for calculation					$N_{FeO}^*$ calcd.	(% FeO)* measd.
	(% MnO)*	Mn*	$\alpha_{Fe}/\alpha_{Mn}$	$\gamma_{MnO}^{[4]}$	$\gamma_{FeO}^{[5]}$		
111	36.3	1.25	79.00	1.0	2.0	5.25	1.60%
112	33.7	11.60	7.62	1.0	2.0	0.34	0.77%
113	33.5	31.80	2.13	1.0	2.0	0.094	0.53%

- 1) “\*” denotes the moment of  $d(\% FeO)/dt = 0$ .
- 2) assume  $\alpha_{Fe}/\alpha_{Mn} = \% Fe/\% Mn$ .
- 3) Mn was calculated according to  $(\% MnO)_i - (\% MnO)^*$ .
- 4)  $\gamma_{MnO}$  and  $\gamma_{FeO}$  were evaluated according to  $B = 1.1$ .

In order to display the rate limiting step of the overall reduction, experi-

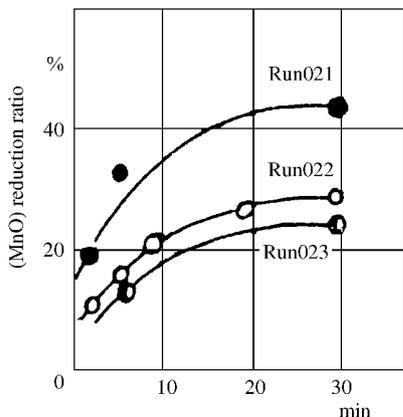
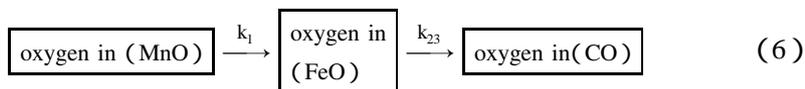


Fig. 4 The effect of initial % S on (MnO) reduction ratio

ments using metal with different %  $\underline{S}$  were designed. This is intended to influence the reduction of (MnO) through the surface active function of  $\underline{S}$ . Fig. 4 shows that reduction ratio abates following the increase of %  $\underline{S}$ . This is surely an evidence indicating that rate limiting step is not (MnO) diffusion, but the interface reaction.

Usually, whether an interface reaction is the rate limiting step or not is judged by means of the variation of interface area. Nevertheless, it can also be judged through the variation of the content of surface active agents. It seems superior than the way of changing crucible diameter, due to the fact that the depth of molten metal and the thickness of slag can be kept without change when the content of surface active agent to be varied a lot.

The basic regularity of reactions in series is a useful mode in analysing which one among the three subreactions gets the slowest rate. The three step model can be simplified as follows



$k_1$  denotes the apparent rate constant of reaction (1). And  $k_{23}$  denotes the overall apparent rate constant of both reactions (2) and (3). In accordance with the pattern of the curve shown in Fig. 3, the relation of  $k_1 < k_{23}$  is possible. In other words, the rate of reaction (1) is likely the slowest. [6]

As well known, the reaction mechanism can also be revealed through the study of reaction order. Figs. 5 and 6 were acquired with a differential method to deal with the experimental data. It was found that carbon addition could cause the variation of reaction order. If there is no carbon addition, all the experiments show apparent second order characteristics. If some carbon is added, it is the apparent first order in the initial stage, no matter the experiment is carried out whether in resistance furnace or in induction furnace. Following the consumption of carbon in slag, the apparent second order appears again. Different curves get different turning point which is caused by different carbon addition as well as different oxidation rate. Thus it is clear that the reaction mechanism for slag involving some carbon should be not the same of that for the slag involving no carbon or only a little carbon.

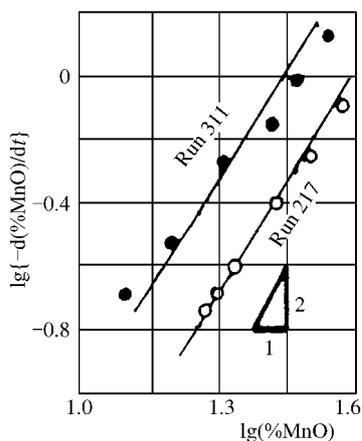


Fig. 5 The apparent reaction order when no carbon addition in slag

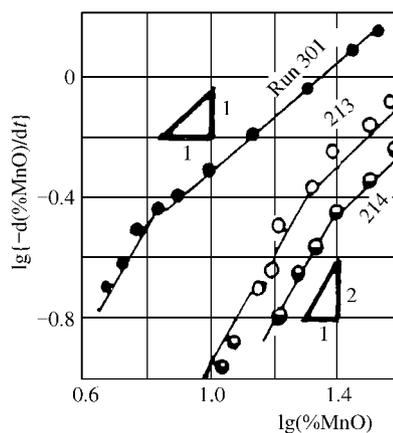


Fig. 6 The apparent reaction order when carbon is added in slag

Whether reaction (1) can exhibit an apparent second order characteristics?

If it can, this should be another evidence to show that reaction (1) is the rate limiting step for the overall process. Suppose the reverse process is possibly to be neglected, then its rate is

$$r = k(1 - \theta)(\% \text{ MnO}) \quad (7)$$

Here,  $\theta$  denotes the occupied ratio along interface by surface active agent Se. The content of Se in the used electrolytic Mn is 0.056%. Its surface active function is known to be as more strong than that of  $\underline{S}$ .<sup>[7]</sup> And the boundary (single molecular) layer of molten steel is of a FeS-like structure even %  $\underline{S}$  is only 0.02%.<sup>[8]</sup> Hence in this experiment,  $\underline{Se}$  may show its influence on the reaction. On the other hand, as Wagner's idea  $\theta$  is not a constant but a variable due to the change of CO evolving.<sup>[9]</sup> And the stronger the stirring caused by CO evolved, the smaller the  $\theta$ .<sup>[10]</sup> Probably, the apparent second order of reaction (1) is just caused by the variation of  $(1 - \theta)$ .

In this investigation, (% FeO) is quite low. And so along gas-slag-metal interface the overall reaction of Eqs. (2) and (3) can be considered as apparent first order.<sup>[11]</sup> But reaction (1) along slag-metal boundary is of apparent second order. Therefore, if  $C$  denotes the mole amount in a slag, then

$$-\frac{dC_{\text{MnO}}}{dt} = k_1 C_{\text{MnO}}^2 \quad (8)$$

$$\frac{dC_{\text{FeO}}}{dt} = k_1 C_{\text{MnO}}^2 - k_{23} C_{\text{FeO}} \quad (9)$$

As apparent rate constant  $k_1, k_{23}$  includes the factor of interface area, finally acquire the following equation. (See Appendix)

$$C_{\text{FeO}} = \frac{k_{23}}{k_1} \left\{ \ln Z + \sum_1 \frac{Q^n}{n \cdot n!} \right\} \exp(-Q) - \frac{C_{\text{MnO } j}}{Z} + \left\{ C_{\text{MnO } j} - \frac{k_{23}}{k_1} \sum_1 \frac{Q^n}{n \cdot n! \cdot Z^n} \exp\left(-\frac{Q}{Z}\right) \right\} \exp(-k_{23}t) \quad (10)$$

$$Q = \frac{k_{23}Z}{k_1 \cdot C_{\text{MnO } j}} \quad (11)$$

$$Z = 1 + C_{\text{MnO } j} \cdot k_1 t \quad (12)$$

Here the subscript  $i$  denotes the initial condition.

Equations (10) ~ (12) were used to describe the experiments. At first,  $k_1$  was calculated pursuant to Eq. (8). And taking  $dC_{\text{FeO}}/dt = 0$ , from Eq. (9)  $k_{23}$  was evaluated. The result is given as Table 4. Finally the variation of (% MnO) and (% FeO) during the whole process can be calculated as the dotted curve in Fig. 3. Surely the agreement is quite well. Of course, this model neglects the reverse processes, so not the effect of % Mn is involved in Eq. (9). But, in fact, it is involved through the evaluation of  $k_1$  and  $k_{23}$ , which depends on experimental results. The agreement is the another evidence indicating the reduction of (MnO) is composed of three sub-reactions, and the rate of the overall process is limited by reaction (1), if no carbon is added in slag. Pomfret recently published a new idea which is similar to us.<sup>[12]</sup> The agreement also points out that the evolution of CO under this experiment condition, unlikely plays a role to limit the overall process.

**Table 4 The rate constant in three step reaction model**

Run	$k_1$	$k_{23}$
111	$8.17 \times 10^{-8} / \text{s}$	$6.70 \times 10^{-5} / \text{s}$
112	$7.60 \times 10^{-8} / \text{s}$	$11.21 \times 10^{-5} / \text{s}$
113	$7.22 \times 10^{-8} / \text{s}$	$15.13 \times 10^{-5} / \text{s}$

#### 4 The Observation of the Reaction Site

The X-TV dynamic metallurgical phenomena displaying device, as Fig. 7 was used to observe the reaction site during the smelting reduction of (MnO). As shown in Fig. 8, under the condition of % Mn < 60% and even the co-existence of the slag-crucible and slag-coke interface, it was found that the reaction product CO usually evolved along slag-metal interface. This leads us to suppose the reaction (3).

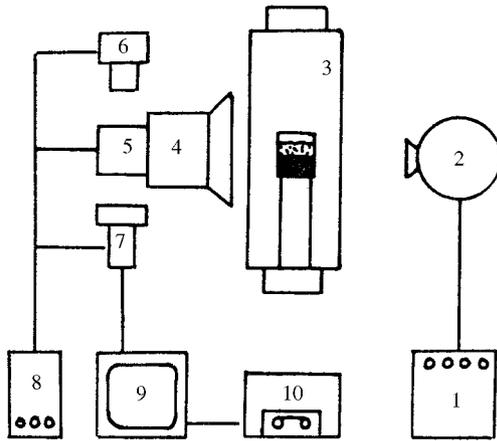


Fig. 7 The X-TV set for dynamically displaying the metallurgic phenomena

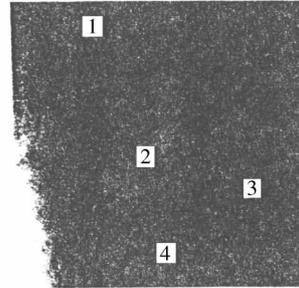


Fig. 8 The evolution site of the reaction product CO

This is a result different from that of Fujita *et al.*,<sup>[13]</sup> however, it coincides with the relevant measurements of reaction rate constant. For example, Fuwa<sup>[14]</sup> and Sato *et al.*<sup>[15]</sup> pointed out the rate constant relating to the reduction with  $\underline{C}$  is much larger than that with solid carbon.

## 5 Conclusion

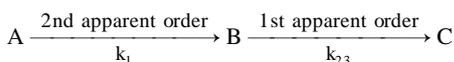
(1) The rate of (MnO) reduction with carbon saturated iron is limited by the interfacial reaction. This is deduced from the following results. Increasing %  $\underline{S}$  makes decrease of interface area, and then causes the relevant lowering down of the reduction rate. Under the condition of %  $\underline{Mn} < 60\%$ , it was viewed by use of the X-TV dynamic metallurgical phenomena displaying device that the reduction product CO usually evolves along slag-metal interface. This is true even in the case of coexistence of slag-crucible and slag-coke interface.

(2) The mechanism of (MnO) reduction with carbon saturated iron was revealed according to the feature of the (% FeO) curve. This indicates that the reduction progresses to follow a three step model. Among the three interfacial-reactions, the rate of reaction (1) is the slowest. The apparent order of this reaction is 2, and that of the overall reaction when no carbon addition in slag is also 2.

(3) According to that reaction (1) is of apparent second order, the basic kinetic equation of reactions in series was deduced. And it was used successfully to describe quantitatively the progression of the reduction process.

## Appendix

Suppose the reactions in series are as follows



Thus

$$-\frac{dC_A}{d\tau} = k_1 C_A^2$$

$$C_A = \frac{C_{A_0}}{C_{A_0} k_1 \tau + 1}$$

$$\frac{dC_B}{d\tau} = \frac{k_1 C_{A_0}^2}{(C_{A_0} k_1 \tau + 1)^2} - k_{23} C_B$$

$$\begin{aligned} C_B &= \exp(-k_{23}\tau) \int \frac{k_1 C_{A_0}^2}{(C_{A_0} k_1 \tau + 1)^2} \exp(k_{23}\tau) d\tau + C \\ &= \exp(-k_{23}\tau) \left[ k_{23} C_{A_0} \int \frac{\exp(k_{23}\tau)}{C_{A_0} k_1 \tau + 1} d\tau - \frac{C_{A_0} \exp(k_{23}\tau)}{C_{A_0} k_1 \tau + 1} \right] + C \\ &= C \exp(-k_{23}\tau) + \frac{k_{23}}{k_1} \exp \left[ -\frac{k_{23}}{C_{A_0} k_1} (C_{A_0} k_1 \tau + 1) \right] \\ &\quad \times \left\{ \ln(C_{A_0} k_1 \tau + 1) + \sum_{n=1}^{\infty} \frac{k_{23}^n (C_{A_0} k_1 \tau + 1)^n}{(C_{A_0} k_1)^n n \cdot n!} \right\} - \frac{C_{A_0}}{C_{A_0} k_1 \tau + 1} \end{aligned}$$

when  $\tau = 0$ ,  $C_B = 0$ , then

$$C = C_{A_0} - \frac{k_{23}}{k_1} \exp \left( -\frac{k_{23}}{C_{A_0} k_1} \right) \sum_{n=1}^{\infty} \left( \frac{k_{23}}{C_{A_0} k_1} \right)^n \cdot \frac{1}{n \cdot n!}$$

Finally,

$$C_B = \frac{k_{23}}{k_1 \exp \left[ \frac{k_{23}}{C_{A_0} k_1} (C_{A_0} k_1 \tau + 1) \right]} \left\{ \ln(C_{A_0} k_1 \tau + 1) + \sum_{n=1}^{\infty} \frac{\left[ \frac{k_{23}}{C_{A_0} k_1} \right]^n (C_{A_0} k_1 \tau + 1)^n}{n \cdot n!} \right\}$$

$$+ \exp(-k_{23}\tau) \times \left\{ C_A - \frac{k_{23}}{k_1} \exp\left(-\frac{k_{23}}{C_A k_1}\right) \sum_{n=1}^{\infty} \left(\frac{k_{23}}{C_A k_1}\right)^n \frac{1}{n \cdot n!} \right\} - \frac{C_A}{C_A k_1 \tau + 1}$$

## References

- [ 1 ] R. J. Pomfret and P. Gieveson : *Ironmaking Steelmaking* , 5 (1987) , 191
- [ 2 ] A. A. Plashevsky and V. N. Mehaelitsu : *Izv , V. U. Z. Chernaya. Metall.* , 10 (1984) , 16
- [ 3 ] N. Shinozaki , K. Ishido , K. Mori and Y. Kawai : *Tetsu-to-Hagané* , 70 (1984) , No. 1 , 73
- [ 4 ] H. Suito and R. Inoue : *Tetsu-to-Hagané* , 70 (1984) , No. 7 , 672
- [ 5 ] E. T. Turkdogan and J. Pearson : *J. Iron Steel Inst.* , 173 (1953) , 217
- [ 6 ] Han Qiyong : *The Kinetics of Metallurgical Processes* , The Publishing House of Metallurgy Industry , Beijing , China , (1983) , 24
- [ 7 ] Chen Jiaxiang : *Handbook of Frequently Used Diagrams and Data for Steelmaking* , The Publishing House of Metallurgy Industry , Beijing , China , (1984) , 412
- [ 8 ] Qu Ying : *The principle of steelmaking* , The Publishing House of Metallurgy Industry , Beijing , China , (1980) , 72
- [ 9 ] Fang Yangyi , Jiang Guochang , Gu Hongtao and Xu Kuangdi : *Shanghai Metals* , 3 (1986) , 47
- [ 10 ] C. Wagner : *The Physical Chemistry of Steelmaking* , ed. by J. F. Elliot , Chapman & Hall. , London , (1958) , 237
- [ 11 ] A. Shinotake , N. Tokumitsu and Y. Hayashi : *Tetsu-to-Hagané* , 73 (1987) , S121
- [ 12 ] R. J. Pomfret : *Proc. of the Centenary Conf. to Celebrate the Establishment of The University of Sheffield's Dept. of Metallurgy in 1984* ; 16-18 , July 1984 , London , The Metal Society , 61
- [ 13 ] M. Fujita , H. Katayama , H. Ishikawa and H. Kajioka : *Tetsu-to-Hagané* , 74 (1988) , No. 5 , 801
- [ 14 ] T. Fuwa : *Bull. Jpn. Inst. Met.* , 26 (1987) , No. 5 , 365
- [ 15 ] A. Sato , G. Aragane , K. Kamihira and S. Yoshimatsu : *Tetsu-to-Hagané* , 73 (1987) , No. 7 , 812

# C-Fe-X (X = Mn, Si, Cr, Ni) 熔体中组元活度的解析<sup>\* 1</sup>

**摘要** 将过剩自由能表达为组元的多项式函数. 以该体系液相区边界条件为基础. 用拟合法确定碳偏 mole 自由能表达式中的参数. 然后, 用“I-D”法给出组元 X 的活度系数. 此法可以确定各 C-Fe-X 系整个液相区中任一组元的活度. 解析结果与文献上的试验结果吻合得很好.

## 符号说明

$X_1, X_2, X_3$ ——C-Fe-Si 系中 C, Fe, Si 的 mole 分数  
 $f_1$ ——C 的偏 mole 自由能  
 $f_1 = f_C - K$   
Y, Z——自变量变换:  $X_1 = 1 - Y$ ,  $X_3 = YZ$   
f——体系总的过剩自由能  
K——C 的活度标准态转换系数

氧化物碳热还原过程的实质是元素之间的竞争氧化反应. 在发展熔融还原技术时, 一个重要的理论预测工作就是计算该竞争氧化的转化温度. 为此, 必须有组元活度的系统数据. 但因为工作量浩大, 费时费力, 还因为涉及多元高合金的试验本身误差较大, 单靠测试很难建立此种数据库. 又由于常用的“相互作用参数”只是针对稀溶液发展起来的, 所以建立上述的数据库只能依赖类似于 Pelton 等和王之昌用于 Cd-Bi-Sn, Cd-Bi-Pb 系的方法, 而用若干点的实测作为校核.

\* 本文合作者: 蒋国昌、张晓兵. 原发表于《金属学报》28(6), B240 ~ B246(1992)

# 1 基本公式及结果——以 1 873 K 下的 C-Fe-Si 系为例

## 1.1 $\alpha_C$ 的公式

按 Pelton 等<sup>[1]</sup>和王之昌<sup>[2]</sup>, 并令  $j' = k' = 5, j' + k' \leq 8$ , 则有

$$f_1 = \sum_2^5 \sum_0^3 A_{jk} Y^j Z^k + \sum_2^4 A_{j4} Y^j Z^4 + \sum_2^3 A_{j5} Y^j Z^5 \quad (1)$$

$$f = F_{10} Y + F_{11} YZ + \sum_2^5 \sum_0^3 F_{jk} Y^j Z^k + \sum_2^4 F_{j4} Y^j Z^4 + \sum_2^3 A_{j5} Y^j Z^5 \quad (2)$$

其中,  $A_{jk}$  和  $F_{jk}$  都是参数, 需由精选的边界条件拟合定值. 以下是这些参数定值的方法及过程.

在 C-Fe 系 ( $Z = 0$  或 12 系) 中有<sup>[3]</sup>

$$f_1(Y, 0) = f_{C(12)} - K = \sum_0^5 A_j Y^j \quad (3)$$

由此式及精选的  $f_{C(12)}$ <sup>[4]</sup>, 用最小二乘拟合法本文作者直接确定了  $K$  及  $A_{20}$ 、 $A_{30}$ 、 $A_{40}$ 、 $A_{50}$  之值. 在 1 873 K 下  $K = 44\ 654.730\ 5$ .

在 C-Fe-Si 三元系中, 有<sup>[2]</sup>

$$Q^{(123)} = f_{C(123)} - K - \sum_2^5 A_{j0} + Y^2 \sum_2^5 F_{k(23)} Z^k \quad (4)$$

Fe-Si 系即 23 系, 亦即  $Y = 1$  系, 有<sup>[1]</sup>

$$f(1, Z) = \sum_1^5 F_{k(23)} Z^k \quad (5)$$

由式(5)及精选的  $f(1, Z)$ <sup>[5]</sup> 拟合确定  $F_{2(23)} \sim F_{5(23)}$ . 再由 C-Fe-Si 系中 C 的饱和线<sup>[6]</sup>及  $X_3 \leq 0.20$  域内  $\alpha_C = 0.025$  的等活度线<sup>[7]</sup> 算出  $f_{C(123)}$ , 这样由式(4) 即可得到若干个  $Q^{(123)}$  之值, 又利用下式<sup>[2]</sup>:

$$Q^{(123)} = \sum_2^5 A_{j1} Y^j Z + \sum_2^5 A_{3k} Z^k \left( Y^3 - \frac{1}{2} Y^2 \right) + \sum_2^4 A_{4k} Z^k \left( Y^4 - \frac{1}{3} Y^2 \right) + \sum_2^3 A_{5k} Z^k \left( Y^5 - \frac{1}{4} Y^2 \right) \quad (6)$$

拟合得： $A_{21} \sim A_{51}$ ， $A_{32} \sim A_{35}$ ， $A_{42} \sim A_{44}$ 和  $A_{52}$ 、 $A_{53}$  共 13 个参数。因为  $k \geq 2$  时有<sup>[2]</sup>

$$F_{k(23)} = - A_{2k} - \sum_3^5 \frac{1}{j-1} A_{jk} \quad (k \geq 2) \quad (7)$$

$A_{22} \sim A_{15}$  四个参数由此确定，拟合得到的全部 21 个  $A_{jk}$  参数见表 1。于是

$$\alpha_c = (1 - Y) \exp\left(\frac{k + f_1^{jk}}{RT}\right) \quad (8)$$

表 1 C-Fe-Si 系 1 873 K 下  $A_{jk}$  参数  
Table 1  $A_{jk}$  Parameters for C-Fe-Si under 1 873 K

j	k					
	0	1	2	3	4	5
2	- 116 427.3	3 199 422	2 534 759	- 6 199 956	6. 541 006 E +07	1. 865 051 E +07
3	19 311.33	- 8 913 055	- 7 687 770	- 2. 343 218 E +07	- 2. 987 73 E +08	- 3. 732 128 E +07
4	106 608.7	8 657 854	- 1 817 260	1. 431 189 E +08	2. 520 774 E +08	0.000 000
5	- 56 220.31	- 2 917 971	7 621 668	- 1. 193 688 E +08	0.000 000	0.000 000

## 1.2 $f_{Fe}$ 和 $f_{Si}$ 的公式——“I-D”法

将经典的先积分后微分方法变换成多项式，即可用电脑计算  $f_{Fe}$  和  $f_{Si}$ ，这就是“I-D”法。

定义  $G = f/Y$ ，所以

$$G = f_{Fe} + Z(f_{Si} - f_{Fe}) - f_c(1 - Y^1) \quad (9)$$

取偏微分，得

$$f_{Fe} = G - Z\left(\frac{\partial G}{\partial Z}\right) - (Y^1 - 1)f_c \quad (10)$$

$$f_{Si} = f_{Fe} + \frac{\partial G}{\partial Z} \quad (11)$$

另一方面,又有

$$G = G_{(Y=1)} - \int_1^Y Y^2 f_c dY \quad (12)$$

由式(1)及(9)得

$$\begin{aligned} G &= f_{Fe_{(Y=1)}} + Z(f_{Si} - f_{Fe})_{(Y=1)} - K(1 - Y^1) \\ &+ \sum_2^5 \sum_0^3 \frac{1}{j-1} A_{jk} Z^k (1 - Y^{j-1}) \\ &+ \sum_2^4 \frac{1}{j-1} A_{j4} Z^4 (1 - Y^{j-1}) \\ &+ \sum_2^3 \frac{1}{j-1} A_{j5} Z^5 (1 - Y^{j-1}) \end{aligned} \quad (13)$$

用此式取 $\frac{\partial G}{\partial Z}$  并和式(10),(11)联立,最后导出

$$\begin{aligned} f_{Fe} &= f_{Fe_{(Y=1)}} + (1 - Y^1)f_1 + \sum_2^5 \sum_0^3 \frac{1}{j-1} A_{jk} (1 - k) Z^k (1 - Y^{j-1}) \\ &- \sum_2^4 \frac{3}{j-1} A_{jk} Z^4 (1 - Y^{j-1}) - \sum_2^3 \frac{4}{j-1} A_{j5} Z^5 (1 - Y^{j-1}) \end{aligned} \quad (14)$$

$$\begin{aligned} f_{Si} &= f_{Si_{(Y=1)}} + (1 - Y^1)f_1 + \sum_2^5 \sum_0^3 \frac{1}{j-1} A_{jk} Z^k (1 - Y^{j-1}) \\ &+ \sum_2^4 \frac{1}{j-1} A_{j4} Z^4 (1 - Y^{j-1}) + \sum_2^3 \frac{1}{j-1} A_{j5} Z^5 (1 - Y^{j-1}) \\ &+ \sum_2^5 \sum_0^3 \frac{k}{j-1} (1 - Z) A_{jk} Z^{k-1} (1 - Y^{j-1}) \\ &+ \sum_2^4 (1 - Z) \frac{4}{j-1} A_{j4} Z^3 (1 - Y^{j-1}) \\ &+ \sum_2^3 (1 - Z) \frac{5}{j-1} A_{j5} Z^4 (1 - Y^{j-1}) \end{aligned} \quad (15)$$

$f_{\text{Si}(\gamma+1)}$  取 Kubaschewski 给出之值<sup>[5]</sup> 最后

$$\alpha_{\text{Si}} = YZ \exp \frac{f_{\text{Si}}}{RT} \quad (16)$$

### 1.3 C-Fe-Si 系的计算结果

1873 K 下 C-Fe-Si 系整个液相区内的等  $\alpha_{\text{C}}$   $\alpha_{\text{Si}}$  线示于图 1, 图 2 是一例, 表明此结果与文献[8]数据吻合.

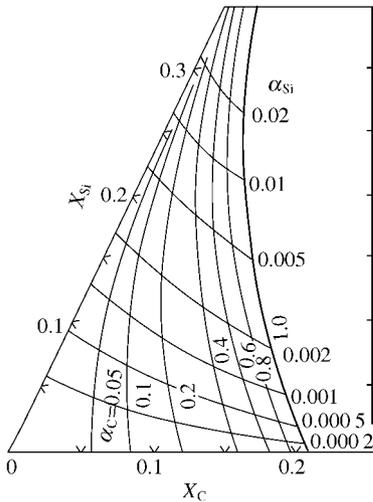


图 1 C-Fe-Si 系 1873 K 下等  $\alpha_{\text{C}}$  和  $\alpha_{\text{Si}}$  线  
Fig. 1 Iso- $\alpha_{\text{C}}$  and  $\alpha_{\text{Si}}$  curves of C-Fe-Si under 1873 K

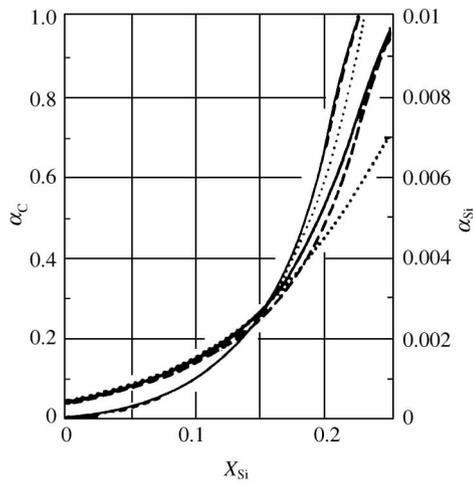


图 2 本文结果与文献比较  
Fig. 2 Comparison about C-Fe-Si ( $X_{\text{C}} = 0.05$ ) under 1873 K

This study  $\alpha_{\text{C}}$  ———,  $\alpha_{\text{Si}}$  ———  
Ref. [8] - - - - -  
Ref. [7] ..... ..

## 2 1873 K 下 C-Fe-Mn 和 C-Fe-Cr 系液相区中的组元活度

上述方法用之于 C-Fe-Mn 和 C-Fe-Cr 两系的等活度线. 仅若干符号及边界条件需作相应的改变<sup>[5-7,9,10]</sup>, 而结果和文献吻合. 这两个三元系的  $A_{jk}$  系数分别列于表 2、表 3.  $f_{\text{C}}$ ,  $f_{\text{Fe}}$ ,  $f_{\text{X}}$  的计算式与 C-Fe-Si 系的类似.

表 2 C-Fe-Mn 系 1873 K 下  $A_{jk}$  参数

Table 2  $A_{jk}$  Parameters for C-Fe-Mn under 1 873 K

j	k					
	0	1	2	3	4	5
2	- 116 427.3	343 123.8	681 719.3	- 293 934.8	191 799.2	- 58 506.10
3	19 311.33	- 75 072.0	- 4 492 809	1 289 622	- 626 198.3	+ 116 806.3
4	106 608.7	- 1 225 317	7 347 861	- 1 174 718	364 597.2	0.000 000
5	- 56 220.31	958 957.6	- 3 533 950	162 036	0.000 000	0.000 000

表3 C-Fe-Cr系 1 873 K下  $A_{jk}$  参数  
Table 3  $A_{jk}$  Parameters for C-Fe-Cr under 1 873 K

j	k					
	0	1	2	3	4	5
2	- 116 427.3	- 36 834.45	54 165.6	- 59 723.01	19 013.37	- 76 774.93
3	19 311.33	18 826.26	- 213 305	171 583.9	157 823.2	146 298.9
4	106 608.7	25 080.29	233 149	- 245 962.5	- 264 286.1	0.000 000
5	- 56 220.31	- 26 375.2	- 80 139.28	181 128.1	0.000 000	0.000 000

### 3 讨论

(1) Palton 等<sup>[1]</sup>及王之昌<sup>[2]</sup>的方法只适用于 C-Fe-Mn 系<sup>[12]</sup>. 用于其他体系时尽管等  $\alpha_c$  线吻合很好, 等  $\alpha_x$  ( $X = \text{Si} \cdot \text{Cr} \cdot \text{Ni}$ ) 偏差显著. 而“ I-D ”法本质上是经典方法, 用之于等  $\alpha_x$  线吻合很好.

(2) 本法适用性很广, 它还可给出不同温度下的等活度线(只要有相应的边界条件). 如利用 C-Fe-Ni 系在 1 873 K 下的边界条件<sup>[4, 5, 7, 13]</sup>, 所得 21 个  $A_{jk}$  参数列于表 4. 其结果也和 Dresler 的吻合.

迄今仍有不少研究者用传统的一阶和二阶相互作用参数方法作出等活度线, 但因多元高合金系的复杂性, 处理不同体系时所需的原始数据和所用的公式会有所不同. 例如, 对 C-Fe-Mn 系, 需要有中等含碳量范围里的数据<sup>[11]</sup>. 而对 C-Fe-Si, Dresler 认为  $\ln a_{\text{Si}}$  必须用下式表示<sup>[8]</sup>:

表4 C-Fe-Ni系 1 823 K下  $A_{jk}$  参数  
Table 4  $A_{jk}$  Parameters for C-Fe-Ni under 1 823 K

j	k					
	0	1	2	3	4	5
2	- 117 516. 5	264 255. 8	120 913. 2	- 78 978. 9	63 716. 63	- 16 010. 22
3	20 960. 51	- 780 249. 1	- 744 449	346 860. 5	- 169 624. 8	36 937. 11
4	106 910. 2	809 197. 5	1 227 123	- 487 757. 4	42 447. 28	0. 000 000
5	- 56 964. 08	- 277 700	- 637 322. 8	290 710. 3	0. 000 000	0. 000 000

$K = 44\ 735. 568\ 7$

$$\ln\alpha_{\text{Si}} = A + BX_{\text{Si}} + CX_{\text{C}} + DX_{\text{Si}}^2 + EX_{\text{C}}^2 + F\ln X_{\text{Si}} + G\ln X_{\text{C}}$$

A~G均是给定的参数. 本法避免了这些弊病. 不再是一种经验性方法. 事实上, 此法不仅能推广到 C-Fe-Si-Mn 和 C-Fe-Cr-Ni 四元系, 并且可望用于归纳炉渣组元活度的试验数据.

(3) 本法保持了 Pelton 等<sup>[1]</sup>及王之昌<sup>[2]</sup>的方法的优点, 即, 既利用了二元系边界条件, 又利用了三元系边界的条件, 而且前者对结果的作用更大(因为 j, k 之值愈小, 该项的值愈大). 另外, 反映  $A_{jk}$  参数(实际上相当于 2~8 阶相互作用参数)和边界条件之间关系的式(1)~(7)符合热力学基本原理. 这使本法给出结果的准确性具有坚实的基础.

## 4 结论

本文报道了一个可靠的、广泛适应的方法. 用之可以给出 C-Fe-X (X = Si, Mn, Cr, Ni) 系整个液相区中的等活度线, 所需的只是该液相区的边界条件.

本文作者在此向王之昌和 W. Dresler 表示深切谢意, 王之昌教授推荐了他的方法, 在此基础上才发展成本文. 而本文所用的若干边界条件是 W. Dresler 教授提供的.

## 参 考 文 献

[ 1 ] Pelton A D, Flengas S N. *Can J Chem*, 1969 ;47 : 2283-2293

- [ 2 ] 王之昌. 中国科学(A), 1986 ;(8) :862-873
- [ 3 ] 王之昌. 私人通讯
- [ 4 ] Hultgren R *et al.* *Selected Values of Thermodynamic Properties of Metals and Alloys.* New York : Wiley. 1973 :485
- [ 5 ] Kubaschewsk O *et al.* , *Metallurgical Thermochemistry. 5th ed.* , Oxford : Pergamon , 1979
- [ 6 ] Elliott J F , Gleiser M , Ramakrishna V. *Thermochemistry for Steelmaking. Vol. II : Thermodynamic and Transport Properties* , London : Addison-Wesley , 1963
- [ 7 ] Darken L S. *Trans Metall Soc AIME* , 1967 ;239 :90-96
- [ 8 ] Dresler W. *ISM* , 1990 :95-99
- [ 9 ] Griffing N R , Forgeng W D , Healy G W. *Trans Metall Soc AIME* , 1962 ;224 :148-158
- [ 10 ] Dresler W. *Electr Furnace Conf Proc* , 1989 ;47 :49-55
- [ 11 ] Dresler W. *Can Metall Q* , 1989 ;28 :109-115
- [ 12 ] 张晓兵. 上海工业大学学报 , 1990 ;11 :490-496
- [ 13 ] Turkdogan E T. *Iron Steel Inst Jpn* , 1956 ;5 :69-72

## Evaluation of Component Activity in C-Fe-X(X = Si , Mn , Cr , Ni)Melts

**Abstract** The parameters in the polynomial expression of partial mole free energy of C were evaluated by value fitting method on the basis of boundary conditions of liquid domain on the system C-Fe-X(X = Si , Mn , Cr , Ni). Then the activity coefficient of the element X may be calculated with the I-D method. The approach suggested is proved to be useful for the activity evaluation of every element in the whole liquid domain of the concerned 4 C-Fe-X ternary systems. The results are found in a good agreement with those of cited previous literatures.

# 碳饱和铁液还原渣中 MnO 的动力学<sup>\* 1</sup>

**摘要** 本文是一个涉及高 [% Mn] 和高 (% MnO) 条件的氧化锰熔融还原动力学的研究. 试验发现, 碳饱和铁液还原渣中 MnO 的过程的限速环节是界面反应. X-TV 冶金现象动态显示仪表明, 反应产物 CO 气泡几乎全在渣金界面上萌芽和长大, 表面活性物质 [% S] 的变化对还原速率有明显影响. 若渣中无碳, 在 (% FeO) 曲线上出现驼峰, 且过程的表现反应级数为 2, 若渣中加碳, 则过程为表观一级. 以串联反应的三步还原模式为基础, 本文对上述现象和规律作了统一的解释.

## 1 引言

用熔融还原法生产高碳锰铁已得到冶金界的重视. 作为钢铁冶炼的基本反应之一, 锰的氧化还原规律已有许多报道, 但这些资料主要局限于低 [% Mn] 及低 (% MnO) 的领域里, 不能适用于熔融还原, 本文介绍高 [% Mn] 和高 (% MnO) 条件下的融态还原动力学研究结果.

## 2 试验装置及方法

部分试验在一个电阻炉中进行, 整个系统示于图 1. 金属料用化学纯的还原铁粉(或电解铜)和电解锰按预定的 Mn/Fe 比配成. 将装有金属的石墨坩埚置于炉内, 并通 Ar(1 L/min) 后开始升温. 达到给定的温度(自控精度  $\pm 5$ ) 且再稳定片刻之后, 将渣料布在金属熔池面上. 渣料系用

\* 本文合作者: 蒋国昌、丁伟中、顾利平、郭曙强、赵柏雄. 原发表于《中国-瑞典冶金科技合作第三阶段共同研究文集》, 沈阳, 1992: 298 ~ 304

化学纯试剂配成,事先经过预熔处理.表1所示是其化学组成.若干试验的渣料内还加有碳粉.渣加入后,按预定的时间间隔用 $\phi 3$  mm的钼棒沾取渣样.每次取出60~100 mg.经破碎和分离金属微粒后用原子吸收光谱测(% MnO)和(% FeO).

另一部分试验是用中频炉做的.设备概况见图2.待金属熔清,即加入经预熔的渣料.若干试验中渣料内还含有碳粒,为维持[% C]的碳粉是用Ar通过一根石墨喷枪喷入的.试验过程中的温度波动小于 $\pm 25$ .渣样用3 mm的不锈钢棒沾取,化学分析方法同上.试验方案见表2.

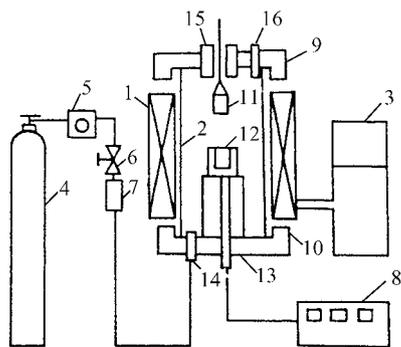


图1 电阻炉试验用的装置系统

- 1—加热元件; 2— $\text{Al}_2\text{O}_3$ 管; 3—控制装置;
- 4—Ar瓶; 5—压力表; 6—阀;
- 7—流量计; 8—毫伏表; 9—水冷盖;
- 10—水冷底座; 11—吊兰(内装渣料);
- 12—石墨坩埚(内装金属液);
- 13—热电偶; 14—Ar进口;
- 15—取样孔; 16—气体出口

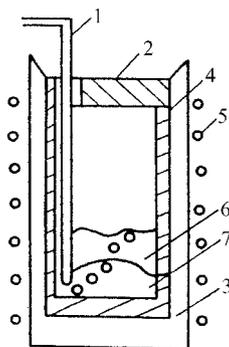


图2 试验用感应炉

- 1—石墨喷枪; 2—石墨盖;
- 3—石墨坩埚; 4—MgO坩埚;
- 5—感应器; 6—渣(350 g);
- 7—金属(1.4 kg)

表1 电阻炉中的试验方案

Run	渣					金属		$t$	
	(% MnO) <sub>i</sub>	(% FeO) <sub>i</sub>	(% MgO) <sub>i</sub>	B	渣量 g	加碳 g	成分		加入量 g
012	52.85	7	$\frac{1}{5}$ (% CaO)	0.9*	20	0	Mn基, [% S] <sub>i</sub> = 0.027	80	1550
022	51.74	7	$\frac{1}{5}$ (% CaO)	0.9*	20	0	Mn基, [% S] <sub>i</sub> = 0.048	80	1550
023	50.67	7	$\frac{1}{5}$ (% CaO)	0.9*	20	0	Mn基, [% S] <sub>i</sub> = 0.079	80	1550
111	40	0	5	1.1	200	0	[% Mn] <sub>i</sub> = 0	600	1550
112	40	0	5	1.1	200	0	[% Mn] <sub>i</sub> = 10	600	1550

(续 表)

Run	渣						金 属		t ,
	(% MnO) <sub>i</sub>	(% FeO) <sub>i</sub>	(% MgO) <sub>i</sub>	B	渣量 g	加碳 g	成 分	加入量 g	
113	40	0	5	1.1	200	0	[% Mn ] <sub>i</sub> = 30	600	1 550
213	42.78	5	6	1.3	20	5	[% Mn ] <sub>i</sub> = 0	80	1 580
214	42.78	5	6	1.3	20	5	[% Mn ] <sub>i</sub> = 30	80	1 580
217	42.78	5	6	1.3	20	5	[% Mn ] <sub>i</sub> = 0	80	1 580

注 :  $B^* = \frac{\text{CaO} + \text{MgO}}{\text{SiO}_2}$  ,  $B = \frac{\text{CaO}}{\text{SiO}_2}$ .

表 2 感应炉中的试验方案

Run	金 属		渣			t ,
	base	[% Mn ] <sub>i</sub>	(% MnO) <sub>i</sub>	B	C-add , g	
301	Fe	0	42.78	1.3	80	1 620
311	Fe	0	42.78	1.3	0	1 620

### 3 反应机理

#### 3.1 三步还原模式

试验发现,只要初渣缺铁,就可看到在反应初期(% FeO)会伴随(% MnO)的下降而升高,且呈现出一个驼峰,见图3.而[% Mn]愈高,则此峰愈低且(MnO)的还原也愈慢.在不同的条件下,已有一些作者<sup>[1~3]</sup>曾报道过此现象.如 Pomfret 等在 CO 气氛下研究了气压变化时(FeO)的行为,而 Пльшевский 等<sup>[2]</sup>研究了温度和(% MnO)初值改变的作用,他们的结果和 Run 111 的(% FeO)峰值特别接近.

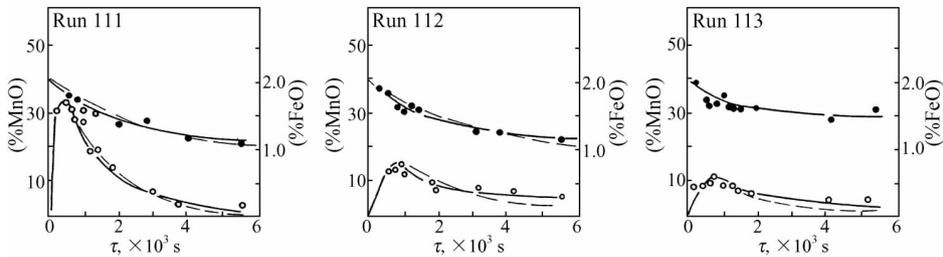
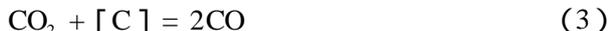


图 3 初渣无碳缺铁时,(FeO)的行为及(MnO)的还原

——动力学模型计算结果; ○—(% FeO)实测值; ●—(% MnO)实测值

图3表明,本试验条件下,(MnO)的还原也是由三个子反应串联而成的,即三步还原模式



这里,反应(1)是铁锰交换反应,其平衡常数为

$$\lg K_{Mn} = -\frac{6440}{T} + 2.95 \quad (4)$$

因此,1550℃下此反应平衡时有

$$N_{FeO} = 0.26 \frac{\gamma_{MnO}}{\gamma_{FeO}} \cdot N_{MnO} \cdot \frac{\alpha_{Fe}}{\alpha_{Mn}} \quad (5)$$

用此式计算和图3所示曲线相应的 $N_{FeO}$ 平衡值,得表3.将其和图3上的 $(\% FeO)_{max}$ 比较,可见反应(1)在热力学上是可能发生的.

表3 反应(1)的热力学可能性

Run	计算用参数					$N_{FeO}^*$ 平衡计算	$(\% FeO)^*$ 实测
	$(\% MnO)^*$	$[ \% Mn ]^*$	$\alpha_{Fe} / \alpha_{Mn}$	$^{[4]} \gamma_{MnO}$	$^{[5]} \gamma_{FeO}$		
112	33.7	11.6	7.62	1.0	2.0	0.34	0.77
113	33.5	31.8	2.13	1.0	2.0	0.094	0.53

注:1. “\*”表示 $\frac{d}{dt}(\% FeO) = 0$ 的时刻;

2. 设 $\alpha_{Fe} / \alpha_{Mn} = \frac{[ \% Fe ]^*}{[ \% Mn ]^*}$ ;

3. 根据 $(\% MnO)_i - (\% MnO)^*$ ,按物料平衡算出 $[ \% Mn ]^*$ ;

4.  $\gamma_{FeO}$ 及 $\gamma_{MnO}$ 均按 $B = 1.1$ 取值.

### 3.2 限速环节

反应按三步原模式进行时,总括速率为何者所限?为探讨这个问题而设计了一个金属含硫量不同的试验,其意在利用 $[S]$ 的表面活性作用作为判据.图4指出, $[S]$ 增加则还原速率减慢.因此(MnO)的扩散不可能是限速环节,是界面反应决

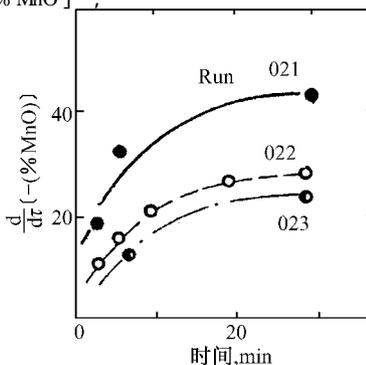
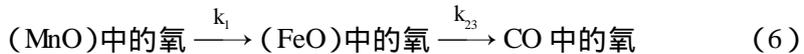


图4 表面活性剂 $[S]$ 对还原的影响

定了过程的总括速率。

界面反应是否为限速环节历来是用改变反应面积作为判据。利用表面活性剂浓度的变化也可导致反应面积的增减。而且和改变坩埚直径的试验方法比较,此法不会引起金属液深和渣层厚度的变化。

图4已指出界面反应是限速环节。但反应(1)~(3)均是界面反应。这可用串联反应的基本规律来作进一步的分析。忽略逆反应,三步还原模式可简化为如下形式:



$k_1$  与  $k_{23}$  均是表现速率常数。因此根据图3上(%FeO)曲线的形状,可以认为  $k_1 < k_{23}$ , 即反应(1)的速率最慢<sup>[6]</sup>。

### 3.3 反应级数

通过研究反应级数来揭示反应机理是众所周知的一种方法。采用微分法处理试验数据得到图5和图6,发现表观反应级数随渣中碳量而变化。渣中不加碳时,电阻炉试验和感应炉试验均得到表观二级反应的结果。而渣中加碳时反应初期呈表观一级特征。随着反应的进行,渣中碳量逐渐消耗,反应又变成表观二级的了。曲线呈现不同的折点是加碳量与碳的氧化速度不同之故。可见,渣中含碳时的反应机理有别于渣中无碳或少碳时的反应机理。

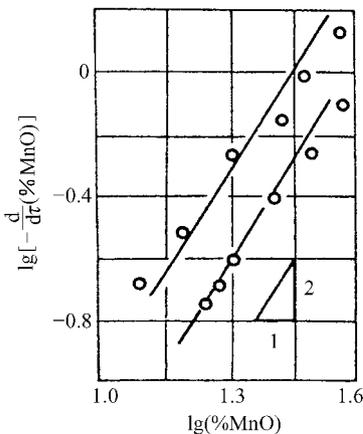


图5 渣中无碳时的表观反应级数

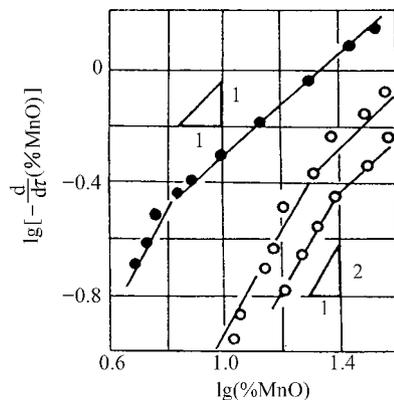


图6 渣中加碳时的表观反应级数

在渣中无碳的条件,反应(1)是否可能也呈现表观二级特征?若是,则

从另一角度证明它限制了总括过程的速率.

作为一个界面反应,若它是不可逆的,其反应速率应为

$$r = k(1 - \theta)(\% \text{MnO}) \quad (7)$$

这里的  $\theta$  是表面活性剂 Se 在渣金界面上的覆盖率,本试验所用电解锰含 Se 约 0.056%, Se 的表面活性作用更甚于  $S^{[7]}$ . 而  $[\% S] = 0.02\%$  时已可使钢液表面单分子层呈 FeS 型结构<sup>[8]</sup>. 所以本试验中  $[Se]$  对反应是有影响的. 另一方面,反应生成物 CO 逸出量的变化会改变  $\theta$  值,并且搅动愈强  $\theta$  愈小<sup>[9]</sup>. 即 CO 逸出量的变化会导致反应(1)呈现表观二级特征. C. Wagner 曾用这种方法讨论过冶金反应的表现级数<sup>[10]</sup>.

### 3.4 模型计算

本试验中的( $\% \text{FeO}$ )很低,筱竹昭彦等认为这种条件下反应(2)与(3)的总括过程是一级的<sup>[11]</sup>,而如上述,反应(1)为二级. 因此,和式(6)相应的动力学基本公式可推导如下:

$$- \frac{d}{d\tau}(\% \text{MnO}) = k(\% \text{MnO})^2 \quad (8)$$

$$\frac{d}{d\tau}(\% \text{FeO}) = k_1(\% \text{MnO})^2 - k_{23}(\% \text{FeO}) \quad (9)$$

求积分得

$$\begin{aligned} (\% \text{FeO}) = & \frac{k_{23}}{k_1} \left( \ln C + \sum_{n=1}^{\infty} \frac{Q^n}{n \cdot n!} \right) \exp(-Q) - \frac{(\% \text{MnO})_i}{C} \\ & + \left[ (\% \text{MnO})_i - \frac{k_{23}}{k_1} \sum_{n=1}^{\infty} \frac{Q^n}{n \cdot n!} C^n \exp(-Q) \right] \exp(-k_{23}\tau) \end{aligned} \quad (10)$$

$$Q = \frac{k_{23}C}{(\% \text{MnO})_i k_1} \quad (11)$$

$$C = 1 + (\% \text{MnO})_i k_1 \tau \quad (12)$$

将此动力学模型用于图 3 所示的两个试验. 首先,利用起始条件由式(8)计算  $k_1$ , 再利用  $\frac{d}{d\tau}(\% \text{FeO}) = 0$  的条件,由式(9)算出  $k_{23}$ . 计算结果见表 4. 然后就可算出 ( $\% \text{MnO}$ ) 与 ( $\% \text{FeO}$ ) 的变化规律. 图 3 所示的虚线即用

此动力学模型计算的结果. 计算和实测吻合, 特别是由式(8)积分所描述的 (% MnO) 变化规律与实测一致, 证明渣中无碳时 (MnO) 的还原确按三步模式进行, 这和 R. J. Pomfret 最近发表的观点<sup>[12]</sup>一致.

表4 三步反应模式中的速率常数

Run	$k_1$	$k_{23}$
112	$5.40 \times 10^{-6} \% s^{-1}$	$7.96 \times 10^{-3} \% s^{-1}$
113	$5.13 \times 10^{-6} \% s^{-1}$	$10.86 \times 10^{-3} \% s^{-1}$

#### 4 反应地点的观察

利用 X-TV 冶金现象动态显示仪(图7)观察了(MnO)熔融还原时的反应地点, 在[% Mn] ≤ 60% 的条件下, 发现反应产物 CO 几乎全在渣金界面上萌发和长大, 即使有渣碳界面共存也是如此, 见图8. 这和藤田正树等的报道<sup>[13]</sup>有别, 但吻合于有关的反应速度常数测定. 例如, 不破祐<sup>[14]</sup>和佐藤彰<sup>[15]</sup>等都指出用[C]还原时的反应速率数显著大于用固态还原时的反应速率常数.

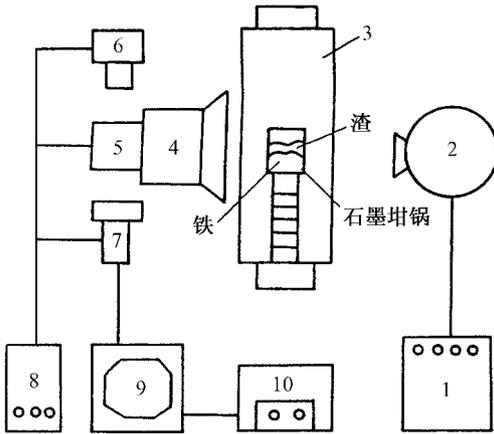


图7 X-TV 冶金现象动态显示仪系统

- 1—X 射线源控制台 ; 2—X 射线源 ;
- 3—MoSi<sub>2</sub> 炉 ; 4—影像增强器 ;
- 5—光学分配器 ; 6—点片照相机 ;
- 7—摄像机 ; 8—X-TV 控制台 ;
- 9—TV ; 10—录像机

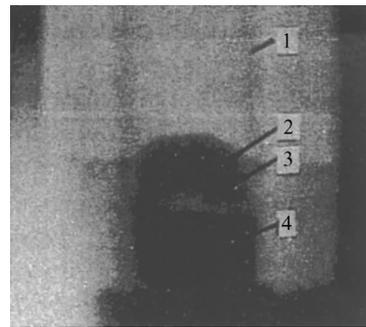


图8 反应产物 CO 的逸出地点

- 1—石墨坩埚 ; 2—渣 ;
- 3—CO 气泡 ; 4—金属

## 5 结束语

(1) 碳饱和铁液还原( $\text{MnO}$ )的过程为界面反应所限速. 这是因为,  $[\% \text{S}]$ 增加, 则界面面积减小, 还原速率相应下降.  $[\% \text{Mn}] \leq 60\%$  条件下, 即使有渣碳界面共存, 用“X-TV 冶金现象动态显示仪”观察到反应产物  $\text{CO}$  仍几乎全在渣金界面上萌芽和长大.

(2) 碳饱和铁液还原( $\text{Mn}$ )的反应机构为还原过程中( $\% \text{FeO}$ )的变化曲线特点所揭示. 它表明该过程按三步反应模式进行. 三个界面反应中,  $\text{Fe}$  与  $\text{Mn}$  的竞争氧化反应速率最慢, 且它是表观二级的, 而渣中无碳时总括反应的表观级数也是 2.

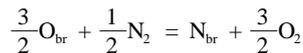
(3) 按  $\text{Fe-Mn}$  竞争氧化反应为表观二级, 导出了串联反应的基本动力学公式, 并成功地用以定量地描述还原过程的推进.

## 参 考 文 献

- [ 1 ] R. J. Pomfret, P. Grievson, *Ironmaking & Steelmaking*, (1978) 5, 191-197
- [ 2 ] A. A. ПльшЕвский, В. Н. Михайлеы Изв ВУЭЧМ, (1984) 10, 16-20
- [ 3 ] 筱崎信也, 石堂善一郎, 森克己, 川合保治 *鐵と鋼*, (1984) 70, 1, 73-80
- [ 4 ] 水渡英昭, 井上亮 *鐵と鋼*, (1984) 70, 7, 672-679
- [ 5 ] E. T. Turkdogen, *J. Pearson Iron and Steel Institute*, (1953) 153, 217-223
- [ 6 ] 韩其勇 *冶金过程动力学*, 冶金工业出版社, (1983) 24
- [ 7 ] 陈家祥 *炼钢常用图表数据手册*, 冶金工业出版社, (1984) 412
- [ 8 ] 曲英 *炼钢学原理*, 冶金工业出版社, (1980) 72-73
- [ 9 ] 樊养颐, 蒋国昌, 顾洪涛, 徐匡迪, *上海金属*, (1986) 3, 47-52.
- [ 10 ] C. Wagner, *The Physical Chemistry of Steelmaking*, by J. F. Elliot, Chapman & Hall Lim, London, (1958) 237-251
- [ 11 ] 筱竹昭彦, 德光直树, 林洋一 *鐵と鋼*, 87-S121
- [ 12 ] R. J. Pomfret, *Proc. of the centenary conf. to celebrate the Establishment of the University of sheffield's Dept of Metallurgy in 1884* 16-18, July 1984, London, *The Metal society* 61-63.
- [ 13 ] 藤田正树, 片山裕之, 石川英毅, 尾岗博幸 *鐵と鋼*, 74 (1988) 5, 801-808
- [ 14 ] 不破祐, *日本金属学会报* 26 (1987) 5, 365-372
- [ 15 ] 佐藤彰, 荒金吾郎, 上平一茂, 吉松右郎 *鐵と鋼*, 73 (1987) 7, 812-819.

# The Equilibrium of Nitrogen between Gas and Slag or Slag and Metal<sup>\* 1</sup>

**Abstract** The thermodynamic behaviour of nitrogen in gas-slag (lime-alumina-silica) system and slag-metal system is studied in this paper. The dissolving reaction of nitrogen from gaseous phase to the molten slag is



br denotes bridging. Based on this, the relationship between nitrogen capacity  $C_{\text{N}_3}$  and slag basicity can be elucidated. The relationships of  $\gamma_{\text{Si}_0.75\text{N}}$  and  $\gamma_{\text{AlN}}$  vs. slag composition in lime-alumina and lime-silica binary systems, and the influence of temperature on them are discussed.

## 1 Introduction

The dissolution of nitrogen in slag is making itself a new research focus in metallurgy. This results from several reasons. First, it is well known from steel-making that slag can prevent nitrogen pickup of molten steel. Surely, this function concerns the dissolvability of nitrogen in slag. Secondly, a new technique idea about using slag in denitrogenation of steel was proposed following the development of nitride ceramics. This undoubtedly brings a lot of profit to the production of ultra pure ferrite stainless steel. Thirdly, nitrogen is an important alloy element in austenitic stainless steel. Perhaps, it will be an economic process that

---

\* In collaboration with Jiang Guochang, Lin Tianying. 4th Int. Con. on Molten Slags and Fluxes, Sendai, Japan, ISIJ, 1992, pp. 221-226

feeding nitrogen through slag. As a fundamental study this paper is devoted to the research of nitrogen behaviour in lime-alumina , lime-silica and lime-alumina-silica systems.

## 2 The experiment method and the results

Fig. 1 shows the equipment used in this investigation. For the equilibrium experiment in gas-slag system graphite crucible was used. 5 g slag material was put inside it. The atmosphere is 0.40 CO-0.60 N<sub>2</sub> which is generally utilized as a standard for the calibration of analytical instruments. The flow rate of this gas was 4 cm<sup>3</sup>/s. The reaction temperature was 1 773 ,1 823 or 1 873 K. A pilot experiment was arranged to determine the time needed for equilibrium experiment. It was performed as adding some Si<sub>3</sub>N<sub>4</sub> into 0.4 CaO-0.4 SiO<sub>2</sub>-0.2 Al<sub>2</sub>O<sub>3</sub> slag for making the intial (% N) to be either lower or higher than the estimated equilibrium value. Fig. 2 indicates the approaching of nitrogen from both sides to each other needs about 14 hrs. Thus ,experiment time was chosen as 18 hrs for gas-slag equilibrium. The results of gas-slag equilibrium experiment is shown in Table 1.

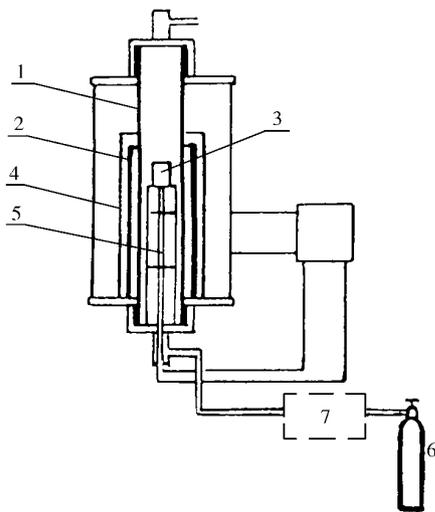


Fig. 1 The experimental set

- |                       |  |
|-----------------------|--|
| 1. alumina tube       | 5. thermocouple  |
| 2. graphite heater    | 6. CO + nitrogen   |
| 3. graphite crucible  | 7. the set for gas de-O <sub>2</sub> , de-H <sub>2</sub> O |
| 4. thermal insulation |  |

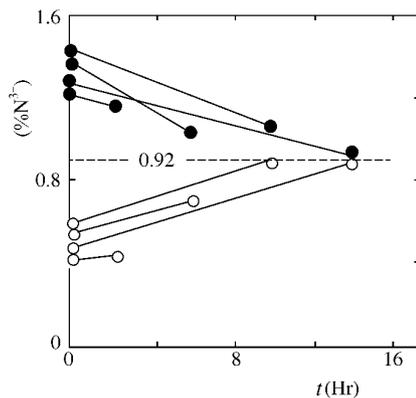


Fig. 2 The variation of (% N<sup>3-</sup>) vs time under 1 823 K and (0.4 CO + 0.6 N<sub>2</sub>)

**Table 1 The results of gas-slag equilibrium experiment**

Temp. (K)	Slag(%)			(% N) exp.	$C_{N^3-} (\times 10^{-13})$
	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>		
1 823	55.0	45.0		0.63	4.78
1 823	40.0	60.0		1.97	14.32
1 823	40.0		60.0	0.28	2.14
1 823	35.0		65.0	0.37	2.78
1 823	40.0	40.0	20.0	0.92	6.92
1 823	50.0	10.0	40.0	0.27	2.04
1 823	30.0	40.0	30.0	1.38	10.47
1 823	45.0	25.0	30.0	0.53	3.98
1 823	55.0	45.0		1.24	9.32
1 873	40.0		60.0	0.56	4.32
1 873	50.0	10.0	40.0	0.60	4.49
1 773	55.0	45.0		0.29	2.17
1 773	40.0		60.0	0.13	0.98

For the equilibrium experiment in slag-metal system alumina crucible was used. There were 5 g slag and 15 g iron. At most, either 0.5% Si<sub>3</sub>N<sub>4</sub> or 0.4% AlN was added in slag before experiment. Iron was killed with Si or Al, and its initial nitrogen content was lower than 0.02%. Ar atmosphere was used in this experiment. The time for this kind of experiment was determined according to Ito<sup>[1]</sup> and Inoue *et al.*<sup>[2]</sup>, as 6 hrs. The results of equilibrium experiment in slag-metal is shown in Table 2.

**Table 2 The results of slag-metal-equilibrium experiment**

Temp. (K)	Slag(%)				Metal(%)			L <sub>N</sub>
	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	N <sup>3-</sup>	Si	Al	N	
1 823	40.0	60.0		0.074	1.58		0.006 2	11.92
1 823	40.0	40.0	20.0	0.073	0.73		0.013	5.60
1 823	40.0	50.0	10.0	0.081	1.51		0.007 4	10.94
1 823	30.0	40.0	30.0	0.061	0.74		0.011	6.03

(cont d)

Temp. (K)	Slag( % )				Metal( % )			$L_N$
	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	N <sup>3-</sup>	Si	Al	N	
1 823	40.0	60.0		0.065	0.90		0.008 5	7.65
1 823	45.0		55.0	0.063		0.018	0.010	6.30
1 823	40.0		60.0	0.065		0.017	0.007	9.29
1 823	55.0		45.0	0.059		0.023	0.016	3.68
1 823	45.0		55.0	0.041		0.012	0.019	2.16
1 823	45.0		55.0	0.082		0.035	0.007 5	10.93
1 873	40.0	50.0	10.0	0.070	1.50		0.007	7.61
1 873	55.0		45.0	0.035		0.18	0.019	1.84
1 773	40.0	50.0	10.0	0.080	1.51		0.005 4	14.81
1 773	55.0		45.0	0.073		0.018	0.011	6.64

Note :  $L_N = (\% N) / \% N$

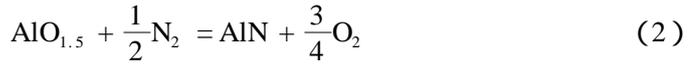
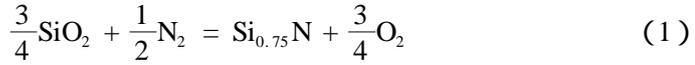
The Kjeldahl method was used in these two experiments for analysing both (% N) and [ % N ]. So this paper does not concern ( % CN<sup>-</sup> ) , but ( % N<sup>3-</sup> ).

### 3 Discussion

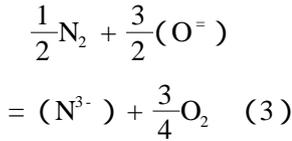
#### 3.1 Gas-slag reaction

Under strong reduction atmosphere , nitrogen can dissolve in slag through a chemical reaction. Referring to this dissolving reaction , however , some contradictory points of view may be found in literatures. Summing up , there are two aspects. One is in what way the partial pressure of nitrogen affects the dissolubility. The other is in what state the nitrogen dissolving in slag behaves. Davies *et al.* [3] and Schwerdtfeger *et al.* [4] reported that the relation of ( % N<sup>3-</sup> ) vs. partial pressure of nitrogen is in equilibrium. As the idea of Ref. 3 , ( % N<sup>3-</sup> ) is in proportion to  $(P_{N_2}/P_{O_2})^{1/2}$  , however , Schwerdtfeger *et al.* claimed it should be in proportion to  $(P_{N_2}/P_{O_2})^{1/2}$ . When the slag is in equilibrium with CO · N atmos-

phere and the partial pressure of nitrogen is high enough, the slag is saturated with  $\text{Si}_3\text{N}_4$  and  $\text{AlN}$ . The chemical stoichiometry indicates that the reactions are



Hence, so far the view point of Schwerdtfeger is the generally accepted one. And it was thought that the dissolving reaction should be



Then the nitrogen capacity was defined as

$$C_{\text{N}^{3-}} = (\% \text{N}^{3-}) \frac{P_{\text{O}_2}^{3/4}}{P_{\text{N}_2}^{1/2}} \quad (4)$$

The  $C_{\text{N}^{3-}}$  listed in Table 1 was evaluated pursuant to Eq. (4). Fig. 3 shows the relation of these  $C_{\text{N}^{3-}}$  values together with the results quoted from literatures [1,3,4,8] vs. slag basicity. It was indicated by Ito and others that this curve is contrary to Eq. (3).

The key problem here is in what state the nitrogen dissolves in slag. Several different opinions were suggested. It is well known, in  $\text{Si}_3\text{N}_4$ ,  $\text{AlN}$  nitride

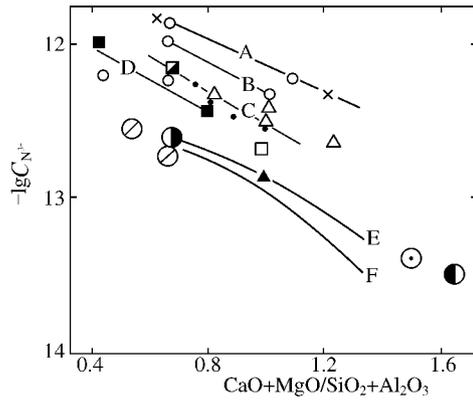
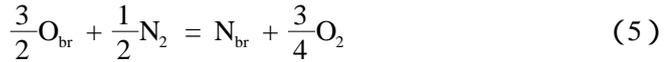


Fig. 3 The relation between  $C_{\text{N}^{3-}}$  and basicity

signal	ref.	experimental condition
○	this work	1 823 K lime-alumina
□	this work	1 823 K lime-silica-alumina (% 40)
■	this work	1 823 K lime-silica-alumina (% 30)
▣	this work	1 823 K lime-silica-alumina (% 20)
×	this work	1 823 K lime-silica
○	[1]	1 823 K lime-silica, lime-silica-alumina
△	[1]	lime-silica-alumina-magnesia
●	[3]	1 823 K lime-silica-alumina (% 20)
▲	[8]	1 873 K lime-alumina
⊙	[1]	1 873 K lime-silica-alumina(sat.)
⊗	[1]	1 873 K lime-silica-magnesia(sat.)
⊖	[1]	1 873 K lime(sat.)-alumina
lineA	sum up	1 823 K lime-silica
B	sum up	1 823 K lime-silica-alumina(% 10)
C	sum up	1 823 K lime-silica-alumina(% 20)
D	sum up	1 823 K lime-silica-alumina(% 30)
E	[4]	1 873 K lime-alumina
F	[8]	1 823 K lime-alumina

ceramics nitroge exists in the cell of Si-N-Si or Al-N-Al ,Furthermore ,a TEM investigation claimed that Si<sub>2</sub>N<sub>2</sub>O was found inside high nitrogen bearing Ca-Si-Al-O-N and Mg-Si-O-N systems<sup>[5]</sup>. This proves that the dissolving nitrogen is existed in Si-N-Si cell in these systems. According to these reports ,the nitrogen dissolving reaction in lime-alumina-silica slag is thought to be as follows



br denotes bridging. Then ,based on the concept of bonding basicity<sup>[6]</sup> the nitrogen capacity should be defined as

$$C_{N^{3-}} = (\% N^{3-}) \frac{P_{O_2}^{3/4}}{P_{N_2}^{1/2}} = \frac{K_{(5)} (B_{O_{br}} Y_{O_{br}})^{3/2}}{\gamma_{N^{3-}}} \quad (6)$$

$B_{O_{br}}$  ,  $Y_{O_{br}}$  is the basicity charateristics and mole fraction of the bridging O<sup>=</sup> anion respectively. As the following Fig. 6 , in lime-alumina binary slags  $\gamma_{N^{3-}}$  is constant. On the other hand , it was proved<sup>[6]</sup> in these slags  $\gamma_{N^{3-}}$  is in proportion with  $(B_{O_{br}} Y_{O_{br}})^{3/2}$ . This is an evidence for the correction of reaction ( 5 ). Mulfinger<sup>[7]</sup> , Shimoo *et al.* <sup>[8]</sup> and Davies *et al.* <sup>[3]</sup> all considered that the dissolving nitrogen is in N<sub>br</sub> state.

### 3.2 The effect of optical basicity and temperature on nitrogen capacity

The effect of optical basicity ( $\Lambda$ ) on  $\gamma_{N^{3-}}$  is shown in Fig. 4. Both the results of this experiment and some literature informations are involved in this relation , and it gives Eq. (7) for 1 823 K.

$$\lg C_{N^{3-}} = - 11.5 \lg \Lambda - 14.28 \quad (7)$$

As the bonding basicity is a revision of optical bsicity , so Eq. (7) coincides with Eq. (6). But it surely gets some differences from that relation supposed by Sommerville.<sup>[9]</sup> The variation of  $C_{N^{3-}}$  against temperature is shown in Fig. 5. And it is deduced as

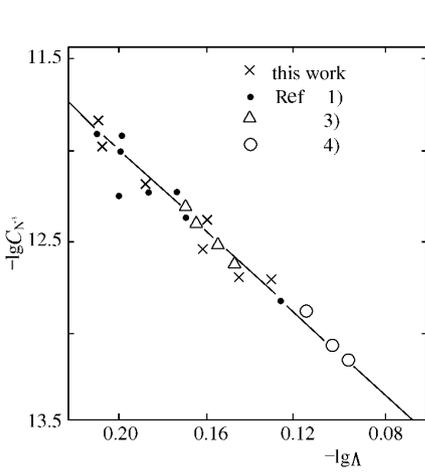


Fig. 4 The relation of  $C_{N^3}$  vs. optical basicity, under 1823 K

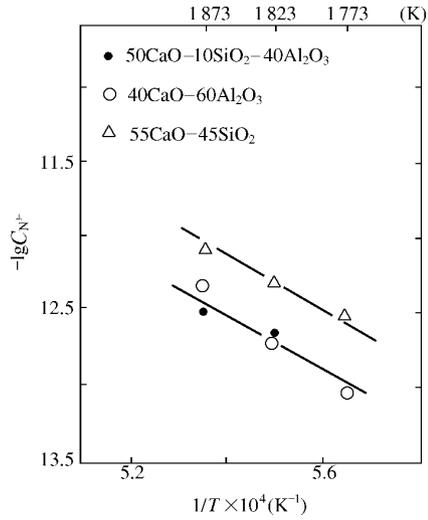
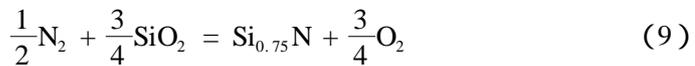


Fig. 5 The effect of temperature on  $C_{N^3}$ .

$$\lg C_{N^3} = -11.51 \lg \Lambda - \frac{22135}{T} - 2.04 \quad (8)$$

### 3.3. The $\gamma_{Si_{0.75}N}$ and $\gamma_{AlN}$ in nitrogen bearing lime-alumina and lime-silica binary slags

The dissolving reaction of nitrogen in lime-silica slag is supposed as



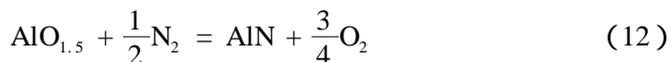
Hence the activity coefficient of this nitride is

$$\gamma_{Si_{0.75}N} = \frac{114MK_{(9)}(\alpha_{SiO_2})^{3/4}}{C_{N^3}} \quad (10)$$

Here  $M$  denotes the sum mole amount of components in 100 g slag.  $K$  is the equilibrium constant.

$$\lg K_{(9)} = -\frac{21926}{T} + 0.737 \quad (11)$$

The dissolving reaction of nitrogen in lime-alumina slag is supposed as



Thus

$$\gamma_{\text{AlN}} = \frac{14MK_{(12)}(\alpha_{\text{AlO}_{1.5}})}{C_{\text{N}^{3-}}} \quad (13)$$

And ,

$$\lg K_{(12)} = - \frac{27\,014}{T} + 2.505 \quad (14)$$

the variation of  $\gamma$  calculated according to equation (10) and (13) vs. slag

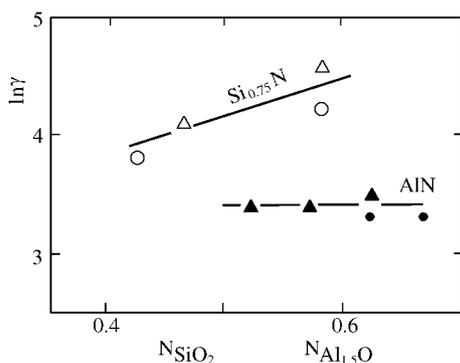
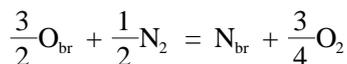


Fig. 6 The relation of nitride activity coefficients vs composition

composition is shown in Fig. 6. The value of  $(\alpha_{\text{SiO}_2})$  and  $(\alpha_{\text{AlO}_{1.5}})$  are quoted from Rein *et al.* [10]. This result is in good agreement with that of Ito *et al.* [1]. The constant  $\gamma_{\text{AlN}}$  in lime-alumina system which might be resulted from the cell structure between  $\text{Al}^{3+}$  cations and  $\text{N}^{3-}$  anions in this slag does not to be changeable. On the contrary, in lime-silica slag, changing %  $\text{SiO}_2$  might possibly cause the formation of double bond between  $\text{Si}^{4+}$  cations and  $\text{N}^{3-}$  anions, and this in turn to vary  $\gamma_{\text{Si}^{0.75}\text{N}}$ .

## 4 Conclusion

The dissolving reaction of nitrogen from gaseous phase to molten slag is the process in which nitrogen replace the bridging oxygen anion.



The corresponding nitrogen capacity should be

$$C_{N^{3-}} = \% N^{3-} \frac{P_{O_2}^{3/4}}{P_{N_2}^{1/2}} = \frac{K_{(9)} (B_{O_{br}} Y_{O_{br}})^{3/2}}{\gamma_{N^{3-}}}$$

Here,  $(B_{O_{br}} Y_{O_{br}})$  is the bonding basicity or an activity index of bridging oxygen anion.

The variation of  $\gamma_{Si_{0.75}N}$  in lime-silica and that of  $\gamma_{AlN}$  in lime-alumina vs. slag composition are in good agreement with that of Ito *et al.* [1]. The reason of these variation is considered as to be possible whether the relevant cell structure is changeable or not.

### Acknowledgement

This paper is supported by the Foundation of National Natural Science of China.

## References

- [ 1 ] K. Ito , R. J. Fruehan : Metall. Trans. 419B (1988) 6 , 419-425
- [ 2 ] R. Inoue , H. Suito : 3rd Intern. Conf. on Molten Slag & Fluxes , Glasgow , U. K. June , 1988 , 77-80
- [ 3 ] M. W. Davies , S. G. Mecherali : Metall. Trans. , 42 (1971) 9 , 2729-1733
- [ 4 ] K. Schwerdtfeger , H. G. Schbert : Metall. Trans. 48B (1977) 12 , 535-540
- [ 5 ] A. Hendry : 3rd Intern. Conf. on Molten Slag & Fluxes , Glasgow , U. K. June , 1988 , 125-129
- [ 6 ] JIANG Guochang , XU Kuangdi : Proceedings of 6th IISC , Nagoya , Japan , Oct. 1990 , Vol. 1 240-247
- [ 7 ] H. O. Mulfinger : J. Am. Ceram. Soc. 449 1 (1966) 9 , 462-467
- [ 8 ] T. Shimoo , H. Kimura , M. Kawai : J. of JIM 436 1 (1972) 8 , 723-727
- [ 9 ] I. D. Sommerville : Proceedings of Intern. Symp. on Foundry Process : Their Chemistry & Physics , Plenum Press , 1988 , 101-122
- [ 10 ] H. Rein , J. Chipman : Trans. AIME 4233 1 (1965) , 415-425

# 渣钢持续接触时脱硫反应的动力学研究<sup>\* 1</sup>

**摘要** 直接由电化学原理导出的电化学模型,以及给出的初始渣钢界面氧位计算方法,可用以定量描述% S ~  $\tau$  曲线. 计算与实测吻合. 脱硫过程中渣钢界面上硫的分配常数  $L_s^*$  和渣钢本体内硫的分配指数  $L_s'$  随界面氧位的下降而不断变化,其规律截然不同.  $L_s^* \sim \tau$  曲线属抛物线类型,而  $L_s' \sim \tau$  曲线属双曲线类型. 与此相应,计算及实测都指出,驱动力参数随时间而变化的曲线呈现一驼峰.

脱硫是炼钢过程的基本反应之一,本文仅就渣钢持续接触条件下的脱硫规律作一探讨.

## 1 限速环节与界面氧位

一般脱硫速度与钢水中含硫量的关系如图1所示<sup>[1]</sup>.

历来都用式(1)来表述脱硫反应的表观速度特征.

$$-\frac{d}{d\tau} \% S = k_1 [ \% S - \% S^* ] \quad (1)$$

此式常被称为经验速率方程. 其中的界面硫量% S\* 是个未定变量,而且所谓速度常数  $k_1$  实

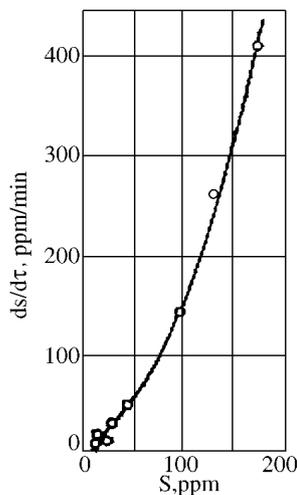


图1 脱硫速度和钢水中含硫量的关系<sup>[1]</sup>

Fig. 1 Desulphurization rate vs % S in melted Steel

\* 本文合作者: 蒋国昌、邓健雄、郭占成、关玉龙. 原发表于《金属学报》26(1), B33 ~ B39(1990)

实际上仅在某一% S 范围里才近似守恒,故难以用式(1)来表述一个% S 变化很大的脱硫过程.仿照 C. Wagner<sup>[2]</sup>的方法,我们改用式(2)来表述.

$$-\frac{d}{d\tau}\% S = k_2 \cdot \% S^m \quad (2)$$

自然,若认为  $k_2$  始终守恒,则  $m > 1$ . 图 1 表明,在% S ≤ 150 ppm 的范围里,渣钢持续接触条件下脱硫的一般规律是,曲线在高% S 段近似于直线,在其低% S 段又接近另一直线,两者之间是一过渡段.这说明,在三个区段中脱硫机理有变化.

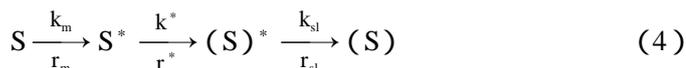
无疑式(2)仍是非线性的,为使问题简单化,令  $m = 1$ ,而定义  $k$  为驱动力参数,  $k$  随% S 变化.

用熔渣脱硫过程的实质是硫和氧通过渣钢界面的电化学迁移.因这一跨越界面的迁移相当快,整个过程的速度受限于相内的传质,界面处于准稳态平衡,即界面上硫的分配系数是

$$L_s^* = \frac{(\% S)^*}{\% S^*} \quad (3)$$

式中,上标“\*”表示界面.

将脱硫过程表示成



这里  $r$  是过程速率,  $r = -\frac{d}{d\tau}\% S$ . 下标  $m$  表示钢侧,  $sl$  表示渣侧. 在钢侧传质限速的条件下有

$$r = r_m = k_m \cdot \frac{A}{W_m} [\% S - \% S^*] \quad (5)$$

$$(\% S) = (\% S)^* \quad (6)$$

这里  $A$  是渣钢界面积,  $W_m$  表示金属重量,相应地用  $W_{sl}$  表示渣重. 根据物质平衡又有

$$\% S^* = \frac{1}{L_s^*} [(L_s^* \rho + W) \% S_0 - W \cdot \% S] \quad (7)$$

式中,下标“0”表示起始条件.  $L_{s0} = (\% S)_0 / \% S_0$ ,  $W = W_m / W_{sl}$ . 因此得到

$$r_m = k_m \cdot \frac{A}{W_m} [(1 + W/L_S^*) \% S - \% S^{**}] \quad (8)$$

$$\ln \frac{\% S - \% S^{**}}{\% S_0 - \% S^{**}} = - k_m \frac{A}{W_m} (1 + W/L_S^*) \tau \quad (\tau \text{ 为反应时间}) \quad (9)$$

$$\% S^{**} = \frac{1}{L_S^*} (L_{S,0} + W) \% S_0 = \% S^* + \frac{W}{L_S^*} \% S \quad (10)$$

在渣侧传质限速的条件下有

$$r = r_{sl} = k_{sl} \frac{A}{W_m} [(\% S)^* - (\% S)] \quad (11)$$

$$\% S = \% S^* \quad (12)$$

由物质平衡得

$$(\% S) = (\% S)_0 + W[\% S_0 - \% S] \quad (13)$$

因此

$$\ln \frac{\% S - \% S^{**}}{\% S_0 - \% S^{**}} = - k_{sl} \frac{A}{W_m} (L_S^* + W) \tau \quad (14)$$

显然,用下式可以归纳式(18)与式(13):

$$\ln \frac{\% S - \% S^{**}}{\% S - \% S^{**}} = - k' \tau \quad (15)$$

钢侧传质限速时

$$k' = k_m \cdot \frac{A}{W_m} (1 + W/L_S^*) = k'_m \quad (16)$$

渣侧传质限速时

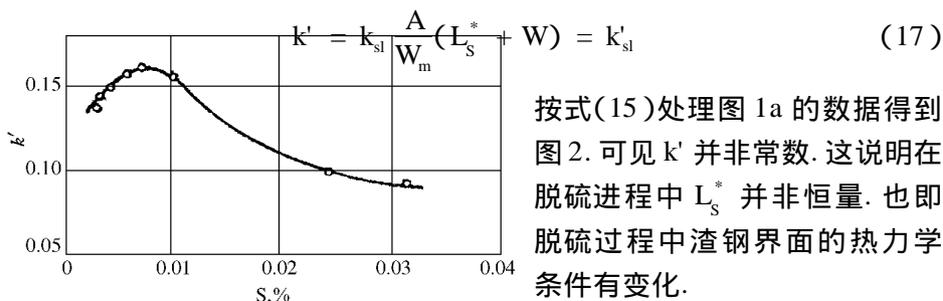


图2  $k' - \% S$  曲线(用文献[1]的数据绘成)

Fig. 2 Driving force parameter,  $k'$  vs  $\% S$  in melted steel

按式(15)处理图 1a 的数据得到图 2. 可见  $k'$  并非常数. 这说明在脱硫进程中  $L_S^*$  并非恒量. 也即脱硫过程中渣钢界面的热力学条件有变化.

因为伴随硫跨越界面的转移必有氧的反向转移. 在高  $\% S$

条件下脱硫速度大,氧跨越界面传至钢侧的速率也大.由于在深度脱硫之前钢水必定要经受深度脱氧,因而氧和脱氧元素的反向扩散致使氧化物在界面以下生成<sup>[3,4]</sup>,即脱硫过程中界面氧位总在下降.为简化起见,令 $\%O^* = a_0^*$

$$-\frac{d}{d\tau}\%O^* = k_0 \cdot \frac{A}{W_m} [\%O^* - \%O] \quad (18)$$

正由于脱硫过程中 $a_0^*$ 不断减小, $L_s^*$ 也就相应地不断变大,从而导致式(15)中 $k'$ 的变值.这样即可解释图2所示的规律.式(17)表明,高%S区内是渣侧传质限速, $k' = k_{s1}$ 逐渐增大;式(16)表明,低%S区内是钢侧传质限速, $k' = k_m'$ 逐渐减小.两区之间,即 $k' \sim \%S$ 曲线上的峰点附近是个混合传质限速的区域.

## 2 可定量描述脱硫过程的电化学模型

脱硫是火法冶金中一个典型的电化学过程,迄今已有不少学者从电化学原理出发讨论过脱硫过程.但这大多是定性的解释.这里我们尝试用电化学模型来定量地描述脱硫过程.

金属液与熔渣一接触,即形成电极体系.一般来说,电化学反应只发生在电介质中,但这里所讨论的是一个电极为液态的体系. A. D. Adamson 指出<sup>[5]</sup>,当两个互不相溶的液相接触时,一个相中的表面活性组分会渗入另一相的边界层中,乃至使其饱和.据此,我们假设电极表面并不在渣钢界面上,而是在钢侧边界层与钢液本体的交界上.即在电化学模型中我们假定电极表面上硫的浓度不是 $\%S^*$ ,而是 $\%S$ .

如上所述,脱硫过程受限于相内的传质.而事实上这个传质过程又是非稳态的.若按 $\frac{d}{d\tau}\%S = -k\%S$ 处理,则直接由电化学得某一时刻的反应速率应该用下式决定<sup>[6,7]</sup>:

$$r = k \cdot \%S_0 \exp(k^2\tau/D_s) \operatorname{erfc}(k\sqrt{\tau/D_s}) \frac{A}{W_m} \cdot 100 \quad (19)$$

此处的 $D_s$ 是S的扩散系数,而 $k$ 并非常数,由下述可见它是恒定的速度常数与可变的过电位 $\eta$ 之某一函数值.所以我们将整个反应时间等分为许多很短的时间间隔来处理.这样,第 $n$ 个时间间隔中的反应速率为

$$r_n = k_n \cdot \% S_{n-1} \exp(k_n^2 \cdot \Delta\tau / D_s) \operatorname{erfc}(k \sqrt{\Delta\tau / D_s}) \frac{A}{W_m} \cdot 100 \quad (20)$$

因而

$$\% S_n = \% S_{n-1} - r_{n-1} \cdot \Delta\tau \quad (21)$$

这里的  $\Delta\tau$  是所取的时间间隔(步长).

按电化学理论,式(19)中  $k_n$  应为反应驱动力的函数:

$$k_n = k_c \cdot \exp\left(\frac{aZF}{RT} \eta_n\right) \quad (22)$$

$k_c$  是不受双电层电场影响的反应速度常数,  $a$  表征电场作用的不对称程度,  $Z$  是在电极上交换的电子数,  $F$  是 Faraday 常数,  $\eta$  是过电位,即电化学反应过程的驱动力. 由于脱硫反应是浓差极化,故可认为有如式(23)所给出的关系:

$$\begin{aligned} \eta_n &= \frac{RT}{ZF} [\ln \% S_{n-1} - \ln \% S_{n-1}^*] + \frac{RT}{ZF} [\ln (\% S)_{n-1}^* - \ln (\% S)_{n-1}] \\ &= \frac{RT}{ZF} \ln (L_{S,n-1}^* / L_{S,n-1}) \end{aligned} \quad (23)$$

这里,  $L_{S,n} = (\% S)_n / \% S_n^*$ .  $(\% S)_n$  可用式(13)计算. 随着反应趋向平衡,即  $n \rightarrow \infty$  时,  $L_{S,n}^*$  和  $L_{S,n}$  都将一致地逼近热力学平衡分配  $L_S$ , 因此  $\eta_{n \rightarrow \infty} = 0$ .

式(22)和(23)清楚地表明反应过程中  $k_n$  是变化的.

为计算  $\eta_n$ , 必须已知  $L_{S,n}^*$ . 为此利用如下的热力学关系:

$$K_s \cdot (\% O^{2-}) = \% O^* \cdot L_S^* = \% O \cdot L_S \quad (24)$$

而知  $L_S^*$  是界面氧位的函数.

$$\% O_n^* / \% O = L_S / L_{S,n}^* \quad (25)$$

即只要已知  $\% O_0^*$ , 则  $\% O_n^* / \% O$  可由式(17)确定. 这是因为对深脱氧的钢水, 可以认为  $\% O$  是恒定的.  $\% O_0$  要根据以描述的试验条件来确定.

设渣中仅 CaO 参与脱硫反应, 则渣的硫容量是

$$C'_S = \frac{(\% \text{CaO})^* \cdot \% O^*}{\% S^* \cdot \alpha_{\text{CaO}}} \quad (26)$$

对于用于钢水二次精炼的渣, 通常可以认为  $\alpha_{\text{CaO}} = 1$ . 另一方面, 相应于  $S \rightarrow (S^*)$  的电流密度可写成

$$i_s = ZFW_m k_s [\% S - \% S^*] / 32 \cdot A \quad (27)$$

或

$$i_s = ZFW_{s1} k_{(S)} [(\% \text{CaS})^* - (\% \text{CaS})] / 72 \cdot A \quad (28)$$

因此导出

$$\% S^* = \frac{\% S + 0.45 W_{s1} \cdot k_{(S)} (\% \text{CaS}) / W_m \cdot k_s}{1 + 0.45 W_{s1} \cdot k_{(S)} C'_S / W_m \cdot k_s \cdot \% O^*} \quad (29)$$

如前所述, 脱硫过程起始时常为渣侧传质限速. 因而

$$\% S_0 = \frac{\% S_0 + 0.45 W_{s1} k_{(S)} (\% \text{CaS}) / W_m \cdot k_s}{1 + 0.45 W_{s1} k_{(S)} C'_S / W_m k_s \% O_0^*} \quad (30)$$

此式中的  $k_{(S)}/k_s$  可用扩散系数之比  $D_{(S)}/D_s$  代替. 这样就能算出  $\% O_0^* / \% O$ .

以上所述即是可用以定量计算  $\% S \sim \tau$  曲线的一个电化模型.

### 3 参数选择和计算实例

我们选用文献[1]中数据作为实例来计算. 计算中所选择的参数如下:

$\% S_0$  0.038%<sup>[1]</sup>,  $(\% S)_0$  0.46%<sup>[1]</sup>,  $L_s$  286<sup>[1]</sup>,  $k_c$  0.0005 cm/s (按电化规律应在  $10^{-3}$  与  $10^{-5}$  之间),  $\Delta\tau$  2s,  $A$  34.2 cm<sup>2</sup><sup>[1]</sup>,  $W_m$  1500 g<sup>[1]</sup>,  $W_{s1}$  250 g<sup>[1]</sup>,  $Z$  2,  $\alpha$  0.5,  $T$  1873 K<sup>[1]</sup>,  $D_s$   $4 \times 10^{-5}$  cm<sup>2</sup>/s<sup>[1]</sup>,  $k_{(S)}/k_s$  0.05<sup>[1]</sup>,  $C'_S$  0.05<sup>[8]</sup>,  $\% O$  0.0004%,  $k_0$  0.425 cm/s<sup>[1]</sup>.

图3a是计算结果之一例, 可见计算与实测吻合得很好. 计算表明, 脱硫过程中  $\% O^* / \% O$  逐渐减小并趋于1.  $L_s^* \sim \tau$  曲线与  $L'_s \sim \tau$  曲线呈现出完全不同的变化规律. 前者呈某种抛物线特征, 后者呈某种双曲线特征. 随着反应的进行两者均逐渐趋近于  $L_s$ , 虽然  $L_s^*$  很快就接近  $L_s$  了.

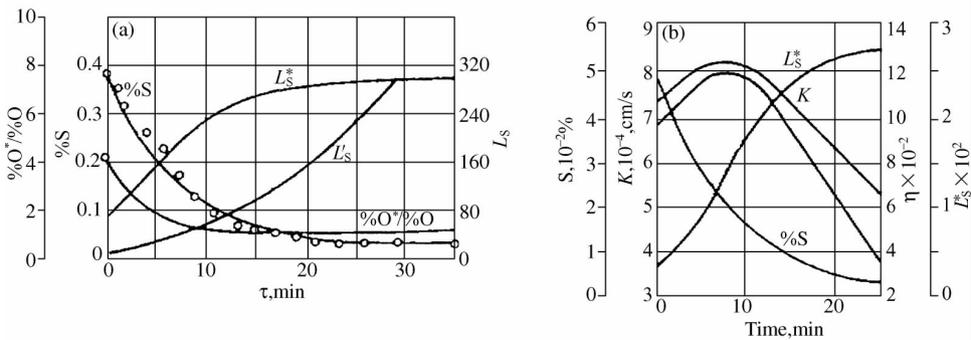


图3 用电化学模型计算的结果

Fig. 3 Results calculated by electrochemical model

(a) from Ref. 1 ; (b) another example

图3b是另一例。除 $\%S_0 = 0.05\%$ 外其他条件均不变。此图指出 $\eta \sim \tau$ 和 $k \sim \tau$ 曲线均有一驼峰，这和图2吻合。

## 4 结论

(1) 对一个渣钢体系来说，若脱硫率很大则可以看到整个脱硫过程能分为三个阶段，且各阶段的脱硫机理有别。即高 $\%S$ 段是渣侧传质限速，低 $\%S$ 段是钢侧传质限速。其间有一个混合传质限速的区域。反应限速环节的这种变化与反应过程中界面氧位的改变密切相关。

(2) 应用电化学方法可直接导出脱硫过程的电化学模型借此模型以及文中给出的初始界面氧位计算方法，可定量地描述 $\%S \sim \tau$ 曲线。计算结果与实测能良好吻合。

(3) 渣钢界面上硫的分配系数 $L_s^*$ 和渣钢本体内硫的分配指数 $L_s'$ 均随界面氧位的下降而上升。 $L_s^* \sim \tau$ 曲线呈某种抛物线特征， $L_s' \sim \tau$ 曲线呈某种双曲线特征。因此 $L_s^*$ 趋近 $L_s$ 要比 $L_s'$ 的快得多。

(4) 用 $\frac{d}{d\tau}\%S = -k\%S$ 可概括脱硫的三个阶段，并更清晰地揭示过程的本质。其中的 $k$ 称驱动力参数，是恒定的速度常数与可变的过电位之函数。它随 $\%S$ 而变且在 $k \sim \tau$ 曲线上有一峰值。

本文为国家自然科学基金资助项目。

## 参 考 文 献

- [ 1 ] Deng Jianxiong(邓健雄), Oeters F. Preprints of 7th Japn-Germany Seminar on Fundamentals of Iron and Steel Making , Duesseldorf , 1987
- [ 2 ] Wagner C. In : Elliot J F ed. The Physical Chemistry of Steelmaking , New York : John Wiley , 1958 : 237-251
- [ 3 ] Pluschkell S W , Dortmund B R , Schuermann E. Arch Elsenhuettenwes , 1981 ; 52( 3 ) : 85-89
- [ 4 ] Ribound P P , Olette M. Proc 7th Int on Vacuum Metallurgy , Vol. II , Tokyo : The Iron Steel Inst of Japan , 1982 : 879-889
- [ 5 ] Adamson A W 顾惕人译. 表面的物理化学 北京 : 科学出版社 , 1984 : 151
- [ 6 ] Bard A J , Faulkner L R. 谷林瑛等译. 电化学方法(原理及应用) , 北京 : 化学工业出版社 , 1986 : 195
- [ 7 ] 田昭武. 电化学研究方法 北京 科学出版社 , 1984 : 24
- [ 8 ] Nicholson A , Howarth D J , Turton J. Ironmaking Steelmaking , 1983 ; 10 : 31-45

## Kinetic Study of Desulphurization Along Metal-slag Interface

**Abstract** An electrochemical model , directly deduced from the principle of electrochemistry , together with the calculation method for initial oxygen potential along the metal-slag interface may be available to quantitatively describe the plot of % S vs time. It was found that during desulphurization both the distribution constant of S along metal-slag interface ,  $L_S^*$  , and distribution index inside the bulk ,  $L_S'$  , vary with the descending of oxygen potential along metal-slag interface. But the plot of  $L_S^*$  vs time is quite different from  $L_S'$  vs time , being of parabola or hyperbola type respectively. The variation of the driving force parameter vs time , obtained either calculated or experimental , plotted as a camel hump.

# 氮在 $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ 渣中的热力学研究<sup>\* 1</sup>

**摘要** 本文借助于光学碱度概念,对  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  熔渣中氮的稳定性进行了研究.结果表明,气相中氮不是与渣中自由氧离子作用,而是与网络结构作用而进入熔渣.根据氮与网络结构  $\text{SiO}_2$  或  $\text{Al}_2\text{O}_3$  之间的反应,提出了熔渣氮容量的新定义.根据渣中氮的行为,结合一系列的试验结果,得到了 1 823 K 时  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  渣的氮容量计算公式 ( $\lg C_N = -11.721gA - 14.26$ ) 和三元渣系的等氮容量曲线.

## 1 前言

钢中的氮对钢材的物理性能和机械性能有很大的影响.在某些情况下,它的存在是有益的,例如,氮形成氮化物细化晶粒,改善了合金钢的高温机械性能,但在大多数情况下,氮的存在是十分有害的,例如,产生时效硬化和降低钢材的轧制性能等等.因此为了防止氮的危害,应最大限度地控制钢中氮含量.

在炼钢的许多环节中,钢液不同程度地吸入氮,但是到目前为止,却没有行之有效的脱氮方法.为了了解大气中氮通过渣层向钢液传氮的程度和预测使用熔渣对钢液脱氮的可能性,必须获得渣中氮行为的有关知识.近年来,对于  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  渣中氮的行为已进行了许多研究,并取得了一些结果,但许多试验结果对氮在熔渣中的行为未能作出正确的解释.本文应用一个新概念——光学碱度  $A$ ,对渣中氮的行为进行了研究,并获得氮进入熔渣的机理及存在形式.

\* 本文合作者:凌天鹰、蒋国昌.原发表于《钢铁研究学报》2(1),13~19(1990)

## 2 光学碱度的概念

熔渣由碱性氧化物和酸性氧化物组成。根据熔渣结构的研究,熔渣中存在着共价键和离子键,氧以下列形式存在于渣中:

- (1) 自由氧离子  $O^{2-}$  ;
- (2) 形成共价键的氧离子  $O^0$ 。

若渣中是纯碱性氧化物,氧与阳离子之间是离子键,则氧以自由离子  $O^{2-}$  存在,即氧是自由的或只受不大的束缚;或是酸性氧化物,氧与阳离子之间大多是共价键,氧受束缚大,渣中  $O^0$  的浓度比例大。

1978年 J. A. Duffy 等人首先提出了光学碱度的概念<sup>[1]</sup>,随后被广泛运用到冶金熔渣的研究中。光学碱度是一个衡量熔渣中氧离子相对自由程度的指标,通过光谱分析的方法测定熔渣中氧将其部分电子施舍给示踪剂(如  $Pb^{2+}$  等)的能力。对于碱性渣,渣中氧离子以  $O^{2-}$  形式存在的浓度大,自由程度也大,则光学碱度值大;对酸性渣,氧离子以  $O^0$  形式存在的浓度大,自由程度低,则光学碱度数值小。

设纯 CaO 渣的光学碱度  $A_{CaO} = 1$ ,冶金中常见氧化物的光学碱度值列于表 1<sup>[2]</sup>。

表 1 氧化物的光学碱度  $A$

氧化物	K <sub>2</sub> O	Na <sub>2</sub> O	BaO	Li <sub>2</sub> O	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	MnO	Cr <sub>2</sub> O <sub>3</sub>	FeO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>
$A$	1.15	1.10	1.08	1.05	1	0.92	0.68	0.95	0.69	0.93	0.69	0.48	0.38	0.29

冶金过程中熔渣大都是多元渣系,对于多元渣系的光学碱度,可按(1)式进行计算。

$$\begin{aligned}
 A = \frac{1}{B} & (N_{CaO} \cdot A_{CaO} + N_{MgO} \cdot A_{MgO} + N_{FeO} \cdot A_{FeO} \\
 & + N_{MnO} \cdot A_{MnO} + 2N_{SiO_2} \cdot A_{SiO_2} + 3N_{Al_2O_3} \cdot A_{Al_2O_3} \\
 & + 3N_{SO_3} \cdot A_{SO_3} + 5N_{P_2O_5} \cdot A_{P_2O_5}) \quad (1)
 \end{aligned}$$

式中  $B = N_{CaO} + N_{MgO} + N_{FeO} + N_{MnO} + 2N_{SiO_2} + 3N_{Al_2O_3} + 3N_{SO_3} + 5N_{P_2O_5}$  ;  
 $N$ ——熔渣中各组元的摩尔分数。

### 3 气相-熔渣平衡试验结果

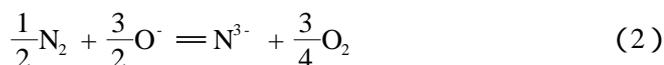
在 1 823 K 温度下,将  $N_2$ -Ar-CO 混合气体通入试验装置,使气体与石墨坩埚中的熔渣反应并达到平衡.根据以前的研究,氮在熔渣中是以  $CN^-$  和  $N^{3-}$  形式存在.由于化验分析方法的限制, $CN^-$  的分析经常不太精确,所以本文只限  $N^{3-}$  的研究.

表 2 是  $CaO-SiO_2$ 、 $CaO-Al_2O_3$  二元系和  $CaO-SiO_2-Al_2O_3$  三元渣系气渣平衡试验的结果.

表 2 1 823 K 时气-渣平衡试验数据

试验者	$P_{N_2}$	$P_{CO}$	$P_{Ar}$	CaO	$SiO_2$	$Al_2O_3$	$N^{3-}$	$C_{N^{3-}}$ $\times 10^{-13}$
	atm			%				
K · Ito <sup>[3]</sup>	0.22	0.78	0	40.1	59.9	0	0.38	13
	0.38	0.62	0	40.0	50.0	10	0.57	10
	0.58	0.42	0	40.0	40.0	20	0.74	6.1
	0.58	0.42	0	50.0	40.0	10	0.54	4.4
M. W. Davies <sup>[4]</sup>	0.50	0.40	0.10	46	42	12	0.668	2.93
	0.55	0.25	0.20	55	33	12	0.703	2.71
K. Schwerdtfeger <sup>[5]</sup>	0.10	0.20	0.70	40	0	60	0.269	1.75
	0.10	0.20	0.70	45	0	55	0.213	1.38
	0.10	0.20	0.70	50	0	50	0.138	0.90
	0.10	0.20	0.70	55	0	45	0.085	0.55
T. Shimoo <sup>[6]</sup>	0.40	0.30	0.30	40	0	60	0.298	1.78
	0.40	0.30	0.30	50	0	50	0.159	0.95
K. Schwerdtfeger <sup>[7]</sup>	0.25	0.25	0.50	55	0	45	0.140	0.83

为了比较不同气相组成下熔渣中氮的稳定性,引入了氮容量的概念.类似于熔渣的其他容量概念(如硫容量、磷容量和碳容量等)<sup>[8]</sup>,根据气体-熔渣的离子反应式(2),可定出如式(3)所示的氮容量  $C_{N^{3-}}$  表达式.



$$C_{N^{3-}} = (\% N^{3-}) \frac{p_{O_2}^{\frac{1}{2}}}{p_{N_2}^{\frac{1}{2}}} = k_2 \frac{\alpha_{O_2}}{f_{N^{3-}}} \quad (3)$$

式中  $k_2$ ——反应(2)的平衡常数；

$\alpha_{O_2}$ ——熔渣中  $O^{2-}$  的活度；

$f_{N^{3-}}$ ——渣中  $N^{3-}$  的活度系数。

由于试验时渣中含有一定的碳,并置于石墨坩埚中,当含有 CO 的混合气体与熔渣平衡时,平衡氧分压由反应(4)决定。



$$\Delta G^0 = -114400 - 85.77T \text{ J/mol}^{[9]} \quad (5)$$

根据气相组成,渣中  $N^{3-}$  的浓度和由式(4)、(5)计算的氧分压  $p_{O_2}$ ,由式(3)就可计算出熔渣的氮容量,如表 2 所示。

图 1 表示 1823 K 温度下熔渣的氮容量与碱度的关系。从图 1 可看出,在所有的情况下,熔渣的氮容量均随碱度的增加而减小。在同样的碱度下,二元系 CaO-SiO<sub>2</sub> 的氮容量最大,并随着 Al<sub>2</sub>O<sub>3</sub> 浓度的增加而减小,氮容量最低的是 CaO-Al<sub>2</sub>O<sub>3</sub> 二元渣系。

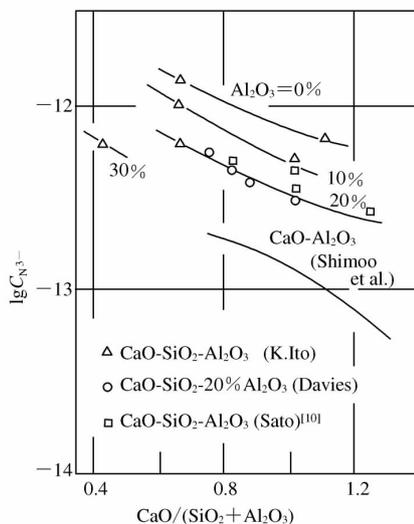


图 1 1823 K 时 CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> 渣的氮容量与碱度的关系

## 4 试验结果讨论

### 4.1 渣中氮的行为

如前所述,根据反应(2)可定义出如式(3)所示的熔渣氮容量。从式(3)可看出,熔渣氮容量与  $p_{N_2}^{\frac{1}{2}}/p_{O_2}^{\frac{1}{2}}$  成正比,这一点已在许多试验研究中<sup>[4~6,10]</sup>得到了证明。

从式(3)还可得出,在一定温度下,氮容量与 $\alpha_{O^{2-}}$ 也成正比。因 $\alpha_{O^{2-}}$ 通常随碱度增加而增大,所以根据方程(3)从理论上讲氮容量应随碱度增加而增大。但是,许多实验结果<sup>[3~7]</sup>都与此相反(如图1所示)。如果气相中的氮是按照式(2)所示的反应进入熔渣的话,势必应该随着碱度的提高, $N^{3-}$ 的活度系数 $f_{N^{3-}}$ 比 $\alpha_{O^{2-}}$ 的活度系数增加快,这样才能解释一系列实验的结果,但这又不大可能。

根据表1中各氧化物的光学碱度,将表2中各个熔渣组成按(1)式折算成光学碱度,得到熔渣光学碱度与氮容量的

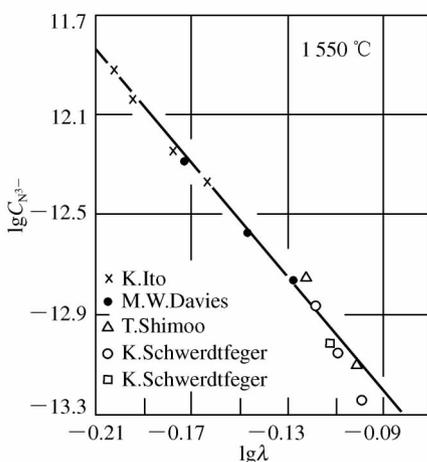
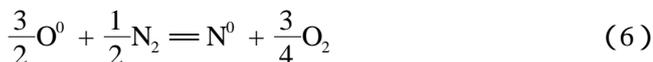


图2 熔渣氮容量与光学碱度的关系

对应关系,如表3所示。将表3中的数据绘成图2,从图中可以看出,氮容量与光学碱度之间存在着反比关系。随着光学碱度减小,氮在熔渣中的稳定性,即氮容量增大。正如前所述,光学碱度减小,意味着熔渣中的氧以 $O^0$ 形式存在的浓度比例增加,这时氮容量随之增大,说明气相中的氮并不是如式(2)所示那样与熔渣中 $O^{2-}$ 反应,而是与网络结构中 $O^0$ 反应,形成新的网络结构。式(6)表示氮取代网络结构中氧而溶解进入渣中反应的离子方程式。

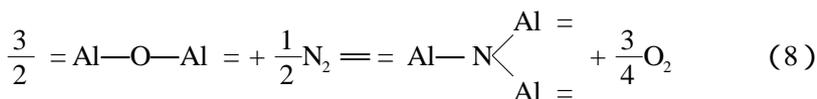
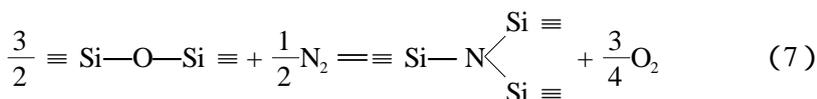
表3 熔渣的光学碱度和氮容量

光学碱度 $\Lambda$	氮容量 $C_{N^{3-}} \times 10^{-13}$	$\lg \Lambda$	$\lg C_{N^{3-}}$	光学碱度 $\Lambda$	氮容量 $C_{N^{3-}} \times 10^{-13}$	$\lg \Lambda$	$\lg C_{N^{3-}}$
0.628	13	-0.202	-11.89	0.766	1.38	-0.116	-12.86
0.641	10	-0.193	-12	0.779	0.90	-0.108	-13.05
0.667	6.1	-0.176	-12.22	0.793	0.55	-0.100	-13.26
0.687	4.4	-0.163	-12.35	0.793	0.82	-0.100	-13.09
0.673	5.45	-0.172	-12.26	0.75	1.78	-0.122	-12.75
0.715	2.71	-0.146	-12.57	0.775	0.95	-0.111	-13.02
0.746	1.75	-0.127	-12.76				



式中  $N^0$ ——网络结构(诸如  $\equiv Si-N \begin{matrix} \swarrow Si \equiv \\ \searrow Si \equiv \end{matrix}$  和  $\equiv Al-N \begin{matrix} \swarrow Al \equiv \\ \searrow Al \equiv \end{matrix}$  中的氮离子).

对于  $CaO-SiO_2-Al_2O_3$  熔渣,与离子反应(6)对应的分子结构反应为



根据反应(6)氮容量可以重新定义成如式(7)所示的形式

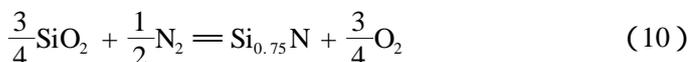
$$C_N = (\% N^{3-}) \cdot \frac{p_{O_2}^{\frac{1}{2}}}{p_{N_2}^{\frac{1}{2}}} = k_6 \frac{\alpha_{N^0}}{f_{N^0}} \quad (9)$$

式中  $k_6$ ——反应(6)的平衡常数;

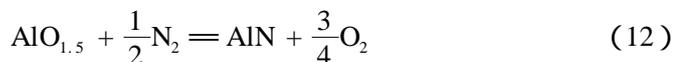
$f_{N^0}$ ——以  $N^0$  形式存在于渣中的氮的活度系数.

从反应(6)和式(7)都可以看到,随着熔渣光学碱度的提高,熔渣中  $O^0$  浓度随之降低,浓度降低抑制了气相中氮向熔渣中传递的反应,从而熔渣的氮容量下降,这个结论与试验结果相符.

对于三元系  $CaO-SiO_2-Al_2O_3$  熔渣,与离子反应式(6)对应的分子反应可用式(10)和式(12)表示,氮在熔渣中以  $Si_{0.75}N$  和  $AlN$  的形式存在.



$$\Delta G^0 = 419\,280 - 14.1T \text{ J/mol}^{[9]} \quad (11)$$



$$\Delta G^0 = 516\,560 - 47.91T \text{ J/mol}^{[9]} \quad (13)$$

#### 4.2 CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> 渣系氮容量及应用

为了了解钢液被熔渣覆盖时钢液吸氮的程度和预测使用熔渣对钢液脱氮的可能性,必须要有一个足够大的浓度范围内的熔渣氮容量.遗憾的是现在根本还没有完整的数据,当然可以一一测定,但由于平衡试验需要很长时间,工作量非常大.本文根据熔渣中氮的行为和机理,结合一系列试验结果,得到了三元渣系 CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> 的氮容量计算公式:

$$\lg C_N = - 11.72 \lg A - 14.26 \quad (14)$$

根据式(14),可以计算出 1 823 K 时各种熔渣组成的氮容量.计算得到的 CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> 渣的等氮容量曲线如图 3 所示.

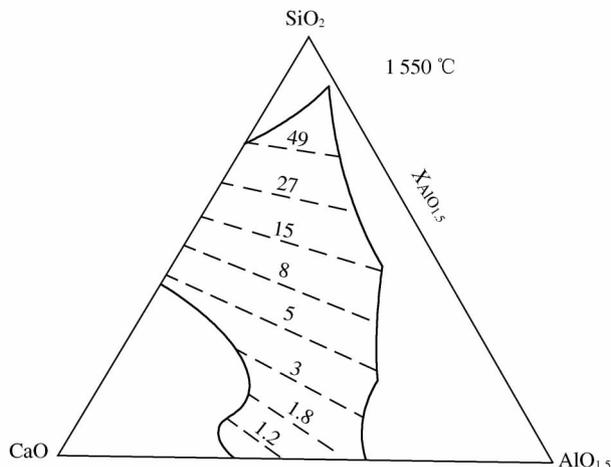


图 3 CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> 渣系等氮容量曲线

(图中数字为氮容量 × 10<sup>13</sup>)

在炼钢和精炼过程中,为防止大气中的氮直接向钢液中传递,通常采用熔渣覆盖保护.根据上面的讨论,当熔渣的氮容量值较大时,气相中的氮较多地进入熔渣,会通过熔渣传递给钢液,因此在选择保护渣时,应根据图 3 选择氮容量较低的熔渣,这样方可起到真正的隔绝作用.

由于目前还没有行之有效的脱氮方法,因此有必要探讨熔渣对钢液脱氮的可能性.使用熔渣脱氮时,渣-钢间氮的平衡分配比,可根据式(19)计算得到.

$$\frac{1}{2}N_2 = N \quad (15)$$

$$\Delta G^0 = 3\,600 + 23.9T \text{ J/mol}^{[9]} \quad (16)$$

$$k_{14} = [N]f_N/p_{N_2}^{\frac{1}{2}} \quad (17)$$

$$C_N = \frac{(\% N^0)p_{O_2}^{\frac{3}{4}}}{p_{N_2}^{\frac{1}{2}}} = \frac{(\% N^0)k_{14}}{[N] \cdot f_N} \cdot p_{O_2}^{\frac{3}{4}} \quad (18)$$

$$L_N = \frac{(\% N^0)}{[N]} = \frac{f_N}{k_{14}} \cdot C_N \cdot p_{O_2}^{-\frac{3}{4}} \quad (19)$$

钢-渣界面的氧分压  $p_{O_2}$  受如下反应中某一个决定：



$$\Delta G^0 = -947\,700 + 198.7T \text{ J/mol}^{[9]} \quad (21)$$



$$\Delta G^0 = -256\,100 + 53.68T \text{ J/mol}^{[9]} \quad (23)$$



$$\Delta G^0 = -843\,620 + 163.4T \text{ J/mol}^{[9]} \quad (25)$$

从式(19)可以看出,在一定温度下  $L_N$  与  $C_N$  和  $p_{O_2}^{-\frac{3}{4}}$  成正比,只要控制很低的  $p_{O_2}$  和选择较高  $C_N$  的熔渣,采用熔渣脱氮在热力学上是可行的.例如对于摩尔百分组成的 26% CaO、63% SiO<sub>2</sub>、10% Al<sub>2</sub>O<sub>3</sub> 熔渣,其氮容量  $C_N = 27.9 \times 10^{-13}$ . 当  $[Al] = 0.01\%$  时,根据式(24)、(25),计算出氧分压  $p_{O_2} = 1.65 \times 10^{-18} \text{ atm}$ , 则

$$L_N = \frac{1}{0.004\,45} \times 27.9 \times 10^{-13} \times (1.65 \times 10^{-18})^{-\frac{3}{4}} = 1\,361$$

可见  $L_N$  是相当大的.

## 5 结论

根据  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  熔渣与  $\text{N}_2\text{-CO-Ar}$  混合气体平衡试验结果,借助于光学碱度概念,对熔渣中以氮化物形式存在的氮的稳定性进行研究,得到以下几点结论:

(1) 气相中氮进入熔渣时,不是与熔渣中自由氧离子  $\text{O}^-$  作用,而是与网络结构作用,形成  $\text{Si-N}$  或  $\text{Al-N}$  新网络结构.

(2) 根据熔渣中氮的行为,结合一系列试验结果,得到在 1 823 K 时熔渣氮容量的计算式:

$$\lg C_{\text{N}} = - 11.72 \lg A - 14.26$$

(3) 根据氮在熔渣-钢液之间的分配热力学研究,熔渣对钢液脱氮在理论上是可行的.

## 参 考 文 献

- [ 1 ] Duffy, J. A., Ingram, M. D. and Sommerville, I. D., *J. Chem. Soc., Faraday Trans. I*, 14(1978), 1410
- [ 2 ] Sosinsky, D. J. and Sommerville, I. D., *Met. Trans. B*, 17B (1986), 331
- [ 3 ] Ito, K. and Fruehan, R. J., *Met. Trans. B*, 19B (1988), 419
- [ 4 ] Davies, M. W. and Meherali, S. G., *Met. Trans.*, 2(1971), 2729
- [ 5 ] Schwerdtfeger, K. and Schubert, H. G., *Arch. Eisenhüttenwes.*, 45(1974), 649
- [ 6 ] Shimoo, T., Iida, T., Kimura, H. and Kawai, M., *Nippon Kinzoku Gakkai-Shi*, 36 (1972), 723
- [ 7 ] Schwerdtfeger, K., Fix, W. and Schubert, H. G., *Ironmaking and Steelmaking*, 5(1978), 67
- [ 8 ] Wagner, C., *Met. Trans. B*, 6B (1975), 405
- [ 9 ] Turkdogan, E. T., *Physical Chemistry of High Temperature Technology*, Academic Press, New York, NY, 1980
- [ 10 ] Choh, T., Hanaki, Y., Sato, T. and Inouye, M., *Trans. Iron & Steel Inst. Jpn*, 13 (1973), 218
- [ 11 ] Mulfinger, H. O., *J. Amer. Ceram. Soc.*, 49(1966), 462

## Thermodynamics of Nitrogen in CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> Slags

**Abstract** The stability of nitrogen as the nitride in CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slags was studied in this paper by means of optical basicity concept. The results showed that nitrogen did not react with “free” oxygen ions but with network former, i. e. SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> and then entered into slags. A new definition of nitride capacity was proposed based on the reaction between nitrogen and the network formers. This capacity could consistently explain the experimental results. The empirical calculating formula of nitride capacity and the iso-C<sub>N</sub> lines diagram in CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slags at 1 823 K were developed based on the behaviour of nitrogen in CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slags.

# 含碳锰矿团块及铬矿团块还原过程的检测和研究方法<sup>\* 1</sup>

**摘要** 本文介绍了含碳锰矿团块和铬矿团块还原过程中还原率的在线检测方法. 通过化学物相分析可分别测出金属还原率和金属化率, 矿相和结构研究可揭示铬、锰矿团块还原过程的进展程度及反应机制. 简介了团块内部气孔特性的测定及全方位信息在固相还原研究中的重要性.

## 1 还原率的在线检测

铁矿团块还原过程的实验室研究大都采用热天平作为测定还原率的手段, 这种方法也被用于研究铬矿团块的还原过程. 但是, 将它用于锰矿团块的还原过程研究, 则由于锰的蒸发会造成较大的误差.

老式的热天平需用 kg 级的团块进行试验. 这一方法的改进之一是使用石英弹簧, 见图 1<sup>[1]</sup>, 借此, 只需 g 级的团块就可做试验了, 测定误差自然有明显减小. 更重要的是, 即使试验的气压条

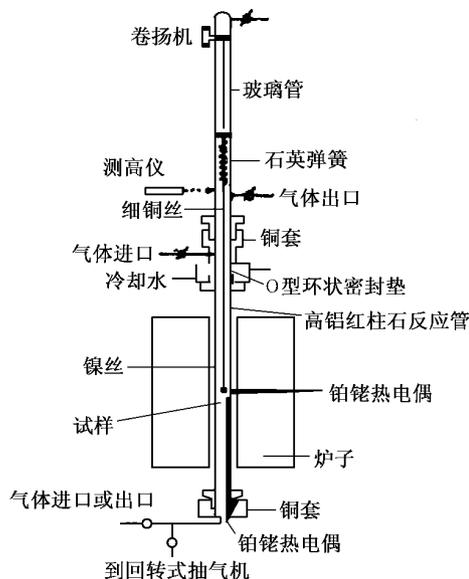


图 1 石英弹簧式热天平

\* 本文合作者: 蒋国昌、徐建伦. 原发表于《铁合金》, (2) 27 ~ 29, 19(1990)

件改变,测定也可连续地进行<sup>[2]</sup>.目前,先进的热天平之灵敏度可达 $10^{-5}$  g的水平,但其准确率却还只限于0.1%<sup>[3]</sup>.除了设备固有的误差因素外,还原时团块内结晶水和挥发分的析出也可能是一个重要的误差起因.

除了热天平之外,逸出气体分析法是另一类在线检测技术.因为要在分离逸出气体的组成之后才作计量,所以试样中结晶水等的析出一般不致有大的影响.这一类测定又可分为两种方法.

一种是直接测量气相组元的浓度,再辅以气体流量的计测就可转换成mol 累计量.红外吸收、气相色谱以及质谱等都属这一系列.例如,日本曾报道过在铁矿还原研究中应用四重极型气相质谱仪作在线检测<sup>[4]</sup>,除了CO及CO<sub>2</sub>外,还可测定H<sub>2</sub>、H<sub>2</sub>O、CH<sub>4</sub>、C<sub>2</sub>H<sub>2</sub>和Ar,每隔3秒测定一次,准确度在2%以内.红外吸收法的准确度也不相上下,其浓度读数的误差约为 $\pm 0.1\%$ .若逸出气体的组成不复杂,则仅使用色谱仪中的部件——热传导检测器(TCD)作在线检测也是可以的,见图2<sup>[5]</sup>,但其测定值的标定较为麻烦.

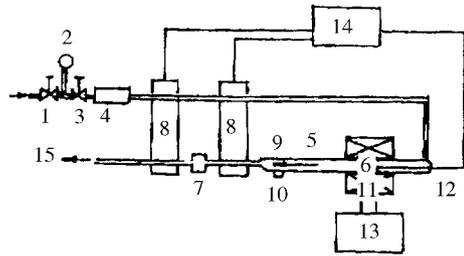


图2 TCD法测还原率

- |           |           |
|-----------|-----------|
| 1. 压力调节器  | 2. 压力表    |
| 3. 大流量控制阀 | 4. 气体净化装置 |
| 5. 反应容器   | 6. 试样     |
| 7. 捕集器    | 8. 热传导测试仪 |
| 9. 铁片     | 10. 磁铁    |
| 11. 炉子    | 12. 热电偶   |
| 13. 温度调节器 | 14. 记录仪   |
| 15. 薄膜测量仪 |           |

第二种是气体吸收法.如用KOH水溶液吸收CO<sub>2</sub>,借pH值的变化来记

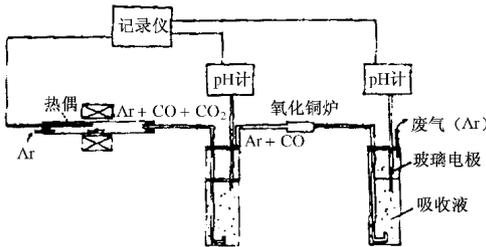


图3 气体吸收法测还原率试验装置

录CO<sub>2</sub>的mol量( $n_{CO_2}$ )就是一例,见图3.这是一个比较易行且经济的方法.但要得到精确的测定,尚需解决如下矛盾.首先,所用的吸收液必须能充分吸收CO<sub>2</sub>.KOH水溶液是熟知的CO<sub>2</sub>吸收液,它与CO<sub>2</sub>反应的平衡常数足够大,但是反应进行得不快.

提高KOH水溶液的起始pH值是促进反应加快之一策.但pH值大于12后,%KOH与pH值之间已呈非线性关系,并且起始的pH值越大则相应于相

等的  $n_{\text{CO}_2}$  之  $\Delta\text{pH}$  就越小,此时 pH 值的读数就会有较大的误差。

这一矛盾可从以下几方面来解决:

① 若试验中 pH 值大于 12,则先绘出 % KOH 和 pH 之间的标准曲线,而且每换一次电极标准曲线应重新作一次;

② 按照库仑法,在  $\text{CO}_2$  输入吸收瓶时同步地输入等 mol 量的  $(\text{OH}^-)$ ,使测定过程中吸收液的 pH 值保持不变,借所耗电量计算相应的  $n_{\text{CO}_2}$  [6];

③ 利用催化剂加快 KOH 水溶液与  $\text{CO}_2$  的反应,另外改变吸收瓶中的温度和压力条件也可显著加快吸收速度 [7],这样吸收液的起始 pH 值可望适当减小;

④ 与 KOH 水溶液相比,乙醇胺水溶液吸收  $\text{CO}_2$  的速度相当快 [7],并且对应相同的  $\text{CO}_2$  吸收量,它的  $\Delta\text{pH}$  较大。

另一个矛盾是,若吸收瓶中液面较低,则气泡滞留时间不足,从而影响吸收率。增高液面则需要加强团块还原用电阻炉的密封;在吸收瓶中加入挡板以阻拦快速上升的气泡,则吸收液的循环流动也会受阻,因而测定会出现滞后。所以吸收瓶结构的设计也是十分重要的。根据化学反应工程学的原理可以预料,使吸收液呈微小的液滴逆向通过气相是最有效的吸收途径。

由于气体吸收法是直接测定 mol 累计量,所以从还原过程的在线检测来看,这可能发展成为测定误差较小的一种方法。

作者在研究固相还原的过程中,应用和改进了气体吸收法,并用碳酸盐分解法对测定值作了校正。

## 2 化学物相分析法

团块在还原中一般总包含高价氧化物到低价氧化物的转变及低价氧化物继续被还原成金属或碳化物两个过程。所以还原率(失氧率)与金属化率是两个不同的概念。应用前节介绍的在线检测方法只能测得还原率。要区分还原率和金属化率就只能依靠化学物相分析法。

日本和我国对铬矿团块的化学物相分离研究均已成功,据报道其误差约为 1% [8]。关于锰矿团块,湖南省冶金材料研究所已能在锰矿含铁量为 5% ~ 20% 的条件下测出还原过程中的总锰量、 $\text{MnO}$  及金属化(包括碳化物)的锰量之变化,并提出了试样制备的规程。

### 3 预还原团块的矿相和结构研究

无论是铁矿还是锰矿、铬矿团块的还原研究论文,近年来都或多或少地包含有矿相及结构研究的成果.除了传统的光性矿物学方法外,扫描电镜、电子探针、X光衍射和图像分析等现代测试仪器都得到了广泛应用.目前最先进的则是利用扫描电镜直接观察铁矿的还原<sup>[9]</sup>.

矿相及结构研究之所以重要,是因为如下一些为揭示还原过程进展程度及反应机制的信息只能依赖这些研究来提供.

(1) 反应析出相(金属相、碳化物相)的特征——开始形核的条件,核心出现的位置,它们的形状、粒度、分布及成分的变化<sup>[10~13]</sup>.

(2) 氧化物相结构和组成的变化特征——气孔及龟裂的发展、膨胀现象、元素的迁移及局部富集、低熔点相的出现、反应阻挡层的形成<sup>[14~20]</sup>.

(3) 碳粒和其他相的接触状态,碳粒消失的条件.

### 4 团块内部气孔特征的测定

在显微镜下固然可以观察到一些团块内部气孔的特征,然而仅仅这些信息还不足以揭示反应规律.问题在于气孔按其半径的分布对气-固反应有决定性的影响<sup>[21]</sup>.这是在铁矿及其团块的还原研究中业已证实的结论.气孔按其半径的分布及其分布规律在还原过程中的变化都应该依靠汞压入法来测定.

在锰矿和铬矿含碳团块的还原过程中,气-固反应究竟有多大作用仍是有争议的问题.无疑,查明还原速率等和小气孔表面积之间的关系可望有助于最后解决该争论.

### 5 全方位信息在固相还原研究中的重要性

一般来说固相还原反应的研究要比研究熔体之间的反应更为复杂.原因在于反应发展的不均衡性,仅仅一种方法不可能提供足够的信息.气体吸收法虽能记录还原过程释放出来的 $\text{CO}_2$ ( $\text{CO}$ )之mol量,但必须同时依靠X光衍射测出原始矿相组成之后才可能计算还原率.所以,为了揭示固相还原的进展程度和反应机制,必须将各种测试及研究相互配合,力求取得全方位的

信息.

## 参 考 文 献

- [ 1 ] 片山博等. 日本金属学会志 ,1976 ,40(10) ,993-999
- [ 2 ] 片山博等. 铁と钢 ,1985 ,71(9) ,1094-1101
- [ 3 ] 宋鸿恩. 《热天平》,计量出版社 ,1985
- [ 4 ] 秋山友宏等. 铁と钢 ,1983 ,S763
- [ 5 ] 寺山清志等. 日本金属学会志 ,1981 ,45(9) ,901-908
- [ 6 ] B. V. 林切夫斯基. 《冶金实验研究方法》. 冶金工业出版社
- [ 7 ] F. C. Riesenfeld *et al.* Gas Purification ,Gulf Pub.
- [ 8 ] 徐素芯等. 冶金分析与测试 ,1983(2) 78-80
- [ 9 ] 小林睦弘等. 铁と钢 ,1985 ,71(9) ,1102-1109
- [ 10 ] 稻见隆等. 铁と钢 ,1981 ,S670
- [ 11 ] T. Maeda *et al.* Trans ISIJ. 1984 ,24 ,B-4
- [ 12 ] N. A. Barcza *et al.* Elec. Furn. Proc. 1971 ,83-93
- [ 13 ] Jiang Guo Chang. Proc. of Shenyang Symp , on Smelting Reduction. 1986 , Sept , 173-190
- [ 14 ] 片山博等. 铁と钢 ,1986 ,72(10) ,1513-1520
- [ 15 ] 片山博等. 日本金属学会志 ,1986 ,50(11) 993-998
- [ 16 ] 杨兆祥等. 钢铁 ,1986 ,21(8) 5-13
- [ 17 ] 陆暘等. 钢铁 ,1985 ,20(11) ,10-17
- [ 18 ] T. Elkasabgy. Trans ISIJ ,1984 ,24 ,612-621
- [ 19 ] W. J. Rankin *et al.* Arch Eisenhuettenwes ,1979 ,50(9) ,373-377
- [ 20 ] U. F. Chije *et al.* Ironmaking & Steelmaking ,1986 ,13(1) ,3-8
- [ 21 ] 徐建伦. 湖南冶金 ,1988 ,(1) ,1-5

## Method for Examining Reduction Process of Carbon Bearing Chrome-Ore Agglomerate and Manganese-Ore Agglomerate

**Abstract** An on-line method for detecting the degree of reduction in reducing process of carbon bearing manganese-ore agglomerate and chrome-ore

agglomerate is described. The degree of metal reduction and metallization may be determined respectively by chemical phase analysis. The mineragraphic method can reveals progress and mechanism of the reducing process. The determination of gas porosity chracter in these agglomerate and the importance of omnibearing information in solid reduction are simply introduced.

# 含碳铬矿团块和锰矿团块 还原过程的催化<sup>\* 1</sup>

**摘要** 综述了含碳铬矿团块和锰矿团块还原过程催化的研究成果. 添加  $\text{Na}_2\text{B}_4\text{O}_7$  等催化剂能促进铬矿团块的还原. 其催化机理的主要观点是催化剂的加入促进了 Boudouard 反应的进行和改善了气相、固相的扩散条件.

在矿的固相还原领域里, 应用催化的方法促进过程动力学是近年来的一个重要动向. 无论是铬矿、铁矿乃至  $\text{SiO}_2$  的还原<sup>[1]</sup>, 均已有人作了专门的催化研究.

## 1 含碳铬矿团块还原过程的催化

片山博等研究了  $\text{Na}_2\text{B}_4\text{O}_7$ 、 $\text{NaF}$ 、 $\text{Na}_2\text{CO}_3$ 、 $\text{NaCl}$ 、 $\text{CaB}_4\text{O}_7$ 、 $\text{B}_2\text{O}_3$ 、 $\text{CaF}_2$ 、 $\text{CaCl}_2$  及  $\text{K}_2\text{CO}_3$  对铬矿还原的促进作用<sup>[2]</sup>. 图 1 表明, 1 200 下未加催化剂的苏联铬矿只有不足 50% 的还原率, 而加入 1%  $\text{Na}_2\text{B}_4\text{O}_7$  的还原率接近 90%. 在 1 300 下这个规律也已得到证实. 因此, 这一试验表明使用催化剂可带来直接的经济效益. 目前, 用回转窑等生产含碳铬矿团块时还原温度一般要求大于 1 300, 加入催

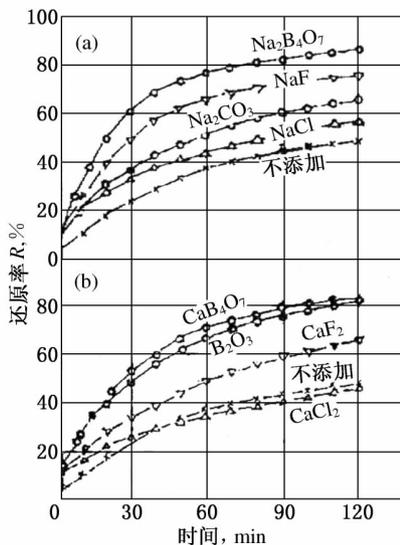


图 1 1 200 下加入 1% 催化剂对苏联铬矿还原率的影响

\* 本文合作者: 蒋国昌、徐建伦. 原发表于《铁合金》(1) 4~8(1990)

化剂则可望在较低温度下得到相同的还原率, 这样可降低能耗. 另外, 目前用回转窑等生产的团块其还原率只有 50%, 原矿中的  $\text{Mg}(\text{Cr}_{0.8}\text{Al}_{0.4})_2\text{O}_4$  多数未还原. 加入催化剂可促进此矿相的还原反应(见图 2 和图 3).

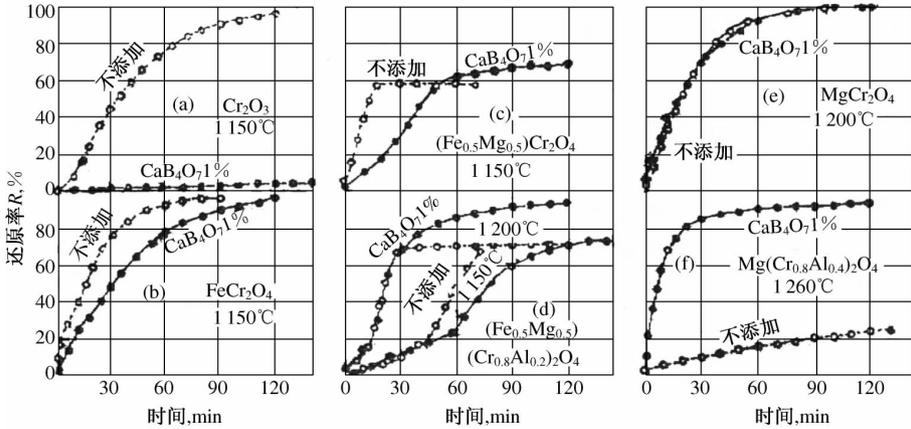


图 2 加入  $\text{CaB}_4\text{O}_7$  对  $\text{Cr}_2\text{O}_3$  及各种合成铬铁矿相还原率的影响

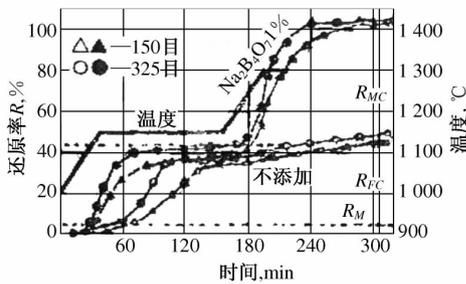


图 3 在二段加入方式条件下加入 1%  $\text{Na}_2\text{B}_4\text{O}_7$  对铬铁矿相(由苏联铬矿分离而得)还原的影响

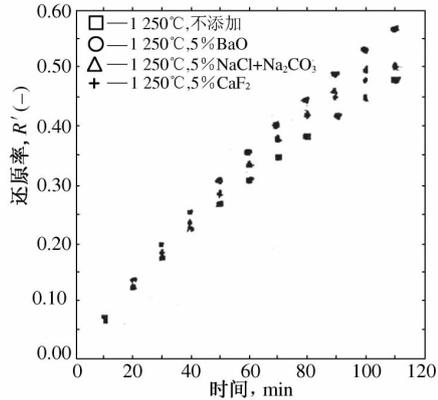


图 4 铬矿还原的催化试验

片山博对催化剂曾做过初步的优选工作. 他们认为加  $\text{Na}_2\text{B}_4\text{O}_7$  最有效, 并且只需加入 1% ~ 2% 即可. 但不同的催化剂有不同的规律. 如 1200 °C 下加 1%  $\text{CaB}_4\text{O}_7$  也很有效. 然而 1250 °C 下加 2% 以上的  $\text{CaB}_4\text{O}_7$  则反而起阻碍作用.

可惜的是所添加的硼酸盐本身也有所还原, 而钢中允许的硼含量仅在微

量范围内,超越此限度则钢的脆性大增,因此工业生产中用硼酸盐作催化剂将会令人忧虑。为此,作者建议考虑 B. Sundelin 以 BaO、CaF<sub>2</sub> 和 Na<sub>2</sub>CO<sub>3</sub> + NaCl 进行的催化试验结果<sup>[3]</sup>。图 4 表明 BaO 是一种有效的催化剂。此外,作者还曾比较过 KCl 等化合物的催化作用,试验表明 KCl 的效果可能优于 Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub><sup>[4]</sup>。

实际上,制团时加入的粘结剂和熔剂也起着某种催化作用,即从催化的概念考虑,球团的渣性也是一个需要研究的课题,而且用于矿热炉的球团其渣性可能与用于高炉或直接合金化的有所区别。

## 2 含碳锰矿团块还原过程的催化

锰矿团块还原过程的催化应从其渣性的调整着手。因为天然锰矿大都是酸性的,锰在其中的活度很低。当然渣系的调整也可在转炉或电弧炉等终还原反应器里进行,但从使用高碱度铁烧结矿可以明显改善高炉炼铁的技术经济指标的事实不难看出,渣性的调整应在预还原过程中完成。从这个意义上说,固相还原中的催化对尔后的熔融还原过程并非没有作用。

根据我国高炉冶炼锰铁的经验<sup>[5]</sup>,可以认为调整渣性的基本要求是 CaO/SiO<sub>2</sub> = 1.5,且 MgO 为 8% ~ 12%。还应指出,这一调整对球团的强度也是有利的。K. Г. Сорокин 等<sup>[8]</sup>和 М. И. Громов 等<sup>[7]</sup>的观点与此是相吻合的。

用盐类促进含碳锰矿团块还原过程的研究是有意义的。目前,即使加了碳的锰矿团块(工业产品)的还原也只能进行到生成 MnO 的状况,这可望通过加入某种盐类而得到改善。只是这一研究现在仅在起步阶段,所以需要引用铁矿固相还原中的催化研究作为借鉴。

碱金属和碱土金属对铁矿的固相还原有促进作用,这是早为冶金界了解的事实,但主动地利用这种作用则是近年来的进展。这些工作集中于钾盐和钠盐的应用。试验表明,钾盐和钠盐可以多种方法加入团块。将它们的蒸汽引入反应器,事先用其水溶液浸渍碳粉或矿粉等均能有效地催化还原。究竟是由 Fe<sub>2</sub>O<sub>3</sub> 到 Fe 的各个阶段都被加速了呢,还是仅某些或某个阶段被促进,目前各家的观点尚不统一。因为其催化作用的强弱很可能还与别的工艺因素(还原温度、矿石的煅烧处理、反应器内的总气压等)有关。

考察铁矿团块还原的催化研究还可得到另一个重要的启示,即钠盐和钾

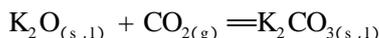
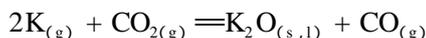
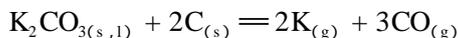
盐的存在会导致异常膨胀,团块的强度甚至可能因此而损失殆尽.幸运的是钠盐、钾盐对强度的影响很可能会因原矿中的脉石量的增加而减弱.如З. И. Некрасов等指出铁矿球团若含脉石10%左右,则加入Na、K盐时球团强度反而会增加<sup>[8]</sup>.而锰矿的脉石量一般远大于10%,所以加入Na、K盐对含碳锰矿团块强度的威胁应该较小.

### 3 催化剂的作用机制

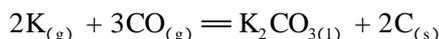
碱金属、碱土金属对铁矿固相还原的催化,曾用这些添加剂会引起Fe-O晶格畸变来解释,并认为添加剂的离子半径愈大则催化作用愈强. $Ba^{++}$ 和 $K^{+}$ 的试用即由此而来.

然而这并不是一个得到公认的观点.如Y. K. Rao等指出,除非长时间地加热无碳的铁矿和碱金属盐之混合物,否则不会有可观的碱金属离子渗入铁氧化物晶格中去.

另一种较流行的观点是碱金属主要通过促进Boudouard反应而起作用.Y. K. Rao等<sup>[9]</sup>也持此看法,并且认为实际反应为如下三个步骤:



毕学工等<sup>[10]</sup>做过一个有趣的试验.他们用K和CO的混合气体还原无内配碳的铁矿矿块(尺寸为10~20 mm),发现K有明显的催化作用.显然这个作用与Boudouard反应无关.该试验发现了两个重要的事实:一是还原后的矿块内直到其芯部均检出有K存在,或者是进入氧化铁的晶格内或者与脉石作用形成渣相.З. И. Некрасов等和T. Elkasabgy<sup>[11]</sup>也有类似的发现.二是混合气体含K愈多,则还原后矿块内就有更多的碳黑出现,他们认为这是反应



的结果.因为矿相分析检出了 $K_2CO_3$ ,所以证实此反应存在是可靠的.由这两个试验结果可以认为:K领先渗入铁矿矿块,再通过碳沉积反应将碳黑输送到“反应地点”.K的催化作用可能就是这样的.

中川大等<sup>[12]</sup>和H. Itaya等<sup>[13]</sup>的观点与毕学工等的观点接近,也认为是

促进气相扩散之故. 因为他们发现加有催化剂时矿块气孔率增加很多.

中川大等还观察到加有催化剂时析出相的形态与无催化剂时不同. 片山博等在铬的还原催化研究中有类似的发现. 他们指出催化剂加入量增大时矿相结构的特征有明显变化. 如在加入 5%  $\text{Na}_2\text{B}_4\text{O}_7$  的条件下, 自始至终只在“铬铁矿”粒子的外缘有金属相析出, 并且它特别粗大, 而矿粒芯部却几乎观察不到金属相(本文作者曾观察到相同的现象<sup>[14]</sup>). 以  $\text{MgO-Al}_2\text{O}_3$  为主要成分的“反应阻挡层”也出现于不同的部位, 且最终移到矿粒芯部(图 5). 据此, 片山博等认为  $\text{Na}_2\text{B}_4\text{O}_7$  能催化  $\text{MgO-Cr}_2\text{O}_3$  还原的原因之一是固相扩散得到促进.

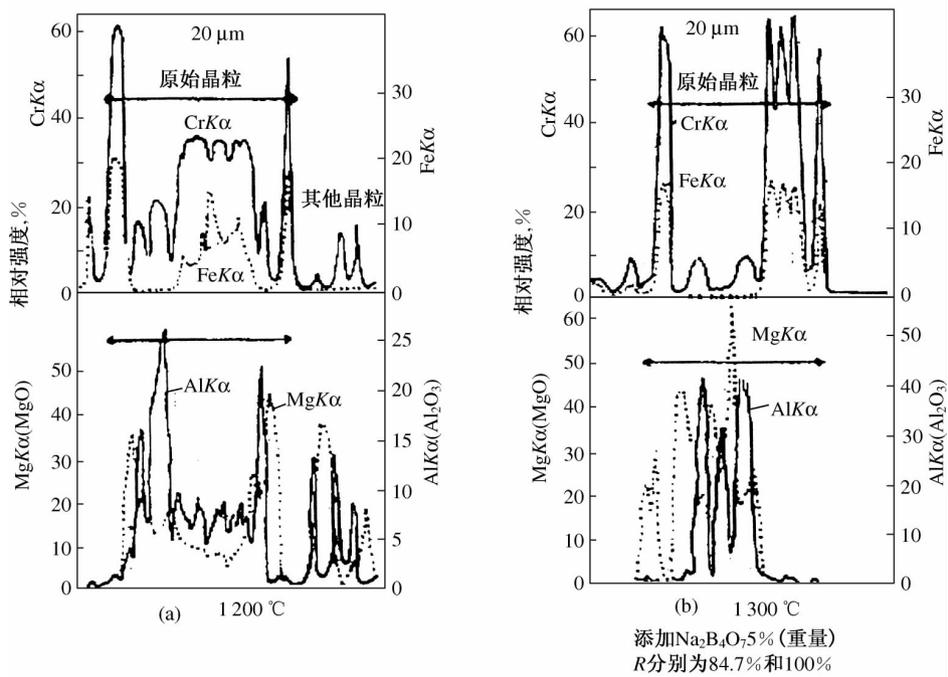


图 5 伊朗铬矿加催化剂还原后的 EPMA 线扫描

新日铁在研究铬矿熔融还原时也曾确认  $\text{MgO-Al}_2\text{O}_3$  阻挡还原的作用<sup>[15]</sup>. 可见在含碳铬、锰团块中加入催化剂对终还原过程也有潜在的促进作用. 充分利用团块固相还原过程调整其化学组成和矿相结构, 应该看作是该过程的主要任务之一.

## 参 考 文 献

- [ 1 ] 戴维等. 第三届冶金过程动力学和反应工程学学术会议论文集(下) ,1986 ,59-71
- [ 2 ] 片山博等. 铁と钢 ,1986 ,72(10) ,1513-1520
- [ 3 ] B. Sandelin. In : Internal report of KTH NEUT-SUT cooperation on smelting reduction. 1987 ,7
- [ 4 ] 顾利平等. (内部资料 将在上海工业大学学报上发表)
- [ 5 ] 余逊贤. 锰. 长沙黑色冶金矿山设计研究院出版 ,1980
- [ 6 ] К. Г. Сорокин , Др. Теория и практика мет . Мн. 1980 ,105-112
- [ 7 ] М. И. Громов , Др. Теория и практика мет . Мн. 1980 ,112-127
- [ 8 ] З. И. Некрасов , Др. Ст аль. 1976(11) ,973-979
- [ 9 ] Y. K. Rao *et al.* Ironmaking & Steelmaking ,1984 ,11(6) ,308-318
- [ 10 ] 毕学工. 北京钢铁学院硕士论文
- [ 11 ] T. Elkasabgy. Trans ISIJ ,1984 ,24 ,612-621
- [ 12 ] H. Nakagawa *et al.* Trans ISIJ ,1985 ,25 ,1021-1024
- [ 13 ] H. Itaya *et al.* Trans ISIJ ,1975 ,15 ,429-435
- [ 14 ] 蒋国昌等. 上海工业大学学报 ,1987 ,(4) ,406-414
- [ 15 ] H. Yamana *et al.* 铁と钢 ,1983-S833

## The Catalysis in Reducing Process of Carbon Bearing Chrome-Ore Agglomerate and Manganese-Ore Agglomerate

**Abstract** Research achievements of catalysis in reducing process of carbon bearing chrome-ore agglomerate and manganese-ore agglomerate are summarized. The addition of catalyst such as  $\text{Na}_2\text{B}_4\text{O}_7$  etc can facilitate the reduction. The main viewpoint of catalytic mechanism is that the catalyst promote the Boudouard reaction and improves the diffusion condition of gas and solid phase.

# A Kinetic Study on Nitrogen Pick-up of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ System from Furnace Atmosphere<sup>\* 1</sup>

## Introduction

Nitrogen is harmful for most kinds of steel. During steelmaking process, covering steel bath with molten slag is frequently used to restrain the nitrogen pick-up of steel. Unfortunately, it is impossible to completely avoid nitrogen pick-up, because nitrogen will penetrate through the slag layer. So far, only few of basic research concerning this utilized technology has been published. Hence, it is quite difficult to optimize this technology.

The nitrogen transferring from atmosphere to steel through molten slag is such a process composed of two sub-processes in series. One is nitrogen pick-up of molten slag from atmosphere and another is nitrogen pick-up of steel bath from molten slag. For simplification, it is better to analyse the two sub-processes separately in advance. This paper is devoted to the nitrogen pick-up of molten slag from atmosphere.

---

\* In collaboration with Jiang Guochang, Lin Tianyin. Reprinted from NEUTISUT-HUT Symp. on Process Metallurgy, P. R. China, May 23-25, 1990. pp. 119-125

## 1 The Experiment Installation and Method

The experiment installation is shown in Fig. 1. In every small graphite crucible there were 6 g pre-melted slag, which was made of pure chemical materials. After the furnace was sealed, the crucibles were heated under Ar. When the given temperature was reached, a pre-deoxidized and dried CO-N<sub>2</sub> mixture was used, composition of which is  $X_{\text{CO}} = 0.4$ ,  $X_{\text{N}_2} = 0.6$ . Then the experiment started, and for every one hour one crucible was taken out from furnace. The nitrogen content in slag was measured by means of Kjeldahl method. Therefore in this paper only (N<sup>3+</sup>) is involved.

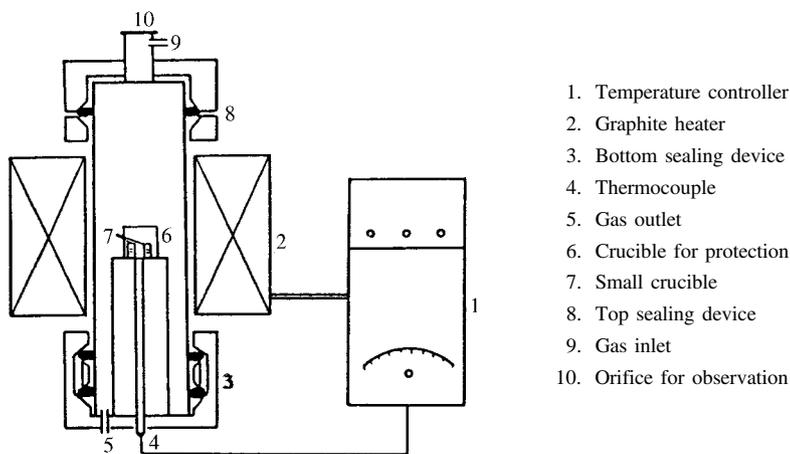


Fig. 1 The experimental installation

## 2 Experimental Results

### 2.1 The Influence of Gas Flow

For acquiring the influence of gas flow rate just along slag surface, an experiment involving 40% CaO-20% Al<sub>2</sub>O<sub>3</sub>-40% SiO<sub>2</sub> slag and various gas flow was carried out.

Fig. 2 shows that the nitrogen pick-up rate under 1550°C is a constant even the

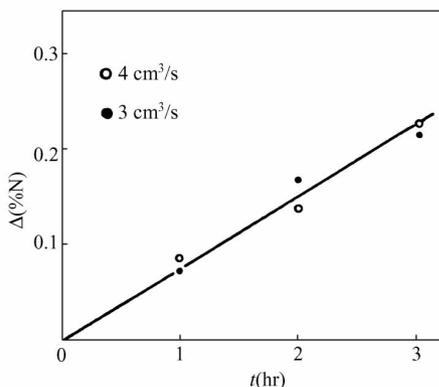


Fig. 2 The influence of gas flow on nitrogen pick-up of slag (40% CaO-40% SiO<sub>2</sub>-20% Al<sub>2</sub>O<sub>3</sub>)

gas flow is changed from 4 cm<sup>3</sup>/s to 8 cm<sup>3</sup>/s.

$$\frac{d(\Delta\%N)}{dt} = k \quad (1)$$

Toshio Shimmo *et al.* [1] ran a similar experiment with 50% CaO-50% Al<sub>2</sub>O<sub>3</sub>. The pure nitrogen gas flow was varied in 4-33 cm<sup>3</sup>/s. They claimed to find an influence of gas flow on nitrogen pick-up of slag even the gas flow is limited in the range of

4-8 cm<sup>3</sup>/s. Of course, this is a completely contradict result. This may be caused by that the experiment conditions are different. Among several factors, perhaps the most significant one is that the nozzle for nitrogen blow was fastened above the slag, surface only 40 mm by them. In that case, the variation of gas flow might cause different stirring in molten slag, not only the gas flow rate along slag surface was changed.

## 2.2 The Influence of Temperature

Under 1 500, 1 550, 1 600°C, the variation of nitrogen content of the slag versus time is a line, as shown in Fig. 3. Fig. 4 indicates the relation of rate constant (k) of nitrogen pick-up against temperature. According to this way, the active energy is 180 kJ/mol. This value is almost equal to that of Shimmo *et al.* In fact, this value locates in the diffusion active energy range of slag components [2].

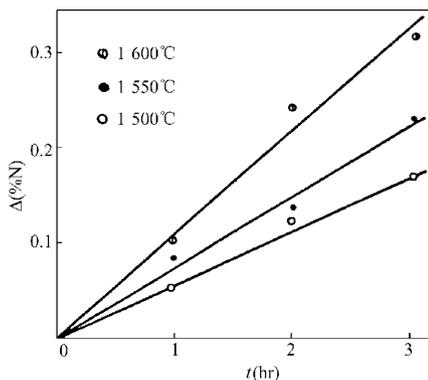


Fig. 3 The influence of Temperature on nitrogen pick-up of slag (40% CaO-40% SiO<sub>2</sub>-20% Al<sub>2</sub>O<sub>3</sub>)

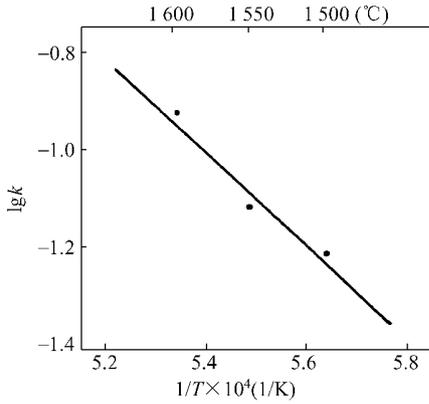


Fig. 4 The influence of temperature on rate constant of nitrogen pick-up of slag

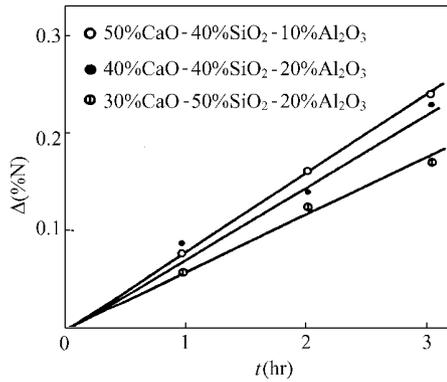


Fig. 5 The influence of slag composition on its nitrogen pick-up

### 2.3 The Influence of Slag Composition

Fig. 5 is the variation of nitrogen content of slag with different composition under 1 550°C. It is clear that nitrogen pick-up ratio is a constant in every case. The influence of variation of slag composition comes from two aspects. One is the change of slag viscosity. Fig. 6 indicates that the viscosity under 1 800°C of the three slags shown in Fig. 5 gets a linear relationship with the corresponding nitrogen pick-up rate. On the other hand, however, the nitrogen capacity does not concern the corresponding nitrogen pick-up rate reasonably.

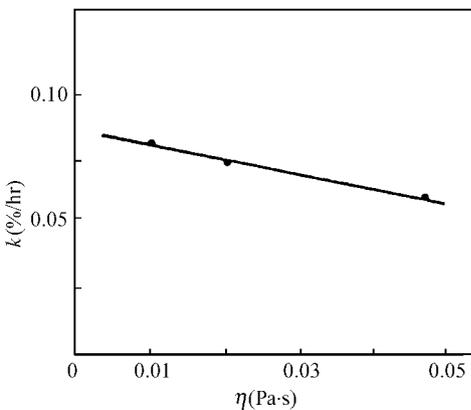


Fig. 6 The influence of slag viscosity on rate constant of nitrogen pick-up of slag

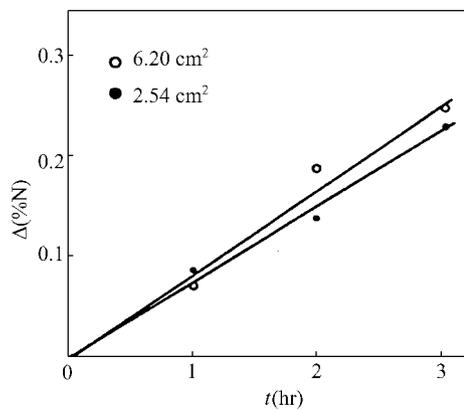


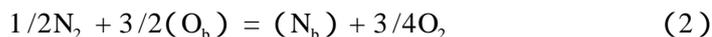
Fig. 7 The influence of interface area on nitrogen pick-up of slag (40% CaO-40% SiO<sub>2</sub>-20% Al<sub>2</sub>O<sub>3</sub>)

## 2.4 The Influence of Interface Area

Under 1 550°C , if the slag amount is kept unchangeable the variation of nitrogen content in slag caused by the changing of gas-slag interfacial area is shown in Fig. 7. It is noticed that , the increase of nitrogen pick-up rate is not in proportion to that of interfacial area. Shimmo *et al.* studied the same influence under 1 550°C with 40% CaO-40% SiO<sub>2</sub>-20% Al<sub>2</sub>O<sub>3</sub> and got a nonlinear relation too<sup>[1]</sup>.

## 3 Discussion

It was pointed out by the authors that the desolving reaction of nitrogen from atmosphere in molten slag is :



Here , O<sub>b</sub> , N<sub>b</sub> , denote bridging oxygen and nitrogen respectively.

Shimmo *et al.* claimed that the rate limiting step is the interface reaction. As well known , to judge whether the interface reaction is a rate limiting step , the best way is to measure the variation of reaction rate following the variation of interface area. As aforementioned , our result and the result of Shimmo *et al.* both indicate the variations are not in proportion. So the interface reaction can not be the rate limiting step.

According to our results the rate limiting step is mass transfer inside slag. This is because :

(1) The active energy of nitrogen pick-up falls on the diffusion active energy level of slag component.

(2) The rate is strongly influenced by slag viscosity.

Shimmo *et al.* ran an experiment about the influence of mechanical stirring on nitrogen pick-up rate , and found there was an obvious effect. Notwithstanding , this experiment was run under a gas flow of 33 cm/s. As the matter of fact , in this case the molten slag got a sufficient agitation even there was no any mechanical stirring.

If the rate is limited by mass transfer inside the molten slag , then

$$\frac{d(\Delta\% N)}{dt} = k' [(\% N)^* - (\% N)] \quad (3)$$

Owing to the fact that interface reaction is not the rate limiting step,  $(\% N)^*$ , the nitrogen content of slag along interface can be considered as a constant. Therefore the relation in Fig. 8 is acquired. And Fig. 1-7 are all the initial periods of Fig. 8 under different conditions.

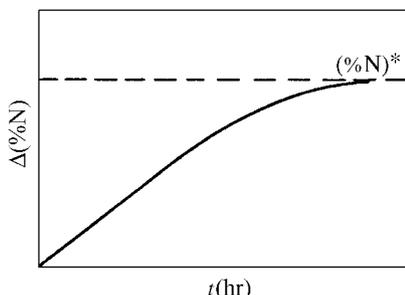


Fig. 8 The relationship of nitrogen content in slag versus reaction time

Adopting Eq. (3) and  $k' = (A/V)K$ , it is possible to calculate the nitrogen mass transfer coefficient. In this calculation,  $(\% N)$  can be acquired by means of the following equation<sup>[5]</sup>.

$$\lg(\% N) \frac{P_{O_2}^{\frac{1}{4}}}{P_{N_2}^{\frac{1}{2}}} = - 11.51 \lg A - \frac{22\ 135}{T} - 2.14 \quad (4)$$

Here,  $A$  denotes the optical basicity. The calculation results for this experiment is shown as follows:

Slag Composition	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
	50	40	10	40	40	20	30	50	20
TK		2 823		1 773	1 823	1 873		1 823	
$K \times 10^{-5}$ (cm/s)		3.19		1.81	1.97	2.27		0.78	

## 4 Conclusion

The nitrogen pick-up process of molten slag from atmosphere of 40% CO + 60% N<sub>2</sub> is limited by mass transfer in slag. The active energy is 180 kJ/mol. The mass transfer coefficient is  $(0.78 - 3.19) \times 10^{-5}$  cm/s.

## References

- [ 1 ] Shimmo *et al.* , J of JIM 1972 ,36(8) ,728-733
- [ 2 ] Han Qiyong , Kinetics of Metallurgical Process. Metallurgical Industry Publisher , 1983 , 253
- [ 3 ] Chen Jiexiang , The Handbook of Frequently Used Diagram , Table And Data for Steel-making , Metallurgical Industry Publisher , 1984 , 204
- [ 4 ] Jiang Guochang *et al.* , A Discussion on Basicity of CaO-SiO<sub>2</sub> and CaO-Al<sub>2</sub>O<sub>3</sub> Binary Systems Based on Bonding Structure
- [ 5 ] Lin Tian Yin , Master Thesis of SUT , 1990

# A Discussion on Basicity of CaO-SiO<sub>2</sub> & CaO-Al<sub>2</sub>O<sub>3</sub> Binary Systems Based on Bonding Structure<sup>\* 1</sup>

**Abstract** A modification of optical basicity based on bonding structure is developed in this paper. The bonding basicity is defined as

$$B = \sum B_{ij} X_{ij}$$

Here,  $X_{ij}$  denotes the mol-fraction of oxygen anion in bond (i—O—j).  $B_{ij}$  denotes its basicity characteristics.

A thermodynamic model is developed to calculate  $X_{ij}$  in the whole liquid region. Some XPS and Raman-Spectroscopy results agree with this calculation very well.

In the liquid region,  $B_{ij} X_{ij}$  is just the activity of that bond. Some linear regularities between them were deduced theoretically. And the agreements with the data published in literatures all are good.

A discussion on desulphurization in CaO-SiO<sub>2</sub> is performed pursuant to bonding basicity. The sulphur in slag behaves in two states: (Si—S—Ca) and (Ca—S—Ca). An equilibrium relation between them is shown to be decided by basicity. This can be used to explain the variation of  $\gamma_{\text{CaS}}$  versus basicity.

The equilibrium constant of dissolving reaction of H<sub>2</sub>O in CaO—SiO<sub>2</sub> is calculated based on bonding basicity.

A linear regularity between  $(B_{22} X_{22})^{3/2}$  and the reported capacity of N<sup>3-</sup> is found. Here, 22 is used to denote (Al—O—Al). This regularity proved that the N<sup>3-</sup> dissolving in CaO-Al<sub>2</sub>O<sub>3</sub> is just the one inside the bond (Al—N—Al).

---

\* In collaboration with Jiang Guochang. Reprinted from Proc. 6th Int. Iron & Steel Congr., ISIJ, Oct. 21–26, 1990, Nagoya, Japan, Vol. 1, pp. 123–130

## 1 The Contribution of Optical Basicity and Its Inadequacy

In pyrometallurgy, slag basicity is one of the essential and frequently used concepts. Since long before, however, it has been only possible to be calculated with empirical equations due to a poor knowledge on microstructure of slag.

The optical basicity which is introduced into metallurgy by I. D. Sommerville made a great progress. According to this concept, basicity is considered as the binding up force acting upon oxygen anion in slag, and it can be detected by using of ultraviolet absorption spectrum as well as photoacoustic spectroscopy<sup>[1]</sup>. From the view point of slag microstructure, the binding up force depends on that the oxygen anions present in which bond and how much they are. For example, in optical basicity the “ionic bond” Ca—O—Ca and “covalent bond” Si—O—Si are considered with  $\lambda_{\text{CaO}}$  and  $\lambda_{\text{SiO}_2}$ . In fact, it was proved through XPS (or ESCA), NMR, Raman spectrum and infrared emission spectrum that the bond Si—O—Ca exists in CaO-SiO<sub>2</sub> system yet<sup>[2]</sup>.

Besides, all of SiO<sub>2</sub> exist as SiO<sub>4</sub><sup>4-</sup> only in the region of  $N_{\text{SiO}_2} < 1/3$ . Where  $N_{\text{SiO}_2} > 1/3$ , more complex Si—O anions in chain or ring are formed through polymerization. Several kinds of polymer can be found in a slag with a given composition. The influence of this structure variation was described with “group optical basicity” introduced by J. A. Duffy<sup>[3]</sup>. Certainly, the bond energy of Si—O—Me will be different for different basic cation Me. If Ca, Mg, Mn, Fe coexist in slag then a Si—O complex anion must have several values of “group optical basicity”. Therefore, the practical utilization of “group optical basicity” will not be easy, so we prefer to attribute all kinds of complex Si—O anion to the relative amount of different bonds. As do so, the argument of molecular theory, ionic theory and which degree of polymerization is avoided, and the basic point is put on some bonds which are doubtless. On the other hand, the calculation is simplified.

Using (11), (14), (44) to denote Si—O—Si, Si—O—Ca, Ca—O—Ca respectively, the “modified optical basicity” or “bonding basicity” of CaO-SiO<sub>2</sub> binary system can be defined as

$$B = B_{11}X_{11} + B_{14}X_{14} + B_{44}X_{44} \quad (1)$$

According to Eq. (1) the calculation of basicity is attributed to the relative amount of different bonds  $X_{ij}$  and the characteristics of oxygen anion in these bonds  $B_{ij}$ . In addition, Eq. (1) makes sense that the difference between optical basicity and bonding basicity is the different element. Optical basicity takes various kinds of compound as its element, but bonding basicity takes various kinds of bond, or various environments of oxygen anion as element.

## 2 The Characteristics $B_{ij}$ of CaO-SiO<sub>2</sub>

As R. Dron's opinion<sup>[4]</sup>, the variation of polymerization degree causes the bond energy to be changed. For example, the bond energy of Si—O—Si in SiO<sub>3.5</sub><sup>3-</sup> should be different from that in SiO<sub>2.5</sub><sup>-</sup>. And the same is for Si—O—Ca. It seems that  $B_{11}$  and  $B_{14}$  should vary with the increase of  $N_{\text{SiO}_2}$ . On the other hand, the increase of  $L_{\text{Si-O}_b}$  and  $L_{\text{Si-O}_{nb}}$  in Na<sub>2</sub>O-SiO<sub>2</sub> system caused by changing  $N_{\text{SiO}_2}$  from 1 to 0.33 all are smaller than 1/16<sup>[5]</sup>. Here  $L$  is the length of Si—O bond. The subnote "b" and "nb" denote bridging oxygen and non-bridging oxygen respectively. Thus, the variation of bond energy in CaO-SiO<sub>2</sub> system caused by changing  $N_{\text{SiO}_2}$  can be neglected. Therefore, in liquid region we take  $B_{44} = 1$ ,  $B_{14} = 0.74$ ,  $B_{11} = 0.48$  to follow that in optical basicity.

## 3 The Calculation of $X_{ij}$ in CaO-SiO<sub>2</sub> System

Under the condition of that the slag is solidified in glass state the values of  $X_{ij}$  can be measured with XPS or Raman spectrum<sup>[2,6]</sup>. Apart from this, several theoretical models are possibly used in the calculation  $X_{ij}$ <sup>[7-10]</sup>. Here it is a model based on thermodynamics.

The summary mole amount of oxygen anion in CaO-SiO<sub>2</sub> system is

$$n_{(\text{O})} = n_{\text{CaO}} + 2n_{\text{SiO}_2} \quad (2)$$

Take

$$X_{\text{CaO}} = n_{\text{CaO}}/n_{(\text{O})} \quad (3)$$

$$X_{\text{SiO}_2} = 2n_{\text{SiO}_2} / n_{(\text{O})} \quad (4)$$

$$X_{ij} = n_{ij} / n_{(\text{O})} \quad (5)$$

And from the balance of bond amount , get

$$2X_{\text{CaO}} = 2X_{44} + X_{14} \quad (6)$$

$$2X_{\text{SiO}_2} = 2X_{11} + X_{14} \quad (7)$$

As C. J. B. Fincham *et al.* pointed out , among three bonds inside CaO-SiO<sub>2</sub> melt the following reaction exists

$$(11) + (44) = 2(14) \quad (8)$$

The prior thermodynamic study of this reaction was performed by G. W. Toop and his colleagues<sup>[11]</sup>. Nevertheless this model has to be revised. Pursuanting to C. R. Masson's opinion<sup>[12]</sup>, the variation of standard free energy for Eq. (8) should be taken into account , and it should be developed to be possibly used in high  $N_{\text{SiO}_2}$  region involving ring-shaped Si—O complex anion. Besides , in that model mol fraction was used but not activity. This also should be revised. Considering that  $(B_{ij}X_{ij})$  can be taken as another type of activity as it will be discussed in following section thus , we took.

$$\frac{(B_{14}X_{14})^2}{(B_{11}X_{11})(B_{44}X_{44})} = \exp(-\Delta G^0 / RT) \quad (9)$$

Here ,  $\Delta G^0$  is the variation of the free energy of Eq. (8) , the standard state of which is pure liquid CaO and SiO<sub>2</sub>. In addition , under different slag composition the same Eq. (8) represents different polymerization reactions. So this  $\Delta G^0$  should vary itself to follow the increase of  $N_{\text{SiO}_2}$ .

In a binary system  $AB$  , the standard free energy of formation of a mole intermediate compound  $A_\alpha \cdot B_\beta$  is

$$G_{10}^0 = RT \left( \ln a_A^\alpha + \ln a_B^\beta \right) \quad (10)$$

Owing to the fact that the variation of polymerization degree is possibly to be considered as the formation of corresponding intermediate compounds , so Eq. (10) can be used to calculated  $\Delta G^0$  in Eq. (9). The following items were also taken in-

to account in calculation.

a) The  $\alpha_{\text{CaO}}$  and  $\alpha_{\text{SiO}_2}$  reported by Rein *et al.* [13] were used. And Kappor's data [14] was used in conversion of standard state.

b) In some intermediate compound, as CaO, SiO<sub>2</sub>, the included (11) bond does not take part in the reaction (8). It only give a contribution to the entropy of formation of that compound because the existence of (14) bond causes it to be polarized in some degree.

The  $\Delta G^0$  which can be used directly in Eq. (9) is given in Fig. 1.

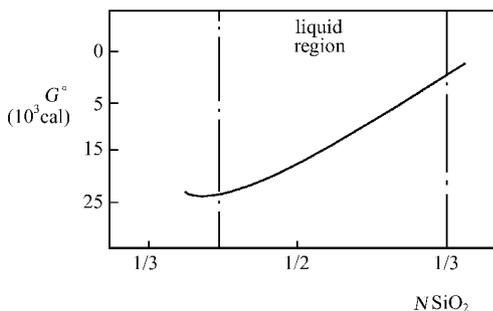


Fig. 1 The value of  $G^0$  used in Eq. (9), 1 600°C

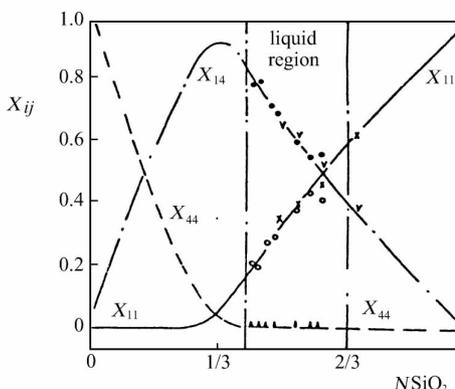


Fig. 2 The comparison of calculation and experiment of  $X_{ij}$  in liquid region (1 600°C) of CaO-SiO<sub>2</sub> system Raman spectra

Based on Fig. 1 and Eq. (9),  $X_{ij}$  can be calculated. The result and the measurements through Raman as well as XPS spectrum were shown in Fig. 2. They coincide with each other pretty well. And it was proved that the calculation developed in this paper can be successfully used in high  $N_{\text{SiO}_2}$  region.

#### 4 The Bonding Basicity in CaO-Al<sub>2</sub>O<sub>3</sub> Binary System

The bonding basicity in CaO-Al<sub>2</sub>O<sub>3</sub> system is defined as

$$B = B_{22}X_{22} + B_{24}X_{24} + B_{44}X_{44} \quad (11)$$

Here, (22), (24), (44) is used to denote the bonds of (Al—O—Al), (Al—

O—Ca) , (Ca—O—Ca) respectively.

When melted CaO and Al<sub>2</sub>O<sub>3</sub> are mixed together a reaction as follows is suggested

$$(22) + (44) = 2(24) \quad (12)$$

In spite of that complexing bond exists in a melt containing Al<sub>2</sub>O<sub>3</sub> , it does not take part in reaction (12). Consequently , as the first step complexing bond need not to be accounted in the calculation  $X_{ij}$ . In this case , get

$$\frac{(B_{24}X_{24}')^2}{(B_{22}X_{22}')(B_{44}X_{44}')} = \exp\left(\frac{-G^0}{3RT}\right) \quad (13)$$

Because the calculation of  $X_{ij}$  in CaO-SiO<sub>2</sub> indicated it could be simplified , the  $G^0$  of Eq. (13) is taken as the free energy of formation of 3CaO-Al<sub>2</sub>O<sub>3</sub> , using pure liquid CaO and Al<sub>2</sub>O<sub>3</sub> as standard.

In molten CaO-Al<sub>2</sub>O<sub>3</sub> , one Al<sup>3+</sup> ion gets one complex bond. For this complex bond , the oxygen anion in (24) acts as a donor. Once a time the complexing bond forms , no difference can be found between it and the corresponding covalent bond. Therefore , two complex bond (O—Al) can be considered as one (22). The mole fraction of complex bond is  $X_{CP} = 2/3X_{Al_2O_3}$ . Thus

$$X_{22} = \frac{X_{22}' + \frac{1}{2}X_{CP}}{1 + \frac{1}{2}X_{CP}} \quad (14)$$

$$X_{24} = \frac{X_{24}'}{1 + \frac{1}{2}X_{CP}} \quad (15)$$

$$X_{44} = \frac{X_{44}'}{1 + \frac{1}{2}X_{CP}} \quad (16)$$

Here  $X_{Al_2O_3}$  ,  $X_{22}'$  ,  $X_{24}'$  ,  $X_{44}'$  , were defined either similar to Eq. (4) or to Eq. (5). The calculation result of Eq. (14)–(16) was shown in Fig. 3.  $B_{22}$  ,  $B_{24}$  ,  $B_{44}$  , was evaluated pursuanting to Table 1 as

$$B_{22} = 0.67 \quad B_{24} = 0.82$$

**Table 1 The basicity characteristics of bonds in CaO-Al<sub>2</sub>O<sub>3</sub>**

bond	combining energy of 1st of oxygen atom (e. v. )*	basicity characteristics based on combining energy of O <sub>1s</sub>	optical basicity given in Ref.		
			$\theta$	$\Theta$	$\Theta$
Ca—O—Ca	528.53	1.0	1.0	1.0	1.0
Al—O—Ca	529.80	0.82			0.85
Si—O—Ca	530.61	0.72			0.74
Al—O—Al	531.00	0.67	0.61	0.68	0.70
Si—O—Si	532.38	0.48	0.48	0.47	0.48

Note : \* The data was taken from J. of JIM 1984 ,48(12) ,1179-1186 and J. of JIM 1987 ,51(12) ,1152-1158

—2rd Int. Symp. on Met. Slags & Fluxes 1984 ,1015-1026

$\theta$ —J. of JIM 1986 50(5) 456-461

$\Theta$ —J. Non. Cryst. Solids 1976 ,21 ,373-410

## 5 Discussion

### 5.1 The relation between bonding basicity and component activity inside liquid region

Just as optical basicity , the bonding basicity is a measure of binding up force acting upon oxygen anion. In other words , bonding basicity is another expression of oxygen activity in slag. So there should be some coverting relations among  $B_{ij}$   $X_{ij}$  and  $\alpha_{CaO}$  as well as  $\alpha_{SiO_2}$ .

Certainly , in liquid region of CaO-SiO<sub>2</sub>  $\alpha_{CaO}$  uniquely concerns bond(14). On account of that the binding up force acting on oxygen O<sub>nb</sub> , caused by Si<sup>4+</sup> is much stronger than that caused by Ca<sup>++</sup> thus ,

$$\bar{G}_{CaO} = G_C^0 + RT \ln \alpha_{CaO}^{\alpha_1} = G_{CB}^0 + RT \ln (B_{14} X_{14})^{\alpha_2} \quad (17)$$

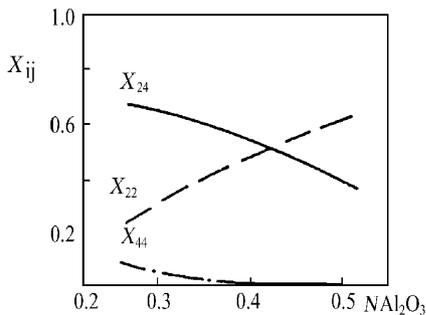


Fig. 3 The calculated value of  $X_{ij}$  in liquid region (1600°C) of CaO- $Al_2O_3$  system

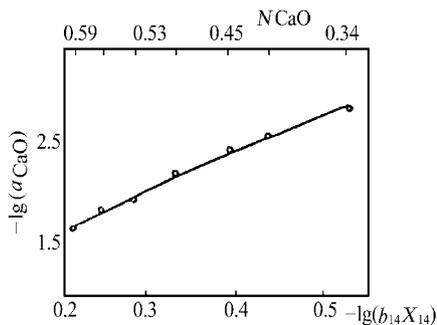


Fig. 4 The bonding basicity relationship of  $(B_{14}X_{14})$  and  $\alpha_{CaO}$  in liquid region (1600°C) of CaO- $SiO_2$  system

Here,  $\overline{G}_{CaO}$  is the partial mole free energy of CaO;  $G^0$  is the free energy in standard state. According to Eq. (17), get

$$\alpha_3 \lg \alpha_{CaO} = \lg(B_{14}X_{14}) + \Delta G_C^0 \quad (18)$$

Fig. 4 is the evidence indicating that Eq. (18) is correct.

It is suggested that  $\alpha_{SiO_2}$  uniquely concerns  $(B_{11}X_{11})$ . However, the data of  $\alpha_{SiO_2}$  is given in pure solid  $SiO_2$  standard, and the standard of  $(B_{11}X_{11})$  is solid CaO. Obviously they have to be converted to use  $2CaO \cdot SiO_2$  as their standard. In this case  $\alpha_{SiO_2}'$  and  $(B_{11}'X_{11})$  were used. Pursuant to R. H. Rein<sup>[13]</sup>,

$$\alpha_{SiO_2} = 0.084 \alpha_{SiO_2}' \quad (19)$$

On the other hand, it was supposed that

$$B_{11}' = \frac{B_{11}}{B_{14}} = 0.65 \quad (20)$$

Taking  $\overline{G}_{SiO_2}$  to express the partial mole free energy of  $SiO_2$ , from

$$\begin{aligned} \overline{G}_{SiO_2} &= G_S^0 + RT \ln \alpha_{SiO_2}^{\beta_1} \\ &= G_{SB}^0 + RT \ln (B_{11}'X_{11})^{\beta_2} \end{aligned} \quad (21)$$

got

$$\beta_3 \lg \alpha_{\text{SiO}_2}' = \lg(B_{11}' X_{11}) + \Delta G_S^0 \quad (22)$$

Fig. 5 is the evidence showing that Eq. (22) is correct.

Fig. 6 & Fig. 7 are the similar relationships in CaO-Al<sub>2</sub>O<sub>3</sub> binary system.

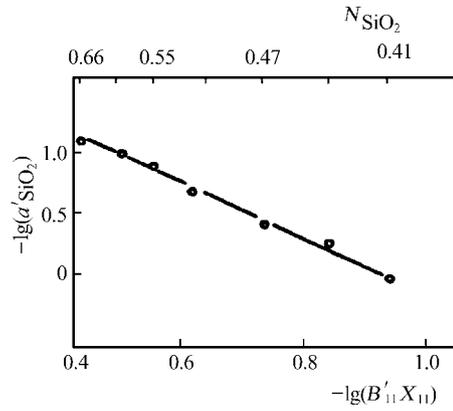


Fig. 5 The relationship of bonding basicity ( $B'_{11} X_{11}$ ) and activity  $\alpha_{\text{SiO}_2}'$  in liquid region (1 600°C) of CaO-SiO<sub>2</sub> system

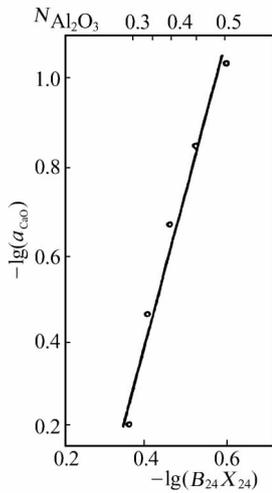


Fig. 6 The relationship of bonding basicity ( $B_{24}X_{24}$ ) and activity  $\alpha_{CaO}$  in liquid region of CaO- $Al_2O_3$  system (1 600°C)

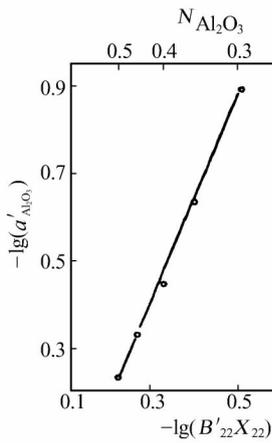


Fig. 7 The relationship of bonding basicity ( $B'_{22}X_{22}$ ) and activity  $\alpha_{AlO_{1.5}}$  in liquid region of CaO- $Al_2O_3$  system (1 600°C)

Through the analysis in this section the following can be concluded that the characteristics  $B_{ij}$  is another type of activity coefficient.

## 5.2 A discussion about desulphurization with CaO-SiO<sub>2</sub> system based on bonding basicity

As the general accepted point of view, the species taking part in desulphurization is ( $O^{2-}$ ), or we say the bond (44). In liquid region, however,  $X_{44}$  approaches to zero. F. D. Richardsop pointed out that the bond (44) taking part in desulphurization comes from the dissolution of bond (14)<sup>[15]</sup>. This means in summerized reaction it is bond (14) which takes part in desulphurization. In spite of this, a non-linear relation was found between ( $B_{14}X_{14}$ ) and  $C'_S$ . One can realise its reason through an analysis of  $\gamma_{CaS}$ .

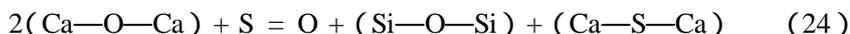
Doubtlessly, the stability of CaS is weaker than that of CaO, and the same is between  $SiS_2$  and  $SiO_2$ . Based on this, the  $\Delta G^0$  of CaS-SiS<sub>2</sub> binary system seems less minus than that in Eq. (9). Then we can estimate that (Si—S—Ca) and (Ca—S—Ca) possibly coexist in a widened secop. On account of that the average electrominus of (Ca—S—Ca) is 1.36 and that of (Si—S—Ca) is 1.

65 , (Ca—S—Ca) is more active than (Ca—S—Si). To explain the increase of  $\gamma_{\text{CaS}}$  resulted from the increase of basicity , it is supposed that the products of desulphurization may be two : (Si—S—Ca) and (Ca—S—Ca). In addition , the higher the basicity , the more the bond (Ca—S—Ca).

If we keep the interfacial electrolytical reaction is still



then the summerized reaction of desulphurization may be two :



Concerning them , the sulphur capacity should be :

$$C_{\text{S}(24)}' = X_{(\text{Ca—S—Ca})} \cdot \alpha_{\text{O}} / \alpha_{\text{S}} = \frac{K_{24} (B_{14} X_{14})^2}{(B_{11} X_{11}) \cdot \gamma_{(\text{Ca—S—Ca})}} \quad (26)$$

$$C_{\text{S}(25)}' = X_{(\text{Si—S—Ca})} \cdot \alpha_{\text{O}} / \alpha_{\text{S}} = K_{25} \frac{(B_{14} X_{14})}{(B_{11} X_{11}) \cdot \gamma_{(\text{Si—S—Ca})}} \quad (27)$$

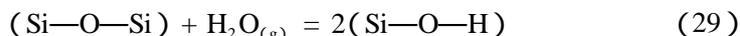
As aforementioned ,  $B_{ij}$  in bonding basicity is another type of activity coefficient. Thus  $\gamma_{(\text{Ca—S—Ca})} / \gamma_{(\text{Si—S—Ca})}$  is a function of  $B_{(\text{Ca—S—Ca})} / B_{(\text{Si—S—Ca})}$  , and it approaches to a constant. From

$$\frac{X_{(\text{Ca—S—Ca})}}{X_{(\text{Si—S—Ca})}} = \frac{K_{24} \cdot \gamma_{(\text{Si—S—Ca})}}{K_{25} \cdot \gamma_{(\text{Ca—S—Ca})}} (B_{14} X_{14}) \quad (28)$$

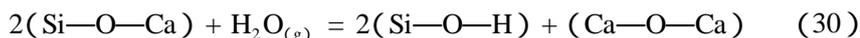
it is clear that the higher the basicity , the greater the  $X_{(\text{Ca—S—Ca})}$ .

### 5.3 The equilibrium constant of dissolving reaction of H<sub>2</sub>O in slag CaO-SiO<sub>2</sub>

The dissolvability of H<sub>2</sub>O in CaO-SiO<sub>2</sub> reported by T. Fuwa<sup>[16]</sup> was widely accepted. And the dissolving reaction was considered as following<sup>[16]</sup> , if  $N_{\text{SiO}_2} > 0.5$  ,



if  $N_{\text{SiO}_2} < 0.5$  ,



The equilibrium constant of Eq. (29) and (30) can be calculated based on the reported dissolvability and bonding basicity.

The calculated constants are shown in Table 2. This is an evidence to prove the reported investigation is correct.

**Table 2 The equilibrium constant of the dissolving of water vapour in CaO-SiO<sub>2</sub> binary system**

$N_{\text{SiO}_2}$	0. 61	0. 55	0. 50	0. 46	0. 44
(H <sub>2</sub> O) ppm	407	391	375	422	465
$X_{(\text{Si-O-H})}$	0. 101 7	0. 097 7	0. 093 7	0. 105 5	0. 116 3
$B_{11}X_{11}$	0. 245	0. 21	0. 18	0. 14	0. 106
$B_{14}X_{14}$	0. 36	0. 41	0. 47	0. 53	0. 58
$K_{29}$	0. 11	0. 12	0. 13		
$K_{30}$			0. 105 $X_{44}$	0. 104 $X_{44}$	0. 106 $X_{44}$

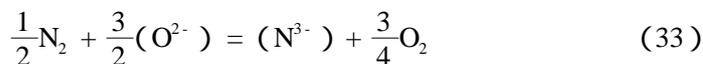
Note : Temperature 1 600℃  
 $P_{\text{H}_2\text{O}} = 289 \text{ Torr}$

$$K_{29} = \frac{X_{(\text{Si-O-H})}^2}{P_{\text{H}_2\text{O}}(B_{11}X_{11})} \quad (31)$$

$$K_{30} = \frac{X_{(\text{Si-O-H})}^2(B_{44}X_{44})}{P_{\text{H}_2\text{O}}(B_{14}X_{14})^2} \quad (32)$$

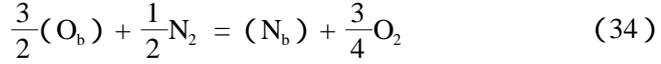
#### 5. 4 A discussion about the dissolve of $\text{N}^{3-}$ in CaO-Al<sub>2</sub>O<sub>3</sub> system based on bonding basicity

The dissolving reaction of  $\text{N}^{3-}$  in slag was suggested<sup>[17]</sup> as



In contrast to this , the measured capacity of  $\text{C}_\text{N}^{3-}$  was found being dropped to follow with the increase of slag basicity. In fact , the saturation of AlN was detected in slag containing Al<sub>2</sub>O<sub>3</sub> if the partial

pressure  $P_{N_2}$  is high enough<sup>[17]</sup>. As well known, nitrogen in AlN exists in Al—N—Al bond, thus the following dissolving reaction may be supposed.



$N_b$  denotes the nitrogen in Al—N—Al. And correspondingly the nitrogen capacity is

$$C_N^{3-} = (\% N^{3-}) \frac{P_{O_2}^{\frac{3}{4}}}{P_{N_2}^{\frac{1}{2}}} = K_{34} \frac{(B_{22}X_{22})^{3/2}}{\gamma_{N^{3-}}} \quad (35)$$

As it was pointed out by *K. Ito et al.*<sup>[17]</sup>,  $\gamma_{AlN}$  in CaO-Al<sub>2</sub>O<sub>3</sub> is constant, so  $C_N^{3-}$  should be in proportion to  $(B_{22}X_{22})^{3/2}$ . Fig. 8 was used to show the relationship between the measured  $C_N^{3-}$  by *K. Schwertfeger et al.*<sup>[18]</sup> and the concerned  $(B_{22}X_{22})^{3/2}$ . The line indicates that Eq. (34) is correct. Certainly, this line does not pass through the original point of coordinated axes. This is because between  $(B_{22}X_{22})$  and  $\alpha_{N^{3-}} = \gamma_{N^{3-}} (\% N^{3-})$  there must have a constant, as eg. (18) or (22).

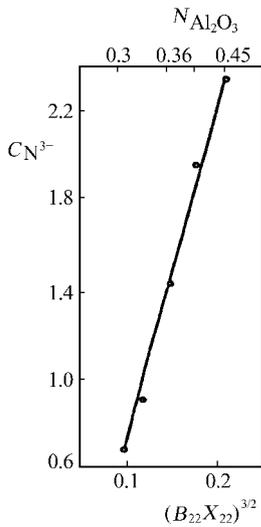


Fig. 8 The relationship of bonding basicity  $(B_{22}X_{22})$  and measured nitrogen capacity  $C_N^{3-}$  (1 600°C)

## 6 Conclusion

A modification of optical basicity based on bonding structure is suggested in this paper.

A thermodynamic model developed as a revised and widened model of G. W. Toop *et al.* is used to calculate  $X_{ij}$ . In liquid region the characteristics  $B_{ij}$  are evaluated as optical basicity. The bonding basicity in CaO-SiO<sub>2</sub>, CaO-Al<sub>2</sub>O<sub>3</sub> is defined as

$$B = B_{11}X_{11} + B_{14}X_{14} + B_{44}X_{44}$$

$$B = B_{22}X_{22} + B_{24}X_{24} + B_{44}X_{44}$$

Obviously various bond or various environments oxygen anion are used as element.

The property and utilization of bonding basicity are discussed in this paper.

(1) In liquid region, ( $B_{14}X_{14}$ ) only represents the activity of CaO. A reasonable converting relation between them is deduced. And the same is found between ( $B_{11}'X_{11}$ ) and  $\alpha_{\text{SiO}_2}'$ . Here the standard of  $\alpha_{\text{SiO}_2}'$  and ( $B_{11}'X_{11}$ ) all are 2CaO-SiO<sub>2</sub>. So  $B_{11}$ ,  $B_{14}$  are the other types of activity coefficients, and the bonding basicity is just the activity of that bond. The similar relationships were displayed in CaO-Al<sub>2</sub>O<sub>3</sub> system.

(2) Comparing with optical basicity, a discussion about desulphurization in CaO-SiO<sub>2</sub> is performed based on bonding basicity. It is considered that bond (44) directly takes part in the interfacial reaction, even it approaches to zero in liquid region. The sulphur in slag, however, behaves in two states: (Si—S—Ca) and (Ca—S—Ca). An equilibrium relation between them is suggested to be decided by basicity. This can be used to explain the variation of  $\gamma_{\text{CaS}}$ .

(3) The equilibrium constant of dissolving reaction of H<sub>2</sub>O in CaO-SiO<sub>2</sub> is calculated based on bonding basicity.

(4) A linear regularity between ( $B_{11}X_{22}$ )<sup>3/2</sup> and the measured capacity  $C_{\text{N}^3}$  indicates that the N<sup>3-</sup> dissolving in CaO-Al<sub>2</sub>O<sub>3</sub> slag is that inside the bond Al—N—Al.

## Acknowledgement

This paper is supported by The Chinese National Foundation of Natural Science.

The authors are very grateful to Prof Wei Shon-Kun for his helpful discussion.

## References

- [ 1 ] Jiang Guo Chang. The sulphur capacity and optical basicity of slag. Trans. of SUT. 1989 , NO. 3 , 257-266
- [ 2 ] K. Izoguchi , *et al.* Structure analysis of NaO ( or CaO )-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> glasses by X-ray photoelectron spectroscopy , J. of JIM , 1984 , 48 , 12 , 1179-1186
- [ 3 ] J. A. Duffy , *et al.* An interpretation of glass chemistry in terms of the optical basicity concept , J. Non-Cryst. Solids , 1976 , 21 , 373-410
- [ 4 ] R. Dron. Acid-base reaction in molten silicates. J. Non-Cryst. Solids , 1982 , 53 , 267-278
- [ 5 ] P. Balta , *et al.* An introduction of physical chemistry of glass ( in Chinese version ) , 1983 , 161-170 ; 220-235
- [ 6 ] Y. Tsimawalo , *et al.* Analysis of CaO-SiO<sub>2</sub> and CaO-SiO<sub>2</sub>-CaF<sub>2</sub> glasses by Raman spectroscopy , J. Non-Cryst. Solids , 1981 , 41 , 369-378
- [ 7 ] H. Gaye , *et al.* Modeling of the thermodynamic properties of complex metallurgical slags , 2nd Int. Symp. on Met. Slags & Fluxes , 1984 , 89-106
- [ 8 ] A. D. Pelton , *et al.* Computer assisted analysis of the thermodynamic properties and phase diagram of slags , 2nd Int. Symp. on Met. Slags & Fluxes , 1984 , 281-294
- [ 9 ] P. Sastri , *et al.* Application of the central atoms model to aluminosilicate melts , 2nd Int. Symp. on Met. Slags & Fluxes , 1984 , 377-391
- [ 10 ] T. Yokokawa , *et al.* Free energy of solution in binary silicate melts , Trans. JIM , 1969 , 10 , 3-7
- [ 11 ] G. W. Toop , *et al.* Activities of ions in silicate melts , Trans. AIME , 1969 , 224 , 873-887
- [ 12 ] C. R. Masson. The chemistry of slags — An overview , 2nd Int. Symp. on Met. Slags & Fluxes , 1984 , 4-44
- [ 13 ] R. H. Rein *et al.* Activities in the liquid solution SiO<sub>2</sub>-CaO-MgO-Al<sub>2</sub>O<sub>3</sub> at 1 600°C , Trans. AIME , 1965 , 233 , 415-425

- [ 14 ] M. L. Kappor , *et al.* The calculation of thermodynamic values and structural properties of liquid binary silicate systems , *Arch Eisenhuettenwes* , 1974 , 45(10) , 663-669
- [ 15 ] F. D. Richardson. Physical. chemistry of melts in metallurgy , Academic Press , London , 1974 , 291-307
- [ 16 ] T. Fuwa. A laboratory investigation about hydrogen in steel during steel-making , *Trans. JIM* , 1977 , 16(10) , 661-673
- [ 17 ] L. Ito , *et al.* Thermodynamics of nitrogen in CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slags and its relation with Fe-C<sub>sat</sub> melts , *Metall. Trans.* 1988 , 19B , 419-425
- [ 18 ] K. Schwerdtfeger , *et al.* Solubility of nitrogen in CaO-Al<sub>2</sub>O<sub>3</sub> melts in graphite crucible at 1600°C , *Arch. Eisenhuettenwes* , 1974 , 45(10) , 649-655

# A Laboratory Investigation on the Reduction of Carbon Bearing Mn-Ore Lump in Solid State<sup>\* 1</sup>

**Abstract** An investigation on the reduction of carbon bearing Mn-Ore lump in solid state was carried out with a variety of research methods. The results indicated the process can be divided into stages. The main feature in different stages is discussed in this paper. On the other hand, the reduction is thought to be composed of three sub-processes. The oxide transformation from higher valence to lower valence progresses pursuant to unreacted core model. The metal separation shows a characteristics of typical homogeneous reaction model. The slag phase formation is detected as the observed grape-like sphere. In some cases, these three sub-processes are found to be co-existed in the same sample. The reduction mechanism is also discussed. Essentially, the reduction is a gas-solid reaction in which CO acts as an intermediate agent. The reduction rate in pregnant period is found to be limited by CO and CO<sub>2</sub> transfer inside the lump. For the fast reaction period it is limited by Boudouard reaction as well as CO and CO<sub>2</sub> transfer inside the lump.

## 1 Introduction

The prereduction in solid state is a significant procedure for producing ferro-alloy through smelting reduction in a converter. It is considered that the operation of final reduction can be facilitated a lot by adopting prereduction. On the

---

\* In collaboration with Jiang Guochang, Xu Jianlun. Reprinted from Proc. 6th Int. Iron & Steel Congr., ISIJ, Oct. 21-26, 1990, Nagoya, Japan, Vol. 1, pp. 240-247

other hand , to modify the structure of mineralogic phases with prereduction is an important way to accelerate the final reduction process<sup>[1~3]</sup>. In addition to this , the successful application of metallized iron pellets in BF process<sup>[4]</sup> is a convincing evidence to show that the prereduction for melting HC-FeMn in BF or Mn-Si alloy in SAF will cause an obvious improvement in production indices.

For developing prereduction technology this investigation was performed through an in line measurement of reduction ratio with an off-gas absorption system. After reduction the mineralogic species in the samples were identified by means of a new developed chemical way and X-ray diffraction. The reduced samples were also analyzed with EPMA and optical microscope. The experiment scheme is shown in Table 1. The main composition of used ore is 21.22% T. Fe , 33.57% T. Mn , 14.12% SiO<sub>2</sub>. The useful mineralogic phases are MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>.

**Table 1 Experiment Scheme**

Run	Proportion inside lump			Reduction temperature( °C )	Reaction time ( min )
	ore	lime	carbon		
1	100	20	10	1 000	90
2	100	20	20		90
3	100	20	20 *		90
4	100	20	* *		90
5	100	20	10		60
6	100	20	20		60
7	100	20	10		30
8	100	20	20		30
11	100	20	10	1 100	30
12	100	20	20		90
13	100	20	20 *		90
14	100	20	* *		90
15	100	20	10		60

(cont d)

Run	Proportion inside lump			Reduction temperature(℃)	Reaction time (min)
	ore	lime	carbon		
16	100	20	20	1 200	60
17	100	20	10		30
18	100	20	20		30
21	100	20	10		90
22	100	20	20		90
23	100	20	20 *		90
24	100	20	* *		90
25	100	20	10		60
26	100	20	20		60
27	100	20	10		30
28	100	20	20		30

Notes : \* fine particle

\* \* no carbon addition inside lump , but to be covered with carbon particles

## 2 The Stepwise Characteristics of Reaction and the Function of Fe in Facilitating MnO Reduction

As shown in Table 1 ,there are two groups. Run 1-4 and 11 ,12 ,14 make up a category of weaker reduction cases. And the others are of stronger reduction cases. The in line measured curves of reduction ratio under various conditions are shown in Fig. 1. Obviously ,the whole process in weaker reduction cases can be divided into 3 steps ,namely ,pregnant period , fast reaction period and final period. Comparatively ,the pregnant period in stronger reduction cases is not so clear ,only two periods are considered.

The characteristics and the corresponding evidences of reduction in various periods are shown in Table 2.

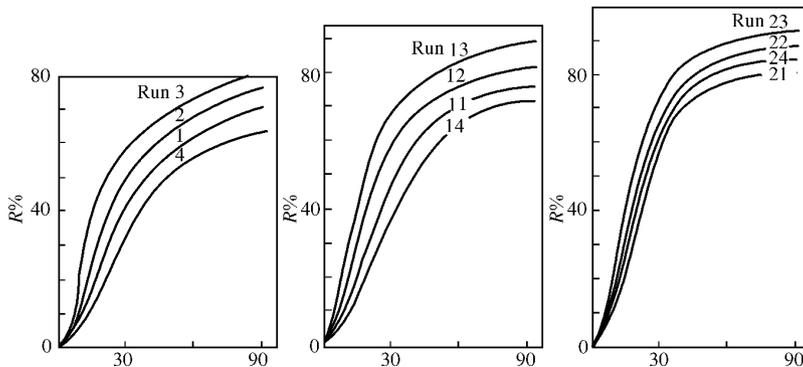


Fig. 1 The in line measured reduction ratio curves

**Table 2 The feature of reduction in various periods and its evidences**

reduction condition	period	reduction features	evidences
weaker	pregnant	<ol style="list-style-type: none"> <li>1. an unstable heat transfer process under a temperature lower than the given one</li> <li>2. <math>MnO_2 \rightarrow Mn_2O_3</math> (incomplete)</li> <li>3. <math>Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO</math> (incomplete)</li> </ol>	<ol style="list-style-type: none"> <li>1. <math>n_{CO}/n_{CO_2}</math> too low, see Fig. 9</li> <li>2. for <math>MnO_2 \rightarrow Mn_2O_3</math> completely <math>R = 17\%</math>, for <math>Fe_2O_3 \rightarrow FeO</math> completely <math>R = 10.6\%</math>, for ending pregnant period the measured <math>R</math> is about 10%</li> </ol>
	fast reaction	<ol style="list-style-type: none"> <li>1. <math>Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO</math> (incomplete)</li> <li>2. <math>Fe_3O_4 \rightarrow FeO \rightarrow Fe</math> (incomplete)</li> </ol>	<ol style="list-style-type: none"> <li>1. for Fe separation completely <math>R = 32\%</math>, for <math>MnO_2 - MnO</math> completely <math>R = 34\%</math>, at the end of this period <math>R = 45\% - 50\%</math></li> <li>2. metallic Fe was detected</li> <li>3. Fig. 2</li> </ol>
	final	<ol style="list-style-type: none"> <li>1. <math>Mn_3O_4 \rightarrow MnO</math></li> <li>2. <math>FeO \rightarrow Fe</math></li> </ol>	<ol style="list-style-type: none"> <li>1. the final <math>R = 66\%</math></li> <li>2. Fig. 2</li> <li>3. iron based metallic phase, Table 3</li> </ol>
stronger	fast reaction	all reactions happening in weaker reduction to be viewed the progression in various parts differs from each other a lot	<ol style="list-style-type: none"> <li>1. at the end <math>R = 60\% - 65\%</math></li> <li>2. Fig. 2</li> <li>3. Fig. 4</li> </ol>
	final	<ol style="list-style-type: none"> <li>1. main reaction is <math>MnO \rightarrow Mn</math></li> <li>2. no carbide formation</li> <li>3. iron based metal</li> <li>4. slag phase emerges</li> </ol>	<ol style="list-style-type: none"> <li>1. Fig. 2</li> <li>2. Table 3</li> <li>3. Fig. 8</li> </ol>

Note :  $R$ —reduction ratio

The research is supported by The National Foundation of Natural Science.

In this investigation , a phenomenon shown in Fig. 2 , that the content of MnO in lumps tends to decrease but the metallizing ratio is increased more even if the temperature is only higher than 1 100℃ , was found. This is resulted from that much iron is contained in the used manganese ore. Fig. 3 displays the so called element shift phenomenon in micro region during reduction process. Namely , iron separates in advance and this in turn causes the increase of % Mn in the adjacent residual oxide phase. Then the content of Mn in separated metallic phase gradually goes up. In fact , as indicated by EPMA ( Table 3 ) the separated metallic phase in the sample reduced in stronger cases for 90 min is still iron based. Hence from the begining to the end the activity of manganese in separated metallic phase is always quite low. This consequently causes a lower starting temperature of reaction in this experiment , and this is exactly the way of Fe co-existing in ore to promote the reduction of MnO.

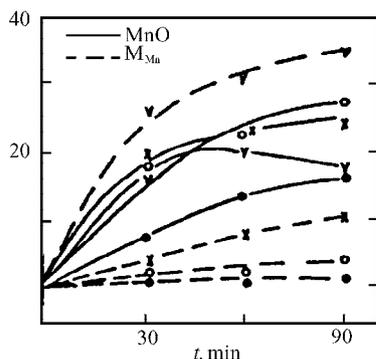


Fig. 2 The chemical way analyzed % MnO inside lump and metallizing degree

reduction temperature	ore: carbon inside lump
1 000℃	. 100: 10
1 100℃	. 100: 10
1 100℃	x 100: 20
1 200℃	v 100: 20

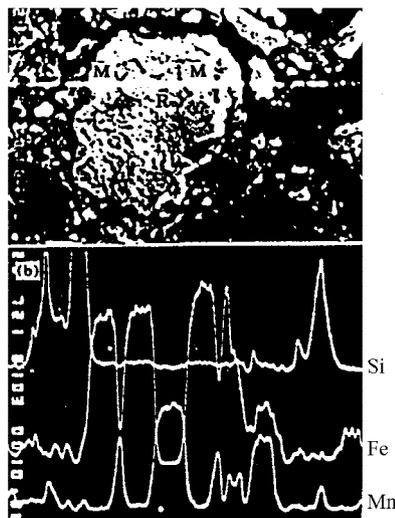


Fig. 3 The element shift phenomenon in micro region during reduction ( detection of EPMA )

**Table 3 The EPMA point measurement result of metallic phase**

Run	22	28	3	23
% Fe(average)	73.08	97.11	97.43	85.66
% Mn(average)	20.73	0.98	0.52	11.55
% C	0.91-1.03	0.67-0.86	0.57-1.32	1.37-2.35

### 3 The Three Subprocesses

The whole reduction process was revealed as composed of three sub-processes : the transformation of oxide from higher valency to lower valency , the separation of metal and the formation of slag phase. Fig. 4 indicates that  $Mn_2O_3$  ,  $Mn_3O_4$  , MnO and Fe coexist in the sample of Run 2. In that of Run 22 , however , not only the formed slag phase but also some residual oxide with higher valence can be viewed.

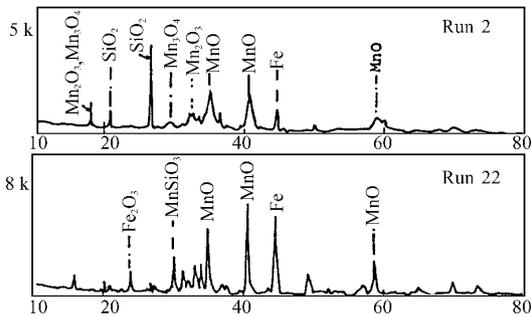


Fig. 4 The X-ray diffraction results of Run 2 and 22

This phenomenon points out that these three sub-processes develop simultaneously in the whole sample , meanwhile in view of a micro region they happen one by one.

#### 3.1 The characteristics of transformation of manganese oxide from higher valency to lower valency

Fig. 5 is the typical feature of the process  $Mn_2O_2 \rightarrow Mn_3O_4$  under optical microscope. And Fig. 6. is that of the process  $Mn_3O_4 \rightarrow MnO$ . For check up , EPMA was used also to make point measurement on the particle shown in Fig. 6. It was found that the proportion of % Mn in the core and in its periphery is about 0.91. This is just the theoretical proportion of % Mn in  $Mn_3O_4$  as well as in MnO. Hence we claim that the transformation of manganese oxide progresses pursuan-

ting to the unreacted core model.

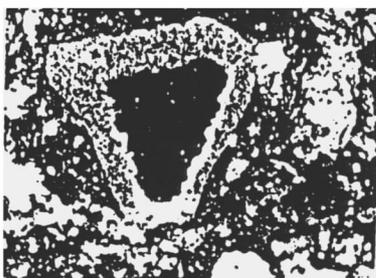


Fig. 5 The characteristics of  $\text{MnO}_2 \rightarrow \text{Mn}_3\text{O}_4$  (1 000°C , 30 min , optical microscopy , polarized light ) obeying unreacted core model , black or dark-brown —  $\text{MnO}_2$  and  $\text{Mn}_2\text{O}_3$  , red-brown —  $\text{Mn}_3\text{O}_4$



Fig. 6 The characteristics of  $\text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$  (1 000°C , 30 min , optical microscopy , polarized light ) obeying unreacted core model , red-brown —  $\text{Mn}_3\text{O}_4$  , green —  $\text{MnO}$

### 3.2 The separation of metallic phase

Initially most of the separated metallic particles are of irregular shaped. And they spread out inside smaller oxide particles or around some bigger oxide particles or near its internal cracks. For a prolonged reaction time or for a stronger reduction condition such a phenomenon , that much but not big separated metallic particles scatter inside larger oxide particles , was revealed as Fig. 7. Certainly this is the feature of a homogeneous reaction. In the strongest reduction case the agglomeration of separated metal was discovered. It is even able to encircle the residual oxide as shown in Fig. 8.

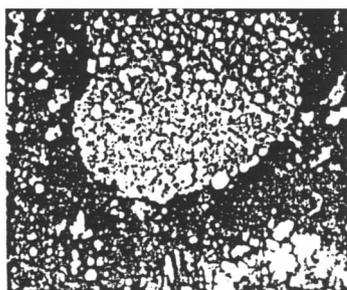


Fig. 7 A phenomenon showing homogeneous reaction model during metal separation

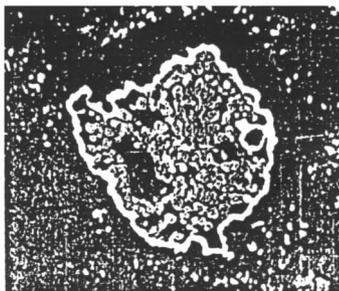


Fig. 8 The agglomeration of metallic phase and the formation of slag phase(optical microscopy)

### 3.3 The formation of slag phase

In Fig. 8 the green residual oxide is clearly of grapelike. Pursuanting to EP-MA it is unreduced MnO. And among the grapelike sphere there is the formed slag phase — a silicate.

## 4 Whether it is a Solid-Solid Reaction or a Gassolid Reaction

According to this experiment the reduction of carbon bearing manganese ore lump is considered to be a gas-solid reaction. This claim can be elucidated based on the following phenomena.

(1) As Fig. 1 the reduction ratio of Run 4 is only slightly smaller than that of Run 1. And it is the same for the comparison between Run 14 and 11. Contrarily, the reduction ratio of Run 24 is larger than that of Run 21. In fact, there were no carbon addition inside the lump of Run 4, 14, 24. If the progression of reduction depended upon the diffusion of carbon in solid state, the reduction ratio of Run 4, 14, 24 should be quite low because the diffusion distance in these cases is quite long.

(2) In weaker reduction cases the transformation of oxide valency progresses during pregnant period and the preceding stage of fast reaction period. It is well known that from  $MnO_2$  to  $Mn_2O_3$  there are a volume expansion of 5%, from  $Mn_2O_3$  to  $Mn_3O_4$  a volume shrinkage of 2.3% comes about and finally from  $Mn_3O_4$  to MnO another volume shrinkage of 11.7% emerges<sup>[5]</sup>. So this transformation has to be accompanied by a dramatical increase of internal porosity and which in turn result in the facilitation of gas transfer inside the oxide phase. If the reduction depended on carbon diffusion in solid state, the increase of internal porosity should obstruct the reaction.

(3) Fig. 5–7 are naturally the evidences claiming that the reduction depends upon the action of CO. Furthermore, the reason of that the reduction to be converted from unreacted core model to a homogeneous reaction model can be considered as the increase of internal porosity.

## 5 The Rate Limiting Ring

### 5.1 The rate limiting ring of pregnant period

In pregnant period the rate limiting ring is related to two features of reduction process. One of them as aforementioned is a poor porosity inside the oxide phase. And the second is that the real reduction condition is even weaker than the given one.

C. Bryk *et al.* reported a paper which concerned the temperature measurement at the center of a carbon bearing iron pellet during its reduction. They indicated that if the temperature of furnace was given as 1 000–1 100°C, for raising the temperature at the center of a pellet with diameter of 19–32 mm up to 900–1 000°C, 10–16 min was needed<sup>[6]</sup>. Thus in this experiment the reduction during pregnant period is such a one progressing under an unstable heat transfer condition. In such a case, the reduction itself is whether a rate limiting ring or one of the rings? A further judgement is needed for this problem.

It is well known, that the following equation is useful for the judgement of rate limiting ring if the reaction progresses along unreacted core model<sup>[7]</sup>.

$$t/t_f = [(1 - R)^{1/3}] + Q^2[1 + 2(1 - R) - 3(1 - R)^{2/3}] \quad (1)$$

Here,  $R$  denotes reduction ratio,  $t$  denotes reaction time,  $t_f$  is the time needed to raise  $R$  to 100%.  $Q^2$  is the criterion for judgement. If  $Q^2 < 1$ , the limiting ring is the transfer of gas through porous solid product layer. As the above discussion, the process during pregnant period does obey unreacted core model. And the resistance for transfer of gas inside lump is similar to that in solid product layer. These two points make us possible to utilize Eq. (1) safely in judgement.

Using  $R_1$  to denote the reduction ratio at the end of pregnant period and  $t_1$  to denote the lasting time of pregnant period we have  $t_f = 100t_1/R_1$ . Taking Run 1 as an example to calculate  $Q^2$  got it was about 25. Therefore, the reduction during pregnant period is controlled by the gas transfer inside lump.

## 5.2 The rate limiting ring of fast reaction period

The relationship of  $n_{CO}/n_{CO_2}$ , the proportion of accumulated mol amount of CO and CO<sub>2</sub> in off-gas, versus reaction time is displayed in Fig. 9. During the fast reaction period of Run 3 and 23 the relationship is linear. Hence the relative releasing amount of CO is linearly increasing. Comparatively, the curve slope of Run 3 is much smaller than that of Run 23. This indicated that these two experiments went forward under different  $P_{CO}/P_{CO_2}$ , the proportion of partial pressure of CO and CO<sub>2</sub>. Since the proportion of Run 3 is smaller, its reduction ratio is lower. The unique difference of the experiments in reduction condition is only that Run 23 got a higher temperature of 200°C. Thus in thermodynamics and kinetics the difference of  $P_{CO}/P_{CO_2}$  is related with the difference of temperature. And  $P_{CO}/P_{CO_2}$  is possibly to be considered as the characteristics of reduction process.

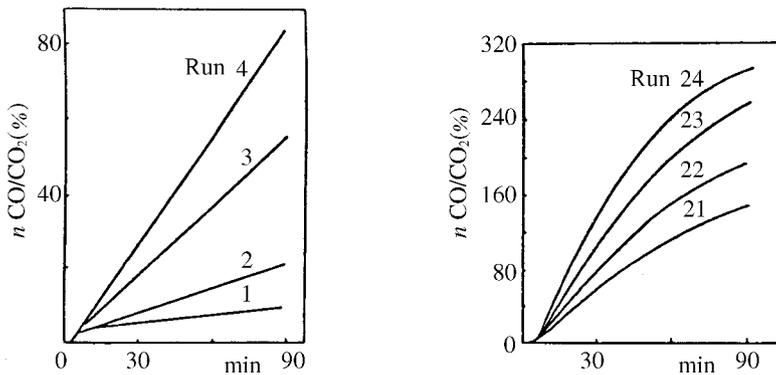
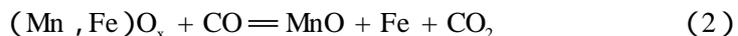


Fig. 9 The proportion of accumulated mol amount of CO and CO<sub>2</sub> in off-gas

It is very difficult to measure directly  $P_{CO}/P_{CO_2}$  inside lump, but it is possible to discuss the feature of  $P_{CO}/P_{CO_2}$  based on Fig. 9. According to Table 2, the reaction in the period the value of  $P_{CO}/P_{CO_2}$  or  $n_{CO}/n_{CO_2}$  in which varies linearly is



Pursuant to the variation of free energy in every steps of manganese transformation from higher valency to lower valency, the equilibrated  $P_{CO}/P_{CO_2}$  under 1 000

$-12\ 000^{\circ}\text{C}$  is lower than  $10^{-4}$ . And under the same temperature that of FeO indirect reduction and Boudouard reaction is 2.0–2.6 and infinite large respectively. Because, in magnitude, the  $P_{\text{CO}}/P_{\text{CO}_2}$  of Run 3 and 23 is only possibly to be compared with that of FeO indirect reduction, the later one can not be the rate limiting ring. The transformations of oxide valency which can not approach to their equilibrium, seem to be limited by the resistance of gas transfer inside lump. On the other hand, however, with that resistance as an unique reason can not explain the difference of reduction rate between Run 3 and 23. Boudouard reaction seems to be the another factor limiting the rate.

The same conclusion can be deduced through the comparison of Run 1 and 21, or Run 2 and 22, or Run 4 and 24.

Based on the above elucidation it is also possible to understand the comparison among Run 1, 2, 3. They were all reduced under  $1\ 200^{\circ}\text{C}$ . The only difference is the average transfer distance of gas inside lump. The average distance of Run 1 is longer than that of Run 2. Because in spite of that the carbon particle with the same size was used in both cases, the carbon addition of Run 1 was less. The average distance of Run 3 is shorter than that of Run 2. Because nevertheless the same carbon addition was used in both cases, the carbon particle used in Run 3 was smaller. This is the reason to elucidate why the  $P_{\text{CO}}/P_{\text{CO}_2}$  or  $n_{\text{CO}}/n_{\text{CO}_2}$  of Run 1 is the smallest, that of Run 3 is the largest. This is also the way to understand why the reduction ration of Run 1 is the lowest, that of Run 3 is the highest. Certainly, this discussion confirms the role of gas transfer inside lump again.

The same conclusion can be deduced through the comparison among either Run 11, 12, 13, or Run 21, 22, 23.

Surprisingly, nevertheless the reduction ratio of Run 4 is lower than that of Run 1, its  $P_{\text{CO}}/P_{\text{CO}_2}$  or  $n_{\text{CO}}/n_{\text{CO}_2}$  is even higher than that of Run 3. It should be noticed that there were no carbon addition inside the lump of Run 4. It was reduced under the cover of carbon particles. Surely, the average transfer distance of Run 4 is much longer than that of Run 1. This should cause a much smaller  $P_{\text{CO}}/P_{\text{CO}_2}$  for Run 4. The carbon amount used in Run 4, however, is much more than that in Run 1. This makes a better probability for  $\text{CO}_2$  to react with carbon, so more CO emerges from Boudouard reaction. Corresponding to this, in Fig. 9

Run 4 gets a curve even over that of Run 3. Doubtlessly, in the case of Run 4 CO should form outside the lump. Only little of this CO can penetrate into the lump due to the flow of carrier gas. Hence the  $n_{CO}/n_{CO_2}$  of Run 4 is impossible to be considered as the reduction potential inside the lump.

The same analysis can be made for Run 14 and 11. Notwithstanding, if the temperature is high enough, then much more CO emerging outside can penetrate into the lump. This is brought about by two factors. One of them is the increased gas diffusion coefficient under a higher temperature. The another is a larger porosity caused by a quick volume variation of oxide during reduction under a higher temperature. Through this way it is possible to understand why the  $P_{CO}/P_{CO_2}$  and in turn the reduction ratio of Run 24 may be higher than that of Run 21.

For check up, Eq. (1) was used again. Here  $R$  denotes the carbon consumption. And the oxidation of carbon particle was thought to be a process obeying unreacted core model due to the high temperature and the fine particle. Considering that in the case of more carbon addition the mol amount of oxygen and carbon is almost equal to each other in this experiment, and the offgas mainly is CO during fast reaction period, so it is reasonably to take the measured reduction ratio as the consumption ratio of carbon. Take Run 22 as example, the calculated  $Q^2$  is about 3. This result is in good agreement with the above discussion.

## 6 The Conclusion Remarks

It is indicated that the prereluction of carbon bearing manganese ore lump is composed of three sub-processes. Namely the transformation of oxide from higher valency to lower valency, the separation of metallic phase and the formation of slag phase. The transformation of oxide was proved to be a process obeying unreacted core model and the separation of metallic phase was thought to be pursuant to homogeneous reaction model. For a whole sample, these three sub-processes progress simultaneously, however, in a view point of micro region they happen one by one.

According to the reduction condition the whole process can be divided into

2 or 3 periods. The main reactions happening in these periods were discussed and the final reduction ratio of these periods was given.

The mechanism of prereduction was analysed. It is claimed that CO plays a role of intermediate reduction agent. The rate in different periods is controlled by different factors. The rate of pregnant periods is controlled by gas transfer inside a lump. During fast reaction period it is limited by Boudouard reaction as well as gas transfer inside lump.

## References

- [ 1 ] Jiang Guochang , Xu Kuangdi , Shanghai Metal , 1988(2) , 3-12
- [ 2 ] Jiang Guochang , Internal Report of Dept. of Process Met all. KTH Sweden , R12/86 , 1986-07025
- [ 3 ] Jiang Guochang , Xu Jianlun , Xu Kuangdi , Proc. of 2nd National Experts' Meeting on Smelting Reduction , Beijing , June , 1988
- [ 4 ] A. N. Lamm , A Calculating Analysis of Modern Process of Blast Furnace ( in Chinese ) , The Metallurgical Industry Publishing Corp. 1987 , p. 82
- [ 5 ] Li Guangyi , Master Thesis of Shanghai Univ. of Technology , 1989
- [ 6 ] C. Bryk , W-K. Lu , Ironmaking and Steelmaking , 1986 , 13(2) , 70-75
- [ 7 ] Mo Dingcheng , Metallurgical Kinetics , The publisher of Middle South Univ. of Technology , 1987 , 193-208

# 锆在钢液精炼过程的行为研究<sup>\* 1</sup>

**摘要** 本文通过感应炉试验研究,介绍了锆对钢液脱氧、净化和夹杂物构成变化的作用,并与钙作了对比,结果表明锆可替代钙用于钢的终脱氧,终点氧可达0.0005%以下,并可使 $\text{Al}_2\text{O}_3$ 夹杂变质为 $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ 复相夹杂。

## 1 前言

铝和钙是目前钢液精炼中最常用的净化剂。和铝比较,锆的脱氧、脱氮能力更强,和钙相比,锆在钢水中的溶解度较钙高数千倍,而蒸气压又低10个量级,所以在钢液精炼过程中锆易得到充分利用。另一方面,锆对钢中的硫化物夹杂也有某种变质作用。为了探索在喷射冶金中应用锆作为一种新型粉剂的可能性,有必要进一步研究它在钢液精炼过程中的行为。

## 2 试验研究方法

试验在中频感应炉中进行,钢水量为15~20 kg,所用原料是40号碳钢。炉料熔化后,造 $\text{CaO} \cdot \text{CaF}_2$ 渣预脱氧使渣变白后,用ZrSi合金加锆。合金组成是21.34% Zr和46.40% Si,其余为Fe。一俟锆加入熔池,即开始用Mo/MoO<sub>2</sub>探头测定氧位。同时又用真空吸管取样,由宝钢总厂的Leco仪测定总氧量,余下的试样供夹杂物检验之用。试验中使用了本校的JCX-733型电子探针及上海交大自制的金相图像分析仪。

\* 本文合作者:壮云乾、蒋国昌、郭雷。原发表于《上海金属》,12(5) 24~26(1990)

### 3 脱氧试验的结果及讨论

共进行了四次 Zr 脱氧试验. 脱氧曲线示于图 1 和图 2. 由图可见: 锆是一种强脱氧剂, 脱氧终止时氧位可降低到 0.000 5% 以下, 总氧量在 0.001 0% 左右. 热力学计算表明, 此时的氧位是由 % Zr 控制的. 以第四次试验为例, 终点时 % Zr = 0.03, % O = 0.000 4.

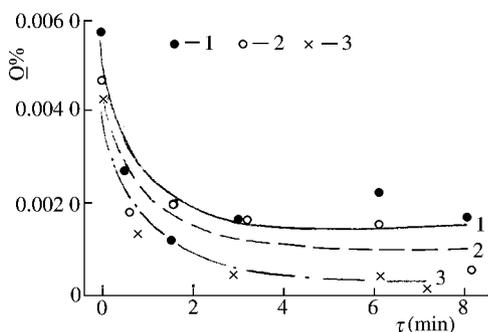


图 1 三次脱氧试验(加 0.15% Zr, 1600 ~ 1650)中的脱氧曲线(浓差电池测定结果)

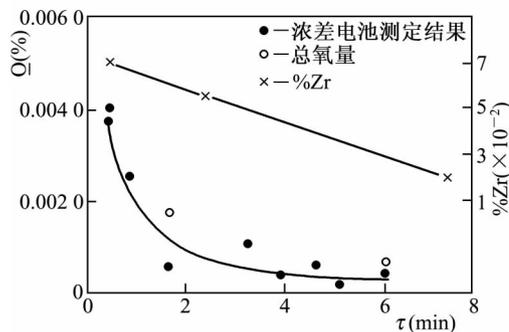


图 2 第四次试验(加 0.07% Zr, 1630)的脱氧曲线和 % Zr 的变化

$$\lg f_{Zr} = - 12 \cdot \% O = - 0.004 8$$

$$f_{Zr} = 0.99$$

$$\lg f_O = - 0.160 \% O - 0.21 \cdot \% Zr = - 0.07$$

$$f_O = 0.85$$

$$K = 0.99 \cdot \% Zr (0.85 \cdot \% O)^2 = 3.47 \times 10^{-9}$$

这里的相互作用参数均取日本学术振兴会推荐值<sup>[1]</sup>, 而该会又给出

$$\lg k = - 57 000/T + 21.8$$

1 900 K 下,  $k = 6.31 \times 10^{-9}$ , 与试验结果相当接近. 考虑到测定误差及计算中忽略了 C、Al 等元素的影响, 可以认为在试验条件下 Zr—O 之间已达成平衡.

锆加入后 3 min 左右 Zr—O 之间可达成平衡. 本试验是在感应搅拌条件

下进行的脱氧速率较快,由数据处理得出氧含量随时间的变化为

$$\ln \% \underline{O} = -0.24\tau + 3.8$$

即脱氧速率常数为  $R = 0.24 \text{ min}^{-1}$ .

本试验中研究了 Zr 加入量为 0.07% 及 0.15% 对脱氧的影响. 但图 1 与图 2 表明, 它们的终点氧量几乎是一样的. 这是因为:  $\underline{Zr}-\underline{O}$  平衡曲线上有一个  $\% \underline{O}$  最低的点, 计算指出此点是  $\% \underline{Zr} = 0.10\%$  相应的  $\% \underline{O}$  为 0.000 2%, 见图 3. 如果只要求目标氧位低于 0.000 5%, 那么 Zr 加入量可按 0.03%  $\underline{Zr}$  控制.

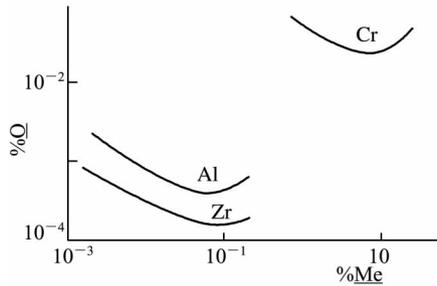


图 3  $\underline{Zr}-\underline{Ca}$  平衡曲线(1600 )

试验中还在 Zr 与 Ca 加入量相等的条件下比较了它们的脱氧效果, 见表 1. 虽然起始氧量较低, 用 Zr 脱氧时也达到 61.4% 的效率, 和用 Ca 脱氧时的相近. 这说明用 Zr 取代 Ca 来脱氧是有希望用于实际生产的.

表 1 Zr 与 Ca 脱氧的比较

脱氧剂	$\% \underline{O}_i$	$\% \underline{O}$		$\frac{\% \underline{O}_i - \% \underline{O}_e}{\% \underline{O}_i} (\%)$
		首次加入后	二次加入后	
Ca	0.010 5	0.007 0	0.003 5	66.6
Zr	0.007 0	0.003 6	0.002 7	61.4

## 4 夹杂物的变化

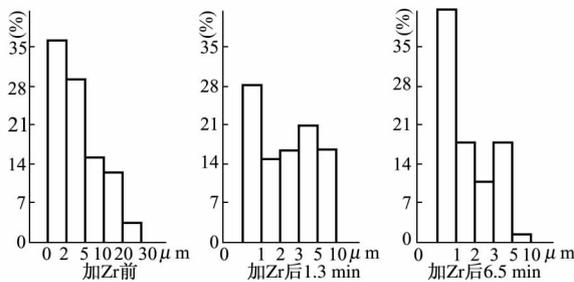


图 4 铁脱氧过程中夹杂物粒度分布的变化

图 4 是用金相图像分析仪测定试验 4 中脱氧产物粒度分布的结果. 测定所用的试样是用真空吸管采取的. 这种方法可以用来观察脱氧过程中夹杂物的相对变化. 但因为试样冷却较快, 夹杂粒度的绝对值要比

用标准方法测定夹杂时的小。

从图 4 可见,加入 ZrSi 后,脱氧产物的粒度是先变大,然后再变小的。这说明,在感应搅拌条件下, Zr 的脱氧产物至少有相当一部分是通过凝聚长大而排除的。这和电子探针的检测结果吻合。由于用 Al 预脱氧,加 Zr 之前是  $\text{Al}_2\text{O}_3$  夹杂,加入 Zr 后则变成  $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  复相夹杂,这证明了 Zr 对  $\text{Al}_2\text{O}_3$  夹杂有和 Ca 类似的变质作用。

表 2 比较了加 Zr 量不同时夹杂物平均粒度的变化,不难发现, Zr 加入较多时夹杂较小,这符合于脱氧的普遍规律,即加入量增多时钢水单位体积内所含的夹杂核心数  $N$  较大,而夹杂的终极半径  $r$  就取决于  $N$ 。

表 2 不同加 Zr 量对夹杂平均直径的影响

加 Zr 量(%)	0.07	0.15	0.25
平均直径( $\mu\text{m}$ )	3.08	2.35	1.87

E. T. Turkdogau 指出如下的规律:

$$r = 0.23N^{-1/3} (\% \underline{O}_i - \% \underline{O}_e)^{1/3}$$

设起始氧位  $\% \underline{O}_i$  是 0.004 0 ~ 0.005 0%, 终点氧位  $\% \underline{O}_e$  是 0.000 5%, 则

$$r = (0.034 \sim 0.037)N^{-1/3}$$

## 5 结束语

(1) 锆是强脱氧剂,脱氧能力超过铝。本试验条件下终点氧位在 0.000 5% 以下,总氧量 0.001 0% 左右。

(2) 锆可取代钙用于终脱氧。在起始氧位为 0.003 0% ~ 0.004 0% 的条件下加 0.03% Zr 即可。

(3) 本试验条件下,加锆 3 min 后 Zr 与 O 即达成平衡。原先用 Al 预脱氧时生成的  $\text{Al}_2\text{O}_3$  夹杂被 Zr 变质而成  $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  复相夹杂,所以含锆的脱氧产物有相当一部分是通过凝聚长大而排除的。

## 参 考 文 献

[ 1 ] 日本学术振兴会 19 委. 制钢反应の推奖平衡值

[ 2 ] E. T. Turkdogan. 钢的脱氧 提高钢质量的途径. 上海科技情报所编, 1973

## An Investigation on the Behaviour of Zr in the Process of Steel Refining

**Abstract** An investigation of the effects of Zr on deoxidation , cleanness and change of inclusion formation in molten steel was carried out in an induction furnace. It was demonstrated that in stead of Ca , Zr can be used as a final deoxidizer , resulting in the final oxygen content less than 0.000 5% . And moreover , the inclusion of  $\text{Al}_2\text{O}_3$  type was modified to form a complex inclusion of  $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  after ZrSi being added.

## 铁液透过熔渣层吸氮的动力学研究<sup>\* 1</sup>

**摘要** 氮在熔渣中有一定的溶解度,在熔渣与铁液间有一定的分配比。因此可把铁液透过熔渣吸氮的过程分解为两个子过程:熔渣由气相吸氮以及渣中的氮向铁液迁移。比较各种条件下两个子过程的速率现象,就可控制铁液吸氮的速率。本文研究了温度、渣组成、界面积等因素对铁液经由CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>渣系吸氮的影响。结果表明,两个子过程的律速环节均是氮在渣中的传输。本文还分别给出了它们的活化能及传质系数,在此基础上提出了铁液通过渣层吸氮全过程的数学模型。

氮是钢中常存微量元素,取决于冶炼方法及钢的成分,通常含量在0.004%~0.04%之间<sup>[1]</sup>。氮除了在奥氏体不锈钢、沉淀硬化不锈钢和热强钢中具有稳定奥氏体和弥散强化等有益作用外,多数情况下都对钢的性能有害。特别是70年代以来,由于超纯铁素体不锈钢、超低碳深冲用钢及石油管线用钢等钢种的出现并得到广泛应用,对钢中含氮量提出了愈来愈严格的要求,希望能将氮含量降到0.003%,甚至0.002%以下的水平<sup>[2]</sup>。但现有的钢液精炼手段对 $\leq 0.004\%$ 以下氮量的去除收效甚微,难以满足上述要求<sup>[3]</sup>。

为了生产低氮钢,首先要尽力避免钢水吸氮。而用熔渣覆盖熔池是最常用的技术措施。近年来,许多研究发现,不同的熔渣具有不同的氮容量,且氮可在气-渣-钢三相之间传递<sup>[4,5]</sup>。从而启迪人们,可以通过有关的热力学和动力学基础研究来优化渣层的“隔氮”效果。本文报道我们在这方面所进行的工作。

\* 本文合作者:蒋国昌、凌天鹰。原发表于《上海工业大学学报》,11(4),380~388(1990)

## 1 试验方法

试验在气氛可控的高温碳管炉中进行. 装置系统如图 1 所示. 试验包括熔渣由气相吸氮、铁液由熔渣吸氮及熔渣的氮透过率三个部分. 其试验方法如下.

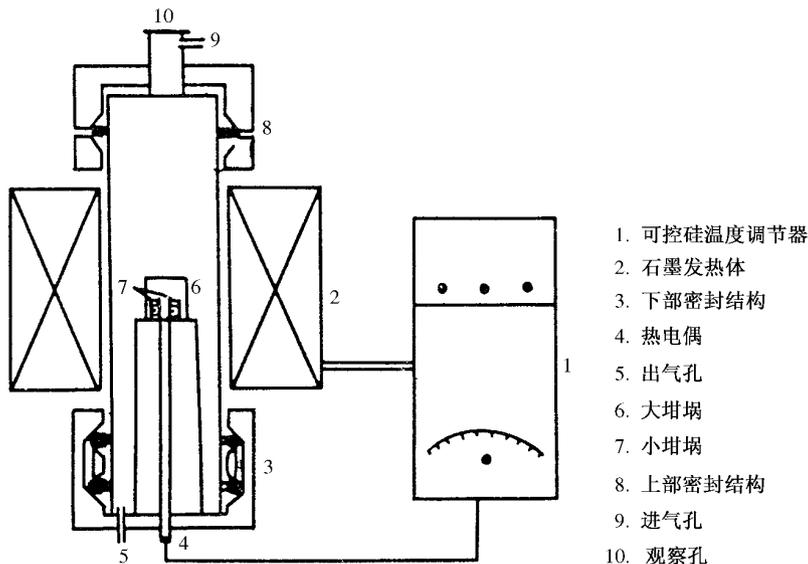


图 1 试验装置图

### 1.1 熔渣由气相吸氮

在图 1 所示的系统中, 每次试验都在炉内放置 3 个石墨坩埚. 内置有用化学纯试剂预熔配制的不同成分  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  渣 6 g, 炉管密封并在氩气气氛下升温至试验温度. 而后再将经过脱氧、去水的分析用标准混合气通入其中, 其组成为:  $x_{\text{CO}} = 0.4$ ,  $x_{\text{N}_2} = 0.6$  ( $x$  表示摩尔分数). 反应温度为 1 500 ~ 1 600 (以 1 550 为基准温度). 试验开始后, 每隔 1 h 取出一个坩埚. 急冷后用经典的 Kjeldahl 法分析渣中含氮量.

### 1.2 铁液从熔渣吸氮

试验装置同上, 但改用刚玉坩埚. 其中置 6 g 含 0.018% Al 的纯铁及含氮 0.3% 的预熔渣. 试验在氩气氛及恒温下进行. 试验开始时, 铁水含氮量为 0.002 3%. 以后每隔 1 h 取出一个坩埚, 分别用 Kjeldahl 法测定渣和铁中的含氮量.

### 1.3 CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> 渣的氮透过速率

在图 1 所示的装置中,放入盛有 6 g 纯铁(含 Al 0.018%)及 6 g 低氮预熔渣的刚玉坩埚.先在氩气氛下加热到预定温度,再改用  $x_{\text{CO}} = 0.4$ ,  $x_{\text{N}_2} = 0.6$  的标定用混合气体取代氩气.开始试验之后,每隔 1 h 取出一只坩埚,用 Kjeldahl 法测定铁中含氮量.

## 2 试验结果

### 2.1 CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> 熔渣由气相吸氮的速度

在这个试验中,曾改变过混合气体流量、温度、熔渣组成、气渣两相的面积等四个参数,其结果分别示于图 2, 3, 4, 及图 5.

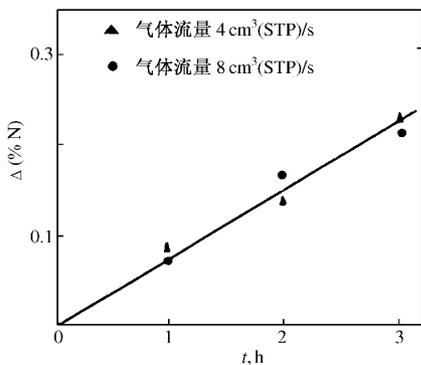


图 2 气流量对熔渣吸氮的影响

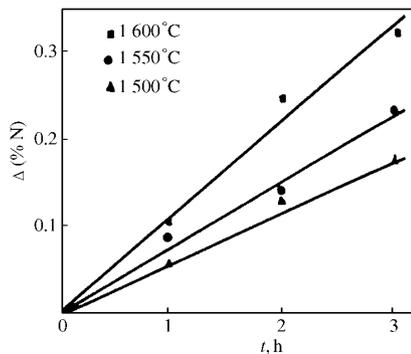


图 3 温度对熔渣吸氮的影响

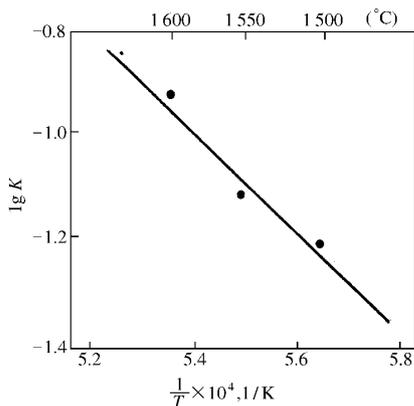


图 4 吸氮速率常数与温度的关系

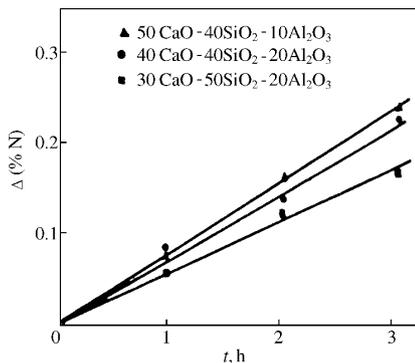


图 5 熔渣组成对熔渣吸氮的影响

图2表明,1550℃时混合气体流量由4 cm<sup>3</sup>/s提高到8 cm<sup>3</sup>/s时40% CaO-40% SiO<sub>2</sub>-20% Al<sub>2</sub>O<sub>3</sub>熔渣的吸氮速率不变.下尾聪夫等曾用50% CaO-50% Al<sub>2</sub>O<sub>3</sub>渣做过类似试验.认为气体流量有明显的影响<sup>[6]</sup>.这是由于该试验将直径6 mm的进气管置于液面正上方40 mm外,气流变化会显著改变渣液内的搅拌程度所致.图3显示了温度从1500℃上升到1600℃时,吸氮速率的明显提高.图4是熔渣吸氮速率常数与温度的关系.依据这种经典的方法,可求得此熔渣由气相吸氮的活化能是180 kJ/mol.它与文献[6]的数据相近,并在熔渣组元扩散活化能的范围之中<sup>[7]</sup>.图5说明不同组分的炉渣有着不同的吸氮速率.而其吸氮速率常数与炉渣的粘度<sup>[8]</sup>有直线关系,粘度愈低,吸氮速率愈大(见图6).改变气渣界面积虽然对吸氮速率有影响(见图7),但两者间无线性关系.这一点与前人的结果<sup>[6]</sup>是一致的.

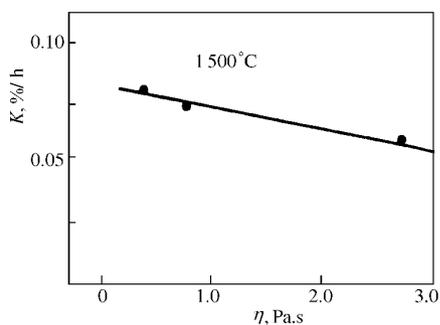


图6 熔渣粘度与吸氮速率常数的关系

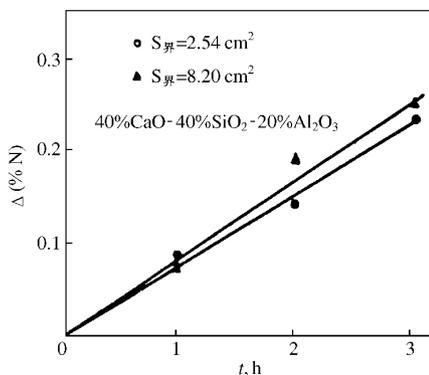


图7 气液界面积对熔渣吸氮的影响

## 2.2 铁液从熔渣吸氮的速度

图8是温度变化对铁液吸氮速率的影响.温度愈高,吸氮愈快.这和渣中氮含量的下降相应.如从图8计算熔渣中氮向铁液迁移的活化能(以平均吸氮速率计),所得之值为145 kJ/mol.图9是将界面积提高2.45倍的影响.发现它虽使吸氮加快,但两者却无正比关系.熔渣组成对吸氮速率的影响见图10.铁液由50% CaO-40% SiO<sub>2</sub>-10% Al<sub>2</sub>O<sub>3</sub>渣吸氮的速率最大.而由30% CaO-50% SiO<sub>2</sub>-20% Al<sub>2</sub>O<sub>3</sub>渣的吸氮速率最小,这和图5的结果是相应的.

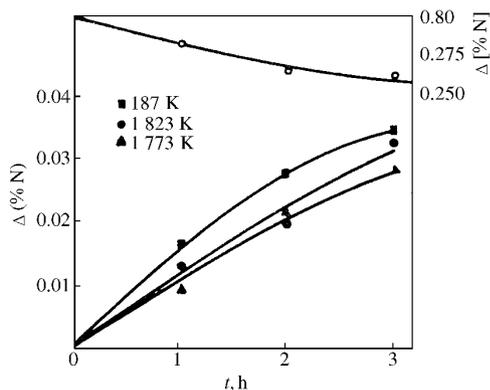


图 8 温度对铁液由渣层吸氮的影响

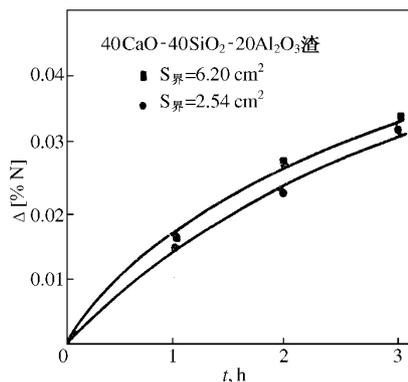


图 9 钢液界面面积对铁液由渣层吸氮的影响

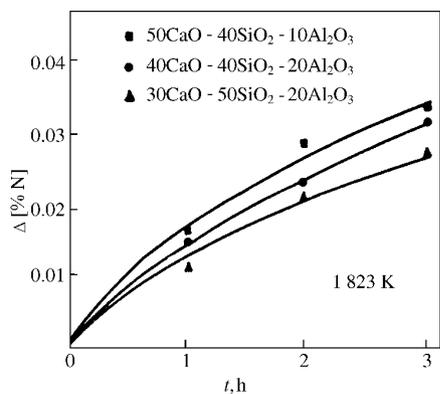


图 10 熔渣组成对钢液由渣层吸氮的影响

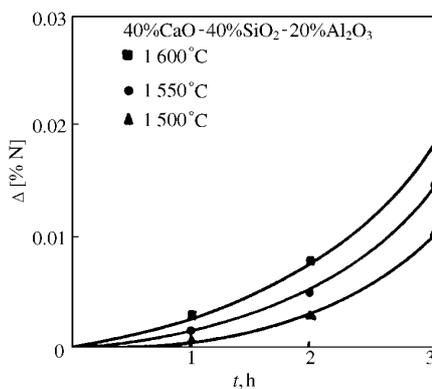


图 11 温度对钢液通过渣层吸氮的影响

### 2.3 CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> 渣的氮透过速率

图 11 是温度对氮透过熔渣渗入铁液的影响. 从图 11 可见, 温度升高, 氮透过熔渣的速率也提高. 图 12 是在不同组成的炉渣中氮透过速率的比较. 看来与前面两个试验类似. 炉渣组成的影响是通过其不同的粘度而体现的. 渣铁界面面积的变化虽然影响氮从熔渣透过的速率, 但与铁水吸氮速率并不呈正比(见图 13).

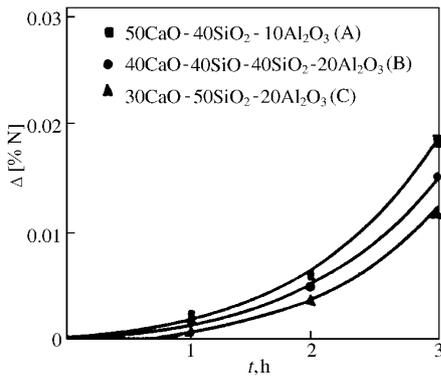


图 12 熔渣组成对钢液通过渣层吸氮的影响

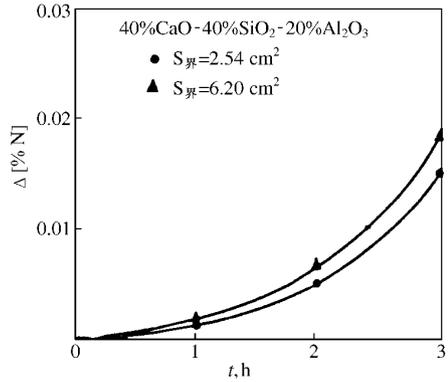
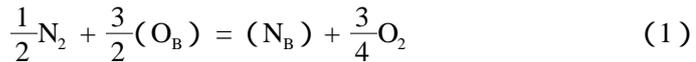


图 13 渣钢界面对钢液通过熔渣吸氮的影响

### 3 讨论

#### 3.1 熔渣从气相吸氮

作者曾指出,熔渣从气相吸氮的反应是气相中的氮置换渣中的“桥氧”而形成“桥氮”的过程<sup>[9]</sup>.即



这个过程的机理可以认为是:

(I) 反应物质( $O_B$ )与  $N_2$  扩散到气-渣界面;

(II) 在气-渣界面上发生反应(1);

(III) 反应产物( $N_B$ )及  $O_2$  分别扩散进入渣相、气相内部.根据本试验的结果(图 2 ~ 图 7) 不难看到该过程的速率受限于氮在渣中的扩散.如是,则经验速率方程应为

$$\frac{d}{dt}(\% N) = k'[(\% N)_{gs} - (\% N)] \quad (2)$$

由于渣的吸氮需 10 余小时才能达成平衡,本试验实际上只是该过程的初始阶段.所以会出现  $\Delta(\% N)$  随时间呈线性变化的结果.

式(2)中的  $(\% N)_{gs}$  是气-渣界面上的氮含量,可用下式<sup>[10]</sup>计算:

$$\lg C_N = \lg (\% N)(P_{O_2}^{3/4} / P_{N_2}^{1/2}) = 11.5 \lg \lambda - (22\ 175 / T) - 8.51 \quad (3)$$

$\lambda$  表示光学碱度. 再利用下式, 可计算出氮在渣中的传质系数  $k_N^s$  :

$$k' = \frac{A}{V} k_N^s \quad (4)$$

$A/V$  表示总值比界面面积.  $k_N^s$  的计算结果示于表 1.

表 1 不同温度下熔渣中氮的传质系数

渣系	50% CaO-40% SiO <sub>2</sub> -10% Al <sub>2</sub> O <sub>3</sub>	40% CaO-40% SiO <sub>2</sub> - 20% Al <sub>2</sub> O <sub>3</sub>			30% CaO-50% SiO <sub>2</sub> -20% Al <sub>2</sub> O <sub>3</sub>
温度 K	1 823	1 773	1 823	1 873	1 823
$k_N^s \cdot \text{cm/s}$	$3.19 \times 10^{-5}$	$1.81 \times 10^{-5}$	$1.97 \times 10^{-5}$	$2.27 \times 10^{-5}$	$0.28 \times 10^{-5}$

### 3.2 铁液由熔渣吸氮

氮电熔渣向渣-铁界面传递的物质流是

$$J_N^s = k_N^s (C_N^s - C_N^{s*}) \quad (5)$$

而氮由渣-铁界面向铁水内部传递的物质流是

$$J_N^m = k_N^m (C_N^{m*} - C_N^s) \quad (6)$$

两式中  $C$  是 mol 浓度, 上标  $m$  为铁水,  $s$  为熔渣,  $*$  表示界面上渣侧或铁水侧. 试验证明 吸氮速率不随界面面积而正比增加. 即界面反应非律速环节. 故在界面上达成平衡

$$C_N^{s*} / C_N^{m*} = L_N \quad (7)$$

稳态传度时,  $J_N^s = J_N^m$ , 所以可导出

$$J_N = \frac{C_N^s / L_N - C_N^m}{1/k_N^m + 1/L_N k_N^s} \quad (8)$$

如将摩尔浓度变化为重量为分数, 则有

$$\frac{d}{dt} \Delta [\% N] = \frac{A \rho_m k_N}{W_m} \left\{ \frac{(\% N)}{L_N} - [\% N] \right\} \quad (9)$$

$$k_N^{-1} = \frac{1}{k_N^m} + \frac{1}{L_N k_N^s} \quad (10)$$

这里  $A$  是界面积  $\rho_m$  是钢水密度,  $W_m$  是钢水重量, 以 40% CaO-40% SiO<sub>2</sub>-20% Al<sub>2</sub>O<sub>3</sub> 渣为例, 此渣系与纯铁间的  $L_N = 5.6^{[10]}$ . 用  $\frac{d}{dt} \Delta [\% N]$  对  $\left\{ \frac{(\% N)}{L_N} - [\% N] \right\}$  作图得一线性关系 (图 14). 由此, 得总传质系数  $k_N = 3.50 \times 10^{-5}$  cm/s.

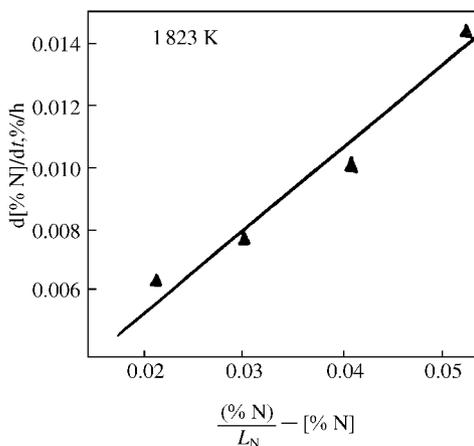


图 14  $\frac{d[\% N]}{dt}$  与  $\left\{ \frac{(\% N)}{L_N} - [\% N] \right\}$  的关系

另外, 由于  $k_N^m \gg k_N^s$ , 所以  $k$  主要由  $k_N^s$  决定. 即此过程的速率也受限于氮在渣中的扩散.

### 3.3 氮透过渣液溶入铁水的速率

铁水通过渣层由气相吸氮的过程可以看作是两个字过程串联的结果. 铁水由熔渣吸氮的子过程有如下关系:

$$\frac{d}{dt} (\% N) = k'' \left\{ \frac{(\% N)}{L_N} - [\% N] \right\} \quad (11)$$

而在熔渣由气相吸氮的子过程中

$$\frac{d}{dt} (\% N) = k' [(\% N)_{gs} - (\% N)] \quad (12)$$

并且在吸氮的初始阶段里  $\frac{d}{dt} (\% N)$  为一常数 ( $D_N$ ). 这两个子过程串联起来时, 自然有

$$\frac{d}{dt} (\% N) = k' [(\% N)_{gs} - (\% N)] - \frac{W_m}{W_s} \frac{d}{dt} [\% N] \quad (13)$$

或在吸氮的初始阶段里

$$\frac{d}{dt} (\% N) = D_N - \frac{W_m}{W_s} \frac{d}{dt} [\% N] \quad (14)$$

由式(11)和(14)又可导出如下的简化式：

$$\frac{d}{dt}[\% N] = \frac{k''}{L_N} D_N t - k''[\% N] \frac{A p_m k_N^s}{W_m} [\% N] \quad (15)$$

设  $t = 0$  时  $[\% N] = 0$ . 则由式(15)积分得

$$[\% N] = \frac{D_N}{L_N \cdot k''} [\exp(-k''t) + k''t - 1] \quad (16)$$

图 11 ~ 13 所示的曲线均服从式(16).

必须再次指出, 式(16)仅适用于吸氮过程的初始阶段. 如果渣受激, 此初始阶段可能很短. 熔渣由气相吸氮子过程的速率不再守恒, 式(16)就无意义了.

事实上, 因为由氮在渣中的传质律速, 可以认为铁水内部氮的分布是均匀的, 而且渣金界面上氮的分配保持热力学平衡. 因此

$$\frac{d}{dt}[\% N] = \frac{A p_m k_N^s}{W_m L_N} [(\% N) - (\% N)_{sm}] \quad (17)$$

这里  $(\% N)$  是渣中的平均含氮量,  $(\% N)_{sm}$  是渣金界面上渣侧的氮含量. 同时由式(3)得

$$\begin{aligned} \frac{d}{dt}(\% N) = & \frac{A p_s k_N^s}{W_s} [(\% N)_{gs} - (\% N)] \\ & - \frac{A p_m k_N^s}{W_s \cdot L_N} [(\% N) - (\% N)_{sm}] \end{aligned} \quad (18)$$

若气相组成恒定, 则气渣界面上渣侧的含氮量  $(\% N)_{gs}$  为一常数. 式(18)只含两个未知数. 为了求解必须引入另一个方程.

由于渣金界面上无氮的积累, 所以它由渣内传至该界面的物质流, 等于它由该界面向金内传质的物质流. 有

$$-k_s \frac{2(\% N)_y}{2y} \Big|_{y=H_s} = H_s = \frac{k_m}{H_m} ([\% N]_{y=H_s}) - ([\% N]_{y=H_m}) \quad (19)$$

这里  $y$  是铅垂线坐标,  $H_s$  表示渣层厚,  $H_m$  表示金属熔池深度. 用  $y = H_s$  表示渣金界面,  $y = H_m$  表示炉底. 由于氮在铁水中的分布可认为是均匀的, 所以

$$\frac{2(\%N)}{2y} \Big|_y = H_s = 0 \quad (20)$$

再加上  $(\%N)_{gs}$  始终保持恒定,于是按菲克第二定律,在假设

$$(\%N)_{sm} = (\%N)_{gs} \left\{ 1 - \operatorname{erf} \left( \frac{H_s}{2 \sqrt{k_N^s t}} \right) \right\} \quad (21)$$

式(17)、(18)和(21)联立构成铁水通过渣层由气相吸氮过程完整的数理模型.此模型可用数值积分方法求解.

## 4 结论

(1)  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  熔渣从 40% CO + 60%  $\text{N}_2$  气相吸氮的过程,由氮在渣相内传质律速.活化能为 180 kJ/mol.氮在渣中的传质系数为  $0.78 \sim 3.19 \times 10^{-5}$  cm/s.

(2) 铁液由  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  熔渣吸氮是非线性关系,其律速环节也是氮在渣中的传输.试验条件下的总传质系数为  $3.5 \times 10^{-5}$ ,活化能为 145 kJ/mol.

(3) 铁液透过渣层由气相吸氮的速率,受限于氮在渣层的传递.在吸氮初期,铁液中氮量的变化服从于

$$[\%N] = \frac{D_N}{L_N \cdot k} [\exp(-k^2 t) + k^2 t - 1]$$

的关系.若  $k_N^s$  很大,则过程速率的描述变得复杂,其数理模型为

$$\begin{aligned} \frac{d}{dt}(\%N) &= \frac{A \rho_m k_N^s}{W_m L_N} [(\%N) - (\%N)_{sm}] \\ \frac{d}{dt}[\%N] &= \frac{A \rho_s k_N^s}{W_s} [(\%N)_{gs} - (\%N)] - \frac{A \rho_m \cdot k_N^s}{W_s \cdot L_N} [(\%N) - (\%N)_{sm}] \\ (\%N)_{sm} &= (\%N)_{gs} \{ 1 - \operatorname{erf} (H_s / 2 \sqrt{k_N^s t}) \} \end{aligned}$$

## 参 考 文 献

[1] В. В. Аверцин. 金属中的氮(中译本). 北京,冶金工业出版社,1981:126-153

- [ 2 ] 徐匡迪. 油气管线用钢的性能要求与工艺技术进展. 上海金属 8(4)1986 :1-11
- [ 3 ] Xu Kuangdi , B. Tivelius. *Secondary steelmaking : review of current processes*. Keynote of Int. Conf. on Influences of Inclusions and Trace Residues on The Working and Serving Performances of Steel. 1985. Canada
- [ 4 ] Ito , K. , Fruehan , R. J. Thermodynamics of nitrogen in CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slags and its reaction with Fe-C<sub>sat</sub> melts. *Metall. Trans.* 198 , 1988 :419-425
- [ 5 ] Hendry , A. *The behaviour of nitrogen in oxide melts*. A paper from Univ of Strathclyde , Glasgow , UK
- [ 6 ] 下尾聪夫 坂田俊晴 木村弘 河合正雄. 黑铅クルシボ中ご熔融したスラグの窒素吸速度に関する二、三の实验. 日本金属学会志 36(8)1972 :728-733
- [ 7 ] 韩其勇. 冶金过程动力学. 北京 冶金工业出版社 ,1983 :253
- [ 8 ] The Committee of Fundamental Metallurgy. *Slag-Atlas*. Verein Deutscher Eisenhuettenleute , 1981 :202
- [ 9 ] Jiang Guochang , Xu Kuangdi. *A discussion on basicity of CaO-SiO<sub>2</sub> and CaO-Al<sub>2</sub>O<sub>3</sub> binary systems based on bondiug structure*. 6th Int. Iron & Steel Congr. , Nagoya , Japan , 1990
- [ 10 ] 凌天鹰. 熔渣中氮的行为研究. 硕士学位论文. 上海工业大学 ,1990

## Dynamic Study of Nitrogen Pick-up of Molten Iron Via Slag Layer

**Abstract** The nitrogen pick-up process of molten iron from furnace atmosphere via a CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag layer is composed of two sub-processes in series : the nitrogen absorption of slag from atmosphere and the nitrogen distribution between slag and metal. The influences of temperature , slag composition and crucible diameter on the rate of the two subprocesses were studied. It was found that the rate limiting ring for these two subprocesses are same , that is , the nitrogen mass transfer in slag layer. The apparent activation energies are 180 and 145 kJ/mol separatively. Based on the kinetic equation of the two sub-processes , a simple equation for the initial stage of the process as well as a sophisticated kinetic equation for the whole process were derived and the former has been used successfully in describing the experimental results.

# 喷粉精炼超低硫钢 工艺的试验研究<sup>\* 1</sup>

**摘要** 本文研究了喷粉精炼超低硫钢的工艺,在试验室中用30 kg感应炉进行的喷粉试验表明,要得到高的脱硫率,首先要控制好顶渣成分和氧化性.而要进一步脱硫到超低硫水平,还必须向钢液中加入脱硫剂.文中对喷吹 CaO、CaSi 粉和 CaO 基复合粉剂在低硫时的脱硫特点及顶渣对脱硫的影响进行了对比试验和讨论.试验中稳定地获得了 [S] < 0.001% 的超低硫钢液.

## 1 前言

随能源开发技术的发展,各种深海用油、气管线、耐高压、低温管线及输送腐蚀性油气管线的需求量越来越大.这种在苛刻环境中工作的管线用钢要求具有抗断裂、易焊接、抗 H<sub>2</sub>S 等腐蚀性气体、一定的低温冲击韧性等性能.大量研究表明,氢致裂纹(HIC-Hydrogen Induced Cracking)是这类钢种的主要破坏形式.通过对断口用扫描电镜分析发现,HIC 易产生在长条状 MnS 夹杂和束状氧化物夹杂周围<sup>[1]</sup>.因此,要生产出满足使用要求的钢,首先要提高钢抗 HIC 的能力.这就需要尽量降低钢中的硫含量,并对钢中残余夹杂物进行变形处理.按照 API 5LX 系列规定的 X-65、X-70、X-80 标准,钢中 [S] < 0.001% ~ 0.002%<sup>[2]</sup>.

\* 本文合作者:林钢、关玉龙、屠宝洪、李士琦、蒋国昌.原发表于《化工冶金》,11(4), 289 ~ 295(1993)

## 2 试验简介

超低硫管线钢属高强度低合金钢,钢水在转炉中初炼、精炼的主要任务是精确控制钢液成分、深度脱硫和对钢中残存夹杂物进行变形处理。国外超低硫管线钢的精炼大多采用喷粉工艺<sup>[3]</sup>。

### 2.1 试验设备

喷粉试验是在上海工业大学冶金材料研究所30 kg中频感应炉上进行的,炉衬为镁砂打结,熔池尺寸 $\phi 150 \times 240$  mm,喷粉罐为本试验室自制的带微型电机振动的有机玻璃质罐。试验室用高碱度渣下喷枪耐材寿命是试验技术上的难点,本试验采用表1的三种配方添加适量钢纤维整体打结自制而成。宝钢钢铁研究所化学室承担了钢中硫的分析,使用的是Laco仪。其余化学分析由上海工业大学冶金材料研究所理化测试中心承担。

表1 喷枪用耐火材料配方

Table 1 Refractory composition for the lance

Formula	Aggregate	Adhesive
I	电熔镁砂、石墨	2127 树脂
II	镁白云石	2127 树脂
III	电熔镁图、鳞片石墨、电熔刚玉颗粒、Si 粉	电熔 Al <sub>2</sub> O <sub>3</sub> 水泥

### 2.2 试验条件

试验顶渣配比为:63% CaO + 27% Al<sub>2</sub>O<sub>3</sub> + 10% SiO<sub>2</sub>。渣量约1.8 kg 相当于60 g渣/kg钢。厂方提供的喷吹粉剂化学成分如表2,复合粉剂中配加的 Al 粉和 CaF<sub>2</sub> 均为化学纯试剂。

表2 喷吹粉剂成分(%)

Table 2 Chemical composition of powder(%)

表2A 钝化石灰

Table 2A Inert CaO

CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MgO	P	S	烧碱	H <sub>2</sub> O	活度
-----	------------------	--------------------------------	-----	-----	---	---	----	------------------	----

94.0	2.5	0.5	0.20	0.5	0.02	0.005	0.25	0.25	7 280 ml
------	-----	-----	------	-----	------	-------	------	------	----------

表 2B 硅 钙 粉  
Table 2B SiCa powder

Composition	Ca	Si	C	P	S	Al
Content	29.333	58.59	0.46	0.032	0.052	2.27

试验喷吹参数如表 3 喷粉时间约 2 分钟.

表 3 试验喷吹参数  
Table 3 Parameters of injection experiment

	Top injection	Fluidization	Carrier gas
Flowrate NI/h	200	200	400
Pressure MPa	0.4	0.4	0.4

### 2.3 试验工艺

图 1 是试验工艺流程 共做了 27 炉试验.

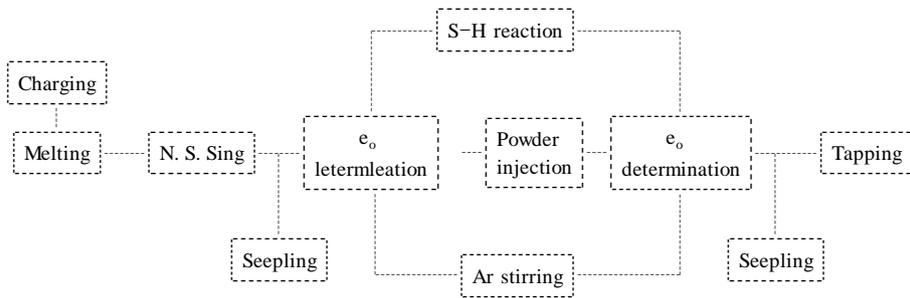


图 1 试验工艺流程图

Fig. 1 Metallurgical principal flowsheet for powder injection experiments

## 3 结果分析讨论

### 3.1 顶渣脱硫

喷粉过程中的化学反应包括粉剂与钢液间的瞬间相接触反应和顶渣

与钢液间的连续相接触反应. 这里先讨论后一种反应的脱硫规律, 即利用未喷粉的几炉试验来讨论顶渣脱硫规律. 下面讨论的脱硫过程是指白渣形成后开始的反应过程(包括渣钢反应与喷粉阶段), 实际上白渣形成过程中也有脱硫反应存在.

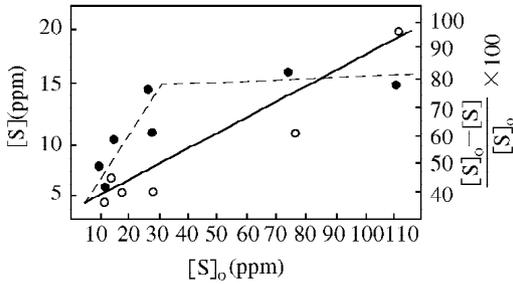


图2 初始硫含量 $[S]_0$ 对脱硫的影响(未喷粉)  
Fig. 2 Effect of initial  $[S]_0$  on desulphurization (without PI) (--- desulfuration rate. —  $[S]$ )

### 3.1.2 顶渣碱度

图3是顶渣碱度 $B$ <sup>[4]</sup>和光学碱度 $\mathcal{N}$ <sup>[5,6]</sup>同最终硫在渣钢间分配系数 $L_s$ 的关系. 同大多数研究结果一致, 当顶渣碱度控制在一定范围时, 其脱硫能力最强, 碱度过大或过小都降低了顶渣脱硫能力. 这是因为低碱度渣硫容量小, 而碱度过高时, 渣中CaO过饱和而析出固相粒子使顶渣变粘, 恶化了顶渣脱硫的动力学条件. 在本试验中, 碱度的最佳值约为 $B \approx 4.0$ ,  $\mathcal{N} = 0.815$ .

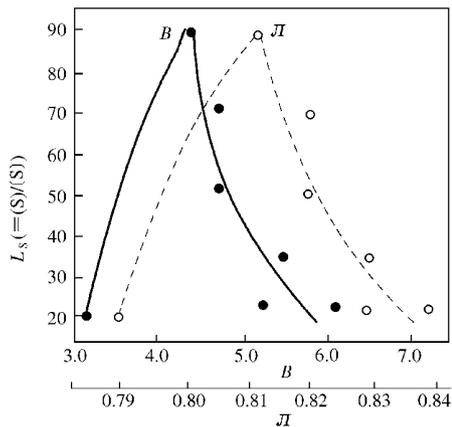


图3 顶渣碱度( $\mathcal{N}$ ,  $B$ )对硫在渣钢间分配系数的关系(未喷粉)  
Fig. 3 Effect of slag basicity ( $\mathcal{N}$ ,  $B$ ) on desulphurization (without PI)

$$B = \frac{X_{Ca^{2+}} + 0.58X_{Mg^{2+}}}{X_{SiO_2} + 0.5X_{Al_2O_3}}, X \text{— 摩尔分数};$$

$$\mathcal{N} = N_{CaO} + 0.92N_{MgO} + 0.66N_{Al_2O_3} + 0.94N_{FeO} + 0.95N_{MnO} + 0.47N_{SiO_2},$$

$$N_{M_xO_y} = \frac{Y \cdot X_{M_xO_y}}{\sum (Y \cdot X_{M_xO_y})}$$

### 3.1.3 顶渣氧化性

顶渣氧化性强弱用渣中不稳定性氧化物(FeO, MnO)含量来表示. 从试验结果中可以看出, 只有弱氧化性渣才能脱硫到较低的水平(图4). 正如文献中的结论: 尽管纯 FeO 也有脱硫作用<sup>[7]</sup>, 但当渣中 FeO 很低时, 降低其含量对脱硫是非常有利的<sup>[3]</sup>.

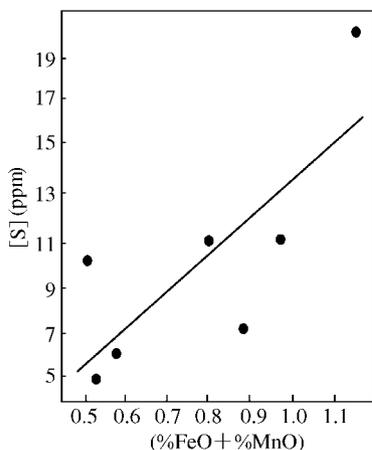


图4 顶渣氧位(% FeO + % MnO)对脱硫的影响(未喷粉)

Fig. 4 Effect of oxygen potential (% FeO + % MnO) on desulphurization (without PI)

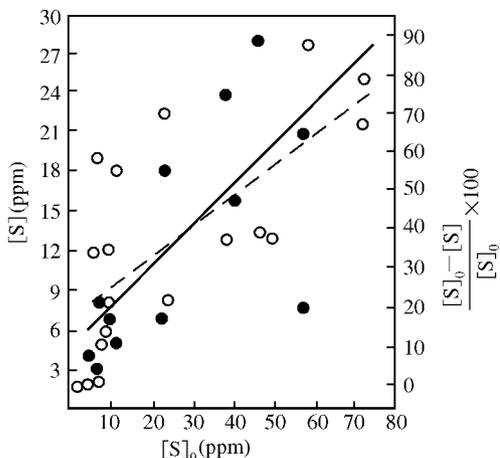


图5 喷粉前硫含量[S]<sub>0</sub>对脱硫的影响

Fig. 5 Effect of initial [S]<sub>0</sub> on desulphurization (with PI)

○ — [S]  
● — desulphurization rate

## 3.2 喷粉脱硫

顶渣脱硫只是喷粉过程脱硫反应的一部分, 此外还有粉剂与钢液间的反应. 下面讨论的喷粉脱硫包括两种相接触反应同时进行的结果.

### 3.2.1 喷粉前钢中硫含量[S]<sub>0</sub>

图5表明喷粉前后钢中硫含量成正比. 同样, 初始硫愈高, 脱硫率越大, 但仍然有限. 因此要得到超低硫钢必须有低硫初炼钢液作保证.

### 3.2.2 顶渣化学成分

图6、7是钢中初始硫含量相近时各炉顶渣碱度R(= % CaO / % SiO<sub>2</sub>)和渣指数M<sub>s</sub>(= % CaO / (% SiO<sub>2</sub> · % Al<sub>2</sub>O<sub>3</sub>))与喷粉过程脱硫率的关系. 显然

在试验范围内,顶渣碱度  $R$  和渣指数  $M_s$  的提高有利于脱硫. 这与文献[3]介绍的  $M_s = 0.25 \sim 0.35$ 、 $R = 4 \sim 6$  时渣系脱硫能力最强的结论是一致的. 顶渣化学成分不但决定了其本身的脱硫能力,而且影响着最终的脱硫效果. 因而有人认为最终决定钢中硫含量的是顶渣组成<sup>[8]</sup>. 但从这次试验看,顶渣化学成分等因素远不及钢中初始硫含量对最终脱硫结果影响显著. 这一方面是因为这些因素都控制在一个较好的范围,波动不大;另一方面低硫时进一步脱硫很困难,需各种因素的最佳配合,它们相互制约,单一因素作用不突出.

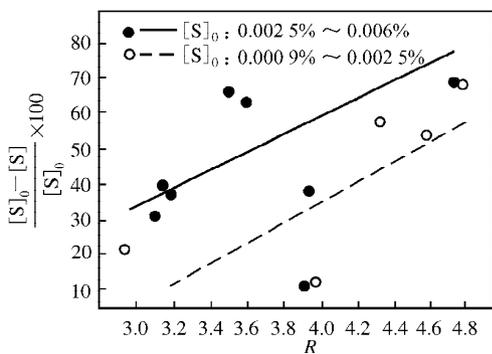


图6 顶渣碱度( $R$ )对脱硫的影响

Fig. 6 Effect of slag basicity on desulphurization (with PI)

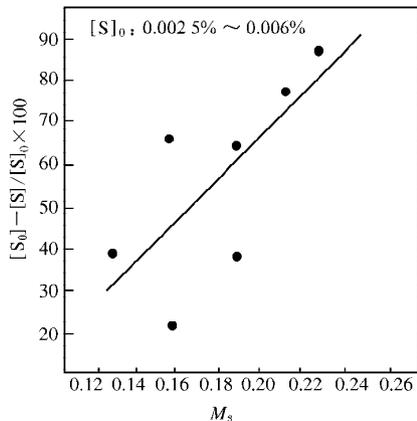


图7 渣指数  $M_s$  对脱硫的影响

Fig. 7 Effect of slag index ( $M_s$ ) on desulphurization (with PI)

### 3.2.3 喷吹粉剂种类

大量研究结果表明,低硫时脱硫反应限制性环节是钢液中硫的传质<sup>[3,4,8]</sup>. 故粉剂与钢液间的瞬间相接触反应是脱硫的关键. 影响瞬间相接触反应的因素很多,这里着重讨论粉剂种类的影响. 因试验炉数有限,不能对试验结果做大量统计分析,同时考虑到钢中初始硫  $[S]_0$  对脱硫结果影响显著,表4将不同初始硫含量的炉次放在一起讨论.

表4中I区三炉  $[S]_0$  较高,脱硫率也较大. 喷  $\text{CaSi}$  的两炉脱硫率稳定在65%,而喷复合粉剂的一炉脱硫率达86%. 一般认为  $\text{CaSi}$  的脱硫能力比  $\text{CaO}$  强,这除了与  $\text{CaSi}$  有更强的脱氧能力有关外,还因为  $\text{CaSi}$  在钢液中上浮时分解为钙液滴和钙气泡,比固体  $\text{CaO}$  颗粒有更好的脱硫动力学条件. 但是,由于感应炉熔池浅,钙液滴和钙气泡在钢液中滞留时间短,故感应炉中  $\text{CaSi}$  利用率不高. 氧化钙基复合粉剂中配加一定的  $\text{CaF}_2$  和  $\text{Al}$  粉,降低了熔

池氧位,  $\text{CaF}_2$  降低了粉剂表面反应产物层熔点, 因而复合粉剂比  $\text{CaO}$  脱硫效果好.

表 4 不同条件喷粉脱硫比较  
Table 4 Experimental results (with powder injection)

Region	No.	De-S agents	top slag								[ % S ] <sub>0</sub> - [ % S ] × 100	
			( % FeO )	( % MnO )	R	B	M <sub>s</sub>	A	[ % S ] <sub>0</sub>	[ % S ]	[ % S ] <sub>0</sub>	
I	2#	CaSi (130 g)	0.60	0.31	3.59	3.61	0.19	0.80	0.0057	0.0021	63.21	
	5#	CaSi 100 g	1.05	0.56	3.49	3.68	0.16	0.80	0.0072	0.0025	65.3	
	4#	C. A. 50 g	0.49	0.22	4.86	3.68	0.23	0.80	0.0058	0.0008	86.2	
	9#	CaSi 150 g	0.92	0.25	3.15	3.18	0.13	0.79	0.0046	0.0028	39.1	
II	13#	CaSi 100 g	0.39	0.19	3.94	2.97	0.19	0.78	0.0048	0.003	37.5	
	11#	C. A. 100 g	0.67	0.25	3.19	2.31	0.14	0.79	0.0038	0.0024	36.8	
III	7#	CaSi 150 g	0.69	0.56	2.94	3.72	0.16	0.8	0.0023	0.0018	21.7	
	14#	C. A. 150 g	0.39	0.13	4.75	3.57	0.2	0.8	0.0023	0.0007	69.6	
IV	10#	CaO 70 g	0.53	0.12	4.32	3.88	0.23	0.81	0.0007	0.0003	57.1	
	12#	CaO 70 g	0.43	0.12	4.59	3.84	0.23	0.81	0.0011	0.0005	54.5	
	16#	CaSi 130 g	0.43	0.09	6.08	4.01	0.24	0.81	0.001	0.0008	20	
	17#	CaSi 100 g	0.57	0.23	4.9	4.08	0.23	0.81	0.0009	0.0007	22.2	
	6#	CaSi 120 g	0.83	0.17	3.91	3.13	0.21	0.79	0.0009	0.0008	11.1	
	20#	CaSi 100 g	0.42	0.11	8.6	4.83	0.35	0.82	0.0006	0.0004	3.33	
V	19#	C. A. 120 g	0.76	0.13	9.06	5.21	0.38	0.83	0.0005	0.0008	0	
	22#	CaSi 50 g	0.66	0.19	7.37	4.26	0.28	0.81	0.0004	0.0004	0	
	23#	CaSi 150 g	0.65	0.66	7.74	4.89	0.34	0.83	0.0002	0.0003	0	

Note : C. A. —Composite agent ,80% CaO + 15%  $\text{CaF}_2$  + 5% Al

II 区几炉 [ S ]<sub>0</sub> 约 0.0038% ~ 0.0048% 脱硫率比 I 区低, 复合粉剂与 CaSi 脱硫效果差不多. 考虑到喷 CaSi 一炉 [ S ]<sub>0</sub> 较高, 故仍可认为此时复合粉剂比 CaSi 脱硫率高.

III 区 [ S ]<sub>0</sub> 为 0.0023%, 喷复合粉剂一炉远比喷 CaSi 炉次高, 这除了与前面分析粉剂种类方面的原因外, 还与该炉顶渣成分和氧化性控制较好有关. III 区两炉甚至比 II 区炉次脱硫率高, 这说明初始硫以外别的因素对脱硫的影响也是明显的.

IV区的六炉初始硫仅7~11 ppm,这时喷CaSi只有10%~30%的脱硫率,而喷CaO两炉脱硫率稳定在55%。超低硫时CaO比CaSi有更强的脱硫能力,这是目前未曾报道过的,而这样低硫时的脱硫试验本身也未见报道,我们从下面几方面来解释这个结果:(1)感应炉中CaSi利用率低。(2)超低硫钢液中硫可能主要是残存的硫化物,这时脱硫的主要途径应是去除硫化物,而CaO比CaSi有更强的去除夹杂物能力,这就表现为较高的脱硫能力。(3)超低硫钢液一般都经过钙处理,钢液中溶解的钙硫热力学平衡值较大,即 $\alpha_s \cdot \alpha_{Ca} = 1.7 \times 10^{-5}$ <sup>[9]</sup>,因而CaS均相形核很困难,喷入固体CaO颗粒为CaS非均相形核创造了条件。(4)超低硫时的脱硫还必须考虑粉剂本身的含硫量,因为粉剂未必能完全上浮。这次试验所用CaSi比CaO含硫量高近10倍(表2)。由上面的分析我们可以认为,虽然目前尚不能确认超低硫时CaO比CaSi有更强的脱硫能力,但可得到如下的启示:研究超低硫时的脱硫规律除应考虑脱硫化学反应本身以外,还应考虑粉剂去除钢中夹杂物能力大小等其他因素。

V区的初始硫已极低,从试验结果看,此时喷吹CaSi和复合粉剂均无明显的脱硫效果。

#### 3.2.4 顶渣氧位

顶渣氧位对脱硫的影响可从表4中清楚地看到。将喷吹同种粉剂的5#、2#和11#、14#炉次对比,初始硫低的炉次仍有较高脱硫率,这与各炉次顶渣氧化性是有明显关系的。显然,要得到高的脱硫率,必须有低氧化性的顶渣,因此超低硫钢生产中要求严格控制氧化性转炉渣的下渣量。

#### 3.3 喷枪寿命

喷枪寿命主要决定于包裹耐火材料寿命,试验室用高碱度渣下喷枪耐火材料,要求具备耐高温、耐钢液和高碱度渣浸蚀和冲刷及一定的抗热震性能。这次使用表1中三种配方的喷枪除配方II寿命较差外,其余两种喷枪经整修后均可再次使用,尤以配方III使用效果更佳。

## 4 结论

(1)  $[S] < 0.001\% \sim 0.0015\%$  的超低硫钢液完全可由喷粉处理而得,但须有低硫初炼钢液作保证。

(2) 顶渣碱度和氧化性是影响脱硫的重要因素,顶渣成分控制好,其本

身有很强的脱硫能力.

(3) 感应炉中 CaSi 粉的利用率不高,氧化钙基复合粉剂有较强的脱硫能力.

(4) 超低硫钢液的脱硫,不仅要考虑脱硫化学反应本身,还应考虑粉剂去除夹杂物能力等其他因素对最终脱硫效果的影响.

(5) 试验室用高碱度渣下喷枪耐火材料以电熔材料为佳.

## 参 考 文 献

- [ 1 ] H. Ohtani *et al.* The development of high strength steels for X-70 to X-100 grade pipe. Paper
- [ 2 ] N. Noziki *et al.* Proceedings of the International Conference of HSLA Steels , Shanghai , 1985 : pp. 485-491
- [ 3 ] 徐匡迪. 上海金属 ,1986 , No. 7 : pp. 1-11
- [ 4 ] 张岚等. 上海工业大学学报 ,1987 , No. 4
- [ 5 ] 中村荣. 日本金属学会会志 ,1986 , Vol. 50 : p. 441
- [ 6 ] 横川敏雄. 日本金属学会会志 ,1986 , Vol. 1 : p. 3
- [ 7 ] 赵玉祥. 冶金热力学动力学(上). 北京钢铁学院出版社 ,1982
- [ 8 ] G. Gatellier *et al.* Int. Calcium Treatment Symp. , 30 , Univ. of Strathclyde Glasgow , June , 1988

## Laboratory Research on Refining Ultra-low Sulfur Steel by Powder Injection

**Abstract** Technique was studied of refining ultra-low sulfur steel by powder injection with a laboratory 30 kg induction furnace. Experimental results show that proper basicity and low oxygen potential of the top slag are two important factors for achieving a high level of desulfurization. Still , powder injection is a must to obtain ultra-low sulfur steel. Ability of three kinds of powder ; CaO , CaSi and CaO-based composite were tested. Utilization of CaSi powder was lower than the composite powder due to the shallow pool of steel in the furnace. The desulfurizing capacity of CaO-based composite powder was increased

significantly due to  $\text{CaF}_2$  and Al powder additive. It is noticed that CaO was more efficient in desulfurization than CaSi powder when sulfur concentration was very low in the steel, that suggests that ability of removing impurity inclusions and other mechanisms are also important factors besides chemical reactions in desulfurization by powder injection. The effects of the composition and the oxygen potential of the top slag on desulfurization were studied as well. In this work, it was proved a regular practice to obtain ultra-low sulfur steel with  $[\text{S}] < 0.001\%$ .

# 含碳锰矿团块固态还原的阶段反应特征<sup>\* 1</sup>

**摘要** 含碳团块是固态还原技术中的一个重要发展,采用不同测试手段对含碳锰矿团块固态还原过程进行了分析研究.提出了在弱还原条件下,整个还原过程可分为孕育期、高速反应期和后期三个阶段,但在强还原条件下孕育期不明显,并分析了各阶段中还原进展的程度和反应特征.

由于含碳锰矿团块的固态还原对高炉冶炼碳素锰铁和矿热炉冶炼MnSi合金均可显著改善其生产指标,在锰的熔融还原中也是重要的一个工序,因此我们在这方面进行了系统的研究工作<sup>[1~3]</sup>,并讨论了含碳锰矿团块固态还原各阶段中的反应特征.我们认为只有确定了这些反应的特征以及反应进行的机制和律速环节,才可能再进一步去建立有价值的数学模型.

## 1 试验方法

在试验中,采用气体吸收法完成了还原率和CO、CO<sub>2</sub>相对累计量比例的在线检测,用化学物相分析法确定锰的金属化率.矿相及金属析出相的组成用X射线衍射、电子探针和化学物相分析法研究.用光学显微镜观察还原过程中矿相结构变化和金属相析出特征.试验方案见表1.

---

\* 本文合作者:蒋国昌、徐建伦、李光义.原发表于《上海工业大学学报》,11(3),261~268(1990)

表1 试验方案

试样	团块内的配比 矿: 碳: 焦	还原温度	反应时间 min	试样	团块内的配比 矿: 碳: 焦	还原温度	反应时间 min
1	100: 20: 10	1 000	90	15	100: 20: 10	1 100	60
2	100: 20: 20	1 000	90	16	100: 20: 20	1 100	60
3	100: 20: 20*	1 000	90	17	100: 20: 10	1 100	30
4	100: 20: **	1 000	90	18	100: 20: 20	1 100	30
5	100: 20: 10	1 000	60	21	100: 20: 10	1 200	90
6	100: 20: 20*	1 000	60	22	100: 20: 20	1 200	90
7	100: 20: 10	1 000	30	23	100: 20: 20*	1 200	90
8	100: 20: 20	1 000	30	24	100: 20: **	1 200	90
11	100: 20: 10	1 100	90	25	100: 20: 10	1 200	60
12	100: 20: 20	1 100	90	26	100: 20: 20	1 200	60
13	100: 20: 20*	1 100	90	27	100: 20: 10	1 200	30
14	100: 20: **	1 100	90	26	100: 20: 20	1 200	30

注: \* 焦炭粉为 - 120 目.

\*\* 团块内无焦粉, 团块埋于碳粉内还原.

## 2 结果及讨论

### 2.1 几个子反应的平行推进

光学显微镜观察和 X 射线衍射分析都证明, 含碳锰矿团块的整个还原过程由三个子反应组成, 即氧化物由高价到低价的转变、金属相的析出和渣相的形成. 由图 1 可见  $Mn_2O_3$ 、 $Mn_3O_4$ 、 $MnO$  和  $Fe$  共存于试样 No. 2 之中. 说明并非氧化物由高价到低价的转变完成之后金属相才开始析出. 这两个子反应是平行推进的. 在 No. 22 试样中渣相已形成. 图 2 所示葡萄球是残余矿相, 而球间就是生成的渣相. EPMA 指出其组成是  $MnSiO_3$ <sup>[2]</sup>. 这和图 1 也是吻合的. 另一方面, No. 22 试验中还存在少量的高价氧化锰. 说明该试样内上述三个子反应同时并存.

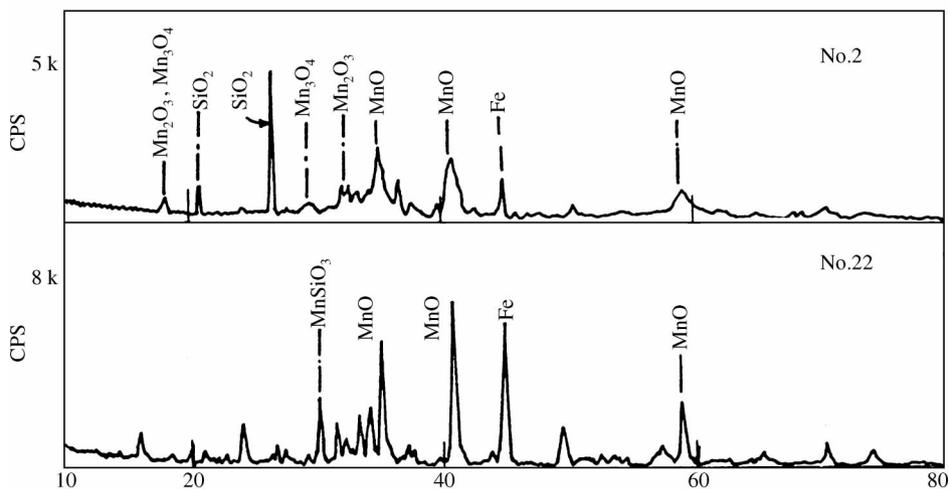


图1 X射线衍射分析结果

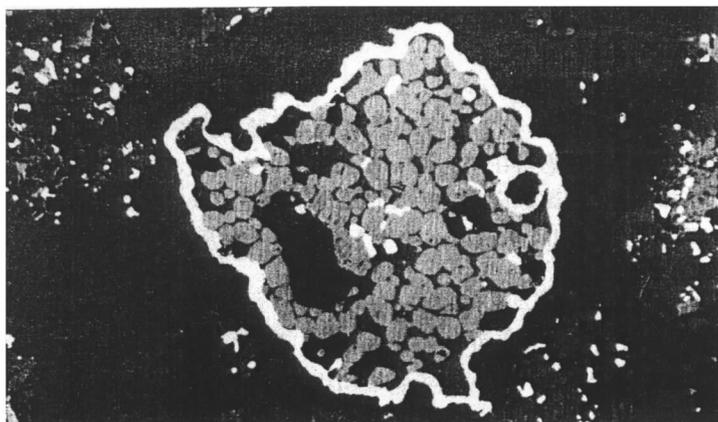
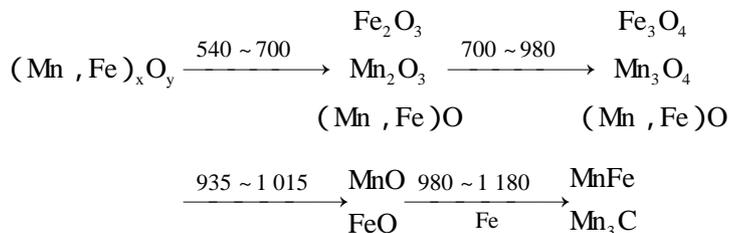


图2 强还原条件下金属析出相的集聚及残余氧化物相变成“葡萄球”的情况

Лади 等<sup>[4]</sup>、寺山清志等<sup>[5,6]</sup>以及 Holta 等<sup>[7]</sup>用纯的氧化锰或锰精矿作为原料研究了其固态还原的特点. 他们指出, 氧化锰的还原由锰从高价到低价的转变与金属相的析出两个子反应组成. 它们又再分为几个步骤, 一一衔接. 对于一个微区来说, 氧化物的降价转变必须领先于金属相的析出. 而当金属有某一析出量时渣相才可能开始形成. 但本试验中, 一个试样的各个微区内还原过程的进展并不均衡. 其起因是:

(1) 试样中各处的原始矿相在组成、结构、致密度等方面有差别, 且还原过程中, 各处的温度条件和还原势也不尽相同;

(2) 某些反应温度区间互相交叉,且都在本试验温度范围内.在原矿为铁、锰共生且 % MnO > 10% 的条件下,Лади 等用差热分析(DTA)指出<sup>[4]</sup>:



显然,后三个反应步骤的温度范围是部分交叉的.图3所示还原率曲线的任一段均包含着几个反应步骤的信息,而非某一步反应的特征.为此以图3为线索将还原过程分为孕育期、高速期和后期进行分析.

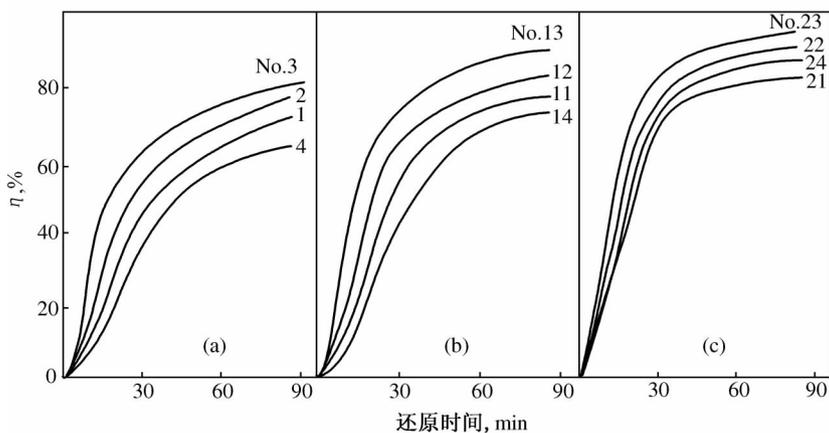


图3 各种条件下的还原率(R)曲线

## 2.2 弱还原条件下的孕育期

由图3,可以把试样 No. 1、2、3、4、11、12、14 试验列为一组,其还原率曲线一特征是有孕育期.而寺山清志等在研究 MnO<sub>2</sub> 的还原时也曾发现有孕育期存在<sup>[5]</sup>.本试验中,孕育期与其后续的高速反应期交接处的还原率约是 10%.孕育期的持续时间最长不超过 15 min.而这段时间里的  $\eta_{\text{CO}}/\eta_{\text{CO}_2}$  小于 10%,特别是反应刚开始约 5 min 内  $\eta_{\text{CO}}/\eta_{\text{CO}_2}$  几乎为零(见图4).

在本试验条件下,试样一进入炉子的高温区,还原过程就伴随着非稳态

传热的开始而起步. Bryk 等<sup>[8]</sup>在研究含碳铁矿团块的还原时曾实测过团块中心的升温曲线. 他们指出, 当炉膛温度为 1 000 ~ 1 100 , 直径 19 ~ 32 mm 的团块中心在 3 ~ 6 min 内可升温到 700 ~ 800 . 但温度升到 900 ~ 1 000 则需时 10 ~ 16 min. 所以说, 本试验中孕育期间的反应实际上是在比预定更弱的还原条件下进行的. 如此情况下,  $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$  的转变可望有某种程度的发展, 但反应放出的大部是  $\text{CO}_2$ <sup>[4~7]</sup>.  $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$  的转变也应该是类似的. 这和图 4 的结果吻合.

按 DTA 的结果<sup>[4,5]</sup>, 虽氧化铁不可能热分解, 但高价氧化锰会发生热分解. 在 No. 4 和 14 试样的孕育期间, 这种热分解可能起了某种作用. 但在其他几种内配碳的试样中可能主要的仍是还原反应.

按本试验所用的原矿计算, 若  $\text{MnO}_2$  全部转变成  $\text{Mn}_2\text{O}_3$ , 相应的还原率是 17%. 若  $\text{Fe}_2\text{O}_3$  全部转变成  $\text{FeO}$ , 相应的还原率是

10.6%. 此两值均大于孕育期终止的标志——还原率达到 10%. 因此, 孕育期间氧化物从高价到低价的转变不可能完成, 也没有金属相析出. 这和寺山清志等<sup>[5]</sup>的结论是吻合的. 他们指出, 600 下,  $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$  需时约 7 min 才能完成. 而  $\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$  在 760 下需时约 17 min 才能完成.

### 2.3 弱还原条件下的高速反应期

对 No. 1、2、3、4 试样取还原率等于 45% 作为高速反应期的终点. 对 No. 11、12、14 则取 50% 为终点. 其延续时间不包括孕育期, 约是 10 (No. 3) 到 30 min (No. 4).

孕育期一结束, 反应速率就迅速增大. 除了团块内部的实际温度这一因素之外, 还必须考虑到团块内矿相物理结构在孕育期间的变化也有重要作用. 这将在另一篇论文中讨论.

图 5 与图 6 表明: 在这高速反应期结束时, % MnO 可达到 10 ~ 20 的水

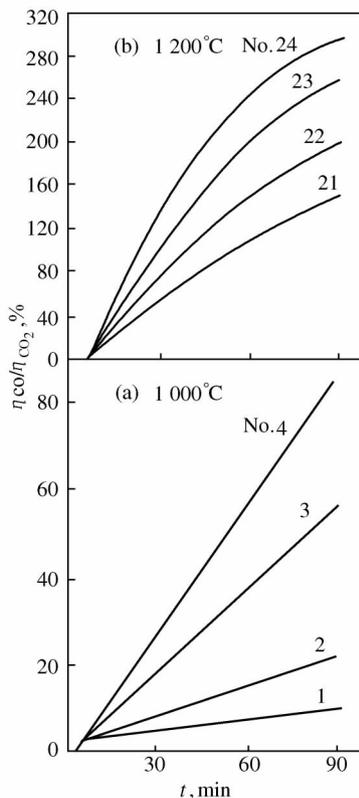


图 4 几种还原条件下的  $\eta_{\text{CO}}/\eta_{\text{CO}_2}$  值

平,而 Mn 金属化率( $\eta_{Mn}$ )在 4% 以下.因此高速反应期间发生的主要是  $Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$  以及  $FeO_4 \rightarrow FeO \rightarrow Fe$  的过程.与这一判断吻合的还有在 No. 8 试样中观察到金属铁开始析出<sup>[2]</sup>.按本试验所用的原矿计算,若 Fe 完全被还原出来,相应的还原率约是 32%.若  $MnO_2$  全部转变成 MnO 相应的还原率是约 34%.作者认为,这表明高速反应期间  $Mn_3O_4 \rightarrow MnO$  及  $FeO \rightarrow Fe$  的过程尚未结束.

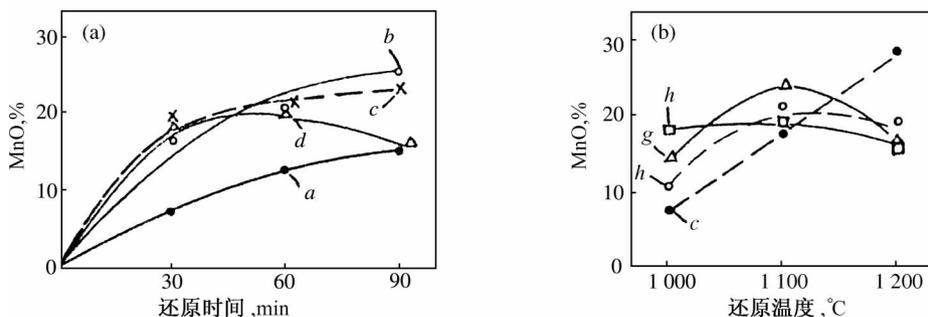


图 5 还原过程中团块内 % MnO 的变化和不同因素的影响

(a) 还原时间的影响

	矿: 焦	
a	1 000	100: 10
b	1 100	100: 10
c	1 100	100: 20
d	1 200	100: 20

(b) 还原温度的影响

	矿: 焦	还原时间(min)
l	100: 10	30
f	100: 20	30
g	100: 20	90
h	100: 20(细)	90

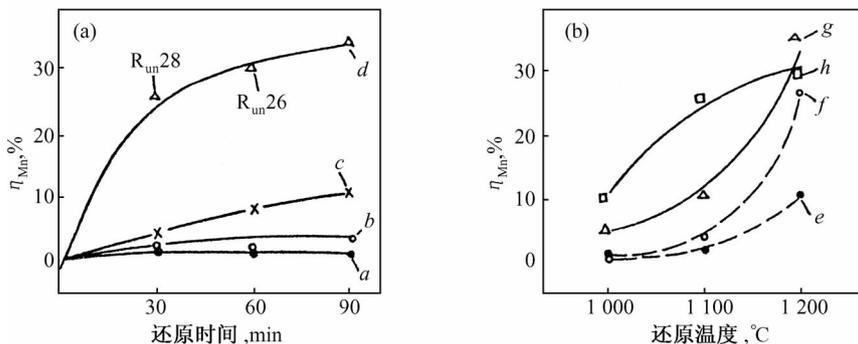


图 6 还原时间(a)和还原温度(b)对 Mn 金属化率的影响(曲线编号同图 5)

$$\eta_{Mn} = \frac{M_{Mn}}{T \cdot Mn} \quad M_{Mn} \text{——还原析出的金属相(Fe-Mn-C)中之含锰量;}$$

$T \cdot Mn$ ——团块内的总锰量

## 2.4 弱还原条件下的反应后期

图 5(a)表明,在弱还原条件下,反应后期中团块内的 % MnO 仍持续升高.但图 6(a)的相应曲线显示出  $\eta_{Mn}$  很小的信息.可见在这个反应后期主要是  $Mn_3O_4 \rightarrow MnO$  的过程.

不同的是,  $FeO \rightarrow Fe$  的过程在此反应后期看来能够完成.因为,除 No. 4 的终点还原率偏低之外,其他的均已超过 66%,见图 3.这就是试样里的金属析出相都是铁基(EPMA)的测定结果,见表 2 的原因.

表 2 金属析出相组成的 EPMA 点测结果

No.	% Fe <sub>(平均)</sub>	% Mn <sub>(平均)</sub>	% C
22	73.08	20.73	0.91 ~ 1.03
28	97.11	0.98	0.67 ~ 0.86
3	97.43	0.52	0.57 ~ 1.32
23	85.66	11.55	1.37 ~ 2.35

## 2.5 强还原条件下的高速反应期

No. 13、21、22、23、24 试样是在还原条件下的试验.其孕育期不明显,所以可将它们分为两期来分析.

X 射线衍射和光学显微镜观察都已证明,在强还原条件下只要较短的保持时间就能取得类似于弱还原条件下经长时间反应才能达到的还原程度<sup>[3]</sup>.而 No. 13、21 ~ 24 试样中,高速还原期的终点为还原率达 60% ~ 65%.这两方面都表明,这一高速反应期中发生了弱还原条件下所有的反应步骤.

这个高速反应期的另一个特点是团块内各处还原程度的参差不齐更加严重.通过 X 射线衍射分析和显微镜观察作者发现在这些试样中不仅有残存的高价氧化锰,而且同时又有大量析出的铁基金属相已开始集聚(见图 2).另外,  $MnO \rightarrow Mn$  也有了某种程度的进展(见图 5 及图 6).

按热力学计算,纯 MnO 碳热还原的起始温度约在 1 400 以上,即使生成的是碳化锰,反应起始温度也只略低于 1 300<sup>[7]</sup>.但寺山清志等在配碳(mol 比)1:1 的条件下(相当于本试验中,矿:焦 = 100:20),将纯 MnO 于 1 150 加热 2 h 得到了金属锰<sup>[6]</sup>.两者之间的矛盾显而易见.本试验条件下,温度高于 1 100 时团块内 % MnO 转为下降而  $\eta_{Mn}$  则大大增加(图 5b 及

$\sigma_B$ ). 这和寺山清志的试验<sup>[6]</sup>有所不同, 但和 Лади 的观点<sup>[4]</sup>一致. 因为本试验所用原矿的 Mn/Fe 比不大. 还原过程中 Fe 领先析出, 同时其毗邻氧化物相内 % MnO 上升. 然后才是金属析出相中 % Mn 逐渐增加<sup>[2]</sup>. 由于金属析出相中  $a_{Mn}$  减小, 反应起始温度比析出纯锰时的低是完全可以理解的. 在这个意义上, 也可以说原矿中含有的铁对 MnO 的还原有促进作用.

## 2.6 强还原条件下的反应后期

该过程的特点可用图 5 和图 6 说明. 由 % MnO 曲线下降而  $\eta_{Mn}$  曲线上升的倾向, 可以判断  $MnO \rightarrow Mn$  是主要反应.

另一方面, 即使在经过 90 min 还原的试样里, 金属析出相仍是铁基的 Fe-Mn-C 合金, 而且其中 % Mn 和 % C 均不高. 这就是为什么在 X 射线衍射分析中没有相应 Mn 谱线检出的原因.

在本试验条件下, 若矿中所含的氧全部转变成 CO, 按计算, 要求矿: 焦 = 100: 21. 所以在本试验中没有生成碳化物的条件, 表 2 即是证明. 并且也没有发现寺山清志等提出的 MnO 还原途中先生成  $Mn_7C_3$  (同时游离碳消失), 后者再和残余 MnO 作用而最终生成 Mn 的现象. 看来这和 Fe 领先析出有关.

除 MnO 的还原之外, 在这个反应后期发生的还有残余氧化物向渣相转变的过程(见图 2).

## 3 结语

在含碳锰矿团块的固态还原各阶段中实际发生的反应很复杂, 往往包含着几个“子反应”的信息.

弱还原条件下的孕育期内发生的是高价氧化物向低价氧化物的转变. 在其后的高速反应期内,  $Mn_3O_4 \rightarrow MnO$  以及  $FeO \rightarrow Fe$  的转变尚未结束. 在反应后期内主要是  $Mn_3O_4 \rightarrow MnO$  的过程. 强还原条件下的高速反应期内发现各种反应步骤同时并存. 在接着的反应后期内主要是  $MnO \rightarrow Mn$  的过程.

本研究工作承陈鉴寅讲师担任 X 射线衍射分析, 诸于良助理工程师负责电子探针测定, 郑芳元高级工程师完成了化学测试, 朱钰如副教授指导了光学显微镜检验. 而气体吸收法是丁伟中讲师提出的, 并作了最初的开拓工作. 特此表示深切谢意.

## 参 考 文 献

- [ 1 ] 蒋国昌 徐建伦 徐匡迪. 冶金部第二届熔融还原专家组会议文集. 铁合金 ,(5)1985 : 23-30 ;(6)1989 :31-34 ;(1)1990 :4-8
- [ 2 ] 朱钰如 ,丁伟中 ,许珞萍 ,蒋国昌 徐建伦 徐匡迪. 含碳锰矿团块预还原过程中的矿相变化及产物的析出. 上海工业大学学报 ,(6)1989 531-538
- [ 3 ] Jiang Guochang , Xu Kuangdi , Xu Jianlun. A laboratory investigation on the reduction of carbon bearing Mn-ore lump in solid-state. *NEUT/SUT-HUT symp. on Process Metall.* May , 1990 , China :210-220
- [ 4 ] Лажин А. Я. , Рижонков Д. И. , Дроздов. Н. М. *Изв ВУЗ ЧМ.* (5)1984 :4-6
- [ 5 ] 寺山清志 ,池田己夫. 日本金属学会志 ,45(9)1981 :901-906
- [ 6 ] 寺山清志 ,池田己夫. 日本金属学会志 ,46(2)1982 :1138-1144
- [ 7 ] Holta , O. , Olsen , S. E. *Electric Furn. Proc.* 43 1985 :273-277

### Characteristics of Various Stages During Solid Reduction of Carbon Bearing Mn-Ore Lump

**Abstract** By means of different measurement methods the reduction of carbon bearing Mn-ore lump in solid state were studied. It is shown that in weaker reduction cases the whole process can be divided into three stages : the pregnant period , the fast reaction period , and the final period. While in stronger reduction cases the pregnant period is not so clear. The progression degree and the feature of reduction in various periods were discussed.

# Bismuth Free Cutting Stainless Steel #410<sup>\* 1</sup>

## Introduction

Free cutting steel is currently made by addition of sulphur or lead. However, sulphur deteriorates the mechanical properties, and lead is a harmful element. Using Bismuth instead of either of these two elements, as a free cutting additive, does not cause pollution problems and degradation of the mechanical properties. This paper presents the preliminary results of investigation on the addition of 0.1% Bi to a stainless steel containing 0.26% C and 11% Cr. Improved machinability was obtained, and mechanical properties were retained for a grade of steel intended for use in the manufacture of ball-pens and their nips.

## Experimental Procedure

Steel grade 2Cr13 (AISI410) was chosen as the starting material. It was melted in a 40 kg induction furnace with non oxidation process. Before tapping, a set amount of crushed Bi-Mn alloy supplied by the Bismuth Institute ( $\pm 80\%$  Bi, balance Mn), was added into the furnace, wrapped in an iron sheet, then stirred.

After holding the molten steel for a short time in the ladle, it was casted at

---

\* In collaboration with Jiang Guo-Chang, Huang Ke-Li, Zhuang Yun-Qian and Yang Sen-Long. Reprinted from *The Bulletin of the Bismuth Institute*, No. 56, pp.7-9 (1989)

a temperature just under 1630°C. The final composition of four heats is listed table I.

The average Bi yield was only about 23% ,as shown in table II.

**Table I The Chemical Composition**

Sample No.	C%	S%	Cr%	Mn%	Bi%
Y2Cr13Bi I	0.173 8	0.005 2	10.95	Increasing	0.01
Y2Cr13Bi II	0.147 5	0.004 2	10.37		0.031
Y2Cr13Bi III	0.227 1	0.003 5	10.98		0.066
Y2Cr13Bi IV	0.252 9	0.004 3	11.42		0.091

**Table II Bismuth Yield**

Sample No.	I	II	III	IV	Average
Yield %	20	20.7	26.4	26	23.25

The test samples used for measuring machinability , anticorrosion and related properties were taken from a cylinder with a forging ratio of 63% ,and were tempered at 700°C for 150 minutes.

## Machinability Tests

### Tool Life Tests

The machinability tests were carried out on a C6150 lathe with a YT14-type cutting tool , and the cutting conditions are listed table III.

**Table III Cutting Conditions**

Rake Angle + 15°	Clearance Angle + 7°	Plane Angle + 75°
Auxillary Angle + 15°	Cutting Edge Inclination - 3°	
$\frac{V}{\text{(Cutting Speed)}}$ 100 m/min	$\frac{f}{\text{(Feed)}}$ 0.204 mm/r	$\frac{a_p}{\text{Back Engagement}}$ 1 mm

The results are shown in Fig. 1.

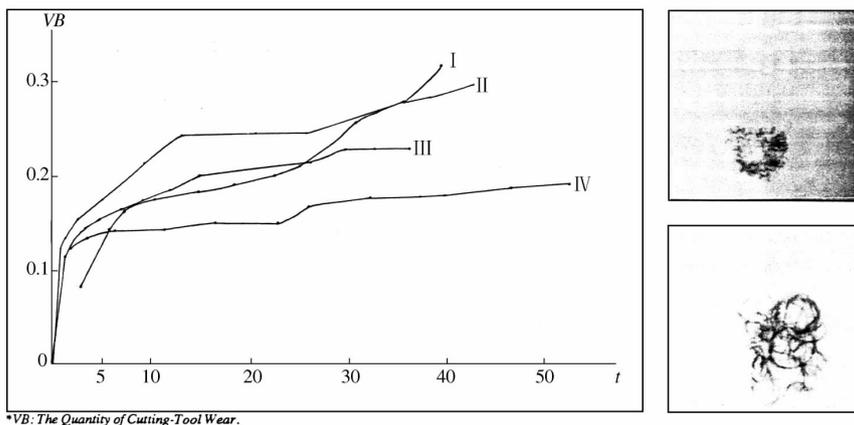
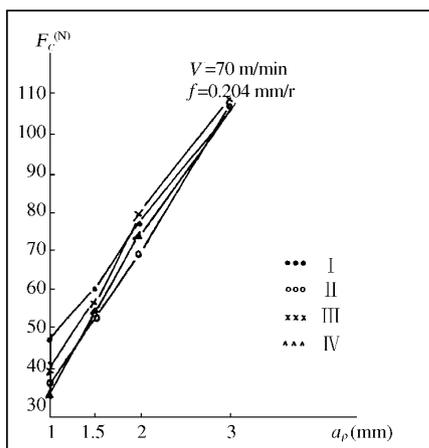


Fig. 1 The Curve of  $VB^*$  (mm)- $t$ (min)

The Shape of Chips

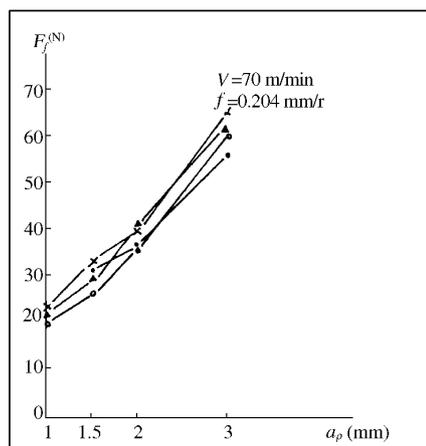
### Cutting Force Test

A kinetic strain gauge type YD-15 was used to measure cutting force and the other testing conditions were the same as for the cutting tool life test. Results are shown in Fig. 2 ,3 ,4 and 5.



\*\* $F_c$ :Cutting Force

Fig. 2 The Curve of  $a_p$ - $F_c^*$



\*\* $F_f$ :Cutting Force

Fig. 3 The Curve of  $a_p$ - $F_f^{**}$

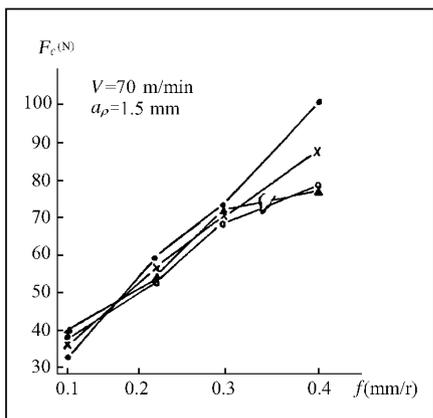


Fig. 4 The Curve of  $f$ - $F_c$

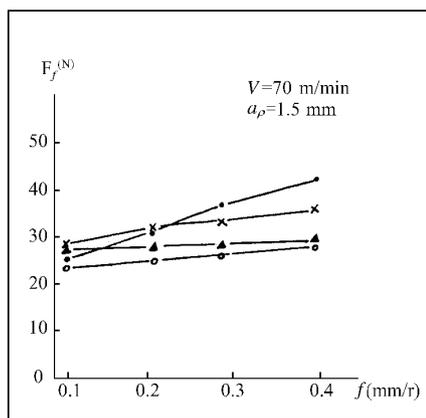


Fig. 5 The Curve of  $f$ - $F_f$

## Chip Formation and Shape

Chips of various shape and length as described in table IV and shown in the photograph above were obtained.

Table IV The Shape of Chips

Sample No.	Shape of Chip	Color
I	Spiral	White
II	Continuous	White
III	Fragmented	Golden Yellow
IV	Fragmented	Golden Yellow

## Mechanical Properties Tests

The tensile test was performed according to Chinese Standard GB228-76 on samples with a L/D ratio of 10.

The HRA , HRB , HRC values were obtained with the Rockwell hardness test , then converted into Brinell hardness.

The results are reported in table V.

**Table V Mechanical Properties**

Sample No.	$\sigma_s$ kgf/mm <sup>2</sup>	$\sigma_b$ kgf/mm <sup>2</sup>	$\delta_{10}$ %	$\phi$ %	Brinell Hardness
1Cr13( #403 )	55	70	25 *	69	195 ~ 220
I	57	72. 6	10. 78	58. 25	242
II	58. 95	69. 8	10. 96	58. 85	227
III	60. 2	79. 3	11. 44	54. 62	253
IV	61. 9	81. 7	12. 85	52. 13	248

\*  $\delta_s$

## Corrosion Tests

Corrosion resistance to salt was tested with a 5% NaCl solution (pH 6. 5 ~ 7) continuously sprayed at  $35 \pm 2^\circ\text{C}$  at a spraying rate of 1 ~ 2 ml/h. Results are reported in table VI.

**Table VI The View of Corrosion Surface**

Time	24 h	48 h	72 h
Sample No.	<i>Corroded</i>		<i>Spots</i>
1Cr13	1	2	4 ~ 5
I	8	16	Almost total surface area.
III	5	12	Over 2/3 of surface area.

## Discussion

There are four key factors determining machinability : Tool life , surface finish , cutting force torque , and shape of chips. Given its low-melting property , the Bi-containing phase is in the molten state during the cutting operations and acts as a chip breaker. This plays an important lubricating role which decreases cutting resistance while extending tool life. The reduced cutting effort also results in a smoother surface requiring lesser finishing steps.

The high carbon ( $C\% > 0.15$ ) and low chromium ( $Cr\% < 11$ ) contents of experimental samples displayed poor corrosion resistance. However, this was not considered to relate to Bi.

Because the vaporization temperature of Bi is low, the Bi yield was generally below 50% for the melts made during this experiment. This will be remedied, however, through an improved method of adding the Bi-Mn alloy.

## Conclusion

Molten steel 2Cr13 (AISI410) was microalloyed with Bi to improve its machinability. The higher the Bi content, the better the machinability. The shape of chips was fragmental when the Bi content exceeds 0.066%.

Although its plasticity is slightly lower, Bi free cutting steel has higher yield and tensile strength, and better hardness properties than 1Cr13 (AISI403).

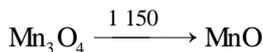
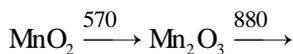
# 锰矿团块还原过程的基础研究<sup>\* 1</sup>

**摘要** 本文介绍了国外锰矿团块还原过程的一些研究成果. 主要讨论了锰矿团块还原过程中锰氧化物由高价到低价的转变、MnO 的还原及其还原速率.

## 1 锰氧化物由高价向低价的转变

天然的氧化锰矿中, 主要的含锰矿相是软锰矿  $MnO_2$ 、硬锰矿  $xMnO \cdot MnO_2 \cdot yH_2O$  和褐锰矿  $Mn_2O_3$ . 碳酸锰矿是另一类天然锰矿, 其主要含锰矿相为菱锰矿  $MnCO_3$ . 不管是哪一类矿源, 在锰矿团块的还原过程中必然存在着锰氧化物由高价到低价的转变.

与  $Cr_2O_3$  不同, 不需任何还原剂, 仅仅加热就可使高价氧化锰转变成低价.



这里的转变温度是由 A. Я. Лади 等用差热分析法测得的, 见图 1<sup>[1]</sup>. 用碳还原时

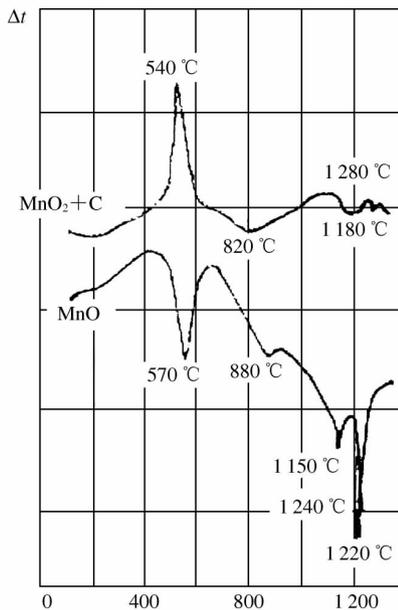
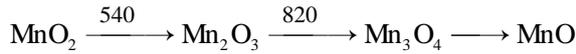


图 1 差热分析结果之一

\* 本文合作者: 蒋国昌、徐建伦. 原发表于《铁合金》, (6), 31 ~ 34 (1989)

这些转变都在较低温度下发生,按图 1 可表示如下:



A. Я. Лади 等认为,  $\text{MnO}_2$  被碳还原时放出总量  $\text{CO}_2$ , 所以这是一个大量放热过程. 而在  $\text{Mn}_2\text{O}_3$  还原成  $\text{Mn}_3\text{O}_4$  的过程中, 既有  $\text{CO}$  又有  $\text{CO}_2$  放出, 图 1 中相应于这一转变的是一低谷, 表明这是一个吸热反应, 即  $\text{CO}$  的量比  $\text{CO}_2$  多. 此曲线没有显现出  $\text{Mn}_3\text{O}_4$  转变成  $\text{MnO}$  的温度, 这是因为放出  $\text{CO}$  的吸热效应和放出  $\text{CO}_2$  的放热效应相抵消之故.

寺山清志等<sup>[2]</sup>在过量配碳 ( $n_{\text{Mn}_2\text{O}_3} : n_{\text{C}} = 1 : 2.5$ ) 的条件下做了差热分析, 见图 2. 他们还用气相色谱法测定了反应逸出的气体组成. 发现在 570 下过量碳和  $\text{MnO}_2$  反应放出的气体中有相当多的  $\text{O}_2$ , 而且该过程的活化能只略大于  $\text{MnO}_2$  热分解的活化能. 这说明即使加有过量的碳, 在该温度下首先是  $\text{MnO}_2$  经热分解转变成  $\text{Mn}_2\text{O}_3$ , 然后才是  $\text{O}_2$  使碳燃烧放出  $\text{CO}_2$ . 只是由于热

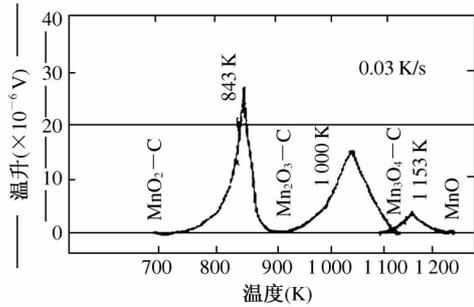


图 2 差热分析结果之二

分解的吸热比燃烧的放热小, 所以过程的总热效应是负值. 关于过量碳和  $\text{Mn}_2\text{O}_3$  的作用, 寺山清志等认为也与温度有关. 温度较低时碳的燃烧不完全, 故有  $\text{O}_2$  剩余. 而在较高温度下逸出的气体才变成  $\text{CO}$  和  $\text{CO}_2$  的混合物. 此过程的热效应和过量碳与  $\text{Mn}_3\text{O}_4$  反应的热效应按图 2 均是负值. 这是寺山清志等的观点, 与 A. Я. Лади 等的观点有矛盾之处.

O. Holta 等用含 40% 挥发分的煤进行了锰精矿 (主要矿相是  $\text{MnO}_2$ ) 的还原研究<sup>[3]</sup> 在 30 /min 的恒速恒温条件下用热天平和气体分析仪进行测定, 发现配碳 6% 时整个过程是分两步完成的.  $\text{MnO}_2$  和  $\text{Mn}_2\text{O}_3$  的还原从 400 开始, 逸出气体全是  $\text{CO}_2$ ;  $\text{Mn}_3\text{O}_4$  的还原始于 700 ~ 750, 起初逸出的气体仍是  $\text{CO}_2$ , 达 900 时才有  $\text{CO}$  可以检出.

他们指出, 逸出气体的组成及还原率取决于配碳量和加热温度, 见图 3. 配碳 2% 时逸出气体中有  $\text{O}_2$  存在, 还原只进行到  $\text{Mn}_2\text{O}_3$  为止, 以后只是热分解. 至少配碳要大于 6%, 当温度升到 1 100 ~ 1 200 时才可能完全转变成  $\text{MnO}$ . 但另一方面, 根据图 4 又指出, 从能量利用的角度来看配碳 4% 最合

理 配碳大于4% 时  $Mn_3O_4$  的还原就变成吸热过程了. 所以他们强调应尽可能利用 CO 而不是 C 来还原  $Mn_3O_4$ .

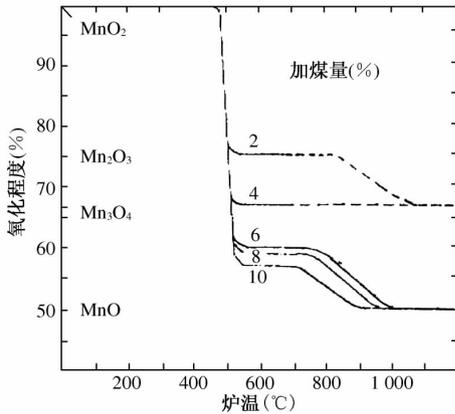


图3 不同条件下锰矿团块的还原率

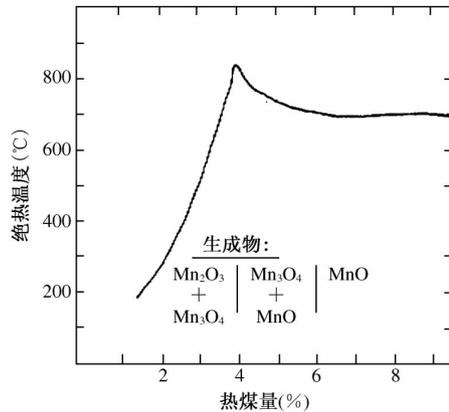
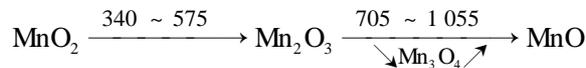


图4 配碳量与高价氧化锰转变过程绝热温度的关系

事实上锰矿或多或少地含铁,而 FeO 也会对上述还原过程发生作用.

A. Я. Лади 等认为有铁共存时,在如下温度区间里转变速率出现峰值:



## 2 MnO 的还原

由热力学数据不难算出反应  $C_{(s)} + MnO_{(s)} = Mn_{(s)} + CO$  的起始温度约 1400 以上. 按 O. Holta 等的意见,即使生成碳化锰,反应的起始温度也只略低

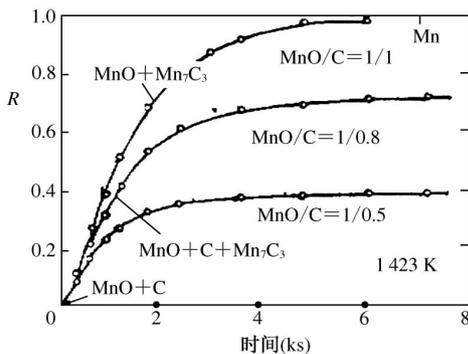


图5 配碳量对 MnO 还原率的影响以及还原过程中反应物生成物的变化

于 1300 . 但寺山清志等的试验表明,配碳为 1: 1 在 1150 下保持 2 小时即可将纯的 MnO 还原成金属锰(若配 1: 2.5, 则所得尽是碳化锰)<sup>[4]</sup>.

寺山清志等在其试验中用 TCD 作还原率的在线检测. 为抑制 Mn 的挥发,纯 MnO 和石墨(经 He 中 1200 加热处理)的混合粉置于有盖的容器内进行还原,且在还原过

程中取样用 X 衍射及电子探针检验还原产物的组成. 他们认为还原过程中的变化可用图 5 表示. 即还原分两步进行, 首先是  $Mn_7C_3$  的生成反应, 而后是  $Mn_7C_3$  与剩余的  $MnO$  作用生成金属锰.

尽管寺山清志等的工作与上述热力学计算有矛盾, 但在有  $FeO$  共存时在该试验条件下  $MnO$  的还原是无疑的. 按 A. Я. Лади 等的数据, 有铁共存时  $MnO$  的还原可在  $600 \sim 1300$  (或  $1000 \sim 1200$ ) 范围内进行.

众所周知, 铬矿只能造球, 而锰矿既可造球也可烧结. 和铁矿一样, 锰矿烧结首先是为了造块以适应高炉或矿热炉冶炼, 其还原率很低. 烧结成品中的主要矿相是黑锰矿 ( $Mn_3O_4$ ) 和锰橄榄石 ( $2MnO \cdot SiO_2$ ). 锰球团有氧化性球团与含碳球团之分. 氧化性球团也以造块为目的, 且以残碳甚低为其特点. 含碳球团的报道目前较少, 尽管各家配碳有所不同, 但在低于  $1200$  还原时, 均认为反应最多只能进行到生成  $MnO$  为止 (即使配碳过量). 成品球团中可以发现有金属球析出, 但其中的含锰量极低<sup>[5]</sup>.

因此可以说, 如果寺山清志等的工作和 A. Я. Лади 等的观点可靠的话, 那么现行的含碳锰矿球团生产技术中必有某些因素阻碍  $MnO$  的还原, 这是需要研究的课题.

### 3 锰矿团块的还原速率

图 6 是高价氧化锰还原过程曲线, 可以看到温度是主要影响因素. 对于  $MnO$  的还原, 除温度因素外碳粉粒度特别是配碳量也有重要作用 (见图 5 和图 7). 用  $Mn_7C_3$  取代碳作还原剂时, 仅前期的还原速率略

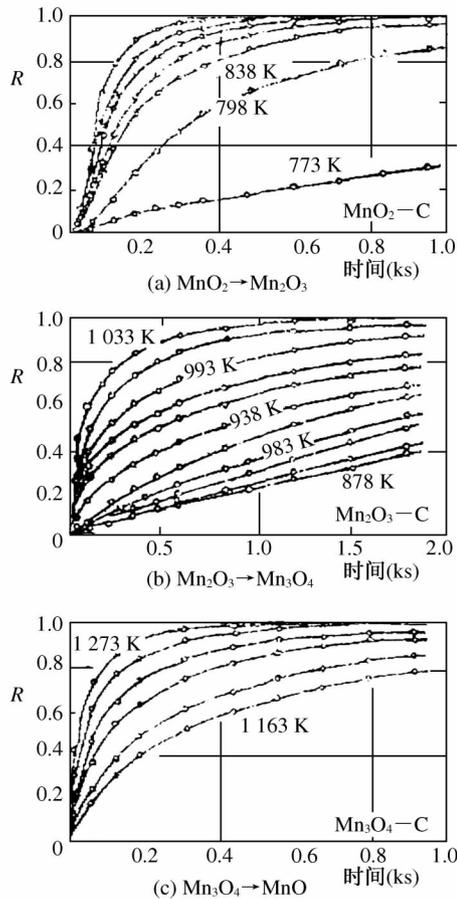


图 6 温度对高价氧化锰(碳还原)还原率的影响

有增加. 这些都是寺山清志等的研究结果.

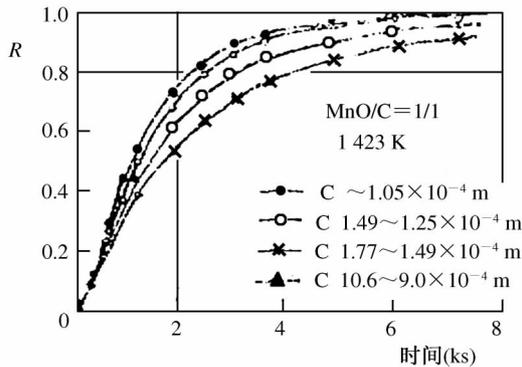


图7 碳粉粒度对 MnO 还原率的影响

含碳锰矿团块的还原动力学目前尚缺系统的研究,有关此动力学的许多规律和现象还未曾仔细考察过,现在还缺乏足够的实验依据去判断反应机制,仅仅依靠速度常数和活化能的计算下断言,说服力是有限的.

## 参 考 文 献

- [ 1 ] А. Я. Лади, Др. Изв ВУЗ ЧМ, 1984(5), 4-6
- [ 2 ] 寺山清志等. 日本金属学会志, 1981, 45(9), 901-908
- [ 3 ] O. Holta *et al.* Elec. Furn. Proc. 1985, 43, 273-277
- [ 4 ] 寺山清志等. 日本金属学会志, 1982, 46(12), 1138-1144
- [ 5 ] J. Relander *et al.* Steelmaking Proc. 1986, 69, 47-49

## Basic Research on Reducing Process of Manganese Ore Agglomerate

**Abstract** In this paper, some research achievements on reducing process of manganese ore agglomerate abroad is introduced. The transformation of manganese oxide from high valence to low valence in reducing process and the reduction of manganoous oxide as well as its reducing rate are mainly discussed.

# 铬矿团块还原过程的基础研究<sup>\* 1</sup>

**摘要** 综合论述了国外铬矿团块还原过程的基础研究成果. 着重介绍了铬铁矿中各组元的还原曲线, 铬铁矿相在还原过程中的结构和成分变化, 并对含碳铬矿团块还原过程中的直接还原和间接还原进行了讨论.

片山博等系统地研究了铬矿团块的还原过程, 1974 年以来, 他们陆续发表了多篇论文, 涉及到多种条件下铬矿团块还原过程的进展和机制. 因此, 以他们的工作为线索不难勾画出目前人们对这一课题的认识.

铬矿中的铬通常存在于复杂的  $(\text{Mg}, \text{Fe})(\text{Cr}, \text{Al}, \text{Fe})_2\text{O}_4$  矿相之中, 一般称此矿相为“铬铁矿”. 从矿物学看, 它是由各种尖晶石相 ( $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ ,  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ,  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  等) 按不同比例组成的. 为了揭示铬矿团块还原过程的基本规律, 先分别观察纯  $\text{Cr}_2\text{O}_3$ 、铁铬尖晶石、镁铬尖晶石和各种“铬铁矿”的还原过程自然是有益的.

## 1 铬铁矿中各组元的还原热力学

铬铁矿中各组元的还原反应起始温度可以按热力学数据计算. 由于生成铬的碳化物的反应比生成纯金属铬易于进行, 所以配碳量高时可望得到高的还原率. 铬铁尖晶石中的  $\text{FeO}$  虽然比纯铁矿难还原, 但仍可领先于  $\text{Cr}_2\text{O}_3$  的还原, 而且领先还原出来的铁对  $\text{Cr}_2\text{O}_3$  的还原有促进作用. 镁铬尖晶石只有在足够高的温度下才能被还原.

\* 本文合作者: 蒋国昌、徐建伦. 原发表于《铁合金》, (5) 23 ~ 30(1989)

## 2 铬铁矿中各组元的还原过程及曲线

纯  $\text{Cr}_2\text{O}_3$  在恒温下的还原规律主要取决于温度的高低和原料粒度的粗细<sup>[1]</sup>。试验表明,  $\text{Cr}_2\text{O}_3$  粒度小于 250 ~ 325 目时, 1 140 ~ 1 170 °C 下可达到 60% ~ 80% 的还原率(图 1)。依赖 X 射线分析, 片山博等指出  $\text{Cr}_2\text{O}_3$  并不像其他氧化物的还原那样有一个由高价到低价的转变, 他们没有发现  $\text{Cr}_3\text{O}_4$  或  $\text{CrO}$  的出现, 也没有检出金属铬或  $\text{Cr}_{23}\text{C}_6$ 。还原生成物仅是  $\text{Cr}_3\text{C}_2$  和  $\text{Cr}_7\text{C}_3$ , 而且这两种碳化物的相对

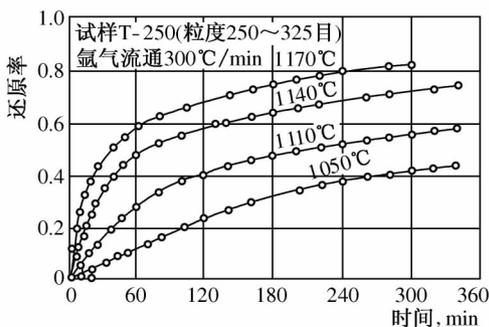


图 1 温度对  $\text{Cr}_2\text{O}_3$  还原的影响

数量与还原温度、氩气流量、原料粒度等因素有关。片山博等认为它们是同时生成的, 只是由于团块内外的  $P_{\text{CO}_2}/P_{\text{CO}}$  值不同, 所以在其内部形成  $\text{Cr}_3\text{C}_2$ , 而在外缘生成  $\text{Cr}_7\text{C}_3$ 。

Y. Maru 等<sup>[2]</sup>曾用  $\text{Cr}_{23}\text{C}_6$  作为  $\text{Cr}_2\text{O}_3$  的还原剂。除了原料粒度和还原温度之外, 他们还发现  $\text{Cr}_{23}\text{C}_6$  的原始气孔率也是影响还原速率的一个重要因素(图 2)。他们的还原产物是金属铬。这之所以有别于片山博等的结果, 看来起因于初始配碳量的差异。

C. M. Голодов 等<sup>[3]</sup>在恒速升温(5 °C/min)和恒温保持条件下比较了不同碳素材料还原  $\text{Cr}_2\text{O}_3$  的作用。尽管不同碳素材料的还原起始温度相近(约在 1 050 ~ 1 100 °C), 但以碳黑的还原反应最有效(见图 3), 这与图 2 是吻合的。此试验所

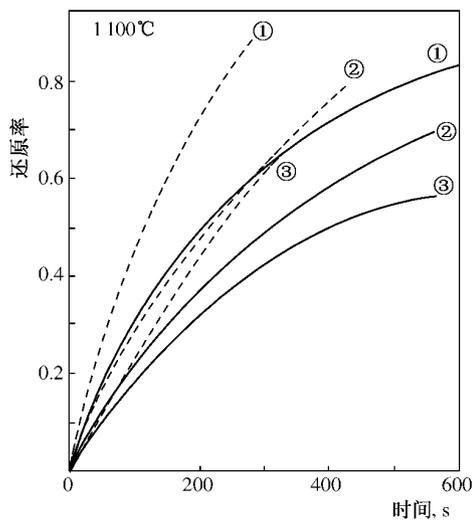


图 2  $\text{Cr}_{23}\text{C}_6$  的粒度和比表面积对  $\text{Cr}_2\text{O}_3$  还原过程的影响

..... 0.39  $\text{m}^2/\text{g}$       —— < 0.16  $\text{m}^2/\text{g}$   
 ① 300 ~ 400 目; ② 200 ~ 250 目; ③ 150 ~ 170 目

得的生成物也是  $\text{Cr}_8\text{C}_2$  和  $\text{Cr}_7\text{C}_3$ , 但与片山博等的观点不同, 他们认为还原前期(低温下)生成  $\text{Cr}_3\text{C}_2$ , 后期才有  $\text{Cr}_7\text{C}_3$  出现.

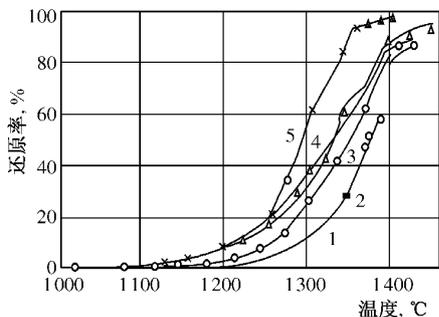


图3 不同还原剂对  $\text{Cr}_2\text{O}_3$  还原的影响

1—石油焦 2—无烟煤 3—半焦 4—石墨 5—碳黑

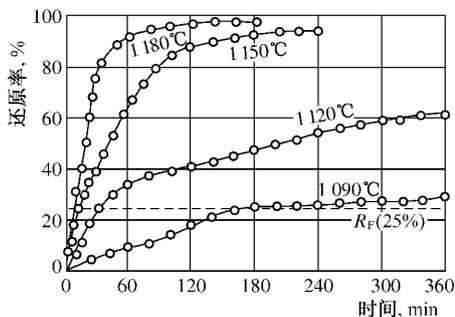


图4 不同温度下  $\text{FeCr}_2\text{O}_4$  的还原规律

( $R_F$  为  $\text{FeO}$  完全还原的还原度)

图4 是片山博等给出的铁铬尖晶石的还原规律<sup>[4]</sup>. 此尖晶石的还原比纯  $\text{Cr}_2\text{O}_3$  容易, 在 1180 下还原率可达 100%, 而后者在 1170 下只有 80%. 1090 还原曲线呈现一个相应于其中的  $\text{FeO}$  被完全还原出来的平阶, 即  $R = R_F$ . 说明在此条件下  $\text{FeO}$  的还原领先. 随着这一过程的推进, 铁铬尖晶石逐渐蜕变成  $\text{Cr}_2\text{O}_3$ . 在  $R < R_F$  的试样中, X 衍射分析指出有  $\alpha\text{-Fe}$  存在, 并且还原所生成的碳化物中铬的含量也随还原率的提高而增加, 初期是  $(\text{Fe}, \text{Cr})_3\text{C}_2$ , 而后变为  $(\text{Cr}, \text{Fe})_7\text{C}_3$ .

但也有一些学者认为此尖晶石中的  $\text{FeO}$  和  $\text{Cr}_2\text{O}_3$  是同步被还原出来的, 在片山博等的论文中也可找到这种见解. 实际上, 由图4 可见, 随着还原温度的升高,  $\text{FeO}$  领先还原的过程很快就能完成, 这就是宏观上往往可看到两者同步还原的原因. 但即使在此条件下, 仍显示出  $\text{FeO}$  促进  $\text{Cr}_2\text{O}_3$  还原的作用.

在  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  的还原过程中, 按照 G. C. Uler 等<sup>[5]</sup>的观点, 此尖晶石里会有  $\text{Cr}^{2+}$  存在. N. S. S. Murti 等<sup>[6]</sup>则认为还原产物中可检出  $\text{Cr}_3\text{O}_4$ . U. F. Chinje 等<sup>[7]</sup>也有类似的发现, 并认为此种含有  $\text{Cr}^{2+}$  的尖晶石和金属铁相接触时会生成一种熔点甚低 ( $< 1000$ ) 的液相, 虽然随着还原率的提高, 此液相逐渐消失, 但它可能是引起团块开裂的一个重要原因.

铬矿常含有  $\text{Fe}_2\text{O}_3$ , 其作用与  $\text{FeO}$  应是一致的.

镁铬尖晶石的还原约于 1200 开始, 然而只要有约 40 的温升, 还原率就可达到 100% (见图5). 温度的这种重大影响正是镁铬尖晶石还原过程的特点, 还原生成物是  $\text{MgO}$  和  $\text{Cr}_3\text{C}_2$ .

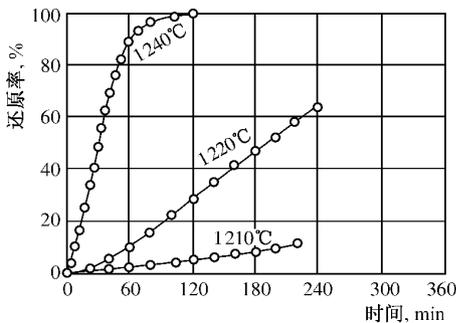


图5 不同温度下  $MgCr_2O_4$  的还原规律

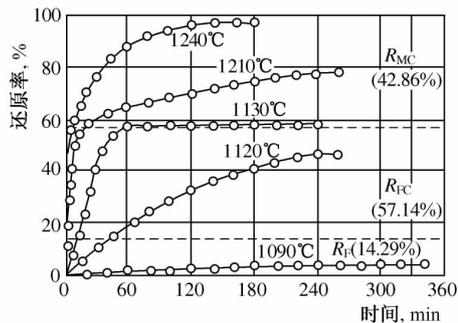


图6 不同温度下  $(Mg_{0.5}, Fe_{0.5})Cr_2O_4$  的还原规律

( $R_F$ 、 $R_{FC}$ 、 $R_{MC}$  分别为  $FeO$ 、 $FeCr_2O_4$  和  $MgCr_2O_4$  完全还原的还原度)

$(Mg_{0.5}, Fe_{0.5})Cr_2O_4$  相的还原规律示于图6. 由 1150 的曲线特征可以推测其中  $FeCr_2O_4$  是领先还原的, 但它的还原与游离态  $FeCr_2O_4$  的还原不同, 反应需在较高温度下开始, 却在较低温度下结束. 由  $>1150$  的曲线特征还可看到, 一旦  $FeCr_2O_4$  被充分还原, 反应速度就显著减小, 这说明  $MgCr_2O_4$  的还原阻力甚大. 另一方面, 由于  $R > R_{FC}$  时还原生成物并不是  $Cr_3C_2$ , 而是  $(Cr, Fe)_7C_3$ , 所以  $(Fe_{0.5}, Mg_{0.5})Cr_2O_4$  中的  $MgCr_2O_4$  的还原与游离态  $MgCr_2O_4$  的还原大体相同.

$(Mg_{0.5}, Fe_{0.5})(Cr_{0.8}, Al_{0.2})_2O_4$  在成分上最接近于天然铬铁矿, 图7 是其还原规律. 显见, 其中  $MgCr_2O_4$  的还原只有在约 1270 以上才能有效地发展. 这应该说是加入  $Al_2O_3$  的结果, 但  $FeCr_2O_4$  的还原看来未受严重影响, 在  $R > R_{FC}$  时此相的还原产物中发现有  $MgO \cdot Al_2O_3$  尖晶石的衍射波峰.

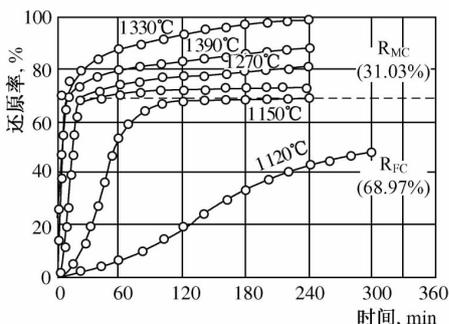


图7 不同温度下  $(Mg_{0.5}, Fe_{0.5})(Cr_{0.8}, Al_{0.2})_2O_4$  的还原规律

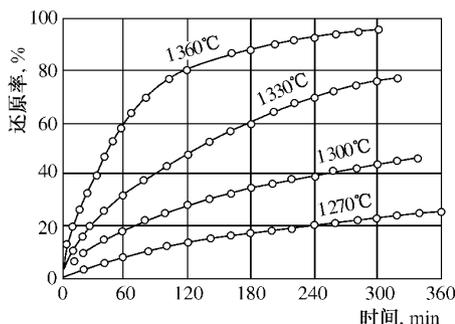
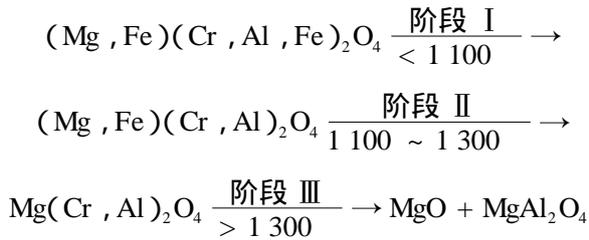


图8 不同温度下  $Mg(Cr_{0.8}, Al_{0.4})_2O_4$  的还原规律

图 8 是  $\text{Mg}(\text{Cr}_{0.6}, \text{Al}_{0.4})_2\text{O}_4$  的还原规律, 这一矿相的还原需要 1 300 以上的高温, 还原生成物中除了  $\text{Cr}_3\text{C}_2$  和  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  之外, 还有游离的  $\text{MgO}$ .

片山博等还用由天然矿石中分离出来的“铬铁矿”作了研究. 毫无疑问, 以上所引述的各种还原规律都应在天然铬铁矿的还原中有所反映, 即天然“铬铁矿”的还原照例是分阶段进行的<sup>[8]</sup>.



当然, 在不同的条件下这种分段模式有其变化的可能性. 例如, W. J. Raukin<sup>[10]</sup> 在其试验中发现, 在 < 1 200 条件下铬不会被还原, 反应生成物里有  $\text{Cr}_2\text{O}_3$  检出, 这看来是配碳量较小之故.

片山博在试验中还发现各种天然“铬铁矿”有如图 9 所示的还原规律. 显而易见, 在 1 200 ~ 1 250 前后的还原特点不同. 按片山博之见, < 1 200 条件下的还原率主要取决于气孔率, 气孔率大还原就快. 而高温下的还原率在很大程度上则受原料中  $\Sigma \text{Fe}$  量的影响,  $\Sigma \text{Fe}$  量愈多 (含铬较低) 还原率愈高.

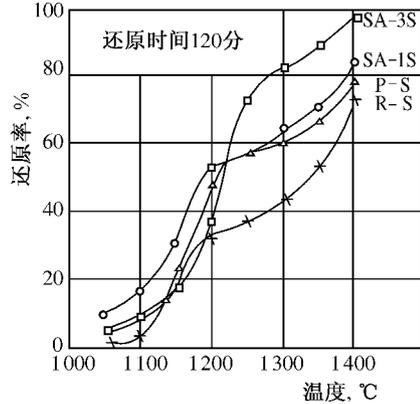


图 9 不同温度下天然“铬铁矿”的还原规律

### 3 天然“铬铁矿”相在还原过程中的结构和成分变化

利用扫描电镜和电子探针揭示还原过程中矿粒结构和成分的变化, 这是还原规律研究中极其重要的一个组成部分. 片山博等<sup>[9]</sup>与 W. J. Raukin 等<sup>[10]</sup>的工作是目前在这方面较为完整的报道. 由于采用了定量分析, 所以他们能够描述还原过程中矿粒内部各元素浓度的变化.

图 10(a)是刚有痕量还原率时的情况, 此时矿粒结构看不出变化, 也没

有明显的金属析出,各元素的分布大体上与原矿一样.

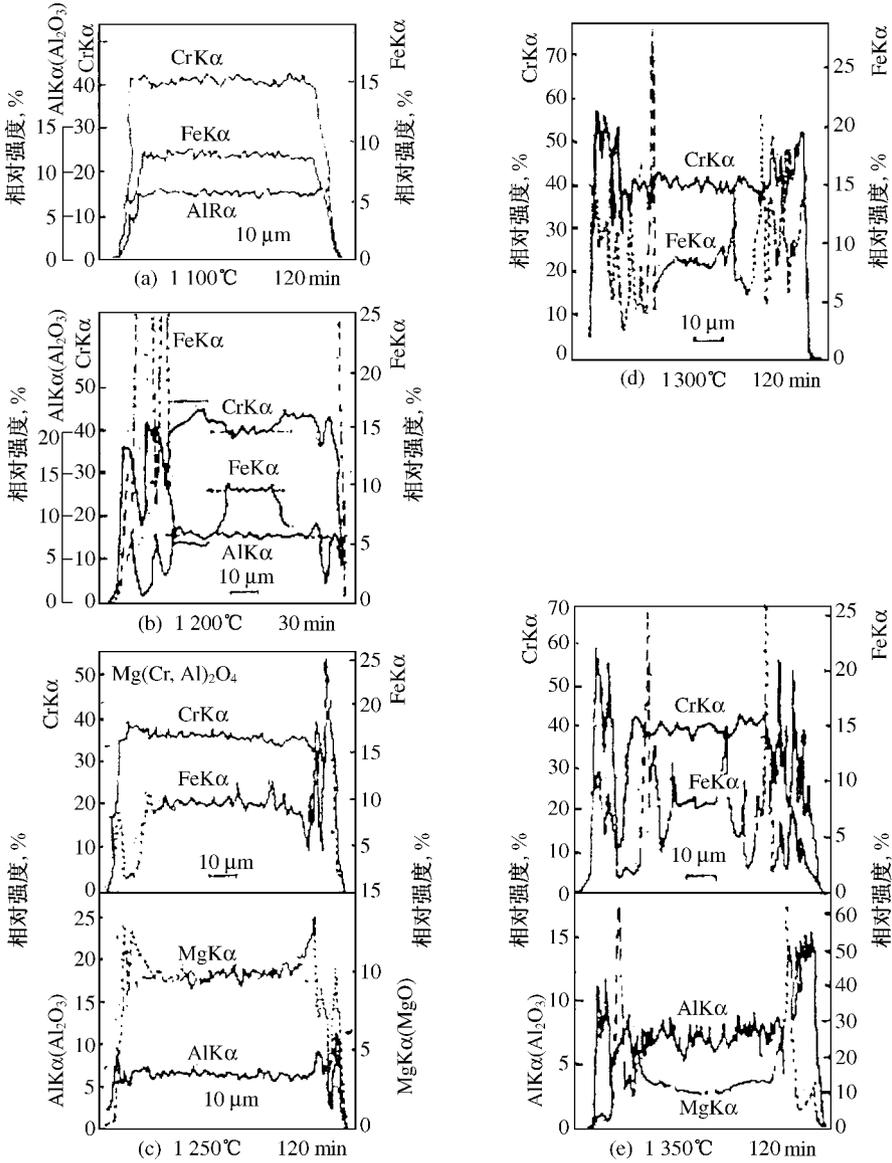


图 10 由苏联铬矿中分离出来的铬铁矿矿相的 EPMA 线扫描  
(图(b)中的水平线表示起始浓度)

图 10(b)是还原率为 20% ~ 40% 时的特征. 此时矿粒结构仍无显著变化,但其外围已可检出金属相,这并不是纯铁相,其中铬约可达 10%. 矿粒直

径比原始尺寸略有缩小,矿粒内各元素分布已有明显变化.外缘部位的含铁量降低了,甚至出现了浓度梯度,这就是这一阶段铁元素由矿粒内向外扩散的实据,正是这个原因使得铬在矿粒外缘部位的浓度升高.然而在紧靠金属析出处铁和铬的局域浓度都降低,在矿粒芯部两者又几乎保持原始浓度.另外,  $\text{Al}_2\text{O}_3$  在矿粒外缘的浓度已可检出.

图 10(c)是还原率为 30% ~ 50% 时的特征.此时矿粒外围的金属相已长大,且其含铬量也增至 10% ~ 20%.矿粒的边界则变得坑洼不平,矿粒内部开始有脉石状金属相析出,可见到气孔变大和增多.  $\text{MgO}$  和  $\text{Al}_2\text{O}_3$  已在矿粒的外缘浓缩,该处有近似于  $\text{Mg}(\text{Cr}, \text{Al})_2\text{O}_4$  的相检出.

图 10(d)的还原率已达 40% ~ 70%,此时矿粒的内外均有更大的金属相检出,外围金属相中含有相当高的铬,内部脉状金属相的含铬量较低.如果原始矿粒较细,此时在尚未还原的矿粒内部含铁量已不大,而存在着铬的浓度梯度,表明铬由内向外的扩散取代了铁的扩散.这一阶段里的其他现象与前一阶段相似.

图 10(e)是还原率更高时的特征,除了与上阶段相似的现象之外,  $\text{MgO}$  和  $\text{Al}_2\text{O}_3$  的浓缩区已十分明显,表明  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  的反应阻挡层已形成.

事实上,金属相一旦析出之后它就一直处于渗碳过程中,只是因为片山博等和 W. J. Raukin 等工作均未能测碳,故难以判断何时由金属相变成碳化物. R. H. Nafziger 等<sup>[11]</sup>认为高还原率的试样中可发现呈异相结构的金属,可能这就表明碳化物的生成.但也可能一开始就是碳化物而不是含碳金属.在不同配碳条件下碳化物究竟何时出现还需要用多种检验方法进行测定.

#### 4 天然铬矿的还原

天然铬矿和由其中分离出来的“铬铁矿”的区别在于前者含有以  $\text{SiO}_2$  为主的脉石.图 11 是天然铬矿的还原规律<sup>[8]</sup>.片山博等认为这一特点正反映  $\text{SiO}_2$  的作用—— $< 1270$  时它对还原起阻碍作用,在高温下它可与  $\text{MgO}$ 、 $\text{Al}_2\text{O}_3$  反应而又促进还原.

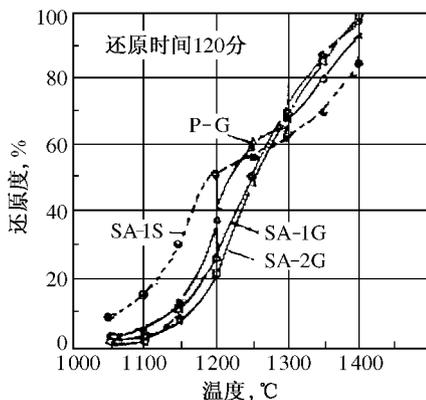


图 11 不同温度下天然铬矿的还原规律

高还原率时天然铬矿内元素的分布特征示于图 12. 由图可知,存在着一个 MgO 高度浓缩的区域,它把已析出的金属相分割成内外两部分. 在原矿的芯部也已充分还原,这里含铁高的金属相和含铁低的混杂在一起. 靠近原矿粒外缘处有 SiO<sub>2</sub> 的峰,这是 SiO<sub>2</sub> 侵入的表现. 据片山博等的看法,1 250 °C 下进行还原时即可观察到这一现象,张南生等称有 2MgO · SiO<sub>2</sub> 生成<sup>[12]</sup>.

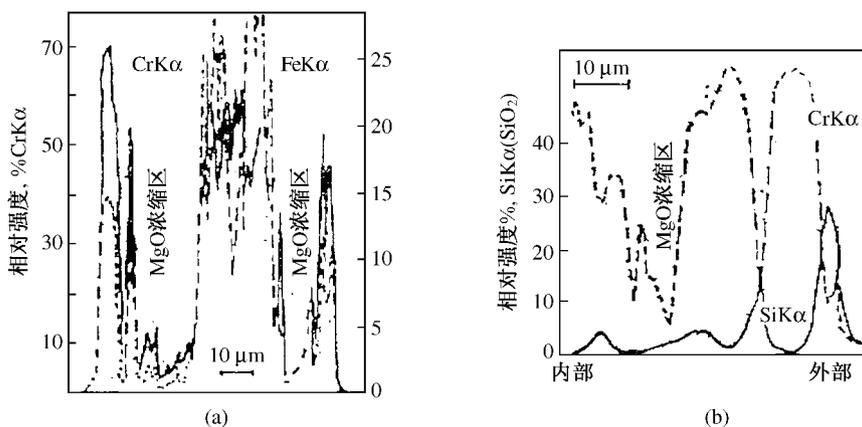


图 12 1 350 °C, 120 min 还原后的 EPMA 线扫描  
(a)—苏联铬矿;(b)—苏联铬矿中的铬铁矿矿相

## 5 直接还原还是间接还原

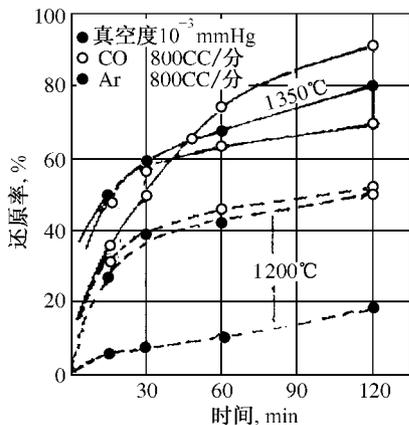


图 13 不同条件下铬铁矿的碳还原

含碳铬矿团块的还原过程是由固体碳直接还原还是由一氧化碳进行间接还原,应该说人们在这一还原途径的研究中迄今还有不少解释不了的结果或相互矛盾的观点,所以这是有待继续深入探索的一个领域,而关键是首先要解决研究方法.

片山博等主要研究了改变气氛或气压的影响,图 13 是他们在 1977 年发表的试验结果<sup>[13]</sup>. 所用的 (Mg, Fe) (Cr, Al, Fe)<sub>2</sub>O<sub>4</sub> 是由天然铬矿分离而

得. 低温下 ( $< 1200 \sim 1250$ ) 主要是通过一氧化碳还原, 而高温下主要是碳通过固相扩散直接还原. 这一观点是他们以此图为依据提出的.

但对此论点并非没有争议.

气体在团块中的渗透有一个临界气孔直径, 此直径与相应气压下的气体分子自由程有关. 在真空下气体分子的自由程变大, 即相应的临界气孔直径变大, 因此一氧化碳能起反应作用的总反应表面积减小, 这就是真空下间接还原受阻的主要原因. 就直接还原作为一个单元反应来说, 真空固然可以促进它, 但对碳的固相扩散很难说有什么作用, 所以真空下以直接还原为主要反应途径只在有限的条件下 (如碳的固相扩散阻力小, 团块气孔也小) 才是可靠的. 图 13 的试验并未用压块, 而是将矿粉、碳粉混匀后装入石墨坩埚. 若假设真空下以直接还原为主, 那么  $< 1200 \sim 1250$  时一氧化碳流动气氛中只有设想以间接还原为主才可理解图 13 所示的规律, 因为若也以直接还原为主则其还原速率应比真空下更小. 然而,  $> 1200 \sim 1250$  时真空下的直接还原不仅比一氧化碳流动气氛中的直接还原快, 也可能快于一氧化碳气氛中的间接还原, 即  $> 1200 \sim 1250$  条件下一氧化碳流动气氛中的反应途径尚难定论.

用一氧化碳还原纯  $\text{Cr}_2\text{O}_3$  的反应驱动力甚小, 只要不大的  $p_{\text{CO}_2}/p_{\text{CO}}$  就足以抑制它. 但用一氧化碳还原无内配碳的  $\text{FeCr}_2\text{O}_4$  时发现铬也有部分还原, 如  $1300$  下保持 5 小时,  $R_{\text{Fe}}$  可达 74%,  $R_{\text{Cr}}$  也可达 8%<sup>[13]</sup>. 1985 年片山博等所发表的在不同的一氧化碳气压下还原含碳  $\text{FeCr}_2\text{O}_4$  的试验结果<sup>[14]</sup> 与图 13 是吻合的. 由此看来, 至少在含碳铬矿团块还原过程的前期, 反应可能是主要按间接还原方式进行的.

然而, 同时发表的在不同一氧化碳气压下还原含碳  $\text{MgCr}_2\text{O}_4$  之试验结果却显示出不同于图 13 的特点. 图 14 表明在  $0.1 \sim 0.2$  atm 条件下还原速率出现极值. 片山博等又用商品球团在不同一氧化碳气压下做了试验<sup>[15]</sup>, 其结果 (图 15) 与图 13 是矛盾的, 且与图 14 也不全一致. 片山博等按间接还原作了解释, 同时又承认尚

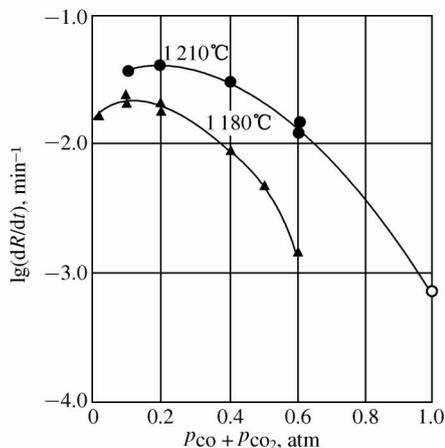


图 14 ( $p_{\text{CO}} + p_{\text{CO}_2}$ ) 对  $\text{MgCr}_2\text{O}_4$  还原速率的影响

难自圆其说.

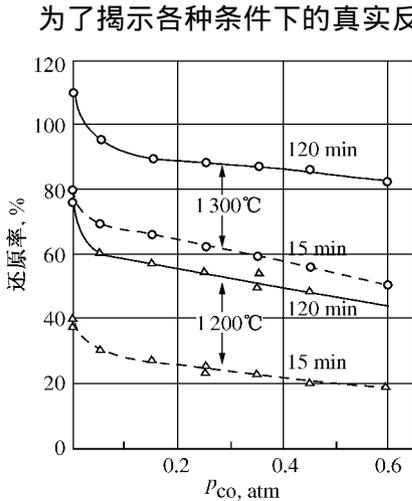


图 15  $N_2$ -CO 气氛中的  $P_{CO}$  对商品球团还原的影响

为了揭示各种条件下的真实反应途径,使用别的研究方法是必需的.前面已介绍了某些条件下含碳铬矿团块的还原率与反应物的气孔率有关,但在这方面发表的文章过于粗糙.作者认为应以汞压入法测孔作为这一研究的基础(在铁矿还原研究中应用此法卓有成效),定量地查核各阶段还原反应速率与气孔(大于临界直径者)内表面积的关系.

为了揭示真实的反应途径,还必须研究微气孔的分布.

前已提到,在过程的中后期,尚未还原的矿粒内部也有生成物析出.但只有检出其在微气孔旁形核,才能有说服力地证实间接还原的贡献.

前还提到,尚未还原的矿粒内有铁的乃至铬的浓度梯度.因此,未反应核和早已析出的生成物之间的边界应是发生单元反应的场所.在此边界上发生的可能是直接还原,也可能是间接还原.因为此界面上也会有微气孔.

在铁矿的还原研究中已证明一氧化碳可进入约 130 Å 的微气孔内起还原作用,所以只有用精细的检验方法才能完成这一研究任务.

因此,含碳铬矿团块的真实还原途径目前尚难断言.作为一种估计,还原前期可能主要通过一氧化碳起作用,而在中后期两种还原途径可能均有贡献.只有依靠研究方法的进一步改进,才可望提出公认的见解.

## 参 考 文 献

- [ 1 ] 蒋国昌. 在上海市金属学会铁合金专业委员会成立大会上的报告, 1988
- [ 2 ] Y. Maru, *et al.*, *Met. Trans.* 1973, 4, 2591-2598
- [ 3 ] С. М. Голодов др. *Изв ВУЗ ЧМ*, 1984(5), 6-9
- [ 4 ] 片山博等. *铁与钢*, 1979, 65(3), 331-340
- [ 5 ] G. C. Ulmer, *et al.* *J. Am. Ceram. Soc.*, 1966, 49, 50
- [ 6 ] N. S. S. Murti, *et al.* *Trans ISIJ*, 1982, 22, 925-933

- [ 7 ] U. F. Chinje , *et al.* Ironmaking & Steelmaking , 1986 , 13(1) , 3-8
- [ 8 ] 片山博等. 铁と钢 , 1974 , 60(9) , 1289-1298
- [ 9 ] 片山博等. 铁と钢 , 1984 , 70(11) , 1559-1569
- [ 10 ] W. J. Raukin , *et al.* Arch. Eisenbutt , 1979 , 50(9) , 373-377
- [ 11 ] R. H. Nafziger , *et al.* Mat. Trans , 1979 , 10B , 5-14
- [ 12 ] 张南生等. 铁合金 , 1980(4) 5-14
- [ 13 ] 片山博. 铁と钢 , 1977 63(2) 207-216
- [ 14 ] 片山博等. 铁と钢 , 1985 71(9) 1094-1101
- [ 15 ] 片山博等. 铁と钢 , 1985 , 71(14) , 1607-1614

## A Basic Study on Reduction Process of Chrome Ore Agglomerate

**Abstract** A comprehensive review on achievements in basic study of reduction process of chrome ore agglomerate at abroad is given. It introduced emphatically reduction curves of each component in chromite and changes in its structure and composition. The direct and indirect reduction in reducing process of carbon contained chrome ore agglomerate is also discussed.

# 超低硫钢冶炼技术的研究<sup>\* 1</sup>

**摘要** 含硫量小于 30 ppm 的超低硫钢是发展石油工业等的紧缺钢材. 为开发这种钢的冶炼技术, 作者用在英国 BSC 公司做的试验数据作了统计分析, 并相应地进行了一些基础研究. 研究指出, 不能单独用  $B = (\% \text{CaO})/(\% \text{SiO}_2)$  或 MI (Mannesmann Index) 来说明顶渣的脱硫效果. 它们有一最佳匹配, 即  $B \approx 7$ ,  $MI = 0.33$ . 最佳的顶渣组成是 58% ~ 62% CaO + 24% ~ 28%  $\text{Al}_2\text{O}_3$  + 8% ~ 12%  $\text{SiO}_2$ . 在 MI 较大时,  $(\% \text{FeO}) + (\% \text{MnO})$  对脱硫效果的影响较弱. 文中对喷吹方案、Ca 利用率和回硫问题进行了分析.

超低硫钢是指硫含量小于 30 ppm 的钢. 随着石油工业的发展, 为了制造能在高压、低温和腐蚀性环境下工作的油、气管线及海洋采油平台, 必须不断降低钢的含硫量<sup>[1]</sup>. 我国石油工业对超低硫钢的需求呼声日高. 为开发这种钢的冶炼技术, 在自然科学基金支持下完成了本基础研究.

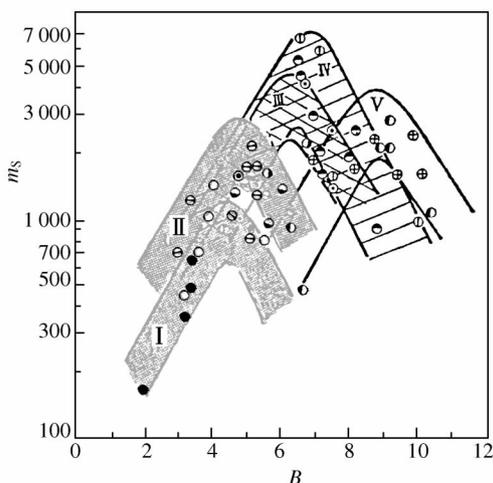
## 1 顶渣碱度

众所周知, 即使是喷粉脱硫工艺, 终点硫含量主要仍取决于顶渣. 而从工艺因素看, 碱度对顶渣脱硫能力的影响最大. 碱度可用很多方式表达, 其中最常用的是  $B = (\% \text{CaO})/(\% \text{SiO}_2)$ . 在钢的二次精炼领域里, 曼内斯曼指数 MI (Mannesmann Index) 也已得到广泛应用.

对在英国 BSC 公司所做的喷粉脱硫数据进行处理后, 发现 B 和 MI 对顶渣脱硫效果的影响是交错的. 在用  $m_s = (\% \text{S})/(\% \text{S} \cdot \% \text{Al}^{2/3})$  表示硫分配

\* 本文合作者: 蒋国昌、郭占成、关玉龙. 原发表于《钢铁》24(8), 12~16(1989)

指数的前提下,将按 MI 值分档,可以看到在每一个 MI 范围内, B 对  $m_s$  的影响都有一个峰值点. 而且将各个优选的 B 值点连接起来,又形成一条具有一峰点的曲线,见图 1. 若将数据 B 值分档,也可看到类似的规律. 这就是说顶渣的控制应从 B 和 MI 两方面提出要求. 例如,对钢的二次精炼用渣,一般要求  $MI = 0.25 \sim 0.35$ <sup>[2]</sup>. 这自然是限于某个 B 值范围的结果. 而本研究中,当  $MI = 0.2$  时也可能脱硫良好<sup>[3]</sup>.



组别	MI	程喷	单喷
I	0.07 ~ 0.15	●	○
II	0.15 ~ 0.20	◐	◑
III	0.20 ~ 0.25	◒	◓
IV	0.25 ~ 0.30	◔	◕
V	0.30 ~ 0.35	⊕	⊙

图 1 碱度和 MI 对硫分配的影响

图 1 所示的规律可用如下回归方程(73 组数据的处理结果)描述:

$$\lg m_s = 7.99 - 20.0(MI - 0.327)^2 - 0.0355(B - 7.15)^2 - 21.06N_{fm}$$

$N_{fm}$  为渣中 FeO 和 MnO 的摩尔分数之和. 此式的相关检验结果:  $U = 25.28$ ;  $Q = 21.17$ ;  $F = 16.0$ ;  $\alpha = 0.05$  时  $\lambda = 4.0$ . 因此,最佳匹配是  $MI = 0.327$ ,  $B = 7.15$ .

以上所揭示的规律可用 O/R 值的变化来说明. O/R 是 Lok 建议采用的指标<sup>[4]</sup>.  $O/R = n_{O_2} / (n_{SiO_2} + n_{Al_2O_3})$ ,  $n$  是摩尔数. 图 2 表明图 1 各曲线峰点的  $m_s$  与相应的 O/R 值成线性关系. 看来, BSC 公司的试验中,最大的 O/R 值出现时,  $m_s$  最大.

由上述最佳匹配可进一步推知最佳顶渣组成应为 63% CaO + 24%  $Al_2O_3$  + 10%  $SiO_2$ . 这和 Shii<sup>[5]</sup>、小仓康嗣<sup>[6]</sup>、Turkdogan<sup>[7]</sup> 的观点一致. 也为本实验室试验<sup>[3]</sup>所证实.

## 2 其他碱度表达式的应用

上述 B 和 MI 均是经验性的碱度表达式. 单用其一难以概括 CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO 四元系的特性. 为此, 又用以 Flood<sup>[8]</sup> 和 Lok<sup>[4]</sup> 两个理论为依据导出的碱度表达式<sup>[3]</sup>作了处理.

$$B_{FL} = \frac{N_{Ca^{++}}^e + 0.58N_{Mg^{++}}^e}{N_{SiO_2} + 0.50N_{Al_2O_3}}$$

$N_{SiO_2}$  和  $N_{Al_2O_3}$  是常用的摩尔分数, 而  $N_{Ca^{++}}^e$  和  $N_{Mg^{++}}^e$  是 Flood 所定义的电当量摩尔分数.

$$N_{Ca^{++}}^e = n_{Ca^{++}} / (n_{Ca^{++}} + n_{Mg^{++}})$$

$$N_{Mg^{++}}^e = n_{Mg^{++}} / (n_{Ca^{++}} + n_{Mg^{++}})$$

图 3 指出  $B_{FL} > 4.5$  时可有良好的脱硫. 这和实验室研究结果<sup>[3]</sup>也一致.

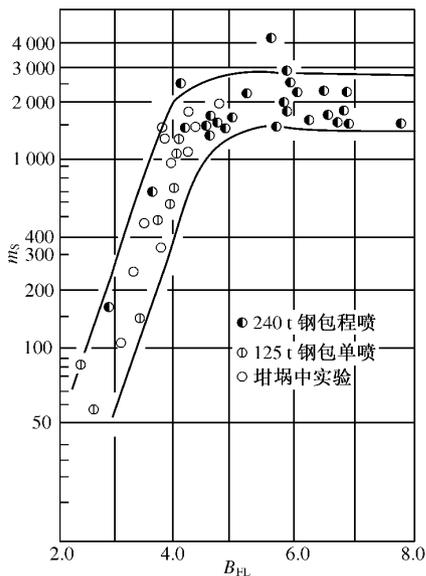


图 3  $B_{FL}$  与  $m_s$  的关系

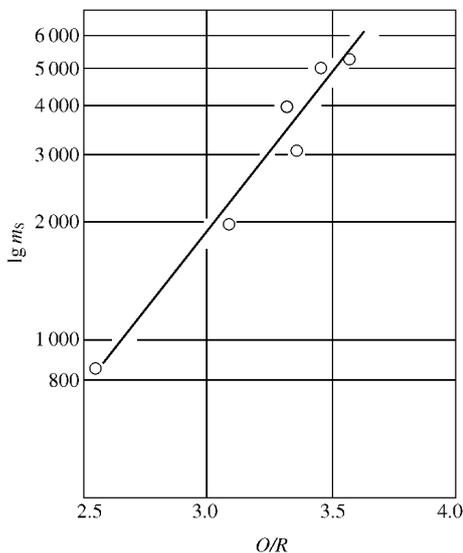


图 2 O/R 值与  $m_s$  的关系

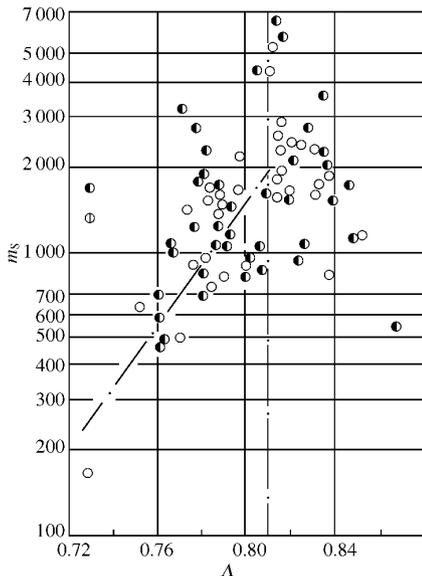


图 4 光学碱度对硫分配指数  $m_s$  的影响

在碱度这一概念的发展中,光学碱度是一个理论基础比较完善且又可实测的新成果<sup>[9]</sup>. Sommerville 等<sup>[10]</sup>曾成功地用光学碱度( $\Lambda$ )概括了7个渣系的硫容量( $C_s$ ) 指出  $\lg C_s$  与  $\Lambda$  之间呈线性关系.

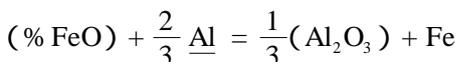
采用中村崇<sup>[11]</sup>的数据处理了在 BSC 公司取得的结果,发现  $\Lambda$  愈大则  $\lg m_s$  愈分散,见图 4. 应注意的是,若脱硫操作终止时反应已接近平衡,则  $m_s$  应是  $C_s$  的函数. 这种条件下,图 4 应和 Sommerville 等的结果吻合. 但迄今已发表的文献中都只限于  $\Lambda < 0.81$  的范围. 在这一范围里,图 4 是接近 Sommerville 等的结果的. 当然,  $m_s$  只是过程参数,所以图 4 中数据的分散度较大是合理的.

另外,在  $\Lambda > 0.81$  的范围里,图 4 的数据更分散. 这一组成实际上已在 CaO 饱和析出线之外. 因此,不可能指望只适用于均相熔渣的光学碱度会明显地影响脱硫指标.

### 3 终渣中的 (% FeO) 和 (% MnO)

图 5 是终渣 (% FeO + % MnO) 对终点硫含量的影响,随着 MI 的增加, (% FeO + % MnO) 的影响减弱. 这一结果并不异常. 因为 MI 增大时,  $a_{FeO}$  是下降的<sup>[12]</sup>.

图 5 表明为使终点含硫量小于 10 ppm, (% FeO + % MnO) 应不大于 0.6%. 此值大体上和钢中的残铝平衡.



$$\Delta G^\circ = -67723 + 17.8T$$

32 组数据的平均值  $\underline{\text{Al}} = 0.039\%$ . 利用以 Thermo-Calc. 程序和修正 IR-SID-Kapor-Frohberg 炉渣模型为基础的计算结果<sup>[13]</sup>,可知相应于最佳顶渣组成的  $\alpha_{\text{Al}_2\text{O}_3}$  约在 0.1 左

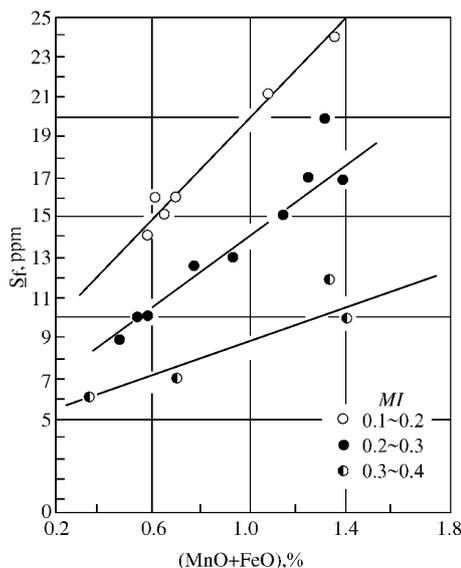


图 5 终渣 (FeO + MnO)% 与终点硫含量的关系

右. 而(FeO)的活度系数约为  $0.5 \times 10^{-3}$ , 所以  $\alpha_{\text{FeO}} = 0.38 \times 10^{-3}$ , 或  $(\% \text{FeO}) \doteq 0.7\%$ .

#### 4 两种喷粉方案的比较

上述数据处理中采用  $m_s$  作为脱硫指标, 由于单喷 CaO 者, 其 %  $\underline{\text{Al}}$  较 CaO-CaSi-CaO 程序喷吹的低, 所以可将两种数据当作一个样本考察. 但实际上两者的脱硫效果是有差异的. 在初始硫量相近的前提下, 采用程序喷粉炼成超低硫的概率较大, 见表 1.

表 1 超低硫钢的炼成率

	初始 % $\underline{\text{S}}$ 70 ~ 60 ppm			初始 % $\underline{\text{S}}$ 50 ~ 40 ppm		
	统计数	% $\underline{\text{S}} < 20$ ppm 的几率, %	% $\underline{\text{S}} < 15$ ppm 的几率, %	统计数	% $\underline{\text{S}} < 20$ ppm 的几率, %	% $\underline{\text{S}} < 15$ ppm 的几率, %
单 喷	15	26.7	0	11	63.6	18.2
程 喷	9	77.8	66.7	23	91.3	60.9

采用逐步回归, 输入 16 个度量, 得到如下规律.

对单喷 CaO 的 50 炉数据

$$\begin{aligned} \lg \frac{(\% \underline{\text{S}})}{\% \underline{\text{S}}} = & - 2.03 + 3.18 N_{\text{CaO}} + 3.09 N_{\text{MgO}} + 0.217 \lg N_{\text{MnO}} \\ & - 0.555 \lg \% \underline{\text{Al}}_f + 5.37(0.11 \% \underline{\text{C}} \\ & + 0.063 \% \underline{\text{Si}} + 0.026 \% \underline{\text{Mn}}) \end{aligned}$$

%  $\underline{\text{Al}}_f$  是终点含铝量. 此式的相关系数  $R = 0.94$ .

对程序喷吹的 51 炉数据

$$\begin{aligned} \lg \frac{(\% \underline{\text{S}})}{\% \underline{\text{S}}} = & 0.968 + 4.06 N_{\text{MgO}} - 5.36 N_{\text{SiO}_2} - 1.53 N_{\text{Al}_2\text{O}_3} \\ & - 0.25 \cdot \lg \cdot N_{\text{MnO}} - 0.197 \lg N_{\text{FeO}} \\ & + 0.155 \cdot Q_{\text{CaO}} + 0.522 \lg t \end{aligned}$$

$Q_{\text{CaO}}$  是 CaO 的喷吹强度 (kg/t),  $t$  是喷粉时间. 此式的相关系数  $R = 0.91$ .

尽管在 BSC 公司的试验中已证实单独喷吹 2.5 ~ 3.0 kg/t 的 CaO 对高

% S 区(% S = 140 ~ 180 ppm) 的脱硫还是有用的, 但因为钢水氧位偏高, 所以炼超低硫钢还得靠程序喷吹.

## 5 Ca-Si 的有效利用率

在 BSC 公司的试验中, Ca-Si(含 28% Ca) 的喷吹强度是 3.05 kg/t. 若假定喷粉期间全靠 Ca 脱硫, 则用于脱硫的 Ca 量是

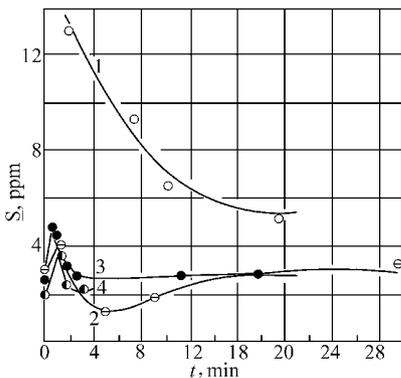
$$\frac{40}{32} \cdot \Delta \% S = \frac{40}{32}(43.7 - 19) \times 10^{-3} = 0.031 \text{ kg/t}$$

因喷 Ca-Si 前先用 Al 脱氧, 故忽略耗于脱氧的 Ca 量. 再考虑到溶于钢水的 Ca 量约为 0.041 kg/t, 从而算出 Ca 的利用率仅为 8.4%.

## 6 回硫

在 BSC 所作的试验中, 曾有 7 个炉号出现回硫现象. 与其他炉号比较, 这 7 炉的特点是: ① 终点硫含量很低, ② 钢中铝的烧损较大. 为了验证回硫现象出现的规律, 利用 30 kg 感应炉进行了程序喷吹试验.

所用的喷粉方案及试验结果示于图 6. 可见, 凡是初始硫量高的炉号都有明显的脱硫. 反之, 则有明显的回硫. 而且回硫均出现于喷吹石灰粉期间. 笔者认为这一试验结果表明: ① 经过喷粉精炼, 硫在渣钢间的分配已接近平衡, 这是出现回硫的基础条件; ② 直接引起回硫的因素是钢水氧的变化, 这和 R. J. Fruehan 的观点<sup>[14]</sup>完全吻合.



符号	喷吹工艺	喷吹量 kg		
		CaO	Ca-Si	CaO
○	程序喷吹	30	150	30
⊖	分层装入一次喷尽	30	250	30
⊙		30	150	30
●		30	150	30

图 6 感应炉喷粉试验中的回硫现象

## 参 考 文 献

- [ 1 ] 徐匡迪 ,上海金属 ,1986 4 2-11 5 ,13-15
- [ 2 ] Holappe ,L. E. K. , International Metal Review ,27(1982) 2. 53-76
- [ 3 ] 张岚 ,上海工业大学学报 8(1987) ,4 ,441-450
- [ 4 ] Lok ,N. V. ,Izv. VUZ Cher. Met. ,1981 ,5 ,167-168
- [ 5 ] Shii ,A. I. , Iron & Steel Maker ,1983 ,7 ,35-41
- [ 6 ] 小仓康嗣 ,钢と铜. 72(1986) 9 ,1309-1315
- [ 7 ] Turkdogan ,E. T. ,Ironmaking & Steelmaking ,12(1985) ,2 ,64-78
- [ 8 ] Flood ,H. ,JISI ,171(1952) ,64-82
- [ 9 ] 蒋国昌 ,上海工业大学学报(待发表)
- [ 10 ] Sommerville ,I. D. ,2nd International Symp. on Met. Slags & Fluxes ,1984 ,1019-1026
- [ 11 ] 中村崇 ,日本金钢镗全志 50(1986) ,5 ,456-461
- [ 12 ] 陈家祥 炼钢常用图表数据手册 冶金工业出版社 北京 1984 636
- [ 13 ] Gustafsson ,S. 国际中小型钢厂会议(资料) ,上海 ,1987
- [ 14 ] Fruehan ,R. J. ,Met. Trans. ,9B(1978) ,287-293

## Investigation on Melting Technology of Ultra-low Sulphur Steel

**Abstract** The ultra-low sulphur steel containing sulphur lower than 30 ppm is an important material in short supply for the developing petroleum industry. In order to improve the melting technology of this steel a statistical analysis based on the experimental results carried out by one of the authors in British Steel Corporation and some relevant fundamental researches were done.

It was found that the influence of  $B = (\% \text{CaO}) / (\% \text{SiO}_2)$  on desulphurization is effected by Mannesmann Index ( $MI$ ), and vice versa. Thus an optimum match was found :  $B = 7$  and  $MI = 0.33$ . For different basicity expressions in desulphurization analysis. It is found that the optimum composition of top slag is 58% -62%  $\text{CaO} + 24\% -28\% \text{Al}_2\text{O}_3 + 8\% -12\% \text{SiO}_2$ . The influence of  $(\% \text{FeO} + \% \text{MnO})$  on desulphurization is weaker if the value of  $MI$  is bigger.

The injection mode , utilization of Ca and resulphurization have also been

discussed.

# 浇注过程钢液吸氮的研究<sup>\* 1</sup>

**摘要** 本文根据模型研究结果,对浇注过程钢液吸氮的现象进行了研究. 研究表明,浇注过程钢液含氮量的变化与注流的长度、水口直径等有关. 在一定的情况下也与钢液本身的物性(诸如表面张力、粘度和密度)有关. 与由于空气卷入钢液氮含量增加相比,通过注流表面吸氮很少,几乎可以忽略不计.

## 1 绪言

近年来,随着冶金技术的不断进步,现在已经能在浇注前将钢液中氮含量降低到很低的水平,因此必须对钢液的浇注过程进行严格的控制,以防止钢液在浇注过程中吸氮.

在钢液浇注过程中,一方面,注流将周围的空气卷入,将其中氮吸进;另一方面,由于注流与空气的直接接触,空气中的氮通过钢液-空气界面向注流中迁移.

本文将对浇注过程中钢液的吸氮机理进行分析,以对浇注过程钢液含氮量的变化进行估算,并分析影响钢液含氮量变化的因素.

## 2 注流的特征

图1表示上注和连铸时注流的流动情况. 图中  $Z_i$  表示浇注开始时注流的落下高度,  $Z$  表示浇注时的注流高度,  $h_i$  表示盛钢桶中钢液的初始高度,  $h$

\* 本文合作者:凌天鹰. 原发表于《钢铁研究》(2), 7~12, 117(1989)

表示浇注过程中盛钢桶钢液的高度  $R_1$  表示盛钢桶的半径 ; $l_0$  表示水口的长度 ;设铸锭截面为正方形  $d$  表示其边长.

### 2.1 钢液的流出速度和流出量

钢液可近似看作不可压缩的流体 ,应用伯努利方程 ,在忽略阻力损失的情况下 ,可求出钢液在水口末端的流出速度  $U_0$  为

$$U_0 = \sqrt{2g(h + l_0)} \quad (1)$$

根据流体流动的连续性方程 ,有

$$-\pi R_1^2 \frac{dh}{dt} = \pi a_0^2 U_0 = \pi a_0^2 \sqrt{2g(l_0 + h)}$$

从而得到

$$\frac{dh}{dt} = - \left( \frac{a_0}{R_1} \right)^2 \sqrt{2g(l_0 + h)} \quad (2)$$

式中  $a_0$  ——水口末端注流的半径  $\mu\text{m}$  ;

$g$  ——重力加速度  $\mu\text{m}/\text{s}^2$ .

根据初始条件  $h|_{t=0} = h_i$  ,对(2)式积分

$$\int_{h_i}^h \frac{dh}{\sqrt{2g(l_0 + h)}} = \int_0^t - \left( \frac{a_0}{R_1} \right)^2 dt$$

整理后得

$$\sqrt{l_0 + h} = \sqrt{l_0 + h_i} - \left( \frac{a_0}{R_1} \right)^2 \sqrt{\frac{g}{2}} t \quad (3)$$

将(3)式代入(1)式 ,则得钢液流出水口的初速度为

$$U_0 = \sqrt{2g} \left[ \sqrt{l_0 + h_i} - \left( \frac{a_0}{R_1} \right)^2 \sqrt{g/2} t \right] \quad (4)$$

钢液的自由流出量为

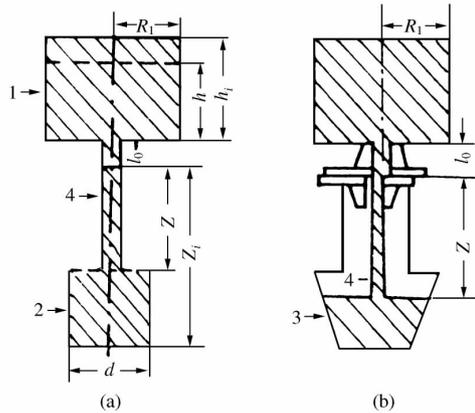


图1 浇注模型

1. 盛钢桶 ;2. 铸模 ;3. 中间包 ;4. 注液

$$g = \pi a_0^2 U_0 \rho \quad (5)$$

式中  $\rho$ ——钢液的密度  $g/cm^3$ 。

## 2.2 注流的落下高度

根据钢液流动的连续性方程可得

$$(h_i - h)\pi R_1^2 = (Z_i - Z)d^2 \quad (6)$$

整理后可得

$$Z = Z_i - \frac{\pi R_1^2}{d^2}(h_i - h) \quad (7)$$

由(4)式求得  $h$  的表达式为

$$h = \left[ \sqrt{l_0 + h_i} - \left( \frac{a_0}{R_1} \right)^2 \sqrt{\frac{g}{2}t} \right]^2 - l_0 \quad (8)$$

将(8)式代入(7)式,从而得到注流落下高度的表达式为

$$Z = Z_i - \left( \frac{\pi R_1^2}{d^2} \right) \left\{ h_i + l_0 - \left[ \sqrt{h_i + l_0} - \left( \frac{a_0}{R_1} \right)^2 \sqrt{\frac{g}{2}t} \right]^2 \right\} \quad (9)$$

## 2.3 钢液-空气的接触界面

设注流在高度  $Z$  处的半径为  $a$ ,则注流-空气的接触面积为

$$F_1 = 2\pi \int_0^Z a dZ \quad (10)$$

根据自由下落注流流动的稳定性理论<sup>[1]</sup>得

$$\frac{2gZ}{U_0^2} + 1 = \left( \frac{a_0}{a} \right)^4 \quad (11)$$

设  $\xi = (2gZ/U_0^2 + 1)^{1/8}$ ,则

$$a = a_0 \xi^{-2} \quad (12)$$

将上式代入方程式(10)得

$$F_1 = 2\pi \int_0^Z a_0 (2gZ/U_0^2 + 1)^{-1/4} dZ \quad (13)$$

整理后可得

$$F_1 = \frac{4\pi a_0 U_0^2}{3g} \left\{ \left[ \frac{2gZ}{U_0^2} + 1 \right]^{3/4} - 1 \right\} \quad (14)$$

### 3 浇注时注流卷入的氮

#### 3.1 浇注时注流卷入空气的速度

注流卷入空气的现象十分复杂,岩田腾吉等人通过模型试验和高速摄影对注流卷入空气进行了研究. 研究表明<sup>[2]</sup>,注流对气体的卷入速度受注流的半径、钢液的浇注速度和注流表面的紊流程度有关,可用下式表示:

$$v_g = 0.02v_1 [(R_c - a)/a_0]^3 \quad (15)$$

式中  $v_g$ ——注流卷入气体的速度  $\mu\text{m}^3/\text{s}$ ;

$a_0$ 、 $a$ ——分别为出口处和高度  $Z$  处的注流半径  $\mu\text{m}$ ;

$R_c$ ——注流的空穴半径  $\mu\text{m}$ ;

$v_1$ ——钢液的浇注速度  $\mu\text{m}^3/\text{s}$ . 可用下式计算得到

$$v_1 = \pi a_0^2 U_0 \quad (16)$$

Sande<sup>[3]</sup>等人通过实验求得  $R_c$  的计算公式为

$$R_c = [(1.14 + 0.0089E_1)^{1/2} - 1.067]^{1/2} \quad (17)$$

式中  $E_1$ ——注流的动能  $\mu\text{erg}$ .

假设注流表面凸出部分动能控制气体吸附<sup>[4]</sup>,则

$$E_1 = 1/2m v^2 \quad (18)$$

式中  $U$ ——钢液流动的线速度  $\mu\text{m}/\text{s}$ .

$$m = \pi\rho\lambda(2a\varepsilon - \varepsilon^2/2) \quad (19)$$

式中  $\lambda$ ——波长,可用式(20)表示:

$$\lambda = 8.38\varepsilon \quad (20)$$

式中  $\varepsilon$ ——钢液在位置  $Z$  处的表面紊流程度.

通过流体流动模型试验和因次分析<sup>[5]</sup>, 可得出钢液流动的表面紊流度

$\varepsilon$

$$\varepsilon = \varepsilon_0 \exp[(2/7)FrWe^{-0.35}(\xi^7 - 1)] \quad (21)$$

$$\ln\left(\frac{a_0}{\varepsilon_0}\right) = 44.3\left(\frac{l_0}{D_0}\right)^{-0.73} Re^{-0.1} \quad (22)$$

式中, We——Weber 数;

Re——Reynold 数;

Fr——Froude 数;

$\varepsilon_0$ ——出口处注流的表面紊流度.

根据流动的连续性方程<sup>[1]</sup>, 在高度为  $Z$  处注流流动的线速度可用下式表示

$$U = U_0 \xi^4 \quad (23)$$

### 3.2 因空气卷入钢液中氮含量的变化

设钢液温度为 1600, 氮气的分压为 0.79 atm, 假定注流周围的空气温度与钢液温度相同, 并设卷入的空气中的氮被注流全部溶解. 则在浇注某一时刻, 注流吸氮量  $\Delta[N]_E^0$  (%) 为

$$\Delta[N]_E^0 = 1.44 \times 10^{-2} v_g / \pi a_0^2 U_0 \rho \quad (24)$$

考虑到卷入的空气中氮不能完全溶解在钢液中, 设  $\eta_E$  为钢液对卷入的空气中的氮的吸收率, 则实际注流的吸氮量  $\Delta[N]_E^0$  (%) 为

$$\Delta[N]_E = \eta_E \cdot \Delta[N]_E^0 \quad (25)$$

浇注前后钢液平均含氮量的变化  $\Delta[\bar{N}]_E$  (%) 为

$$\Delta[\bar{N}]_E = 1.44 \times 10^{-2} G/M_1 \cdot \eta_E \quad (26)$$

式中  $M_1$ ——浇注的钢液重量 t;

$G$ ——浇注期间卷入气体总体积  $m^3$ .

## 4 浇注时注流钢液的吸氮

对于钢液与空气的直接接触, 气相中的氮向注流中的迁移可分为以下三

个步骤：

(1) 空气中的氮通过气体边界层向气-钢界面扩散 其迁移速度为

$$n_g = K_g(P_{N_2,b} - P_{N_2,i})/RT \quad (27)$$

式中  $K_g$ ——氮通过气体过界面的传质系数  $\mu\text{m/s}$ ；

$P_{N_2,b}$ ——气相中氮的分压  $\mu\text{atm}$ ；

$P_{N_2,i}$ ——气-液界面处氮的分压  $\mu\text{atm}$ ；

$R$ ——气体常数  $\mu\text{m}^3 \cdot \text{atm}/(\text{mol} \cdot \text{K})$ ；

$T$ ——气体温度  $\text{K}$ 。

(2) 在界面上氮发生分解、吸附等界面化学反应 其速度为

$$n_r = K_r(C_e^2 - C_i^2) \quad (28)$$

式中  $K_r$ ——界面化学反应速度常数  $\mu\text{m}^3/(\text{mol} \cdot \text{s})$ ；

$C_e$ ——与气相相平衡的平衡氮浓度  $\mu\text{mol}/\text{cm}^3$ ；

$C_i$ ——界面处钢液中氮含量  $\mu\text{mol}/\text{cm}^3$ 。

(3) 氮从界面处向钢液内部的扩散 其扩散速度为

$$n_l = K_l(C_i - C_b) \quad (29)$$

式中  $K_l$ ——钢液中氮的传质系数  $\mu\text{m/s}$ ；

$C_b$ ——钢液内部氮含量  $\mu\text{mol}/\text{cm}^3$ 。

所有的研究都表明 氮在气相中的扩散速度比其他各个环节快很多 对其扩散阻力可忽略不计。设第二和第三步骤的总速度为

$$n_{ov} = K_{ov}(C_e - C_b) \quad (30)$$

式中  $K_{ov}$ ——氮的总传质系数  $\mu\text{m/s}$ 。

设反应稳态进行,  $n_r = n_l = n_{ov}$ , 从而可求得  $K_{ov}$  为

$$K_{ov} = K_l \left[ \frac{\sqrt{4C_b\phi + \phi^2 + 4C_e^2 - (2C_b + \phi)}}{2(C_e - C_b)} \right] \quad (31)$$

式中  $\phi$ —— $K_l/K_r$ ,  $\mu\text{mol}/\text{cm}^3$ 。

考虑到钢中氧对界面反应速度常数的影响  $K_r$  可用下式表示<sup>[6]</sup>

$$K_r = 10f_N/(1 + 953f_O[\text{O}]) \quad (32)$$

式中  $f_N$ 、 $f_O$ ——分别为钢中氮和氧的活度系数；

[O]——钢中氧含量, % .

对于注流表面积为  $F_1$ , 氮通过注流表面向钢液内迁移使钢中氮含量的增加  $\Delta[N]_{st}(\%)$  为

$$\Delta[N]_{st} = 1400F_1 n_{ov} / (\pi a_0^2 U_0 \rho) \quad (33)$$

由于注流表面吸氮, 钢中平均氮含量的增加  $\Delta[\bar{N}]_{st}(\%)$  为

$$\Delta[\bar{N}]_{st} = 1400 \sum F_1 n_{ov} \Delta t / (M_1 \times 10^4) \quad (34)$$

## 5 计算结果及讨论

### 5.1 流体物性对钢液吸氮的影响

(1) 表面张力的影响. 对于注流落下初始高度分别为  $Z_1 = 50$  cm 和 250 cm 的条件下, 设钢液密度  $\rho = 7$  g/cm<sup>3</sup>, 粘度  $\mu = 0.05$  g/(cm·s) 表面张力分别为  $\sigma = 1000$ 、1500 和 1800 dyn/cm  $\Delta[\bar{N}]_E^0$  与  $U_0$  的关系如图 2 所示. 从图中可看出, 随着表面张力的增加  $\Delta[\bar{N}]_E^0$  减小. 这个现象在  $D_0$  较小及  $Z_1$  较小的情况下不明显.

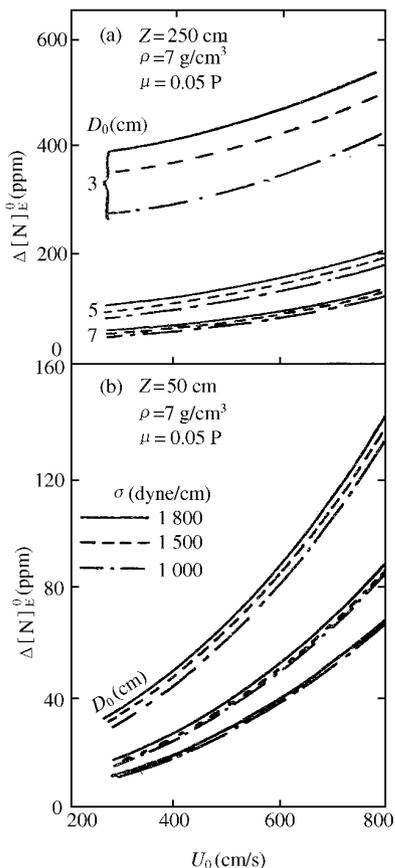


图2 钢液表面张力对钢液氮含量变化  $\Delta[N]_E^0$  的影响

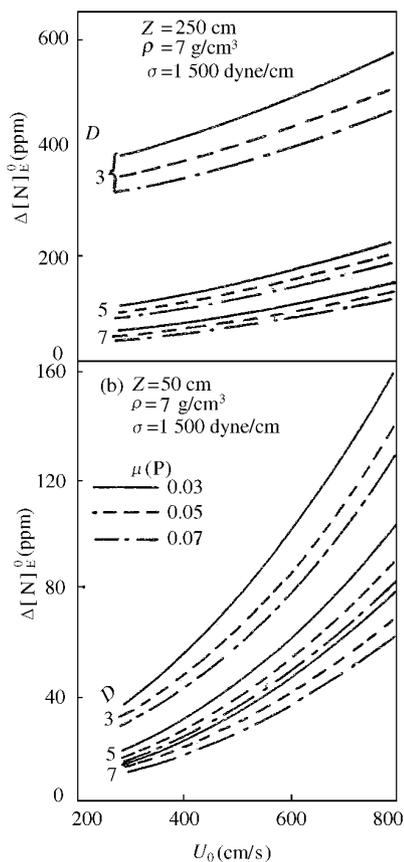


图3 钢液粘度对钢液氮含量变化  $\Delta[N]_E^0$  的影响

(2) 粘度的影响. 设钢液的密度  $\rho = 7 \text{ g/cm}^3$  表面张力  $\sigma = 1500 \text{ dyn/cm}$ , 粘度分别为  $\mu = 0.03, 0.05$  和  $0.07 \text{ g/(cm} \cdot \text{s)}$  通过计算得到如图3所示的关系, 可以看到, 随着粘度的增大  $\Delta[\bar{N}]_E^0$  减小.

(3) 密度的影响. 密度变化对  $\Delta[\bar{N}]_E^0$  的影响很小, 可以忽略不计.

## 5.2 浇注过程钢液吸氮量的变化

设卷入空气中的氮全部进入钢液中, 即  $\eta_E = 1$ , 钢中氮含量的变化与时间的关系的计算结果如图4所示. 计算条件为:  $R_1 = 150 \text{ cm}$ ,  $h_1 = 250 \text{ cm}$ ,  $d = 88.6 \text{ cm}$ ,  $D_0 = 5 \text{ cm}$ ,  $l_0 = 30 \text{ cm}$ ,  $Z_1 = 250 \text{ cm}$ . 计算结果表明, 随着浇注的进行, 由于水口出口处钢液流动线速度  $U_0$  下降, 注流落下高度  $Z$  的减小,

注流卷入周围空气的数量减少,  $\Delta [N]_E^0$  相应减小, 同时注流的表面积  $F_1$  减少,  $\Delta [N]_{st}$  也相应减小. 从计算结果还可看到, 由于空气卷入钢液含氮量的增加  $\Delta [N]_E^0$  远远大于通过注流表面的吸氮量  $\Delta [N]_{st}^0$ .

### 5.3 钢中氧对氮含量变化的影响及吸

众所周知, 钢液中氧是表面活性元素, 它们会向钢液表面富集, 占据表面的空位, 从而阻碍吸氮.

根据取样测定<sup>[7]</sup>, 浇注过程中钢液氮含量的变化与氧含量的关系如图5所示. 严格来说, 这些测定值是  $\Delta [\bar{N}]_E$  和  $\Delta [\bar{N}]_{st}$  的和. 但正如上面得到的,  $\Delta [\bar{N}]_{st}$  的数值很小可忽略, 可以近似认为测量值即等于  $\Delta [\bar{N}]_E^0$  的测量值.

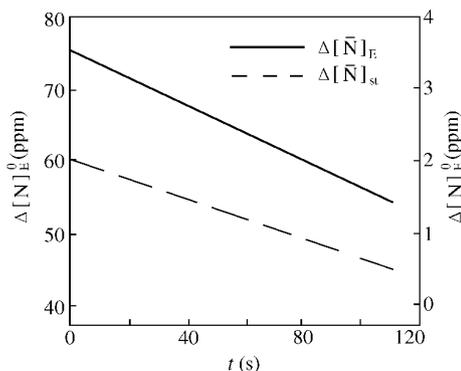


图4  $\Delta [N]_E$  和  $\Delta [N]_{st}$  与时间的关系

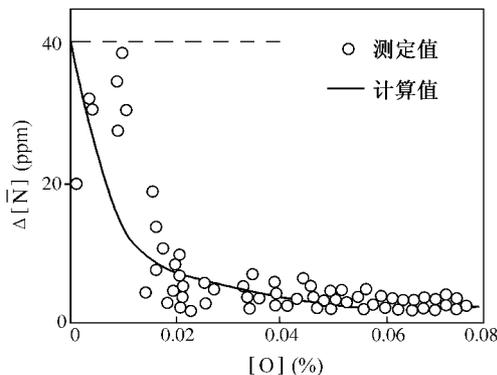


图5 浇注时钢液吸氮与钢中氧含量的关系

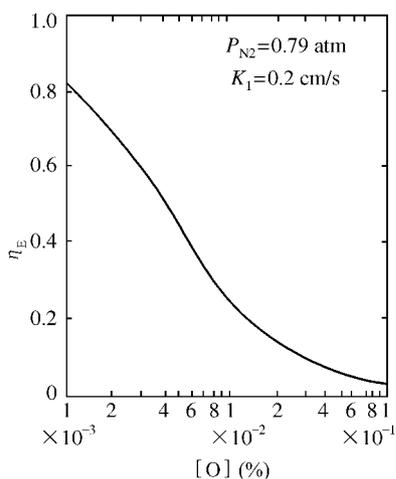


图6 氮的吸收率  $\eta_E$

根据模型计算出  $\Delta[\bar{N}]_E^0$  的值为40 ppm,对于任意的钢中氧含量,根据方程式(31)和(32),可以计算出  $K_{ov}$  的数值,再根据  $K_{ov}$  的数值,利用公式  $\eta_E = K_{ov}/K_{ov}^0$  确定出  $\eta_E$  的数值,结果如图6所示,这样根据方程式(25)可计算出  $\Delta[\bar{N}]_E$  的数值,如图5所示.从图5可以看到,  $\Delta[\bar{N}]_E$  的计算值与实测值十分相符;另外还可得到,在  $[O] = 0 \sim 0.02$  范围内,  $\Delta[\bar{N}]_E$  随  $[O]$  的增大而急剧减小,当  $[O] > 0.02$ ,  $\Delta[\bar{N}]_E$  随  $[O]$  的变化趋于平缓.

#### 5.4 浇注条件对钢液氮含量变化的影响

(1) 注流落下的初始高度  $Z_i$ .  $Z$  与钢液吸氮量的关系如图7所示.可以看到,随着  $Z_i$  的增加,  $\Delta[\bar{N}]_E$  和  $\Delta[\bar{N}]_{st}$  都随之增加.

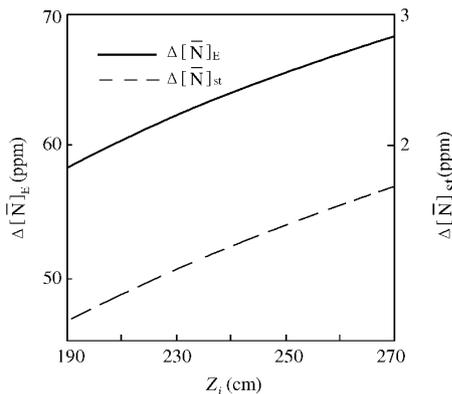


图7 注流落下初始高度对  $\Delta[\bar{N}]_E$ 、 $\Delta[\bar{N}]_{st}$  的影响

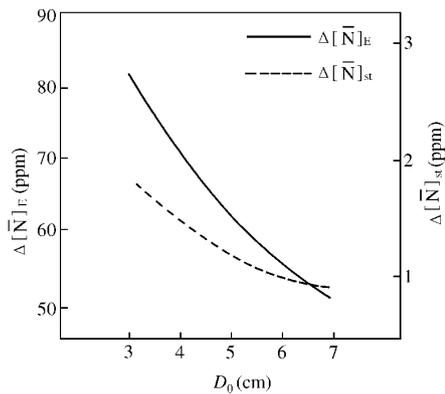


图8 水口直径变化对  $\Delta[\bar{N}]_E$ 、 $\Delta[\bar{N}]_{st}$  的影响

(2) 水口直径  $D_0$ . 水口直径  $D_0$  与钢液含氮量变化的关系如图8所示. 从图8可以看出, 随着水口直径的减小,  $\Delta[\bar{N}]_E$  和  $\Delta[\bar{N}]_{st}$  都随之增加. 通常水口直径的影响要比注流落下初始高度的影响大.

## 6 结论

根据理论计算和实际取样分析, 研究了钢液在浇注过程中氮含量的变化, 得到如下结论:

(1) 钢液浇注时, 钢液的表面张力和粘度等物性对钢液氮含量变化均有一定的影响;

(2) 浇注时, 因空气卷入钢液氮含量变化比注流表面吸氮引起的氮含量变化大得多, 后者几乎可以忽略不计;

(3) 浇注条件对氮含量变化有较大的影响, 随注流落下高度增大和水口直径减小钢中氮含量的增量明显增大.

## 参 考 文 献

- [ 1 ] T. Kurabayashi : Trans. Japan Soc. Mech. Eng. ,25(1959). 1266
- [ 2 ] 岩田腾吉,长隆郎,井上道雄:铜と钢 68(1982) p. 1922

- [ 3 ] E. van de Sande , J. M. Smith , and J. J. J. van Oord : J. Appl. phys. , 45 ( 1974 ) , p. 748
- [ 4 ] Katsuyoshi , IWATA , Takao CHOH , and Michio INOUYE : Trans. ISIJ , 23 ( 1983 ) , p. 224
- [ 5 ] 长隆郎 , 岩田腾吉 , 井上道雄 : 铜と钢 , 68 ( 1982 ) , p. 2461
- [ 6 ] M. BYRNE and R. BELTON : Metall. Trans. B , 14 ( B ) ( 1983 ) , p. 441
- [ 7 ] 石墨守幸 , 大久保益太 : 铜と钢 , 55 ( 1969 ) , p. 492

# 氧化锰的熔融还原动力学问题<sup>\* 1</sup>

**摘要** 本文对 R. J. Pomfret、A. A. Плыщеский 以及作者自己的试验结果作了综合分析. 指出(MnO)的还原可用三步模式说明, 并且其中 Fe、Mn 间的交换反应可能是速度最慢的一个环节. 作者还为进一步定量地论证三步模式在实际还原过程中的贡献提出了研究方法, 对还原过程中的副反应与不同还原剂的作用也作了讨论.

## 符号说明

(MnO), $Mn$ ——渣中和金属中的 锰	$\tau$ ——反应时间
C——金属中的碳	$k_1$ ——反应(1)的表观速度常数
$C_{(s)}$ ——以固体存在的碳素	$k_{23}$ ——反应(2)和(3)的总括表 观速度常数
$a$ ——活度	$i$ ——表示起始值
T——温度	max——表示峰值
P——气体压力	B——碱度
N——mol 分数	

## 1 引论

锰的氧化及还原是钢铁冶炼过程中的基本反应之一. 在钢铁冶金理论发展过程中, 渣钢间锰的行为已有不少学者曾进行过研究. 这些研究结果主要

\* 本文合作者: 蒋国昌、丁伟中、顾利平. 原发表于《上海工业大学学报》9(1), 80~89 (1988)

局限于(% Mn)和%  $\underline{\text{Mn}}$ 均较低的情况.随着熔融还原新技术的发展,用熔融还原方法生产高碳锰铁或进行锰钢的直接合金化已经得到重视.因此,冶金学家的兴趣转移到了高(% Mn)和高%  $\underline{\text{Mn}}$ 领域.但是,在这一新领域里至少有以下的一些课题有待进一步解决,例如:

(1) 渣的锰容量及高(% MnO)条件下渣中各组元的活度;

(2) 高%  $\underline{\text{Mn}}$ 条件下 Fe-Mn-Si-C 四元系或 Fe-Mn-Si-P-C 五元系中元素的活度;

(3) 高(% MnO)和高%  $\underline{\text{Mn}}$ 条件下的物性参数(粘度、界面张力等);

(4) 反应的机构和律速环节;

(5) Si、Fe 和 Mn 的竞争氧化还原;

(6) 不同还原剂及还原剂不同状态(例如:  $\text{C}_{(s)}$ 、 $\underline{\text{C}}$ 及 CO 等)的作用.

本文是关于氧化锰熔融还原反应动力学方面的评述分析.其中包括近几年内作者的一些工作.

## 2 三步还原模式

### 2.1 Fe、Mn 交换反应

熔融氧化铁的还原反应机构有两种模式,即直接还原模式(被 $\underline{\text{C}}$ 或 $\text{C}_{(s)}$ 还原)和间接还原模式(被 CO 还原).对于氧化锰的熔融还原,除了上述两种假设外,还有三步还原模式也已得到某些研究者的支持.按照这一模式,整个过程由三个反应串联而成,即



显然,这里的反应(2)和(3)合在一起正是熔融氧化铁的间接还原模式,而反应(1)常被称为铁、锰的交换反应,实质上可看作 Fe 和 Mn 的竞争氧化还原反应.

Pomfret<sup>[1]</sup>、Плыщевский<sup>[2]</sup>、筱崎信也<sup>[3]</sup>和本文作者曾分别用不同的试验证实:只要初渣缺铁,就可发现(% FeO)在反应初期随着(% MnO)的下降而升高,并且常呈现出一个驼峰,见图 1<sup>[4]</sup>.这个事实被看作是反应(1)的

直接实验依据.

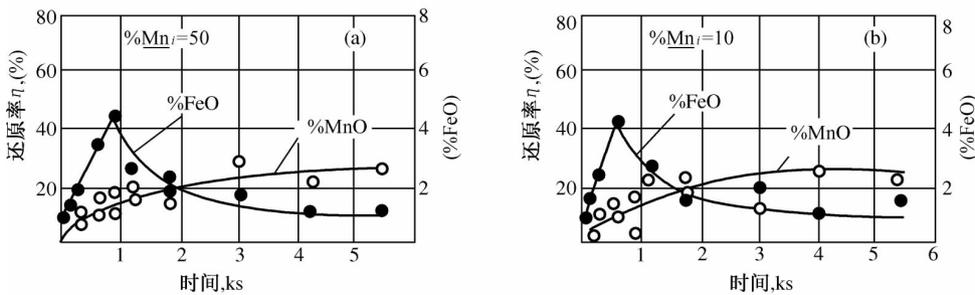


图1 MnO 熔融还原过程中(FeO)的变化

由反应(1)的平衡得

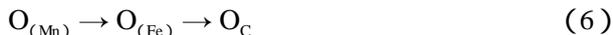
$$\lg \frac{\alpha_{Mn} \cdot \alpha_{FeO}}{\alpha_{MnO}} = -\frac{6440}{T} + 2.95 \quad (4)$$

故 1823 K 条件下, 只要满足

$$\alpha_{FeO} < 0.26 \frac{\alpha_{MnO}}{\alpha_{Mn}} \quad (5)$$

在热力学上反应(1)就是可能的. 以熔融还原法炼制碳素锰铁的终点时, 通常  $(\% MnO) \leq 10\%$  而  $\% Mn = 60\%$ . 根据 Warren 等<sup>[5]</sup>和田中章彦<sup>[6]</sup>的平衡试验, 此时  $\alpha_{MnO} / \alpha_{Mn}$  的量级为 1. 可见, 氧化锰熔融还原过程中  $N_{FeO}$  达到 0.1 左右或更大可由热力学来证实<sup>[7]</sup>. 由此可以预计, 实际过程中反应(1)距离其平衡尚远.

忽略逆过程, 就可用下式表示简化了的三步模式:



这里  $O_{(Mn)}$ 、 $O_{(Fe)}$  及  $O_C$  分别表示以 (MnO)、(FeO) 及 CO 形态存在于反应体系内的氧. 这样, 在  $(\% FeO)_i = 0$  及  $P_{CO, i} = 0$  的起始条件下, 可以导出<sup>[8]</sup>

$$N_{FeO, \tau} = \frac{k_1 N_{MnO, i}}{k_{23} - k_1} [\exp(-k_1 \tau) - \exp(-k_{23} \tau)] \quad (7)$$

这里  $k_1$  是  $O_{(Mn)} \rightarrow O_{(Fe)}$  的表观速度常数,  $k_{23}$  是  $O_{(Fe)} \rightarrow O_C$  的表观速度常数. 此式表明,  $(\% FeO) - \tau$  曲线上的驼峰点和  $k_{23} / k_1$  比值有关.  $(k_{23} / k_1)$  愈大,  $(\% FeO)_{max}$  就愈小. 另外, 若  $k_1$  和  $k_{23}$  均变动而保持其比值恒定, 则

$(\% \text{FeO})_{\max}$  不变, 但  $\frac{d}{dt}(\% \text{FeO})$  曲线会显示出完全不同的变化特征<sup>[8]</sup>.

## 2.2 改变 $P_{\text{CO}}$ 的影响

Pomfret 等<sup>[1]</sup>的工作(图 2、3)研究了气压(CO 气氛)变化的影响. 由图 3 可见, 气压升高时 CO 的累计放出量增加, 这正是(FeO)间接还原的证据, 由于气压变化不致直接作用于反应(1)本身, 所以气压升高的总结果是  $k_1$  不变而  $k_{23}$  加大, 从而使  $(\% \text{FeO})_{\max}$  下降.

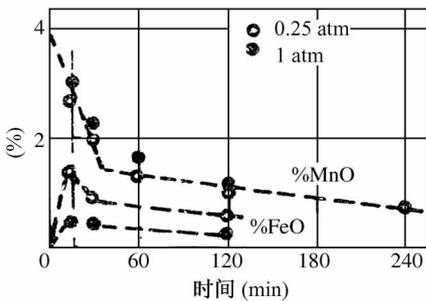


图 2 气压对 (% MnO) 和 (% FeO) 的影响. 35 g 金属, 10 g 含  $\text{SiO}_2$  为 45% 的渣, 石墨坩埚( $\varnothing 9$ )

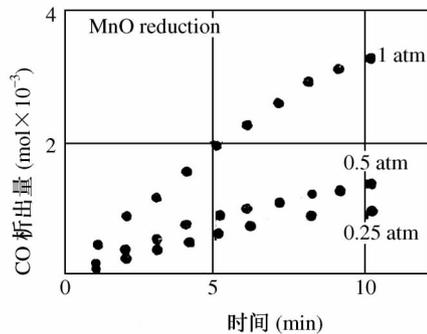


图 3 气压对气体析出量的影响

## 2.3 温度的影响

Плыщевский 等<sup>[2]</sup>研究了温度的影响. 由图 4 可见, 温度升高则  $(\% \text{FeO})_{\max}$  变大. 按 Кондаков 等<sup>[9]</sup>和 Mulholland 等<sup>[10]</sup>的观点, 温度对  $k_{23}$  没有明显的作用. 但温度升高时  $k_1$  作为吸热反应的速度常数照理是应该增大的, 这就是 Плыщевский 等结果的解释.

比较图 1、2 和 4 还可发现一个特点, 从反应开始到  $(\% \text{FeO})_{\max}$  的时间  $\tau_{\max}$  均在 15 min 左右, 因为

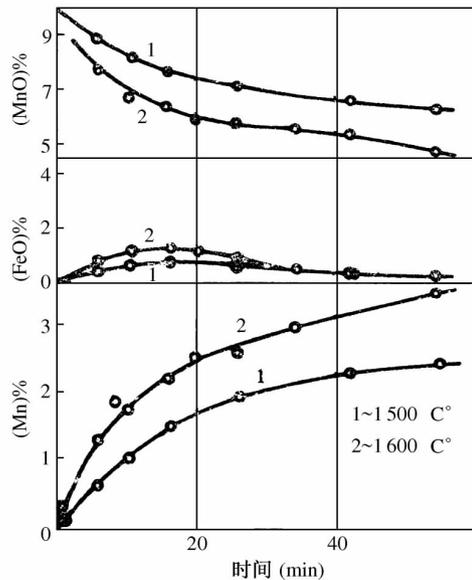


图 4 (% MnO)、(% FeO)、% Mn 随时间变化

$$\tau_{\max} = \frac{\ln q}{k_1(q-1)} \quad (8)$$

这里,  $q = k_{23}/k_1$ . 利用 Taylor 级数展开并取一级近似得

$$\tau_{\max} = \frac{2}{k_1} \left( \frac{N_{\text{FeO}, \max}}{N_{\text{MnO}, i}} \right) \quad (9)$$

在图 2 中,  $\left( \frac{N_{\text{FeO}, \max}}{N_{\text{MnO}, i}} \right) = 0.125$ . 图 4 中此比值约是 0.178, 即 Плыщевский 试验中的  $k_1$  大于 Pomfret<sup>[1]</sup> 的  $k_1$ . 因为前者的试验温度是 1 500, 而后者的是 1 450, 所以推论合理.

#### 2.4 (%MnO)<sub>i</sub> 及 %Mn<sub>i</sub> 的影响

Плыщевский 等还研究了 (%MnO)<sub>i</sub> 的影响. 他们指出 (%MnO)<sub>i</sub> 由 4% 增至 10% 时, (%FeO)<sub>max</sub> 可增加约 150%. 同样, 这也是因为  $k_1$  增加而  $k_{23}$  变化不大之故.

在前人工作基础上, 本文作者研究了 (%MnO)<sub>i</sub> = 40% 条件下改变 %Mn<sub>i</sub> 的影响. 发现 %Mn<sub>i</sub> 增加时 (%FeO)<sub>max</sub> 下降.

#### 2.5 律速环节

综上所述, 可用串联反应的动力学基本规律来描述三步还原模式. 再进一步还可用下式估计律速环节:

$$N_{\text{FeO}, \max} = \frac{N_{\text{MnO}, i}}{q-1} \left[ \exp\left(-\frac{\ln q}{q-1}\right) - \exp\left(-\frac{q \ln q}{q-1}\right) \right] \quad (10)$$

这里 N 是 mol 分数. 式(10)的近似式如下:

$$q = 3 - 2 \frac{N_{\text{FeO}, \max}}{N_{\text{MnO}, i}} \quad (11)$$

不论是 Pomfret、Плыщевский 或本文作者, 对 (%FeO) 的测定均不是连续进行的, 因此很难得到 (%FeO)<sub>max</sub> 的准确值. 尽管如此,  $N_{\text{FeO}, \max} < N_{\text{MnO}, i}$  总是肯定的. 这样由式(11)得到结论:  $k_{23} > k_1$ . 即三步还原模式中反应(1)的速度较慢些. 但差值不大, 故过程的总速度也可能是被混合律速的.

Pomfret<sup>[1]</sup>、筱崎信也<sup>[3]</sup>及本文作者都曾用数学方法探讨了三步还原模式中的律速环节, 得到了不同的结论. 这是由于尽管数学方法没有问题, 但引用了不同的活度系数和扩散参数, 而这些参数又都与试验条件

有关,往往缺乏足够的可比性.本文的研究方法则设法回避这一难点来进行分析探讨.

## 2.6 其他反应模式

尽管三步还原模式有存在的可能性和规律性,但不能确认这是惟一的反应途径.如筱崎信也<sup>[3]</sup>认为只在低碱度和 % C < 2% 时三步还原模式才起主要作用.作者认为如果在按串联反应处理之后再按并联反应处理则不难作出解答.即认为和式(6)平行存在二步还原(或直接还原)模式



按并联反应的基本规律<sup>[8]</sup>,有

$$\frac{O_{C,S}}{O_{C,12}} = \frac{k_s}{k_{12}} \quad (13)$$

这里  $O_{C,S}$  表示按三步还原模式,即式(6)生成的 CO;  $k_s$  是式(6)的总括表观速度常数;  $O_{C,12}$  表示按二步还原模式或直接还原模式生成的 CO;  $k_{12}$  是相应的表观速度常数.因为  $k_s$  在按串联反应处理时可以求出,所以只要通过试验求出  $k_{12}$  就能定量地确知三步还原模式的贡献.

当然,实际上无论是三步还原模式还是其他模式均可能并非严格的一级反应.所以需要采用 n 级反应的公式作为研究的基础.

## 3 二步还原模式

Sommerville<sup>[11]</sup>和 Upodhya 等<sup>[12]</sup>在研究碳饱和铁液还原熔融氧化铁时发现渣中含有一些呈铁素体组织的金属小珠.他们指出这就是熔融氧化铁被间接还原的依据.本文作者曾用 % Mn 不同的碳饱和铁液还原熔融氧化锰.在反应进行 5 min 后将坩埚由炉中取出,快速冷却,发现渣中也有一些金属小珠<sup>[13]</sup>.其化学成分微量分析结果,可见表 1.

表 1 混于渣中的金属小珠之组成

金属熔池	1#			2#		
	% Mn	% Fe	Mn/Fe	% Mn	% Fe	Mn/Fe
Fe-C <sub>sat</sub>	1.8	95.5	0.019	1.6	94.2	0.017

Fe-Mn-C <sub>sat</sub>	79.8	13.5	5.91	79.4	14.3	5.55
Mn/Fe = 2						

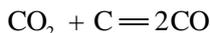
这个结果颇为意外,因为高 %  $\underline{\text{Mn}}_i$  条件下金属小珠中的锰增量 ( $\Delta\% \underline{\text{Mn}} = \% \underline{\text{Mn}}_{\text{珠}} - \% \underline{\text{Mn}}_{\text{熔池}}$ ) 竟然比 %  $\underline{\text{Mn}}_i = 0$  条件下的相应值大得多. 怎样理解这一现象? 看来间接还原模式(即第二步还原模式)可能对此是有作用的.

Volkert 等<sup>[14]</sup>曾明确表示他们的观点: MnO 的间接还原是不可能成立的. 若 MnO 为纯的固态, 还原出来的为液态纯 Mn, 则 Volkert 等的论断完全正确. 这种条件下



$$\Delta F^\circ = 30.850 - 1.17T \quad (15)$$

1823 K 时如果  $(P_{\text{CO}_2}/P_{\text{CO}}) > 10^{-4}$ , 则反应(12)不可能向右进行. 而另一方面, Boudouard 反应



$$\Delta F^\circ = 38900 - 40.1T$$

1823 K 时需  $(P_{\text{CO}_2}/P_{\text{CO}}) > 10^{-4}$  才能向右进行. 但是高温下, 在 MnO 成渣后(由上一节知此种渣内必有 FeO), 其间接还原却是可能的. 由:



$$\Delta F^\circ = 19630 - 5.36T \quad (17)$$

可知,  $(P_{\text{CO}_2}/P_{\text{CO}}) < 10^{-2}$  时一般来说反应(14)可能向右进行. 这和 Boudouard 反应没有冲突.

在 %  $\underline{\text{Mn}}_i \neq 0$  条件下, 反应发生 5 min 后的 (% MnO) 较低而 (% FeO) 较高(和高 %  $\underline{\text{Mn}}_i$  条件下的相应值比较). 所以由于间接还原反应而析出的微粒中 %  $\underline{\text{Mn}}_i$  较小. 另一方面, 我们在渣中发现的金属小珠实际上应该是由更加细小的金属微粒凝聚合并而成的. 它们不像是完全由间接还原反应造成的, 因为其中都含有相当数量的 Fe. 它们也不像是纯粹由于沸腾而从熔池里卷上来的, 因为其 %  $\underline{\text{Mn}}$  显著大于熔池本身之值. 在 %  $\underline{\text{Mn}}_i = 0$  的条件下, 观察到较强的沸腾, 看来由熔池卷至渣中的金属微粒要多得多, 这似乎就是 %  $\underline{\text{Mn}}_i = 0$  条件下, 金属小珠中  $\Delta\% \underline{\text{Mn}}$  较小的原因.

由于在这一试验中没有做金属小珠 % C 的测定,及反应过程中气相组成的测定,所以这一现象还待进一步研究才能阐明真相。

#### 4 直接还原模式

熔融氧化锰还原的总括反应方程式如下:



如果还原反应仅通过这一步就完成,那就是直接还原模式。这一反应途径曾经遭到怀疑,主要是认为反应(18)中包含了三个相(还原剂是C)或四个相(还原剂是固态碳粒),致使这个多相反应只能在非常小的多相共存的界面上发生。

但是即使在氧化铁熔融还原动力学领域里,也有不少学者认为直接还原模式和间接还原模式都有其作用<sup>[15]</sup>。事实上,熔融氧化物和还原剂(特别是碳饱和铁液)并不乏相互接触的机会,所以对直接还原模式的主要忧虑是CO的形核问题。这里,我们认为不能套用钢冶金学中的规律。因为金属熔体中氧位极低,而渣中氧位甚高,并且此种渣往往不是均质的。所以CO完全可能直接在熔渣-还原剂界面(两个相的相界面)上萌发。

Lloyd<sup>[16]</sup>曾用高速摄影的方法证明了这一点。Mulholland<sup>[10]</sup>在用X-TV观察金属液滴落入含氧化铁的熔渣时也得到相同的结论。

对于熔融氧化锰,还没有人用类似的方法做过研究。但是筱崎信也<sup>[3]</sup>用数学运算的方法指出在高% C、高碱度条件下,直接还原模式起主要作用。

#### 5 起主要作用的还原剂

在实验室里用石墨坩埚研究(MnO)的熔态还原时,必须回答石墨坩埚在何种程度上参与了还原反应。根据 Pomfret<sup>[1]</sup>的工作,可以说C的还原作用远超过石墨坩埚。他曾在尺寸相同的石墨坩埚中用不同的渣量做试验。发现渣层厚时虽然渣和坩埚的接触面积增加,但(MnO)的还原反而减慢(图5)。而用Al<sub>2</sub>O<sub>3</sub>坩埚取代同样尺寸的石墨坩埚时(MnO)的还原速度不变。另外,他和 Daines<sup>[17]</sup>都曾发现% C对还原速度有影响(图6)。我们在感应炉试验时也曾发现石墨坩埚和熔渣接触的部位几乎不被侵蚀,而和铁液接触的部位其直径已明显加大。用来向铁液喷吹碳粉的石墨喷枪也显示出相似的侵蚀特

征<sup>[13]</sup>. 这自然和碳粉喷入量太少, 不足以保持C的饱和状态是有关的. 但是, 我们还曾经直接向渣中加入碳屑, 发现这对加速还原很有效. 新日铁公司在发展(Cr<sub>2</sub>O<sub>3</sub>)熔融还原时的经验与此完全一致. 我们以为这表明: 增加反应界面是促进熔融还原速度的第一要点<sup>[18]</sup>. 实验室电阻炉和感应炉中用C还原(MnO)的试验正是由于搅拌强度受限, 致使试验终点时还原率偏低.

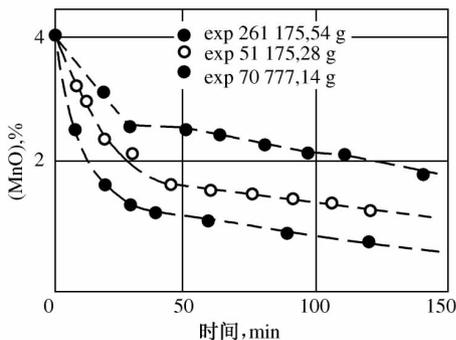


图5 石墨坩埚中渣层厚度的影响

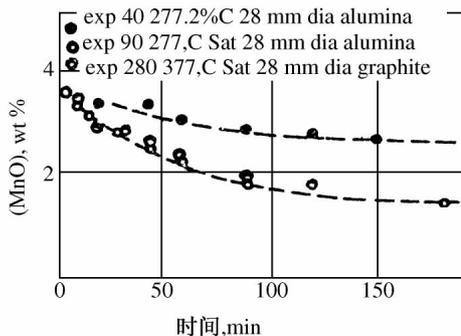
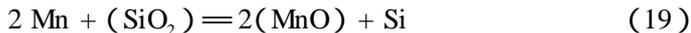


图6 初始含碳量的影响

## 6 副反应的问题

所有的商品 Fe-Mn-C<sub>sat</sub> 中均含有相当数量的Si. 这表明锰矿的还原中必然存在着 Si 和 Mn 的竞争氧化还原问题. 所以任何试验研究都应该考虑到Si的影响.

对于反应



有

$$\lg \frac{(\% \text{Mn}) \cdot \% \text{Si}^{1/2}}{\% \underline{\text{Mn}}} = -1.41 \times B + 1.48 \quad (20)$$

其中 B 为碱度. 设  $B = 1.3$ ,  $(\% \text{MnO})_i = 43\%$ ,  $\% \underline{\text{Mn}}_i = 30\%$ , 则还原氧化锰起始时的  $\% \underline{\text{Si}}_{\text{平衡}}$  可增加到 0.16. 且随  $(\% \text{Mn})$  减少和  $\% \underline{\text{Mn}}$  增加而加大.

图 7 是芦塚正博的试验结果<sup>[19]</sup>. 尽管该熔渣碱度为 1.25, 仍然可以看到 (SiO<sub>2</sub>) 被还原出来. 图 8 是我们按图 7 的数据绘成的. 此图表明在后期反应 (19) 已达到平衡. 在前期因为实测所得的  $\% \text{Si}^{1/2} / \% \underline{\text{Mn}}$  远大于平衡值, 说明

这一阶段里Si有还原(MnO)的能力. 当然, 由于  $n_{Mn}$  和  $n_{Si}$  增量之比远大于 2, 所以(MnO)主要被C还原. 而 % Si 的变化则决定于它的生成速度和消耗速度之差. 前者是



后者即反应(17)之逆过程.

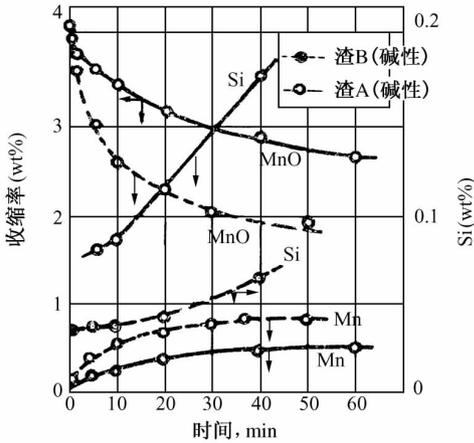


图7 Si和Mn在渣中,金属中的浓度随时间的变化(1550℃)

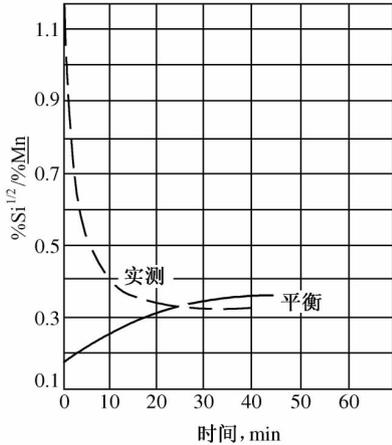


图8 芦塚的实验中Si、Mn的竞争氧化还原规律<sup>[19]</sup>

这种竞争氧化还原的规律是否有普遍性,例如是否适用于不同  $(\% Mn)_i$  和不同  $\% Mn_i$  的情况,看来还不能定论.

## 7 结语

(1) 本文讨论了熔融氧化锰还原反应途径的三种模式. 对于实际的氧化锰熔融还原过程中这三种模式各能作出多大贡献的问题, 本文提出了一种研究方法.

(2) 用串联反应的动力学基本规律可以描述三步还原模式. 借此研究方法可以回避使用可比性不足的活度系数和扩散参数等. 作者用此法得到结论: 三步还原模式中Fe的交换反应可能是速度较慢的一个环节.

(3) 讨论了起主要作用的还原剂, 指出增加反应面积是加速还原的第一要点.

(4) 氧化锰熔融还原过程中必有Si、Mn的竞争氧化还原反应, 任何试验

都必须考虑 Si 的影响.

## 参 考 文 献

- [ 1 ] R. J. Pomfret. *et al.* Kinetics of fast initial stage of reduction of MnO from silicate slag by carbon in molten iron, *Ironmaking Steelmaking*, (5) ,1978 :191-197
- [ 2 ] A. A. Лышевский, др. Кинетика восстановления оксида марганца шихта чугуна. *Изв ВУЗ ЧМ*, (10)1984 :16-20
- [ 3 ] 筱崎信也等. 碳素灰含有する溶鋼によるスラグ中のMnOの還元速度. 鋼と鋼, 70 (1), 1984 :73-80
- [ 4 ] 顾利平. 锰熔态还原时渣中氧化铁变化规律及其他影响因素的研究. 上海工业大学硕士学位论文, 1987
- [ 5 ] G. F. Warran, *et al.* Liquidus temperature and the activities of MnO in slags associated with the Production of high-C FeMn. *Int. Conf. on Ferroalloy*, 1974 :175-185
- [ 6 ] 田中章彦. Mn-C, Mn-Si, Mn-Si-C<sub>sat</sub> Mn-Fe-Si-C<sub>sat</sub> 合金溶液 中の Mn の 活 量. 日 本 金 属 学会 会 報, 41(6) ,1977 :601-607
- [ 7 ] 魏寿琨. 冶金过程热力学. 上海科技出版社, 1980 :42
- [ 8 ] 韩其勇. 冶金过程动力学. 北京. 冶金工业出版社, 1983 :22-24
- [ 9 ] B. B. Кондаков, Др. Исследование кинетики восстановления закиси железа в твердом состоянии при температурах выше 1400, *Изв ВУЗ ЧМ*, (4) ,1960 :23-24
- [ 10 ] E. W. Mulholland, *et al.* Visualization of slag-metal reactions by x-ray fluoroscopy : Decarburization in basic oxygen steel-making *J. Iron & Steel Inst.* (9) ,1973 :632-639
- [ 11 ] I. D. Sommerville, *et al.* Kinetics of reduction of iron oxide in slag by carbon in iron : Part 1, effect of oxide concentration, *Iron making & Steel making* (1) , 1980 :25-32
- [ 12 ] K. Upadhyaya, *et al.* Kinetics of reduction of iron oxide in slag by carbon in iron Part 2. effect of carbon content of iron and silica content of slag. *Ironmaking Steelmaking*, (1) , 1980 :33-36
- [ 13 ] 丁伟中. 熔体中饱和碳对氧化锰的熔态还原研究. 上海工业大学硕士学位论文, 1985
- [ 14 ] G. Volkert 等. 铁合金冶金学. 上海科技出版社, 1978 :350
- [ 15 ] 相马胤和. 铜镪石の溶融还原. 日本金属学会会報, 12(8) , 1982 :620-625
- [ 16 ] G. W. Lloyd, *et al.* Reaction of iron oxide with Fe-C melts. *Ironmaking & Steelmaking*, (1) , 1975 :49-55
- [ 17 ] W. L. Danies, *et al.* Kinetics of MnO reduction from basic slag by carbon dissolved in liquid iron, *Met. Trans. 2*, 1971 :1203-1211
- [ 18 ] Jiang Guo Chang. *A literature Review on Smelting Reduction of Fe-Cr-C*. Internal Report of Dept. of Process Metallurgy, Royal Institute of Technology, Stockholm, Sweden, R.

1986.

[19] 芦塚正博等. 碳素饱和溶鋼による溶融スラグ中のMnO 还原反麻にへひて. 鋼て鋼 , 61(1) ,1975 :36-45

## The Kinetics Problem of MnO Smelting Reduction

**Abstract** The paper makes a synthetic analysis of the results of R. J. Pomfret , A. A. Пгыщевскицц and of the authors. It pointsout that smelting reduction of (MnO) can be explained on the basis of a three step model. The exchange reaction between Fe and Mn might be the stlowest ring. With a view to describing quantitatively the contribution of the three-stap model in actual process , a research procedure is proposed. The additional reaction and the effect of different reducing agents have also been discussed.

# Slag-metal Mixing in a Converter with Combined Blowing , as Applied to Smelting Reduction of Mn<sup>\* 1</sup>

## Introduction

Many research projects have in the last year treated ferroalloy production by smelting reduction. In many tests , a converter has been used as the main equipment.

Metal ore can be charged into the converter either by top addition or by injecting. Top addition seems to be a more practical way. Pellets ( ore and fluxes ) then should be added from the top and carbon powder should be injected into the bath. After being dropped into the furnace the pellets first dissolve in the slag and then react with carbon dissolved in the metal or with solid carbon particles suspended in the slag. Several researchers claim that the reaction with dissolved carbon has a greater reaction rate constant<sup>[1]</sup>. For promoting the reaction with dissolved carbon it is necessary to have good slag-metal mixing in the converter. The purpose of this paper is to describe the characteristics of two different mixing patterns and the control of slag-metal mixing.

---

\* In collaboration with *Jiang Guo Chang , Ding Wei Zhong , Fan Yang Yi.*  
Reprinted from *Scand. J. Metallurgy* 16(1) , pp.42-47(1987)

## A comparison of two mixing patterns and their possibilities

### *The influence of two mixing patterns upon reduction rate*

During the process, two different mixing patterns may emerge. We call them the “upper mixing” . . . the dispersion of metal in the slag layer and the “lower mixing” . . . the dispersion of slag in the molten metal. In steel making, similar mixing patterns also exist. Many scholars have indicated that the influence of these two patterns upon steel refining efficiency is different<sup>[2]</sup>. As a generally accepted idea by steelmakers, the “lower mixing” was considered to be more efficient<sup>[3]</sup>. But for smelting reduction, the direction of element transfer is mainly from slag to metal. Therefore, which system is more efficient has again to be confirmed.

For “upper mixing”, there are two basic equations. The mass balance equation in an element transferring process is:

$$W_s^z \cdot d(X) = \{X_0 - X\} \cdot dW_m$$

The reaction rate equation is:

$$W_s^z \frac{d(X)}{dt} = k'_u \cdot A \cdot \left\{ X - \frac{(X)}{K} \right\} \cdot \rho_m$$

$$A = a_m \cdot W_m = a_m \cdot F_m \cdot t_u / \rho_m$$

If  $k_u = k'_u \cdot a_m \cdot t_u$  then:

$$W_s^z \cdot d(X) = k_u \left\{ X - \frac{(X)}{K} \right\} \cdot dW_m$$

Since  $X_0 - X = k_u \left\{ X - \frac{(X)}{K} \right\}$ ,

$$\int_{(X)_0}^{(X)} \frac{d(X)}{(X) - KX_0} = \int_0^{W_m} \frac{-k_u}{KW_s^z(k_u + 1)} dW_m$$

If  $X_0 = 0$ , then

$$(X)_u = (X)_0 - \exp\left(-\frac{1}{KY_u} \frac{k_u}{k_u + T}\right) \quad (1)$$

From mass balance we get

$(X)_0 - (X) = X/Y_u$  so finally :

$$X_u = (X)_0 Y_u \left\{ 1 - \exp\left(-\frac{1}{KY_u} \frac{k_u}{k_u + T}\right) \right\} \quad (2)$$

For “lower mixing” , the same as above , we get :

$$W_m^s dX = \{(X)_0 - (X)\} \cdot dW_s$$

$$W_m^s dX = k_w \{(X) - KX\} \cdot dW_s$$

$$(X)_0 - (X) = k_w \{(X) - KX\} , \text{ and}$$

$$\int_{X_0}^X \frac{dX}{(X) - KX} = \int_0^W \frac{k_w}{W_s^s (k_w + 1)} \cdot dW_s$$

If  $X_0 = 0$  , then :

$$X_w = \frac{(X)_0}{K} \left\{ 1 - \exp\left(-\frac{k_w}{k_w + 1} KY_w\right) \right\} \text{ and} \quad (3)$$

$$(X)_w = (X)_0 \left\{ 1 - \frac{1}{KY_w} \left| 1 - \exp\left(-\frac{k_w}{k_w + 1} KY_w\right) \right| \right\} \quad (4)$$

Since  $k_u$  and  $k_w$  are both comparatively large values , Eqs. (2) and (3) can be simplified as

$$X_u = Y_u \cdot (X)_0 \{1 - \exp(-1/KY_u)\} \text{ and} \quad (5)$$

$$X_w = \frac{(X)_0}{K} \{1 - \exp(-KY_w)\} \quad (6)$$

Fig. 1 shows the curves described by these two equations. If we suppose  $Y_u = Y_w = \% \text{ SL}$  and the slag basicity  $B = 1.1 - 1.3$  , then  $K$  has a value quite smaller than unity. Thus the independent variable field of these two equations may not exceed  $KY = 1$ . That means under such a condition “upper mixing” seems to be even a bit more efficient.

#### Mixing circulation

It should , however , be indicated that usually  $Y \neq \% \text{ SL}$ . As a rule , a mixing is stable means that after being separated from a mixture every slag drop can be drawn into the molten metal again. For iron droplets the same is true too. There exists thus a flow balance. This may be defined as “mixing circulation”.

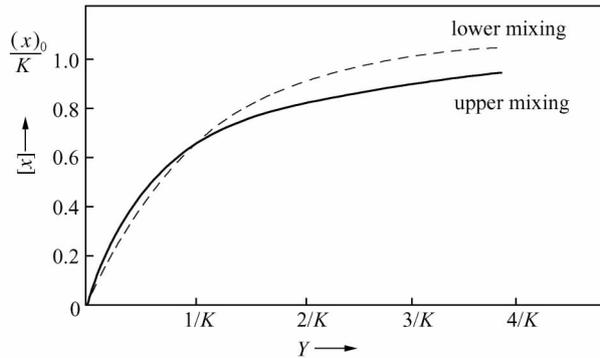


Fig. 1 The influence of mixing ratio on the content in molten metal (calculated values)

Considering that the mixing circulation is always repeated time and again, the increase of  $X$  and the decrease of  $(X)$  can be described by the following equations :

$$X_u, n_m = Y_u \cdot (X)_0 \cdot \{1 - \exp(-n_m/KY_u)\} \quad (7)$$

$$X_w, n_s = \frac{(X)_0}{K} \{1 - \exp(-KY_w)\} \\ (1 + Q + Q^2 + \dots + Q^{n_s}) \quad (8)$$

$$Q = 1 - \frac{1}{KY_w} \cdot \{1 - \exp(-KY_w)\}$$

$$(X)_u, n_m = (X)_0 \cdot \exp(-n_m/KY_u) \text{ and} \quad (9)$$

$$(X)_w, n_s = (X)_0 \cdot Q^{n_s} \quad (10)$$

For a given dispersed phase, the larger mixing ratio the quicker the mixing circulation<sup>[4]</sup>. So the hub of this top-addition process is to find a way to increase  $n$  — the mixing circulation times or  $Y$  — the mixing ratio of dispersed phase.

### Multiple mixing

The mixing phenomenon in a converter is determined not only by the stirring but also by the material properties. Suppose the influence of material properties upon the above two mixing patterns are similar, then according to mixing investigations carried out within chemical engineering, it is possible to promote the dispersion of a heavier phase in a lighter phase by putting the stir-

ring force in the lighter phase. One can also place the stirring force in the heavier phase to promote the dispersion of a lighter one in it<sup>[5]</sup>.

For smelting reduction of Mn, the influence of material properties on the process are usually not the same. Therefore the two mixing patterns have got completely different stabilities.

Under the condition of smelting reduction, the reaction agents are two liquids, slag and metal, and one of the products is a gas. In this case, a concept of "spreading coefficient"  $S$  is often used to describe the stability of a dispersed system<sup>[6,7]</sup>. For  $S_{1/2} < 0$ , that means phase "1" can be dispersed in "2" stably. The larger the negative value, the more stable is the dispersed system.

Since  $S_{m/s} = \sigma_s - \sigma_m - \sigma_{m/s}$ ,  $S_{s/m} = \sigma_m - \sigma_s - \sigma_{m/s}$  and under 1823 K,  $\sigma_m \approx 1.0 \text{ N/M}$ ,  $\sigma_s \approx 0.45 \text{ N/M}$ ,  $\sigma_{m/s} \approx 0.65 \text{ N/M}$ ,  $S_{s/m}$  is just smaller than zero but  $S_{m/s}$  is strongly negative. This indicates, in an intensively agitated state,  $n_s$  is larger than  $n_m$ . Therefore "lower mixing" is more effective.

On the other hand, when "lower mixing" is promoted by putting the stirring force within molten metal, a considerable proportion of "upper mixing" is still able to be kept at the same time. Even inside a slag drop which is drawn into the molten metal, some fine iron droplets can always be found. This phenomenon we define as "multiple mixing". Of course, in this case, "upper mixing" makes its own contribution to the decrease of  $(X)$ .

$$(X) = (X)_{u, n_m} \cdot (X)_{w, n_s} = (X)_0^2 \cdot \exp(-n_m/KY_u) \cdot Q_s^n \quad (11)$$

Based on the above discussion, one may conclude that to promote "lower mixing", getting a multiple mixing system is technically correct.

### The designation of the model and the selection of the materials

It is reasonable to consider that a slag drop is subjected to three forces at its forming moment: surface tension, floating force and shearing stress. So in an agitated bath the main physical factors affecting the slag drop formation are  $\sigma$ ,  $\rho_m$ ,  $\rho_s$ ,  $U$ ,  $L$ ; the basic dimensions are  $M$ ,  $s$ ,  $N$ . Therefore the predominating similar criterion should not be one but two. Along with dimensional analysis we deduced the Weber Number and Corrected Froude Number:

$$We = \sigma/g \cdot \rho \cdot L$$

$$Fr' = U^2 \cdot \rho / g \cdot \Delta\rho \cdot L$$

J. C. Godfrey<sup>[8]</sup> and Shinji Hida<sup>[5]</sup> both agree with this viewpoint.

Because *We* and *Fr* should be obeyed simultaneously, a water mode is only able to correspond to one imagined converter. It was thought that using a smaller converter, about 7T, to do a pilot industrial experiment may be favourable. Thus we decided on the size of our model as in Figs. 2 and 3.

Along with the principle of keeping the proportion of phase densities and viscosities unchanged, we selected the materials for simulation. For the smelting reduction of Mn, the real material properties

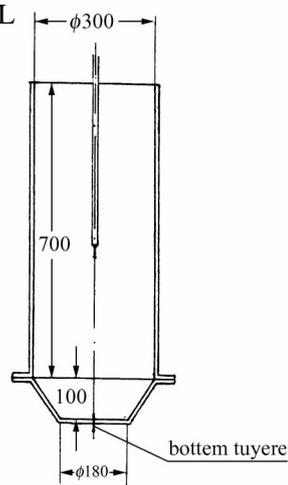


Fig. 2 The model for top-bottom blowing

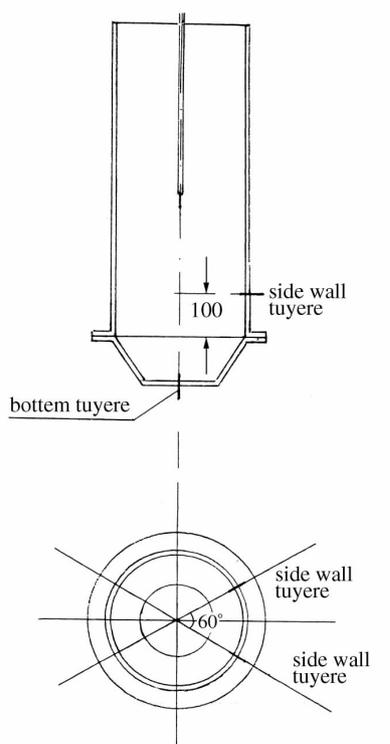


Fig. 3 The model for side wall blowing

are shown in Table 1. For simulating materials we kept  $\rho_m/\rho_s = 1.73$ ,  $\mu_s/\mu_m = 18 - 28$ . In order to study the influence of surface tension, we took  $\sigma = (5 - 16) \cdot 10^{-3}$  N/M.

Because in this simulation we have to keep  $\rho_{\text{water}} > \rho_{\text{oil}}$ , only those surface active agents which can dissolve in oil but not water could be used.

The properties of the simulating materials are also shown in Table 1. After experiment, these properties were measured again and not found seriously changed.

**Table 1 Material properties**

	Molten iron	molten slag	oil A	oil B	oil C	ZnCl <sub>2</sub> + water
$\rho(10^3 \text{ kg/m}^3)$	6.4 - 5.4	3.7 - 3.1	0.87	0.87	0.87	1.53
$\mu(10^{-3} \text{ p}_a \cdot \text{s})$	5	90 - 140	95.35	85.35	67.04	3.5
$s_{m/s}(\text{N/m})$	0.6 - 0.7	0.6 - 0.7	15.9	8.7	5.4	
			$10^{-3}$	$10^{-3}$	$10^{-3}$	
$\rho_m/\rho_s$	1.73	1.73	1.76	1.76	1.76	
$\mu_s/\mu_m$	18 - 28	18 - 28	27.24	24.39	19.15	

**The definition of mixing ratio for “lower mixing” and its measuring method**

Since an intensively agitated state is necessary for slag-metal mixing , only a sniffer tube could be used as a reliable sampling method. Five sniffer

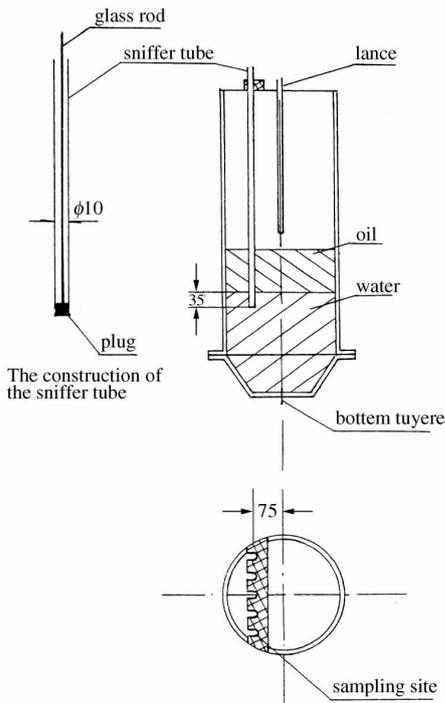


Fig. 4 The sampling site

tubes were located as in Fig. 4. After beginning to blow for 60 s , the mixing state was stable and sampling started. By opening the plug the slag-metal mixture which was below the plug level entered by the tubes. The tube inserted depth was determined by some pilot experiments. The final choice was 35 mm below the static interface for top-bottom combined blowing.

The average volume proportion of oil and water in the sniffer tubes was defined as the mixing ratio for “lower mixing”. According to Shinji Hida<sup>[5]</sup> , and M. A. Magedson<sup>[4]</sup> , we thought we could choose correct process parameters by means of this measurement.

## Experiment designation and data treatment for top-bottom blowing

### *An estimation of ( $n_s/n_m$ )*

The average volume proportion of oil and water in the sniffer tubes was measured after taking out these tubes from the “converter” for five min. This five min proved to be too long for the separation of oil drops from “lower mixing”. But as it was a multiple mixing system, the fine water droplets entrapped within oil drops took a quite longer time for their separation. According to our measurements, the time needed for oil separation was only about 1/10 of that for water. Perhaps this indicated that the mixing circulation ( $n_s/n_m$ ) was about 10 or likely larger.

### *Orthogonal designation and its results*

As an exploratory investigation, the first thing we did was to sift out those critical factors from a lot of others. Orthogonal designation favoured us in simplifying our work.

Table 2 shows the orthogonal form of  $L_{18}(2^1 \times 3^7)$  which was used and the experimental results. It was concluded that the major factors of our experiment were two: amount of bottom gas and slag layer thickness.

**Table 2**  $L_{18}(2^1 \times 3^7)$  orthogonal form and the measurement

	oil thickness ( $10^{-3}M$ )	bottom gas amount ( $M^3/hr$ )	oil type	gas pressure (atm)	bottom tuyere site ( $R$ )	water depth ( $10^{-3}M$ )	top gas amount ( $M^3/hr$ )	top nozzle type	$V_{oil}/V_{water}$
	40	1.6	A	3.0	2/3	250	1.1	3 120	0.325 7
	80	1.1	A	2.5	1/2	250	0.6	1 180	0.511 5
	80	0.6	A	2.5	1	170	1.1	3 120	0.082 0
	100	1.1	A	3.5	2/3	170	1.6	1 180	0.632 0
	100	0.6	A	3.0	1/2	100	1.6	3 120	0.178 1
	40	1.6	A	3.5	1	100	0.6	1 180	0.071 0
	80	1.6	B	3.5	1/2	250	1.6	3 120	0.782 2
	100	0.6	B	3.0	1	250	0.6	1 180	0.220 4
	100	1.6	B	2.5	2/3	170	0.6	3 180	1.077 6
	40	1.1	B	3.0	1/2	170	1.1	1 180	0.055 5
	40	1.1	B	2.5	1	100	1.6	3 120	0.122 8
	80	0.6	B	3.5	2/3	100	1.1	1 180	0.014 7
	100	1.1	C	3.5	1	250	1.1	3 120	0.795 0
	40	0.6	C	2.5	2/3	250	1.6	1 180	0.250 0
	40	0.6	C	3.5	1/2	170	0.6	3 120	0.101 9

(cont d)

	oil thickness ( $10^{-3}M$ )	bottom gas amount ( $M^3/hr$ )	oil type	gas pressure (atm)	bottom tuyere site ( $R$ )	water depth ( $10^{-3}M$ )	top gas amount ( $M^3/hr$ )	top nozzle type	$V_{oil}/V_{water}$
	80	1.6	C	3.0	1	170	1.6	1 180	0.509 9
	80	1.1	C	3.0	2/3	100	0.6	3 120	0.533 3
	100	1.6	C	2.5	1/2	100	1.1	1 180	1.214 2
sum of									
1st class	0.926 9	3.980 6	1.800 3	3.258 1	1.801 1	2.234 1	2.475 0	3.998 6	$\varepsilon = 7.477 8$
2nd	2.433 6	2.650 1	2.273 2	1.822 9	2.833 3	2.458 9	2.487 1	3.479 3	
3rd	4.117 3	0.847 1	3.404 3	2.396 8	2.843 4	2.884 8	2.515 7		
maximum difference	3.190 4	3.133 5	1.604 0	1.435 2	1.042 3	0.750 7	0.040 7	0.519 4	

Following this step, a so-called "range estimation" method was used to see the optimum fluctuation. Table 3 indicates this estimation. It was interesting to find that this "optimum" fell just on the boundary of the independent factor varying area.

**Table 3 The range estimation of optimum mixing ratio**

Optimum condition	The fluctuation of $\frac{V_{oil}}{V_{oil} + V_{water}}$
oil thickness $100 \times 10^{-3}M$	36% - 54%
bottom gas amount $1.6 M^3/hr$	

*Vertex calculation by means of a paraboloid equation*

Based on the results obtained from orthogonal designation, we used a paraboloid equation introduced by a famous Chinese mathematician, Hua Luo Geng<sup>[9]</sup>, to check the results obtained from "range estimation".

Four factors had been chosen and a minicomputer was used to solve a linear equation group with 15 dimensions. We then got the following paraboloid:

$$\begin{aligned}
 Y = & 7.081 6 - 0.361X_1 + 0.083X_2 - 2.83X_3 - 3.079X_4 \\
 & + 0.015X_1X_2 + 0.047 3X_1X_3 - 0.007 5X_1X_4 \\
 & - 0.074X_2X_3 - 0.372X_2X_4 + 2.43X_3X_4 + 0.008X_1^2 \\
 & + 0.077X_2^2 - 1.6X_3^2 + 0.49X_4^2
 \end{aligned}$$

where  $Y$  = mixing ratio ,  $X_1$  = surface tension ,  $X_2$  = slag layer thickness ,  $X_3$  = amount of bottom gas ,  $X_4$  = gas pressure.

The vertex calculated from this paraboloid equation was unexpectedly a minimum value falling on the other side of the independent factor varying area :  $X_1 = 16.74$  ,  $X_2 = 35.5$  ,  $X_3 = 0.97$  ,  $X_4 = 2.17$ .

The above two calculations made us aware of the fact that within the independent factor varying area , the factors produced only a monotonous effect.

#### *The influences of a single factor and discussion*

Figs. 5 and 6 show the influences of bottom gas amount as well as slag layer thickness separately. The agreement with the above estimation was good. Based on these figures , the mixing ratio was found to be 40% -50% .

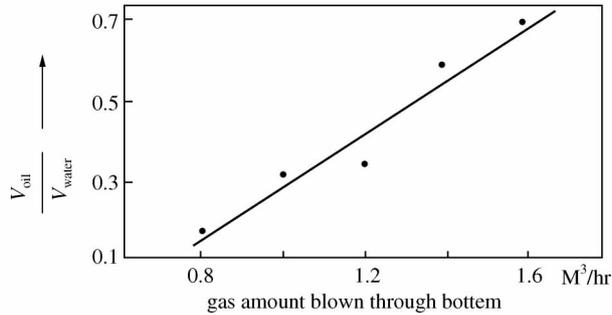


Fig. 5 The influence of bottom gas amount on mixing ratio

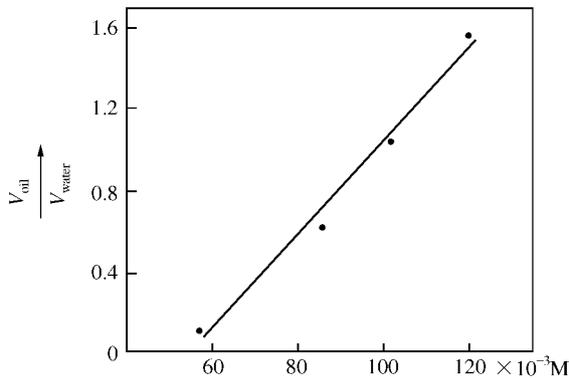


Fig. 6 The influence of oil layer thickness on mixing ratio

According to this investigation , the maximum bottom gas amount was limited by  $0.3 \text{ M}^3/\text{T} \cdot \text{min}$ . It was a bit smaller than that of AOD , and only about

1/3 of the gas amount used in a violently agitated refining furnace ( $0.8 \text{ M}^3/\text{T} \cdot \text{min}$ ). So some experiences were offered for us to increase the bottom gas amount further. On the other hand, as Tsuyoshi Kai<sup>[10]</sup> indicated for bottom blowing, the deeper the bath the weaker the splashing. Since in the case of smelting reduction, the thick slag layer should be taken into account, so a further increase of bottom gas amount is thought to be indicated.

The attractive influence of slag layer thickness was beyond our expectation.

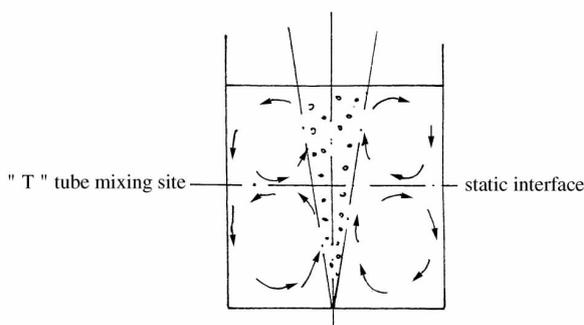


Fig. 7 "T" tube mixing function

But it could be understood by considering that the mechanism drawing the slag drops into the molten metal varied when the slag layer was varied from thin to thick. If the slag layer is thin, the slag is drawn downward mainly by shearing stress on the slag-metal interface.

Oppositely, if it is a thick slag layer, the pumping effect directly happening in the slag layer must make its own contribution causing a strong slag flow inside the slag layer and along the side wall downward. Thus, through a so-called "T" tube mixing function (Fig. 7), the slag drops can be drawn quite far down, approaching the bottom of the converter.

Fig. 6 is important. It indicates that a thick slag layer is favourable for a good slag-metal mixing ratio and consequently may lead to a good reduction of Mn from slag to metal.

### The contribution of side wall blowing

As shown in Fig. 3, the side wall tuyere was put just beneath the interface, so we were not surprised to find this side wall blowing did not show an obvious effect on the mixing ratio. But we also found that oil drops separated from water very quickly as soon as we suddenly stopped the gas flow if only bottom blowing was used (despite whether top blowing was used or not). When a bottom/side-wall combined blowing was used, the time needed for separation was prolonged (Fig. 8).

Pursuant to V. G. Levech's opinion, during the floating up of oil drops, they are always inclined to merge with each other into a larger one, so the initial floating velocity is essential for determining the total separation time<sup>[11]</sup>. From Fig. 8, the initial floating velocity for top-bottom blowing was 8.75 mm/s and that of bottom, side wall blowing was 3.89 mm/s. Using V. G.

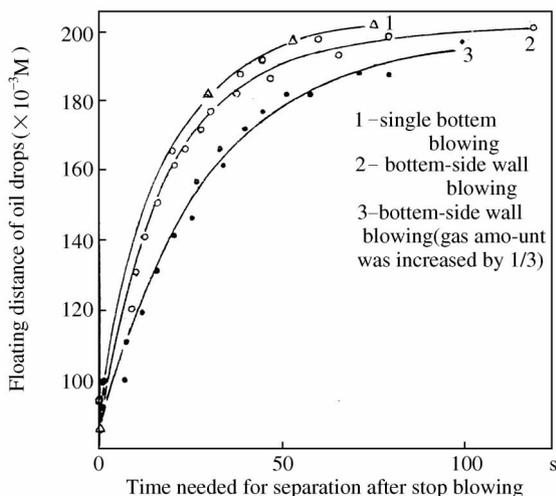


Fig. 8 The effect of side wall blowing

Levech's<sup>[11]</sup> and G. H. Geiger's method<sup>[12]</sup>, we calculated the corresponding size of oil drop to be approximately 1 mm and 0.67 mm. The calculated oil drop size for top-bottom blowing was a bit smaller than the size of oil drops which adhered inside the sniffer tubes at sampling moment. A small slag drop was the significant contribution attributed to side wall blowing.

## Conclusion

Top addition in performing a smelting reduction process in a converter was thought to be the most practical technique. Whether it may succeed or fail, all depends on the slag-metal mixing within the converter.

Based on the analysis of slag-metal mixing characteristics, we claim that by means of a thick slag layer and intensive stirring in a 3 — set tuyeres side wall blowing converter, slag-metal mixing may be fully developed. In this case, the main function of the bottom tuyere (just as AOD tuyere) is to draw slag downwards. Middle side wall blowing (tuyere put beneath static interface) results in small slag drops. A top blowing tuyere put beneath the static slag top surface is mainly useful to perform post-combustion. So slag drops were thought to play an important role in heat transfer downward in this converter blown with three sets of tuyeres.

## Acknowledgement

The authors are grateful to Professor S. Eketorp for his kind help in correction of this paper.

## List of symbols

$X$  — The content of the element in molten metal which is to be reduced

$(X)$  — The content of the element in slag which is to be reduced

$K$  — Equilibrium constant,  $K = (X)/X$

$Y_u$  — The mixing ratio of upper mixing,  $Y_u = W_s^{\Sigma}/W_m$

$Y_w$  — The mixing ratio of lower mixing,  $Y_w = W_s/W_m^{\Sigma}$

$W_s$  — The total dispersed amount of slag

$W_m$  — The total dispersed amount of molten metal

$W_s^{\Sigma}$  — The total weight of all slag in the converter

$W_m^{\Sigma}$  — The total weight of all metal in the converter

$k'_u, k'_w$  — Mass transfer coefficient

$k_u, k_w$  — Reaction coefficient

% SL — Slag percent, % SL =  $W_s^{\Sigma}/W_m^{\Sigma}$

$F$  — The flow ratio of dispersed phases,  $F = dW/dt$

$t$  — Time

$a$  — Average specific surface area

$s$  — Seconds

$S$  — Spreading coefficient

$M$  — Meter

$N$  — Newton

$n$  — The mixing circulation time

$t_u$  — The average retention time of molten metal droplets in slag

$U$  — Velocity

$L$  — Size

$\sigma$  — Interface tension or surface tension

$\rho$  — Density

$\mu$  — Viscosity

Subnotes :

*u* — upper mixing

*w* — lower mixing

*o* — initial

*s* — slag

*m* — metal

*n* — nth mixing circulation

## References

- [ 1 ] Soma T. Trans Jpn Met Soc 1982 :21(8) :620-625. In Japanese.
- [ 2 ] Mori K. Tetsu to Hagane 1964 :50(11) :1826-1828. In Japanese.
- [ 3 ] Moriyama A. Tetsu to Hagane 1969 :55(9) :777-788. In Japanese.
- [ 4 ] Magidson IA. Izv AH SSR (Met) 1981 :6 :15-20. In Russian.
- [ 5 ] Hida S. Mixing theory and application. Chem Ind Publ House 1984. In Chinese , translated from Japanese.
- [ 6 ] Becher P. Emulsion theory and practice. Am Chem Soc/Reinhold Press 1984.
- [ 7 ] Xi ZG. Physicochemistry of surface active agents. Beijing Univ Press (China) 1984. In Chinese.
- [ 8 ] Godfrey JC. Handbook of multiphase systems. McGraw Hill ,New York 1982. Chap 4.
- [ 9 ] Geng HL. Optimum seeking method. Sci Publ House 1981. In Chinese.
- [ 10 ] Kai T. Tetsu to Hagane 1982 :68(14) :100-106. In Japanese.
- [ 11 ] Levech VG. Physicochemical hydrodynamics. Sci Tech Publ House , Shanghai 1965. In Chinese , translated from Russian.
- [ 12 ] Geiger GH. Transport phenoma in metallurgy. Addison-Wesley ,New York 1973.

# 对炉外精炼钢的质量要求及其单元操作<sup>\* 1</sup>

## 1 前言

炉外精炼在现代化的钢铁生产流程中已成为必不可少的一个环节。

本世纪30年代出现了钢包渣洗法(Perrin Process)脱硫、脱氧工艺,到50年代,各种真空处理法(DH、RH)先后问世,并可工业化应用。在1970年以前,几乎所有钢包精炼方法,都已有相当的工业规模,但它的应用尚限于特殊钢的生产,在总钢产量中的比率,不足10%。直到70年代中期,由于能源危机,钢铁工业力求降低成本、提高经济效益,首先是日本,然后是西欧的钢铁企业,出现了两种技术趋势:一是连续铸锭技术的广泛采用,以取代传统的锭模浇注;二是采用大型转炉生产优质钢、特殊钢,以提高产值及利润率。显然,为了使连铸工艺顺行,通过炉外精炼来降低钢中硫、氧含量,以及均匀钢包中的温度、成分,是十分必要的,目前已用“钢水准备”一词来加以概括。现在,铁水预处理+大型氧气转炉+炉外精炼+连铸,已成为国外大型钢铁企业技术改造后的普遍模式。

本文综合近期国内、外炉外精炼的研究进展,结合本人的工作,对炉外精炼钢的质量要求,以及如何通过单元操作来加以保证,作一综合评述。

## 2 对炉外精炼钢质量要求的新动向

对炉外精炼钢的质量要求来自两个方面:一方面是由于炉外精炼可以

\* 原发表于《特殊钢》(4),1~9(1987)

更精确地控制化学成分,同时又可以改善钢及其中夹杂物的机械性能<sup>[1][2]</sup>。所以,导致了用户对炉外精炼钢提出日益苛刻的要求,以适应各种复杂和恶劣的工作条件。另一方面的质量要求来自连铸、轧制、热处理等后道工序。由于钢液质量提高,不仅可以避免某些常见的产品缺陷,还可使浇铸工艺有更大的灵活性。终轧温度降低和轧后冷却制度及产品热处理简化,而产品的性能更加稳定。最近三年以来,对炉外精炼钢质量要求的新动向,可大致归纳如下:

(1) 由于连铸坯尺寸的不断加大,所以对钢中硫含量的限制亦越来越严,其目的不仅是为了防止在连铸坯的凝固时形成白带、裂纹,更重要的是为了改进其热态与冷态的机械性能。现在已有不少厚板用户,提出要求炉外精炼钢能满足 ppm 级硫的要求 ( $S \leq 0.001\%$ )。

(2) 近期对精炼钢质量要求的另一个明显变化,是许多用户提出,要大大降低精炼钢磷的规格,其理由如次:

a. 对于高强韧钢、低碳的 Cr-Ni-Mo 钢和 9% Ni 钢等钢种来说,降低磷含量可避免回火脆性及低温脆性,这是因为磷很低时,晶间偏析减少,晶界得到净化之故;

b. 对于低合金高强度钢的管线用钢来说,磷必须小于 100 ppm (即  $\leq 0.010\%$ ),以防止氢诱导裂纹(HIC)及应力腐蚀裂纹(SCC),对于奥氏体不锈钢来说,如果将磷含量从 200 ppm 降到 20 ppm,则应力腐蚀裂纹可以完全防止。

(3) 用于深冲的高强度冷轧钢板,经常要求很低的碳含量 ( $< 40$  ppm, 即  $\leq 0.0040\%$ )。由于炉外精炼工艺能把碳降到这样低的水平,而又保证钢中氧及氧化物夹杂含量不高,因此,就可以用炉外精炼时钢液脱碳,来取代传统的成品带钢连续脱碳退火的工艺,它不但降低了生产成本,而且大大提高了生产率。此外,这类产品常常还要求非常低的氮含量(例如  $\leq 20$  ppm),这在脱碳退火中是无法达到的,而在氧气转炉激烈脱碳之后,再加上真空下的脱碳则有可能实现。

(4) 对于不锈钢来说,要求碳和氮的固溶量尽量降低,例如  $(C + N) < 100$  ppm 以后,就可以完全防止晶间腐蚀及应力腐蚀。显然,采用炉外精炼使  $(C + N) < 100$  ppm 后,要比传统的用钛、铌来使不锈钢稳定化更为经济,质量更好。

(5) 铝脱氧钢板和铁素体不锈钢的焊缝韧性和夏贝冲击值,可因碳和氮含量的降低而大大改善。如果是要求热塑性的产品,应该避免

高的  $Al \times N$  值,因为连铸坯凝固时,AIN 可能导致钢坯内显微裂纹的形成。

(6) 处于交变载荷下的高强度钢,对氧化物夹杂有越来越高的要求,这是因为它会引起钢的塑性降低、裂纹源形成,并最终导致钢的疲劳寿命缩短。

(7) 从各种不同的使用性能要求出发,提出了对钢中夹杂物形态控制的要求。最初是厚板生产者及 T 型焊接工艺要求钢中硫化物夹杂呈一定的形态。然后 Z 向钢和石油、天然气管线用钢对硫化物的数量及形态提出了更为严格的要求。现在,更多的冶金工作者转向钢包中的合成顶渣加合成渣粉喷吹脱氧工艺的开发<sup>[3]</sup>。同时,又有人重新趋向于复合脱氧剂的应用,例如为防止焊缝的脆性开裂,在焊条钢炉外精炼时应用复合脱氧剂,使精炼后钢中夹杂物呈细小、分散的半塑性状态(铝硅酸锰系列)。初步的结果是令人满意的,也可能会扩大到其他的场合加以应用<sup>[4]</sup>。

据统计<sup>[5]</sup>,精炼钢目前能达到的水平为钢中硫、氧、氢、氮、磷的含量小于 100 ppm,而到本世纪末将低于 30 ppm。到那时,不仅钢的性能会进一步改善,一些目前常见的冶金缺陷,如白点、热裂、回火脆性、焊接裂纹等也可以消除,并减少为防止这些缺陷所采取的一系列工艺措施。

### 3 炉外精炼的单元操作分析

经过二十多年的发展,炉外精炼的方法已有十几种,可归纳成以下单元操作。

#### 3.1 真空脱气及脱碳

迄今为止,各种脱气的动力学理论模型还不能直接适用于高真空条件。脱气过程的实际控制参数仍是真空度、惰性气体吹入速率及处理时间,而后两者的乘积就是吹气量。

对氢的去除来说,已有的生产实践表明,最经济的脱氢真空度是 2 mbar(相当于 1.6 mmHg)。这时,经过 30 分钟处理,不管是 RH<sup>[6]</sup>、DH 还是钢包真空吹氩<sup>[7]</sup>,均可使最终的钢中氢含量达到  $\leq 1.5$  ppm。钢液脱氮,则由于其原子半径较大,同时气/钢表面又大部分被钢中表面活性元素硫、氧所吸附,因此实际效果很差。在没有惰性气体吹入的 DH 装置中,只有起始氮含量大于 80 ppm、深度脱氧及脱硫的钢液,经过长时间反复

提升处理,有可能脱氮 40% ~ 50%,最终含氮量达到 40 ppm 左右,见图 1<sup>[8]</sup>.

至于炉外精炼过程中,干燥无水的炉渣有可能吸收钢液中相当数量的氢和氮则是一个新的概念.炉渣吸收水分的能力,可用水容量  $C_{H_2O}$  来表示:

$$C_{H_2O} = \frac{(H_2O, \text{ ppm})}{(P_{H_2O}, \text{ atm})^{1/2}} \quad (1)$$

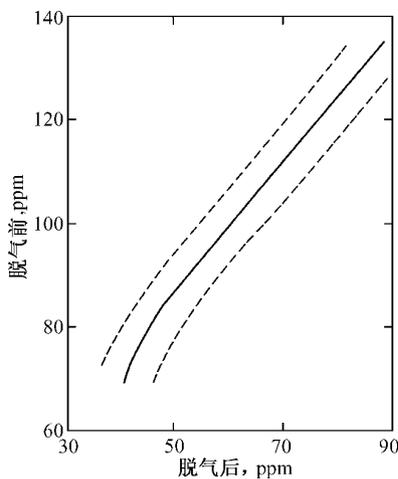


图 1 DH 脱气时钢中氮含量的变化

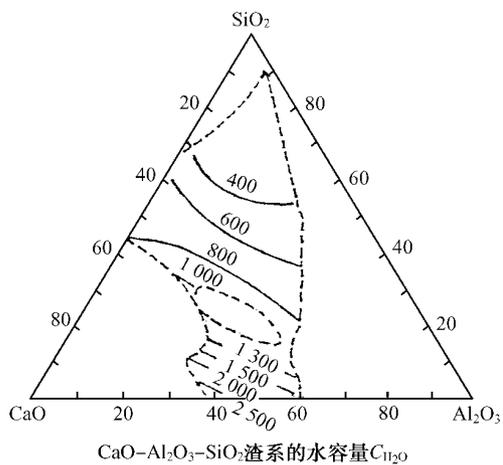


图 2 CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> 渣系的水容量  $C_{H_2O}$

对于 CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> 渣系的水容量数据,可用图 2 表示.由于真空下的  $P_{H_2O}$  极小,所以渣中溶解的(H<sub>2</sub>O)将被不断脱去.而与此同时,如果未彻底脱氧,在真空下钢、渣激烈搅混时,有可能发生下列反应:



从而发生氢从钢到渣,再由渣中以水汽形式逸出的脱气过程.为此,当然应尽量选用水容量低的渣系.一方面是为了使氢从渣到气相的过程加快,另一方面,是这类渣不会吸收大量水分,不至于造成氢从渣到钢的增氢过程.

目前国外深冲用冷变形高强度钢板是先 在转炉中脱碳到 0.04% 左右,然后在 RH 真空室中,利用钢液中的氧量使碳进一步降低,其脱碳动力学可用下式来描述:

$$C_t = C_0 \exp\left(\frac{\dot{q}}{V} \cdot \frac{AK}{\dot{q} + AK} \cdot t\right) \quad (3)$$

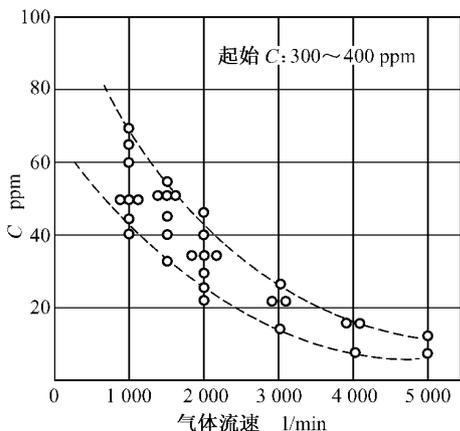


图3 用RH法处理13分钟时气体流速与碳含量关系

式中  $AK$  是脱碳反应的容积系数 (单位时间进行脱碳的钢水容积), 它是 RH 上升管中吹氩流量的函数.

$C_0$ 、 $C_t$  分别起始时及 7 分钟时钢液的含碳量;

$q$  钢液环流速度;

$V$  钢包容积.

这样, 通过最佳吹氩速率及高的环流速度, 可使碳在 10 ~ 15 分钟内, 降到 20 ppm 以下<sup>[9]</sup>. 见图 3.

### 3.2 搅拌均匀化及排除夹杂物

搅拌在炉外精炼中有特殊重要的意义. 不仅是因为钢包特定的形状 ( $D/H = 1$ ) 造成的反应界面小及熔池不易均匀化 (温度、成分), 而且还是促进钢液中夹杂物排除的主要手段. 在不同的炉外精炼工艺中, 采用不同搅拌方式, 它们有气体搅拌、感应搅拌及真空驱动中 (钢液环流) 搅拌.

关于搅拌能量和夹杂物聚合、排除之间的定量关系, 已被模型及试验结果所证实<sup>[10, 11]</sup>. 对于大尺寸的液态夹杂物来说, 它的上浮排除没有热力学困难, 惟一可能的障碍是液态夹杂与钢液间的表面现象, 即高的氧、硫活度的钢液会使得夹杂物与钢液间的相间张力减小. 在这种情况下, 搅拌就要特别当心, 过分强烈的不规则搅拌, 只会导致夹杂物 (或渣滴) 与钢液的乳化, 而不利于夹杂上浮排除. 从另一方面来讲, 如果高浓度的强脱氧剂, 直接与氧化性炉渣接触 (如转炉非挡渣出钢时, 包中加锰铁、硅铁、铝及吹氩搅拌) 再加上搅拌, 就特别容易生成小颗粒的液相夹杂, 并且在钢流的驱使下, 卷入钢液深部.

对于固体夹杂物来说, 它们与钢液的湿润性特别重要. 一般来说, 其浸润角不仅应大于  $90^\circ$ , 使之能形成串群状的大尺寸夹杂, 而且为了最终在钢液搅拌时, 当这类夹杂运动到渣/钢界面时能顺利地排出钢液进入渣相, 浸润角

应越大越好,见图4。这里还应强调一下,钢液中高的氧活度,对刚玉或尖晶石系夹杂物,特别是这类夹杂物含有锰时的排除不利。

以上这些微观现象的分析和观点,再加上清洁钢生产的实践经验,已使炉外精炼工作者明确,在充分防止过氧化的条件下(氩气或真空气氛及还原渣下),对深度脱氧、脱硫的钢液进行适当强度的长时间搅拌,将可获得很纯净的钢液。这在国外,被称为“后搅拌”(Post-stirring)或“清洗搅拌”(Washing-stirring),各清洁钢生产厂家都根据本厂的实际生产条件(钢种、脱氧方法、耐材质量等)制订出相应的搅拌规范。

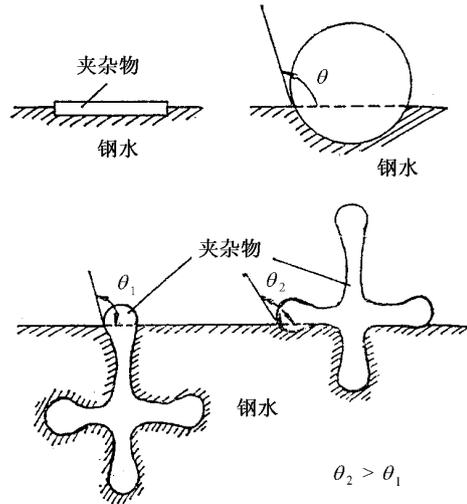


图4 湿润角对夹杂物稳定状态的影响

### 3.3 夹杂物形态控制

不同夹杂物在轧制温度(1000 )时的可变形性及形态如图5所示。

图5中,由中间白色部分组成的夹杂,是生产细线材或丝所必需的,显然它不可能用Al、Ca等强脱氧剂来获得,因为低 $\alpha_o$ 部分(5~20 ppm)相当狭窄,而中等 $\alpha_o$ 区20~90 ppm也容易进入不变形夹杂区,最好能将 $\alpha_o$ 控制在100~110 ppm,这样当 $\alpha_{Si}=0.3$ 时,100%的夹杂物是可变形的。如要将 $\alpha_o$ 控制在这样高而窄的范围内,目前的惟一办法是还原渣下吹Ar搅拌或喷吹渣粉。

另外,对于铝或硅脱氧的钢来说,无论喷吹碱性渣粉或钙处理均可使氧化物夹杂变性,进行形态控

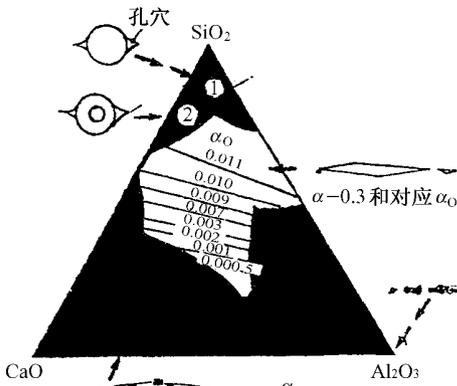


图5 CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>系夹杂物在轧制温度(1000 )下的可变形性。区域1—单相非结晶态不变形夹杂。区域2—与区域1相同,只是其中有非晶态可变形析出相。区域2—结晶态+一个非晶态可变形相。中间白色部分的夹杂组成是在轧制时保持塑性的可变形夹杂。中间的斜线表示当1600、 $\alpha_{Si}=0.3$ 时,要形成塑性夹杂所对应的氧活度。

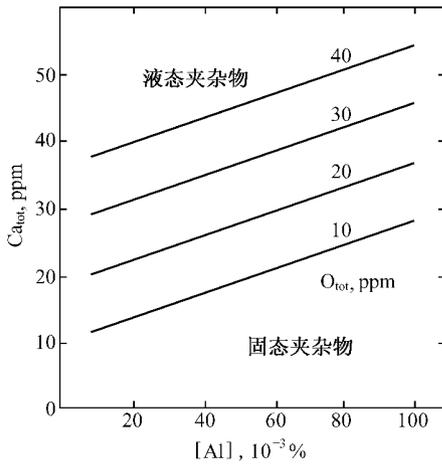


图 6 在铝脱氧钢中使串链状三氧化二铝夹杂变性所需钙量

制. 但若要使硫化物变性, 只能采用钙处理法<sup>[13, 14]</sup>.

夹杂物变性的一个重要应用, 是采用钙处理法使铝镇静钢中固体串链状三氧化二铝夹杂物转变为液态钙铝酸盐夹杂物, 以利于这类铝镇静钢的连铸. 钢中钙、铝、氧含量之间的关系, 如图 6 所示.

当然, 钙处理时, 进入钢中的钙除了与氧作用外, 还要和其他非金属元素作用, 根据 IRSID 最近的研究结果, 其热力学数据, 如图 7 所示<sup>[15]</sup>. 其中

$$\alpha_{Ca} \cdot \alpha_O = 9 \times 10^{-7} \quad (4)$$

$$\alpha_{Ca} \cdot \alpha_S = 1.7 \times 10^{-5} \quad (5)$$

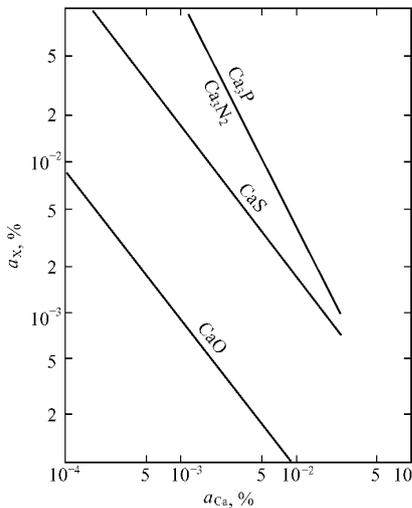


图 7 当存在高 CaO 及 CaS 溶解度脱氧产物时, 钙与钢中元素的平衡(1 600 °C)

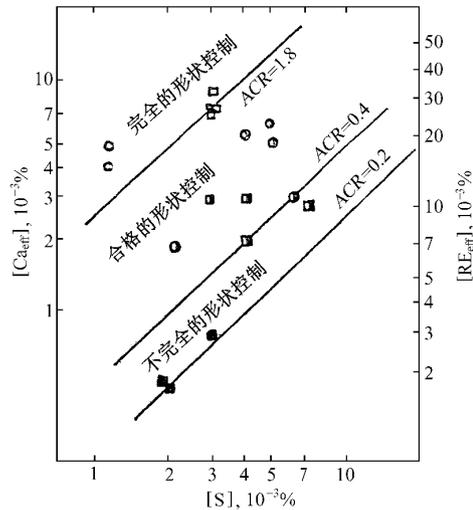


图 8 在低合金高强度钢中, 用钙及稀土控制硫化物形态

不同硫含量时, 采用钙或稀土处理, 使硫化物夹杂变性, 控制硫化物形态的情况, 如图 8 所示<sup>[16]</sup>. 而硫化物夹杂的变性, 是由于 CaS 溶入 MnS 中引起夹杂物硬度增加, 并且在轧制温度下不变形所致. 有研究表明, 如果只希望形

成不变形的硫化物夹杂以提高低合金高强度钢的性能,则不必使 MnS 完全变成 CaS,只要有 5% 的 CaS 进入 MnS 固溶体中,使 Mn/S 达到 0.06 即可。

$$\begin{aligned} \text{ACR} &= (32/40)[\% \text{Ca}_{\text{eff}}]/[\% \text{S}] \\ &= (32/140)[\% \text{RE}_{\text{eff}}]/[\% \text{S}] \end{aligned}$$

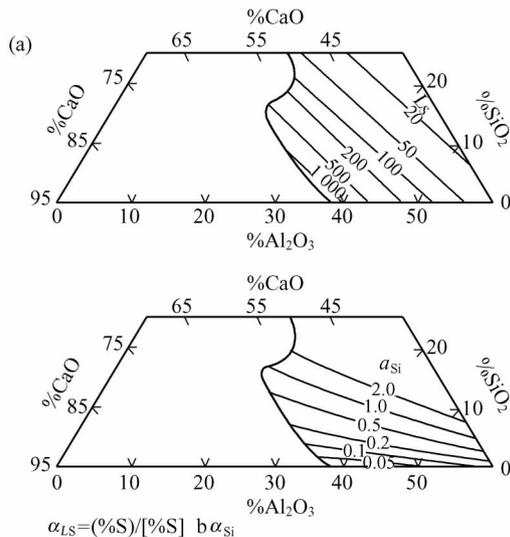
这里  $[\% \text{Ca}_{\text{eff}}]$  及  $[\% \text{RE}_{\text{eff}}]$  指脱氧后剩下的钙及稀土。

### 3.4 顶渣反应

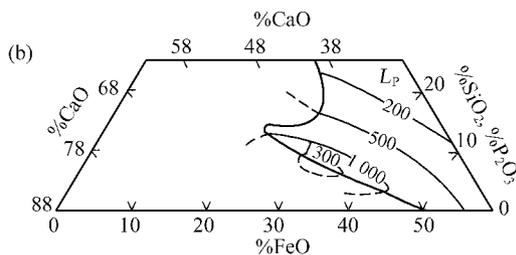
相当一段时间中,冶金工作者认为炉外精炼就是真空、加热及搅拌的组合,最多在某种产品需要前提下加一个喷粉,对于钢包中顶渣的作用有所低估。但近年来,人们重新重视了它不可忽视的、有时是决定性的(如对极低硫、氧钢的生产)作用。但迄今为止,通过顶渣/钢液反应,人们仅能控制硫、磷、氧三个元素,对于它对钢中氢、铝、硅的含量的影响,尚处于不能控制阶段。

#### 3.4.1 精炼渣/钢间的热力学研究结果

根据文献<sup>[17, 18, 19]</sup>所发表的三元或四元渣系中,硫、硅及磷的平衡情况如图 9 所示。



a) 含 Al ( $\alpha_{\text{Al}} = 0.03$ ) 钢与 CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-5MgO 渣间在 1625 °C 时的硫与硅的平衡。



b) CaO-(SiO<sub>2</sub> + P<sub>2</sub>O<sub>5</sub>)-FeO-6MnO-4Na<sub>2</sub>O 渣在1 600 下与钢液之间磷的平衡分配.

图9 渣钢间硫、磷的分配系数及硅活度的平衡情况

从这些平衡图可以使我们看到 ,对应不同精炼目的的最佳顶渣成份.

例如 ,为了深度脱氧及脱硫 ,应该使炉渣碱度达到 3 ~ 5 ( $R = \text{CaO} / \text{SiO}_2$ ) ,  $\Sigma(\text{FeO}) < 0.5\%$  ,而且使炉渣的曼内斯曼指数  $M = R : \text{Al}_2\text{O}_3 = (\text{CaO} / \text{SiO}_2) : \text{Al}_2\text{O}_3 = 0.25 \sim 0.35$ . 这种组成炉渣中的氧活度特别低 ,而三氧化二铝的活度低于 0.001 ,故与此渣相平衡的钢中氧活度将小于  $4 \times 10^{-5}$  (0.5 ppm)<sup>[17]</sup>. 对于低铝镇静钢的一种炉外精炼法 ,就是采用 CaO 饱和的顶渣与低铝 (Al ≤ 0.005% ) 钢液激烈搅拌 ,从而使最终的氧活度 ≤ 5 ppm<sup>[18]</sup>.

综上所述 ,热力学分析结果 ,对应于不同的精炼目的 ,可将最佳顶渣成分推荐 ,如表 1.

表 1 炉外精炼的最佳顶渣成分

精炼目的	最佳炉外精炼顶渣组成 ,%				
	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MgO	FeO
脱 硫	50 ~ 55	20 ~ 25	10 ~ 15	≤ 5	< 0.5
脱 氧	50 ~ 55	10 ~ 15	10 ~ 15	≤ 5	< 0.5
脱 磷	45 ~ 55	(MnO)6	(SiO <sub>2</sub> + P <sub>2</sub> O <sub>5</sub> )6 ~ 10	Na <sub>2</sub> O ≤ 2 , ~ 4	30 ~ 40

### 3.4.2 顶渣/钢液反应的动力学

目前对渣/钢反应动力学的研究 ,已涉及脱硫、脱磷、钢液中铝的消耗及钢中氧的控制等方面 ,在钢包的特殊条件下 ,在没有足够的搅拌强度时 ,钢液中的传质是限制性环节(即化学控制或双电化学作用)<sup>[19]</sup>. 故其动力学公式可用式(6)表示.

$$\frac{d[\% X]}{dt} = - K \frac{A}{V} \left( [\% X] - \frac{(\% X)}{L_x} \right) \quad (6)$$

式中  $A$ ——渣/钢相界面  $m^2$  ;

$K$ ——表观反应速度常数(在一定的液体搅拌条件下) 即

$$K = 500 \left( D_x \frac{Q}{A} \right)^{1/2}, \text{ms}^{-1} \quad (7)$$

$D_x$ —— $X$  组元在钢中的扩散系数  $m^2 \cdot s^{-1}$  ;

$Q$ ——在  $T$  和  $p$  条件下 通过渣/钢界面的真实气体流量  $M^3 \cdot s^{-1}$  ;

$L_x$ ——在  $t$  时间内组元  $X$  在一定温度下所能达到的平衡分配比 ;

$V$ ——钢液体积 ;

$[\% X]$  及  $(\% X)$ ——钢液及渣中  $X$  组元的浓度, wt% .

如果在反应温度下 组元的气化损失极小, 则其脱除比例为

$$R = \frac{[\% X]_0 - [\% X]_f}{[\% X]} \quad (8)$$

引入无量纲数,

$$\lambda = L_x M_{Si} \quad (9)$$

$\lambda$  仅取决于渣/钢成分及渣量  $M_{Si}$  系指每吨钢的渣重, 吨. 再引入一个表征液体搅拌条件的无量纲数  $B$  :

$$B = K \frac{A}{V} \cdot t \quad (10)$$

则

$$R = \frac{1 - \exp[-B(1 + 1/\lambda)]}{1 + 1/\lambda} \quad (11)$$

这也就是说  $R$  可简化为  $\lambda$  及  $B$  的函数, 它们可用图 10 表示. 由图 10 可知影响脱除率的是, 炉渣的性质及数量 ( $B \geq 4$  时, 或图右部分), 或者搅拌能量 (当  $\lambda \geq 14$  时).

### 3.5 钙处理

采用钙处理使钢液脱氧、脱硫及夹杂物形态控制已是一种普遍应用的工艺, 因此不作赘述. 但值得指出的是, 采用钙处理法来脱除钢液中磷、砷、锑、氮等有害元素, 是一个令人感

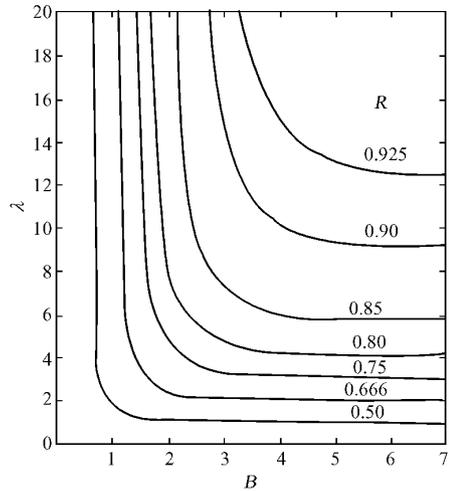


图 10 顶渣反应的效率及影响因素

兴趣的新动向. 向硅钢中加入钙使之脱磷、脱砷等结果见图 11,而在减压(25 bar)及  $\text{CaF}_2$  顶渣下,向 18—8 不锈钢液加入 3% 的钙,可使磷脱除 70%,达到 0.01% 左右,脱砷 95% 达到 10 ppm 左右,脱锑 90% 达到 20 ppm 左右;脱锡 90%,达到 150 ppm 左右,见图 12. 尽管有这些好的试验结果,但成本较高及操作上除渣的困难,仍是广泛应用的一大障碍.

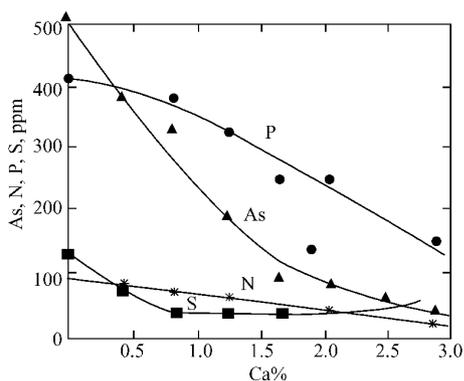


图 11 钙处理对硅钢中残余元素的影响

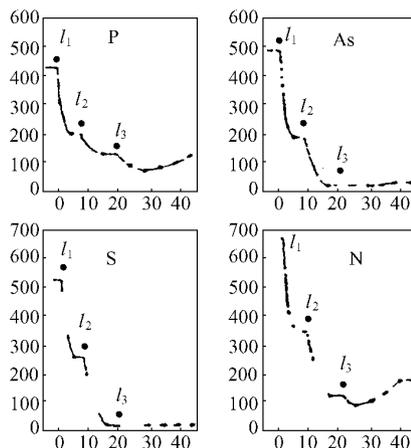


图 12 18—8 不锈钢的钙处理对残余元素的影响

## 4 结论

(1) 炉外精炼正随着转炉生产特殊钢比重的增加,以及连铸比的不断提高而日益普及.与此同时,用户也对炉外精炼钢的质量提出越来越高的要求.目前,对于钢中氧、硫、磷、氢、氮的总含量,已要求低于 110 ppm,预计到 2000 年,这种要求将提高到  $\leq 30$  ppm.

(2) 炉外精炼工艺包含真空脱气及脱碳、搅拌均匀化及夹杂物排除、顶渣脱硫及脱氧、夹杂物形态控制及钙处理等单元操作.真空下的脱氢及脱碳已可定量控制,搅拌均匀化及顶渣脱硫及脱氧可以半定量控制,夹杂物形态控制及夹杂排除的动力学,尚属于定性研究阶段.

(3) 今后炉外精炼工艺研究的重点,在于搅拌方式对不同类型夹杂物去除速率的定量关系,超纯净钢(氧活度  $\leq 1$  ppm,硫含量  $\leq 5$  ppm)精炼过程炉渣与炉衬的行为及其成分优化,以及不同钢种及不同应用条件下的夹杂物形态控制.

## 参 考 文 献

- [ 1 ] T. EMI & Y. IIDA. in Proc Scaninject III' , Vol. 1 , Paper 1. ,1983 Luleä , MEFOS
- [ 2 ] T. OHTAKE. in Proc 7th ICVM Congr , Nov. 1982 , Tokyo , Iron and Steel Institute of Japan 821
- [ 3 ] B. TIVELIUS & K-D , Xu. in Proc Congr on Inclusions and Residuals in Steels , Mar. 1985 , Canada
- [ 4 ] L. DEVILLERS *et al.* in Proc Conf “Effect of Residual , Impurity and Microalloying Elements on Weldability and Weld Properties” , Nov. 1983 , London , The Welding Institute
- [ 5 ] K. KAWAKMI. Transactions ISIJ , 24 ,1984 ,754-759
- [ 6 ] Y. MIZUKAMI , *et al.* 铁と钢 ,1983 69(2) ,A41
- [ 7 ] F. CAUMONT , *et al.* Rev Métall , cah Inf Tech ,1982 ,79 (6) #95
- [ 8 ] CI. OUVRADOU. Le Procédé DH' , Report 83 , 393 , CESSID , Oct 1983
- [ 9 ] N. SUMIDA *et al.* Kawasaki Steel Tech. Rep. 1983 (8) 69
- [ 10 ] S. LINDER. Scand. J. Metall. 1976 3(4) ,137
- [ 11 ] R. VASSE *et al.* in Proc 7th ICVM Congr , Nov. 1982 , Tokyo , Iron and Steel Institute of Japan ,1125
- [ 12 ] Y. SHINSHO *et al.* Trans Iron Steel Inst Jpn ,1982 22(12) B368
- [ 13 ] A. MORIYA *et al.* in Proc Scaninject III , Vol. 2 Paper 32 ,1983 Luleä MEFOS
- [ 14 ] Y. IIDA *et al.* in Proc “Scaninject III ” , Vol. 2 Paper 49 1983 Luleä MEFOS
- [ 15 ] C. GATELLIER , *et al.* Tetsu-to-Hagane ,1984 ,70 (12) , S 872
- [ 16 ] T. EMI *et al.* in Proc 3rd Germany-Japan Seminar 1978 , Düsseldorf
- [ 17 ] T. Usui *et al.* in Proc “Scaninject II ” 1980 , Luleä MEFOS
- [ 18 ] E. T. Turkdogan. Arch Eisenhüttenews 54(1983) Nr 1 , Jan
- [ 19 ] P. V. RIBOUD *et al.* Steel desulphurization in secondary refining' Report

# 连铸钢水的准备<sup>\* 1</sup>

## 1 引言

近年来,客户要求高性能低价格的钢材<sup>[1]</sup>.即要求:均匀的硬度,无宏观的条状裂纹,无表面缺陷,好的冷变形性能(取消加工过程中的热处理),易切削性,更严格的尺寸公差,越来越大的盘卷单重和线材直径,高的疲劳强度,无有害夹杂,高速压延性能,高的可扭转性能,不需热处理,好的延展性.

为实现以上要求,从70年代后期至80年代初,在世界范围内越来越多地采用了钢包精炼工艺.这种工艺介于熔炼炉和连铸机之间,被称为“钢水的准备”,图1为典型“钢水准备”装置.

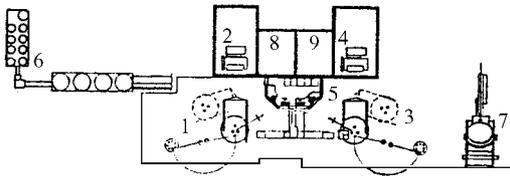


图1 新型钢包炉的布置

1. 1号加热站(活动炉顶式,带感应搅拌器,喷粉装置) 2. 变压器 3. 2号加热站(活动炉顶式,带感应搅拌器,喷粉装置) 4. 变压器 5. 控制室 6. 加合金装置 7. 除渣站 8. 过程控制计算机(二级) 9. 过程控制计算机(一级)

为连铸机作“钢水准备”有如下特点:加合成顶渣或喷粉来脱硫,以改善钢的质量和可浇注性;用浓差定氧来控制脱氧,精确的合金化,并调整浇注温度;吹氩或电磁搅拌,以使成分和温度均匀;对要求氢含量低的钢进行真空脱气;为高质量的钢提高清洁度.

\* 原发表于《上海金属》,9(6),91~100(1987)

## 2 脱硫

在钢铁联合企业中,我们可以对还原性的铁水进行预处理来脱硫,采用适当的工艺可把硫降至 0.003% 以下.

然而,在炼钢过程中,硫很难达那么低,转炉炼成的钢水中的硫含量通常达 0.01% 或更高,同样,电炉炼钢厂出钢时钢水中硫通常最低为 0.01%,经常波动于 0.015% ~ 0.025% 之间.为此,必须考虑进行再脱硫,并把它作为一种必不可少的处理过程.

为了有效地脱硫,有两种处理方法:

(1) 钢水在良好搅拌的条件下与合成顶渣反应,通常用吹氩搅拌和 CaO-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> 顶渣.

(2) 喷吹钙复合物或石灰基粉剂,或者两者顺序喷吹.

顶渣的碱度应在 3 ~ 5 左右,渣指数  $M = (\text{CaO}/\text{SiO}_2) : \text{Al}_2\text{O}_3$  应为 0.25 ~ 0.35 间,见图 2<sup>[2]</sup>.

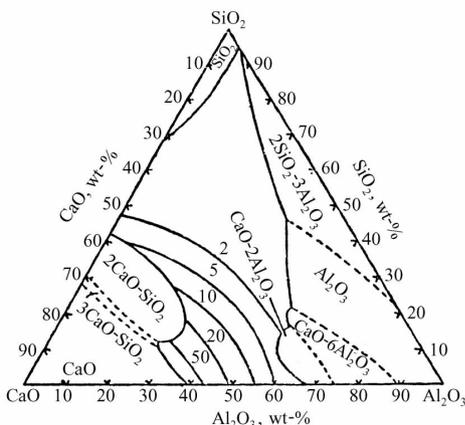


图2 1 600 下,Al<sub>2</sub>O<sub>3</sub>-CaO-SiO<sub>2</sub> 体系中的硫化物容量  $C_s^l$  ( $C_s^l$  的单位为  $10^{-3}$  wt%)

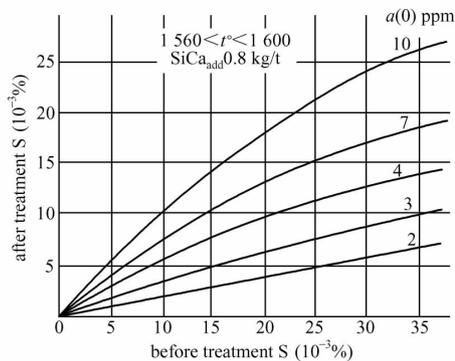


图3 用 Ca-Si 粉脱硫时,脱硫量与氧活度的关系

在钢包喷粉时,如果用 Ca-Si 粉作为脱硫剂,发现有图 3<sup>[3]</sup>那样的氧活度、Ca-Si 加入量和脱硫率之间的关系.碱性炉衬和惰性载气造成的强搅拌有利于很快地脱硫,大生产中可使硫含量降至 30 ppm,图 4<sup>[4]</sup>给出了 240 炉钢包喷粉的结果,采用的粉剂是石灰加萤石,喷粉量 5 kg/t 钢,氩作载气,每分钟 1 Nm<sup>3</sup> 的流量吹 21 分钟,然后再吹吨钢 1.5 kg 的 Ca-Si 进一步提高质量.

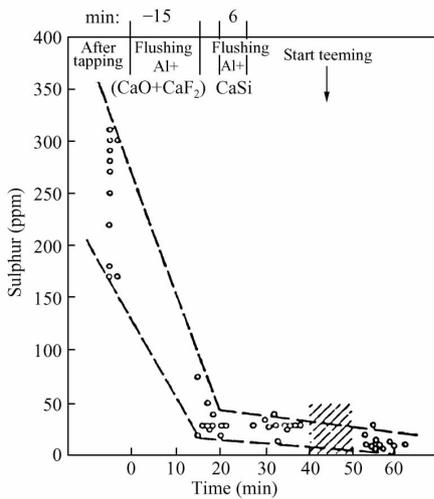


图4 钢包精炼用的典型喷吹脱硫程序

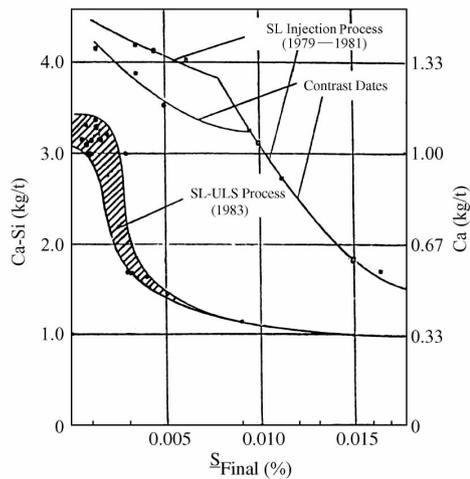


图5 SL-ULS 工艺的脱硫结果

英钢联的莱肯比钢厂采用SL-ULS工艺来处理管线钢,使硫含量低于20 ppm,该厂的生产结果见图5和图6<sup>[5]</sup>。

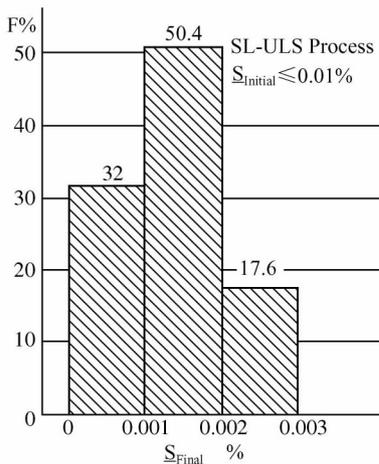


图6 SL-ULS 工艺用于管线钢生产的结果

平均Ca-Si用量约为吨钢3 kg,80%以上的钢中硫含量低于20 ppm。

还可以用钢包炉(VAD,LF或ASEA-SKF)来进行脱硫,用Ca/Al<sub>2</sub>O<sub>3</sub>混合渣系来生产低硫钢(<0.005% S),大部分硫都在出钢时由于渣钢高度混合而被脱除。通常在80 t钢包中随着铁合金和脱氧剂一起加入0.5 t快熔渣(60% CaO,20% CaF<sub>2</sub> 20% Al<sub>2</sub>O<sub>3</sub>),脱硫率可达50%(0.030/0.040降至0.015/0.020% S)。此后,加入0.3 t石灰使渣稠化,以减轻对炉衬的侵蚀。VAD不用来进行深度脱硫,当

要求最高硫含量为0.005%时,在炉内用传统的白渣工艺进行冶炼,使出钢时[S]<0.025%。然后可以采用两种不同工艺:单包操作,加0.5 t合成渣,并进行浅喷,然后再进行VAD处理;另一种是倒包操作,每个钢包中加0.5 t合成渣。

虽然在低硫条件下脱硫会进行得很慢,但VAD中可以进行附带的不是很

强的脱硫,直至渣被硫饱和( $\sim 1.5\% S$ )。然而,由于VAD具有加热能力,如果需要进一步脱硫的话,可以无限制地吹氩搅拌。

### 3 钢包精炼时用的取样和定氧测温系统

在以钢包精炼为代表的精确冶炼的领域中,如何精确地、重现性好地测温和分析成分是至关重要的,为此,测量探头的深度和插入时间必须不变,图7<sup>[5]</sup>所示的斯堪的纳维亚喷枪—ADS自动定深测量系统正是为在钢包中取样和测温而发展的。

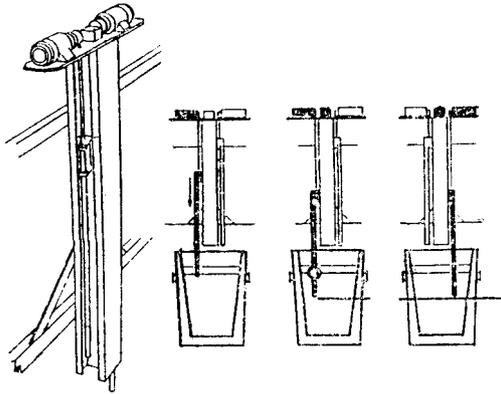


图7 测温取样用的斯堪的纳维亚喷枪—ADS系统

对于用于方坯连铸的SiMn或Si-Mn-Al镇静钢,钢中氧的平衡见图8,该图中有三个不同区域,分别表示不同的氧化物与氧平衡的情况。如果镇静钢由敞式水口的方坯或板坯连铸机浇铸,则铝含量要受到限制,钢中铝含量与水口直径有如下关系式:

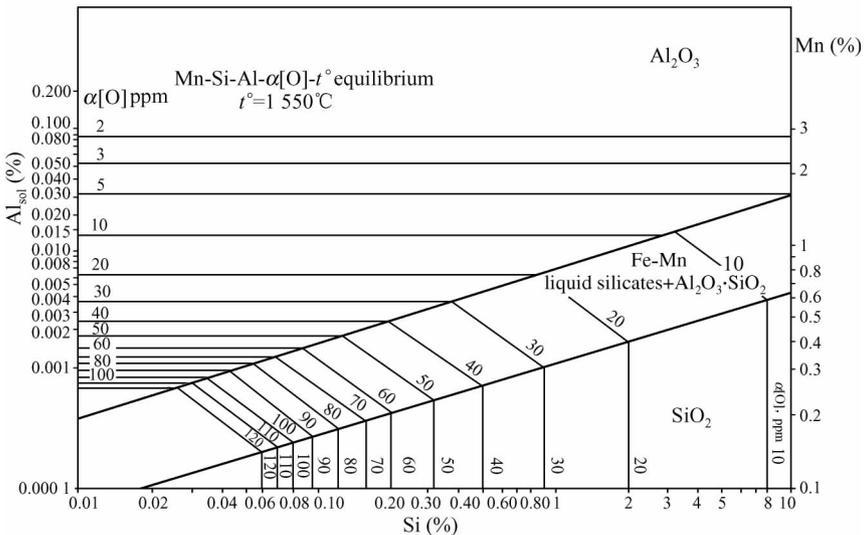


图8 Si-Mn或Si-Mn-Al镇静钢中的氧活度和氧化物夹杂

$$\log Al = - 1.25 + 1.74 \times \log D \quad (1)$$

其中  $D$ —水口直径(mm),  $Al$ —为避免水口堵塞而确定的临界溶解铝含量(%)。

应该指出 这种脱氧方式(Si-Mn 加少量的 Al)不能使钢中的氧降到令人满意的水平 无法避免因凝固过程中碳氧反应而使钢材表面出现气孔等表面缺陷。

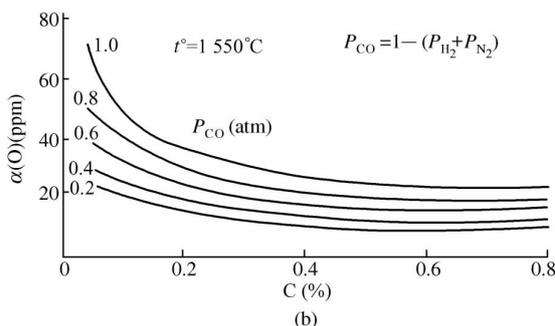
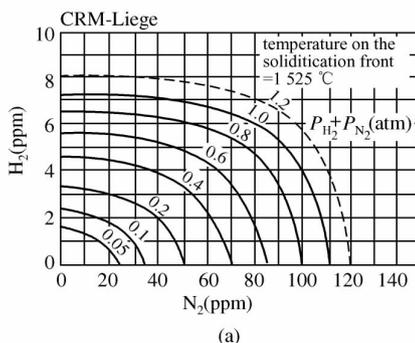


图9 不同脱氧条件的关系

(a)  $N_2, H_2$  含量与压力的关系;

(b) 不同  $CO$  分压下, 钢中碳氧间的关系

接下来,在钢包处理站要测定氧活度,测得的结果与图9所示的脱氧条件进行比较 根据比较结果可以在钢包中进行补充脱氧.图9中(b)表示为了防止产生表面缺陷,创造良好的脱氧条件,钢中的氧和碳应有的关系,由于氮和氢可以减少凝固前沿  $CO$  的分压,因此它们的存在对凝固前沿的碳氧反应有明显影响(即  $P_{CO} = 1 - (P_{N_2} + P_{H_2})$ ).这种压力变化的关系如图9(a)所示,虽然在钢包处理时可以补充脱氧,但由于要保持低的铝含量很困难,因此钢包中氧含量一般总比较高,此时应根据下式补充铝:

$$Al = \frac{0.11 \times [\alpha_{[C],m} - \alpha_{[C],c}] \cdot C_{ap}}{\eta_{Al}} \quad (2)$$

其中  $Al$ —加铝量(kg,由铝丝喂入机加入), $\alpha_{[C],m}$ —探头测得的氧活度(ppm)  $\alpha_{[C],c}$ —按图9算得的氧活度(ppm), $C_{ap}$ —钢包容量(t)  $\eta_{Al}$ —铝的回收率(%).

对于由板坯连铸机浇铸的 Si-Al 或 Al 镇静钢,平衡含量主要要控制 Al.但为得到细的晶粒,溶解铝含量要达到 0.025% ~ 0.060% 在这样高的铝含量下 按图8算得的氧含量可低至 3 ~ 5 ppm 此时存在的不是控制脱氧的问题 而是如何

根据氧活度测量结果来控制钢的清洁度,甚至是控制铝的含量的问题。

上述钢种由小方坯连铸机浇铸时也一样,脱氧过程中的主要问题是如何控制铝含量,这个临界值是很低的(约为0.005%~0.006%溶解铝)。对于敞开水口的小方坯连铸机来说,采用传统的化学或光谱分析方法很难及时地对此加以控制,但由图8可以看到,当主要要控制铝的平衡含量时,用氧活度测定法来控制低的溶解铝含量是很灵敏的,例如当溶解铝含量由0.001%变到0.006%时,相应的氧活度变化值达60 ppm(1550℃下,由80 ppm变至20 ppm),即每增加0.001%的溶解铝,就减少12 ppm。对于板坯连铸机用的Al镇静钢水,也存在着由实际结果整理出的溶解铝与氧活度间的关系(见图10)。图10中的氧活度以平均温度1550℃下测得的电动势值给出,实际使用中采用电动势值时灵敏度更高(溶解铝0.20%~0.060%,电动势-100~-170,而1580℃下相应的活度变化仅为7~3 ppm),这一关系的变异系数为10%左右,即在平均溶解铝为0.05%时,标准离差为0.005%。如果考虑到采用此方法测定溶解铝的速度(15秒),那么这一精度对于大多数场合来说已足够。因此,为了在钢水送去连铸前在钢包处理站快速可靠地控制铝含量,采用定氧探头测定是惟一快速精确的方法,这种关系确定以后,就可以应用钢包冶金设备作出图11的模型,这个图表示了溶解铝与氧测定值(以mV表示)间的关系,如果铝含量太低,或需要增加吹氩搅拌时间(在均匀化所需时间以外再加1至2分钟),则就要补加铝。如果意外地出现铝含量过高的情况,那么铝含量的减少就直接与搅拌强度和包衬材料有关(见图10以黏土和白云石为包衬的例子)。

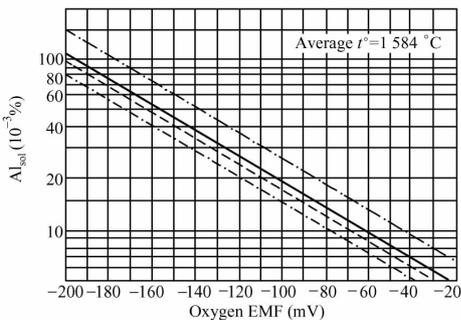


图 10 溶解铝和氧活度间的关系

- 搅拌站中钢中溶解铝含量；
  - - - 搅拌站中钢中总铝含量；
  - · · 用黏土钢包连铸时溶解铝含量；
  - · - 用白云石包衬连铸时溶解铝含量；
- $\alpha_{[O]}$ 在搅拌站测定

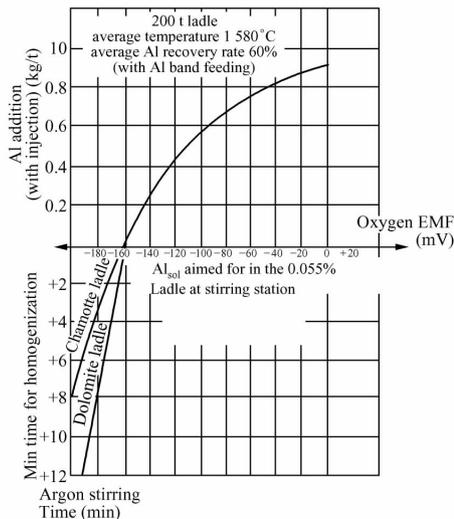


图 11 氧活度与工艺条件间的关系

如果钢包处理站有微机控制,则温度、氧和溶解铝都可以由计算机算出,图 12 是一个典型的计算机模式。

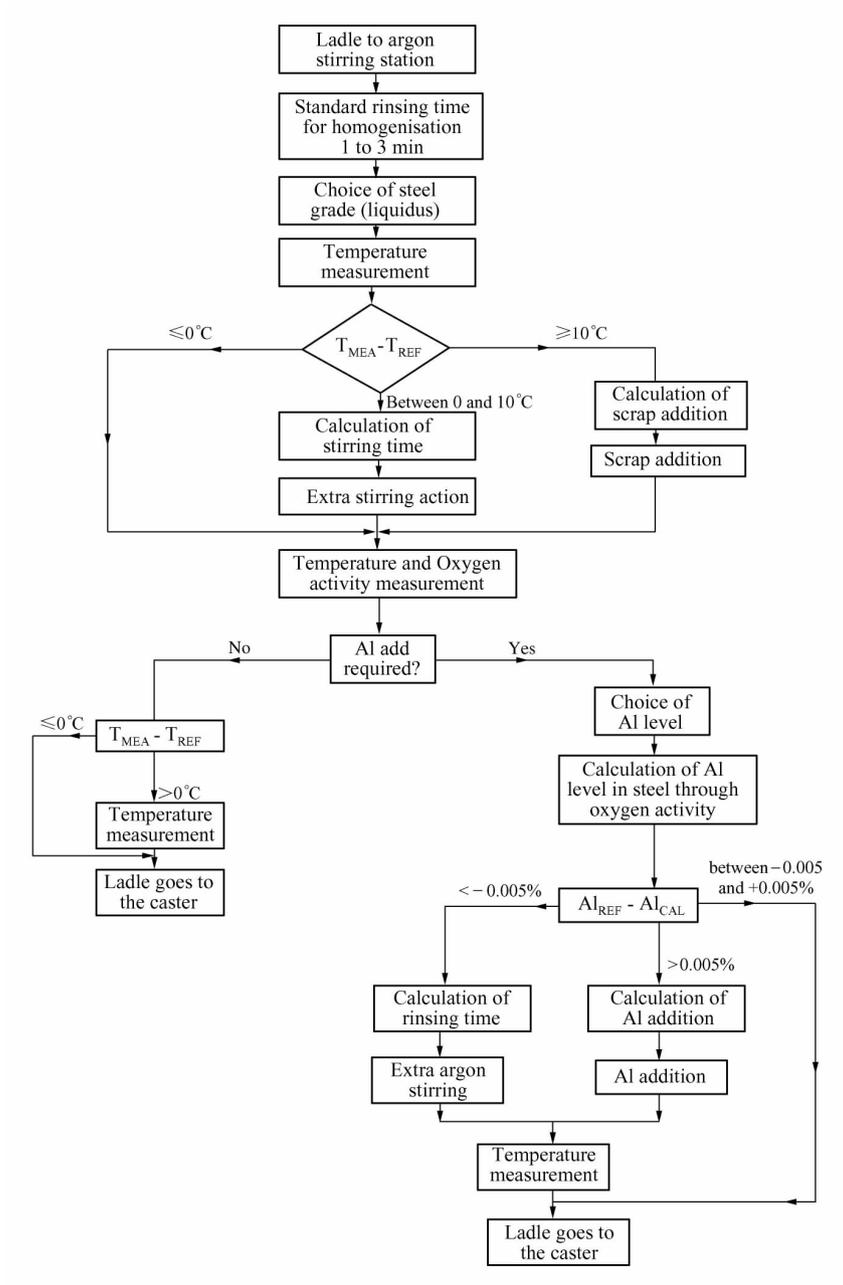


图 12 钢包处理的计算机控制模型

## 4 化学成分控制

如能在真空下吹氩或喷粉时进行成分的微调,就能生产出某些对硬度要求控制很严的钢种,如工程用钢、汽车用钢或轴承钢<sup>[6]</sup>。

### 4.1 碳

碳是一个需予以仔细控制的元素,在这一方面,VAD或LF比以前的钢包成分微调方法优越之处见图13。开始时,控制碳含量的问题主要来自最后分析调整后的碳含量的增加。在钢包处理站对碳含量进行调整,使其有充分的时间(约15分钟)使钢包中的碳充分溶解。

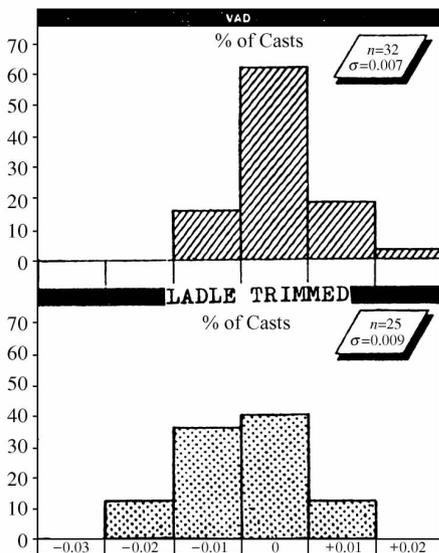


图13 碳含量与目标值的偏差

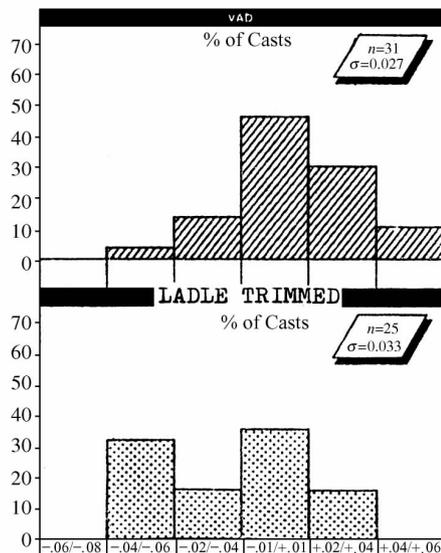


图14 锰含量与目标值的偏差

### 4.2 锰

由于采用了合成渣,并在真空或氩气氛下补加,正常情况下,钢中锰含量无明显下降,VAD中与其他钢包精炼设备中进行成分微调所得到的实际结果与目标值的偏差见图14。在每种设备中都在20分钟内取样检验,结果表明在此期间锰含量无明显减少,这是用了合成渣的缘故。图16给出了锰的收得率。

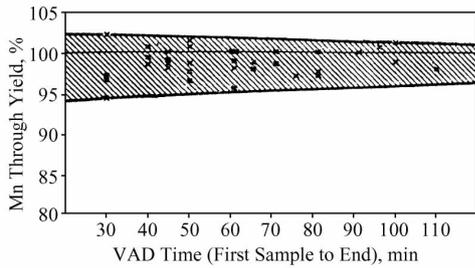


图 15 锰收得率与 VAD 处理时间的关系

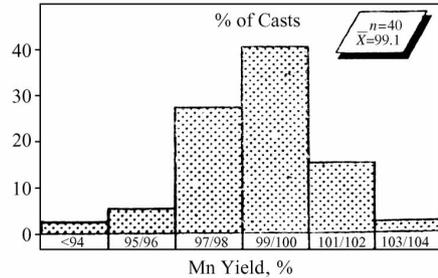


图 16 VAD 处理的锰收得率

### 4.3 铬

钢包中进行成分微调时,重的合金元素问题不大,VAD 中进行铬成分微调比 LF 中稍好些(图 17)。

### 4.4 低比重元素合金化

固体添加剂加入钢水后,最好能沉入钢液,低比重元素的合金化确实有些麻烦。此时,常常要采用喷吹或喂丝法,为了使加入的材料与钢水充分反应,重要的是要使添加剂在良好搅拌的情况下在钢水中很快溶解与均匀化。表 1 给出了采用喷枪深喷时合金粉剂的收得率。

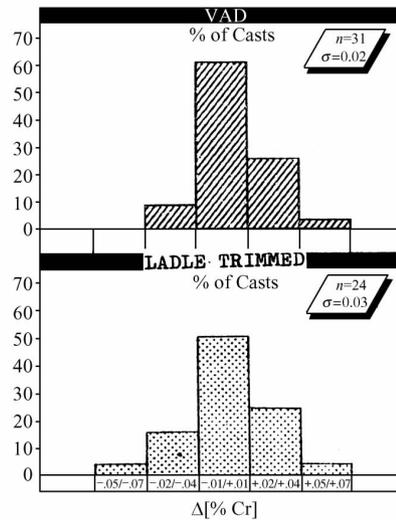


图 17 铬含量与目标值的偏差

表 1 钢包深吹时合金粉剂的收得率

元 素	C	B	Al	Ti	Nb	V	Si
收得率(%)	97	75	90	85	100	100	95

## 5 温度控制

对于连铸的细晶粒钢而言,为能有效地控制温度,钢包炉(VAD, LF 等)的再加热能力是很重要的。温度偏差控制在  $-5^{\circ} \sim +10$  就能消除以前采用真空脱气时常出现的浇冷钢现象(钢水温度低于目标值 5 以

上),见图 18.

当 VAD 的钢包的透气砖装在边壁上时,要保证氩流量大于 $5 \text{ m}^3/\text{h}$ ,并至少吹 5 分钟,这样才能避免冷钢积在钢包底部造成的分层现象.

## 6 连铸用的铝镇静钢

对于采用连铸工艺生产高质量钢的工厂,钢包精炼装置是保证钢水适应连铸要求的关键设备.此外,在浇铸细晶粒钢时,为了保证水口不被堵塞,控制钢水中氧和铝的含量是关键.一些工厂发展了真空处理后向钢包中加钙的工艺,以保证铝镇静钢符合要求,并能顺利浇注.

对于钙添加剂有一个“安全窗”——临界范围(见图 19),低于这一范围,钢水中不能形成适合于连铸的低熔点铝酸钙化合物,高于这一范围,则会形成钙硫化物.影响这一范围大小的主要因素为铝、硫、碳的含量和温度.

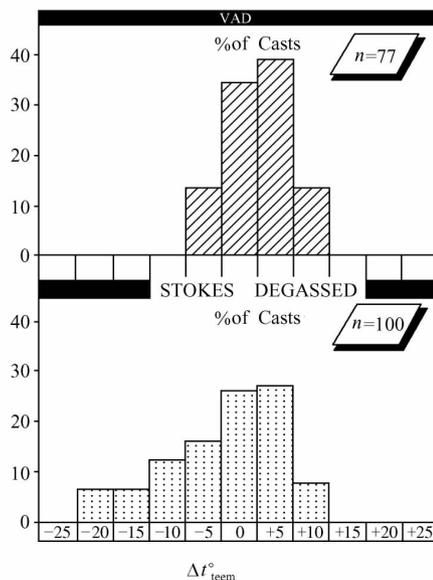


图 18 浇注温度与目标值的偏差

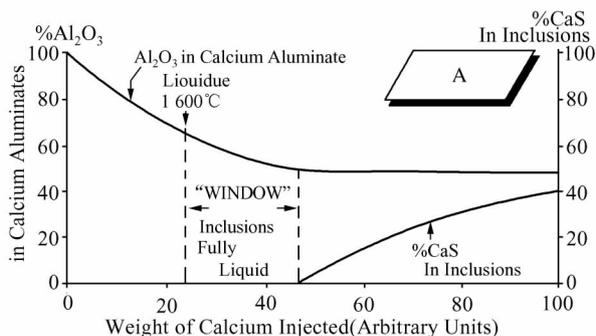


图 19 喷钙处理时夹杂中的成分

A: 1 600 下;初始硫含量 0.02%;  
铝含量 0.02%;低碳钢

图 20 给出了低碳和中碳钢中这一范围中铝和硫的理论关系.对于一定的铝含量,有一个硫含量的临界值,当硫含量高于这一值时,在形成有利于浇

铸的夹杂相( $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ )以前,就会形成硫化钙.图21给出了温度影响的理论计算结果,其影响是很大的,当温度降低时,氧活度下降,促进硫化钙的形成.同时还应注意到,当碳含量增加时,使液相线温度降低,从而使浇注的最佳温度降低.在正常生产中,成功地进行钙处理要求能够很好地控制精炼装置中钢水的成分以及钙的加入.

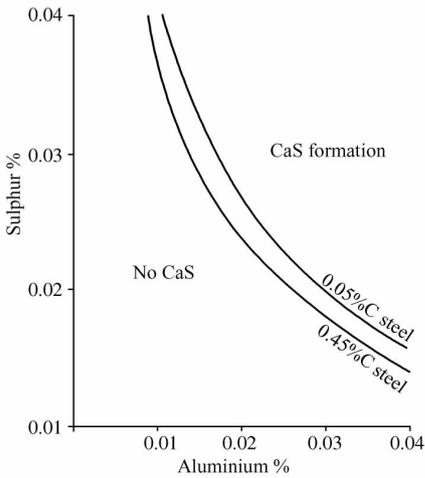


图20 1600下,硫、铝含量对钙硫化物形成的影响

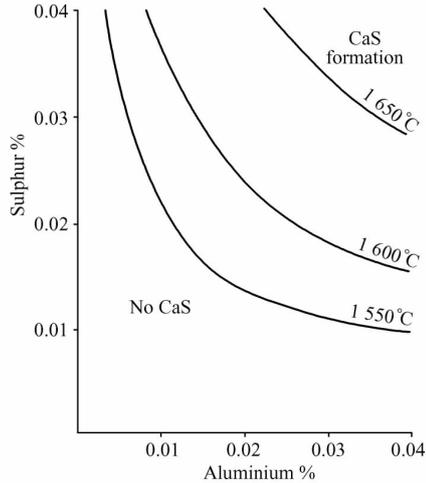


图21  $[\text{C}] = 0.45\%$  的钢中,温度对钙硫化物形成的影响

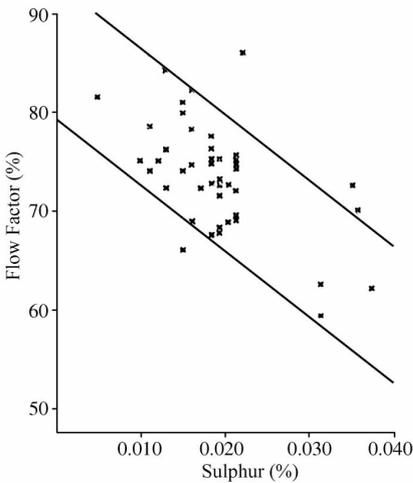


图22 锰钢(36/35/14/F)用硅钙处理后的浇注性能

图22给出了生产C-Mn钢管钢时得到的结果,用流动因子来表示钢水通过水口的情况,流动因子的计算式如下:

$$\text{流动因子} = \frac{\text{(实际注速)}}{\text{(按水口直径和中间包中熔池深度计算理论注速)}}$$

流动因子小于75%表明浇注情况不佳,图中可以看出硫含量对浇注情况有很大影响.对于该种钢,硫含量应控制在0.015%以下.

## 7 结论

采用钢包精炼装置可以满足连铸生产所提出的高生产率、高质量的要求,即更严格地控制成分,满足连铸工艺对温度控制的高要求;与好的模铸技术配合,能提高钢的清洁度;与钙处理设备配合,能够顺利地连铸铝镇静钢。

## 参考文献

- [ 1 ] Kobe Steel, LTD :“ Advanced continuous casting for high quality , long steel products. ” METEC '84 ,Dusseldorf , 22-28 ,July ,1984
- [ 2 ] A. Jequemot :“ cent. DOC ;sider. Inf. Tech. ” 1979 ,36(9) ,1041-1065
- [ 3 ] J. P. Carlens :“ Aluminium , doxidation and desulphurization control in ladle metallurgy for billet and slab caster by means of the oxygen activity measurement with the celox oxygen probe. ” Electro-Nite N. V. Houthalen ,Brussels
- [ 4 ] R. Scheel *et al.* :Secondary Steelmaking for Products Improvement. London ,23-24 ,Oct 1984 ,6. 1-6. 12
- [ 5 ] B. Tivelius & K-D. Xu :“ Secondary steelmaking : review of current processes. ”
- [ 6 ] I. G. Davies *et al.* :“ Secondary steelmaking : Developments on engineering steels at Stocks-Bridge Works ”. Secondary Steelmaking for Products Improvement , London , 23-24 , Oct ,1984

# 喷吹过程中的钢水吸氮规律<sup>\* 1</sup>

**摘要** 对鞍钢第二炼钢厂平炉冶炼和上钢三厂电炉冶炼的 16Mn 钢在喷粉处理过程中的吸氮行为进行了统计分析. 首先对喷吹过程作了现场取样分析, 在此基础上对喷吹过程中钢液吸氮的规律进行了理论分析. 结果证明, 钢中表面活性元素氧和硫的含量对吸氮过程有很大影响, 钢水温度也有明显影响, 钢中氮含量的增加主要是由于气相中的氮通过钢液裸露面为钢液吸收.

## 1 前言

随着喷射冶金技术在我国推广, 许多钢厂的实践都证明, 若无防护措施, 喷粉可导致吸氮. 这一吸氮量与所熔制的钢种无关, 最高将近 20 ppm. 因此我们对鞍钢二炼钢( $100 \times 10^3$  kg 级钢包)和上钢三厂( $20 \times 10^3$  kg 级钢包)的喷吹过程钢液吸氮作了研究和分析.

## 2 大生产数据的统计分析

这一统计分析所处理的是鞍钢二炼自 1982 年 10 月至 1984 年 3 月的 49 炉以及上钢三厂自 1982 年 6 月至 1983 年 7 月的 75 炉 16Mn 钢喷吹 SiCa 的原始数据. 喷吹的工艺条件见表 1.

---

\* 本文合作者: 顾洪涛、蒋国昌、胡立祥、王开亚. 原发表于《上海金属》, 7(6), 15~18 (1985)

表1 16Mn 钢喷粉处理工艺条件

	鞍钢二炼钢				上钢三厂			
	最小值	最大值	加权平均值	统计样本	最小值	最大值	加权平均值	统计样本
吨钢喷粉量(kg)	0.31	3.4	1.99	41	0.80	2.86	1.64	74
喷吹流量(Nm <sup>3</sup> ·h <sup>-1</sup> )	27	50	35.16	40	19.752	29.702	24.548	69
喷粉时间(s)	60	600	343	41	60	275	178.1	74
喷前温度( )	1560	1600	1577	35	1561	1690	1620.81	27
喷吹温降( )	15	45	26.613	31	14	78	48.83	23

按照这些工艺处理的结果,发现喷粉过程中钢水吸氮量平均达到17~19 ppm. 为了研究这一吸氮现象的规律性,用逐步回归法对上述数据作了分析,得到如表2和表3的结果.

表2 鞍钢二炼钢 16Mn 钢喷粉处理增氮量逐步回归分析结果

输入原始变量: $[N]_0, [S]_0, [O]_0, QC, TI, QI, TC, T_0, [N]_e - [N]_0, [S]_e - [S]_0$
回归方程: $[N]_e - [N]_0 = -1.5629[N]_0 + 0.000207474QC + 0.000132499T_0 - 0.000298713 \times TI - 0.001228005TC - 0.200493$
回归平方和: $U = 3.256 \times 10^{-5}$
剩余平方和: $Q = 1.286 \times 10^{-5}$
标准差: $S.D = 9.947 \times 10^{-4}$
相关系数: $R = 0.716814$
F 检验的上置信限: $\alpha = 0.1$

符号说明: T—钢液温度, QC—清洗(空吹)气量, QI—吨粉气量, TC—清洗时间, TI—喷粉时间, PG—吨钢喷粉量, K—平衡常数. 下标: O—喷粉前, e—喷粉后.

表3 上钢三厂 16Mn 钢喷粉处理增氮量逐步回归分析结果

输入原始变量: $[N]_0, [N]_e - [N]_0, [S]_0, [S]_e - [S]_0, QC, [O]_0, [O]_e - [O]_0, [AlS]_0 - [AlS]_e, K_0 - K_1, [Al], T_0 - T_e, PG, TL, QI, TC$
回归方程: $[N]_e - [N]_0 = -0.840605[N]_0 + 7.06673 \times 10^{-5}T_0 - 0.106111$
回归平方和: $U = 8.85468 \times 10^{-6}$

(续 表)

剩余平方和 :  $Q = 1.02033 \times 10^{-6}$

标准差 :  $S.D = 4.51737 \times 10^{-4}$

相关系数 :  $R = 0.896676$

F 检验的上置信限 :  $\alpha = 0.1$

符号说明 : 同表 2.

### 3 喷粉生产实践中的取样分析结果

为了进一步揭示喷吹过程中钢水吸氮的行为, 在两个厂的喷粉过程中取样以研究氮含量的整个变化历程. 图 1 和图 2 所示的是数据比较完全的炉号. 另外, 还取了包盖下方自由空间里的气样作为研究的参考. 图 3 是在上钢三厂所得的结果.

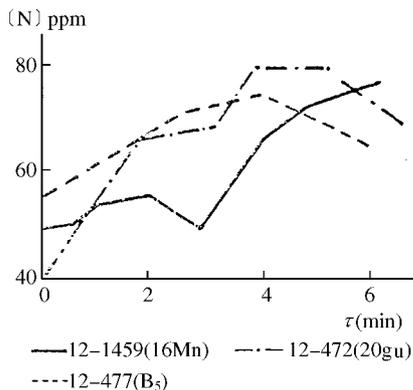


图 1 喷吹过程钢水(N)变化曲线  
(鞍钢二炼钢)

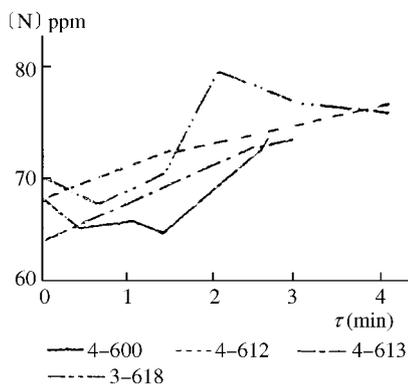


图 2 喷吹过程钢水(N)变化曲线  
(上钢三厂)

### 4 两厂喷吹实践中钢水吸氮的几点规律

由上述回归分析和过程钢样与气样的分析结果可见 :

- (1) 增氮量与原始含氮量有负相关关系 ;
- (2) 增氮量与喷前温度(从而也与喷吹过程中的温度)有正相关关系 ;

(3) 注意到两个厂喷粉时间相差较大(分别为平均5分多钟和平均不到3分钟),而增氮量相差很小(分别平均为约19 ppm和16.8 ppm),可以看到两个厂的吸氮速率相差极大——上钢三厂喷粉过程的平均吸氮速率约为鞍钢的2倍;

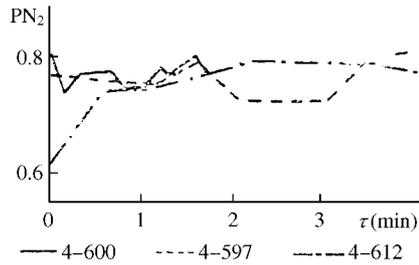


图3 喷吹过程中包内  $PN_2$  变化

(4) 鞍钢的过程氮含量曲线表现出在空吹时有下降趋势,而上钢三厂的相应曲线无此现象.

## 5 两厂的吸氮速率不等的原因分析

### 5.1 表面活性剂的影响

众所周知,钢液中氧和硫是表面活性元素,它们会向钢液表面富集,占据表面的空位,从而阻碍吸氮.

表面活性元素  $i$  在表面和熔体内部的分配服从兰格缪尔等温式<sup>[1]</sup>,从而平衡常数是

$$K_i = Q_i/a_i \cdot (1 - Q_i) \quad (1)$$

而由热力学关系式可得

$$\ln K_i = \frac{\Delta H_i}{RT} + C_i \quad (2)$$

当钢液中有一种以上表面活性元素存在时,总表面覆盖率为<sup>[1]</sup>

$$Q_T = \sum_i K_i a_i / (1 + \sum_i K_i a_i) \quad (3)$$

表面活性元素对吸氮速度常数的影响可用分数  $K_N^F$  来表示,有经验式<sup>[2]</sup>

$$K_N^F = 1.19 \sqrt{1 - Q_T} - 0.19 \quad (4)$$

已知对于硫  $\Delta H_s = -35000 \text{ cal}$ , 1873 K 下  $K_s = 140$ <sup>[1]</sup>; 对于氧  $\Delta H_o = -40000 \text{ cal}$ , 1873 K 下  $K_o = 220$ <sup>[1]</sup>, 代入(2)解得  $C_s = -4.46$  和  $C_o = -5.65$ .

设活度等于浓度,以两个厂的喷前喷后温度、成分的平均值代入(2)~(4),计算得表4.由表中可见,表面活性元素对速度常数的影响很大——可使速度常数降低到无表面活性元素时的一半左右乃至更小.而鞍钢的 $K_N^F$ 小于上钢三厂的对应值.

表4 喷前喷后的 $K_N^F$ 值

	$T_o(K)$	$[O]_o$	$[S]_o$	$(K_N^F)_o$	$T_e(K)$	$[O]_e$	$[S]_e$	$(K_N^F)_e$
鞍钢	1850.2	0.00616	0.0202	0.3252	1824.2	0.00236	0.0132	0.4127
上三	1894	0.00698	0.009375	0.4752	1845.9	0.00258	0.004895	0.5975

## 5.2 温度通过表面活性剂的作用而发生影响

温度可通过改变平衡常数 $K_i$ 值来影响速度分数 $K_N^F$ ,从而改变吸氮速度.由式(2)~(4)可推得:

$$\frac{\partial K_N^F}{\partial T} = \frac{dK_N^F}{dQ_T} \left( \sum_i \frac{\partial Q_T}{\partial K_i} \frac{\partial K_i}{\partial T} \right) = \frac{-0.595 \sum_i Q_i K_i \Delta H_i}{RT^2 (1 + \sum_i K_i Q_i)^2 \sqrt{1 - Q_T}} \quad (5)$$

分别将两个厂的参数代入(2)、(3)和(5),可得表5结果.注意到 $K_N^F$ 是 $10^{-1}$ 数量级的,而两个厂喷吹过程中温度差为 $20 \sim 60$  K,从而可见温度差能使 $K_N^F$ 有约10%的变化.这是可观的.这也是吸氮量与温度成正相关的原因.

表5  $\partial K_N^F / \partial T$  计算值

	$T(K)$	$[O]$	$[S]$	$\partial K_N^F / \partial T$
鞍钢	1836.9	0.00544	0.0167	0.001164
上三	1869.6	0.00606	0.007135	0.001236

## 5.3 喷吹过程中钢水因裸露而吸氮

由表1我们还可看到,上钢三厂钢包容量为鞍钢的五分之一,而喷吹流量则为一半以上,能量密度高于鞍钢,并且喷枪插得也较浅.由水模拟实验知道,这些因素都使上钢三厂钢包裸露的相对比表面积较大,表面更新率较大,所以其吸氮速率高于鞍钢.一般认为喷溅越大吸氮越多,实

实际上要使喷溅产生,必然要有大的搅拌能量,正是激烈的熔体运动,使裸露的相对比表面积增大,表面传质加快,而喷溅本身并不是吸氮的主要原因。

#### 5.4 喷吹时的钢水喷溅主要引起二次氧化

现场观察中,发现喷吹过程中喷溅是严重的(鞍钢更严重),溅起的钢水滴通过“自由空间”后又回到熔池中。这些钢水滴究竟能带回多少氮?

Greenberg 和 Mclean<sup>[3]</sup>发现悬浮熔化的钢水滴下落通过大气时,钢水不吸氮,而下落通过氮分压为 0.54 atm 的 N<sub>2</sub>-Ar 混合气,钢水吸氮约为 10 ppm。Pehlke 和 Elliott<sup>[4]</sup>指出,随着铁中氧浓度的提高,氮的吸收过程在能量上变得越来越困难(0.01% [O] 时, E = 25 kcal · mol<sup>-1</sup>; 0.07% [O] 时, E = 63 kcal · mol<sup>-1</sup>)。有的实验者还在类似的实验中发现铁滴表面有高浓度的氧边界层生成。在这些条件下,吸氮过程就很难进行了,而两个厂在包盖下面自由空间里的气氛据测定全都近于大气,所以喷溅主要是引起二次氧化。

### 6 喷粉实践中钢水吸氮的速度控制环节

钢水吸氮的整个过程可分解为下列步骤:

- (1) 气相中的氮传递到气-液临界面(裸露面);
- (2) 氮在界面上被钢水吸附,并离解为原子;
- (3) 被吸附的氮原子溶解于钢水边界层中;
- (4) 钢水内部氮的传输。

如果整个吸氮反应呈现为一级反应,则积分形式的速度方程是

$$\ln \frac{[N]_p + [N]}{[N]_p - [N]} = A\tau + B \quad (6)$$

这里:[N]<sub>p</sub>—平衡氮量; $\tau$ —反应时间;B =  $\ln \frac{[N]_p + [N]_0}{[N]_p - [N]}$ ; [N]<sub>0</sub>—喷吹前的氮量。

如果整个吸氮过程呈现为一级反应,则应有

$$\ln \frac{[N]_p - [N]_0}{[N]_p - [N]} = A\tau \quad (7)$$

将鞍钢二炼和上钢三厂的几炉数据代入这两个方程进行计算,发现算得

的 A 值均不守恒,变化甚大.可见,这两个厂的喷粉实践中,钢水的吸氮既不是一级反应,也不是二级反应,其速度为混合控制.

## 7 结束语

(1) 弄清了鞍钢二炼钢及上钢三厂现行喷粉实践条件下,钢水吸氮的几点规律.

(2) 论证了上钢三厂的吸氮速率大于鞍钢二炼吸氮速率的原因.

(3) 指出实际喷粉过程中钢水主要是通过裸露面吸氮,而且吸氮速率为混合控制,不能简单地用一级反应或二级反应来描述.

## 参 考 文 献

- [ 1 ] G. R. Belton : Metall. Trans. 7B (1976) , p. 35
- [ 2 ] C. H. Hua & N. A. O. Parlee : Metall. Trans. 13B (1982) , p. 357
- [ 3 ] L. A. Greenberg , A. Mclean : Ironmaking & Steelmaking. 9 (1982) , No. 2 , p. 59
- [ 4 ] R. D. Pehlke & J. F. Elliott : Trans , AIME. 227 (1963) , p. 844

# Secondary Steelmaking : Review of Current Processes<sup>\* 1</sup>

**Abstract** This paper reviews the specific features and applications of existing secondary steelmaking processes. A survey is made of the fundamentals of the refining reactions and their efficiency in terms of the process parameters and the steel composition. The concept of “clean steel” is discussed with the view of summarizing today’s state of the art and the future possibilities. Besides the technical and quality aspects of secondary steelmaking, some economic and productivity factors are given due consideration to understand the past and future progress of the technology.

## INTRODUCTION

The concept of secondary steelmaking or “ladle metallurgy” embraces a variety of treatments applied to molten steel between tapping from the main melting furnace and the final casting. The concept was introduced more than 20 years ago and is today widely applied as a working tool for steelmaking. The number of installations made through the years is illustrated in Fig. 1.

Secondary steelmaking processes have taken over many of the refining steps traditionally performed in the melting furnace, thereby substantially reducing the tap-to-tap time of the furnace. The cost and energy savings obtained are the principal incentives for secondary metallurgy development, in-

---

\* Inclusions and Residuals in steels : Effects on Fabrication and Service Behaviour. Ottawa, Ontario, Canada, 4-5 Mar. (1985) pp. 33-71

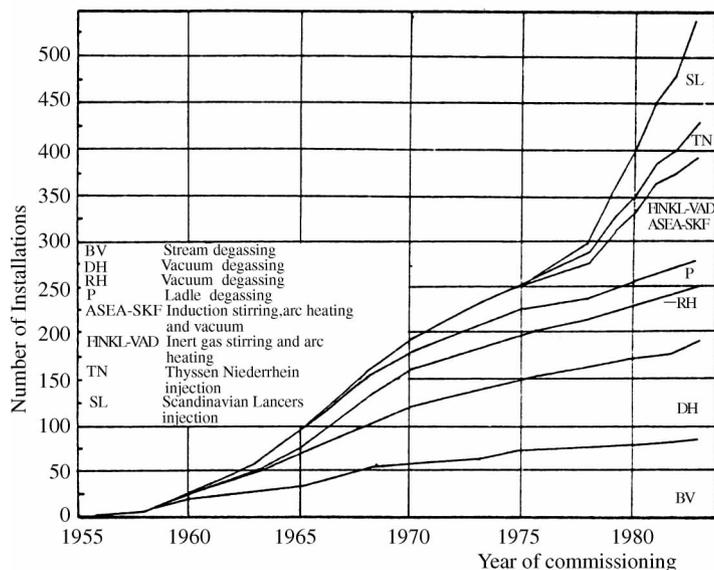


Fig. 1 Annual increase of different types of secondary steelmaking facilities in the world

creased productivity is another. No less important is the demand for better cleanliness of the steel, to meet the market's increasing quality requirements, and to increase the efficiency of the subsequent steps of steelmaking. Technically and economically this development has been very important to the steelmaking industry, which has been suffering from low profits for many years.

Among the variety of secondary steelmaking processes we can distinguish 5 different groups:

- Ladle argon bubbling
- Vacuum degassing (DH, RH, BV, PM processes)
- Ladle furnace refining (ASEA-SKF, FINKL-Mohr, LF)
- Ladle injection (Sc Lanc, TN, Wire feed)
- Stainless refining (AOD, CLU, VOD, RH-OB, VODC)

The historical development of the various secondary steelmaking processes is summarized in Fig. 2. The specific objectives and approaches of the different processes are given in Fig. 3.

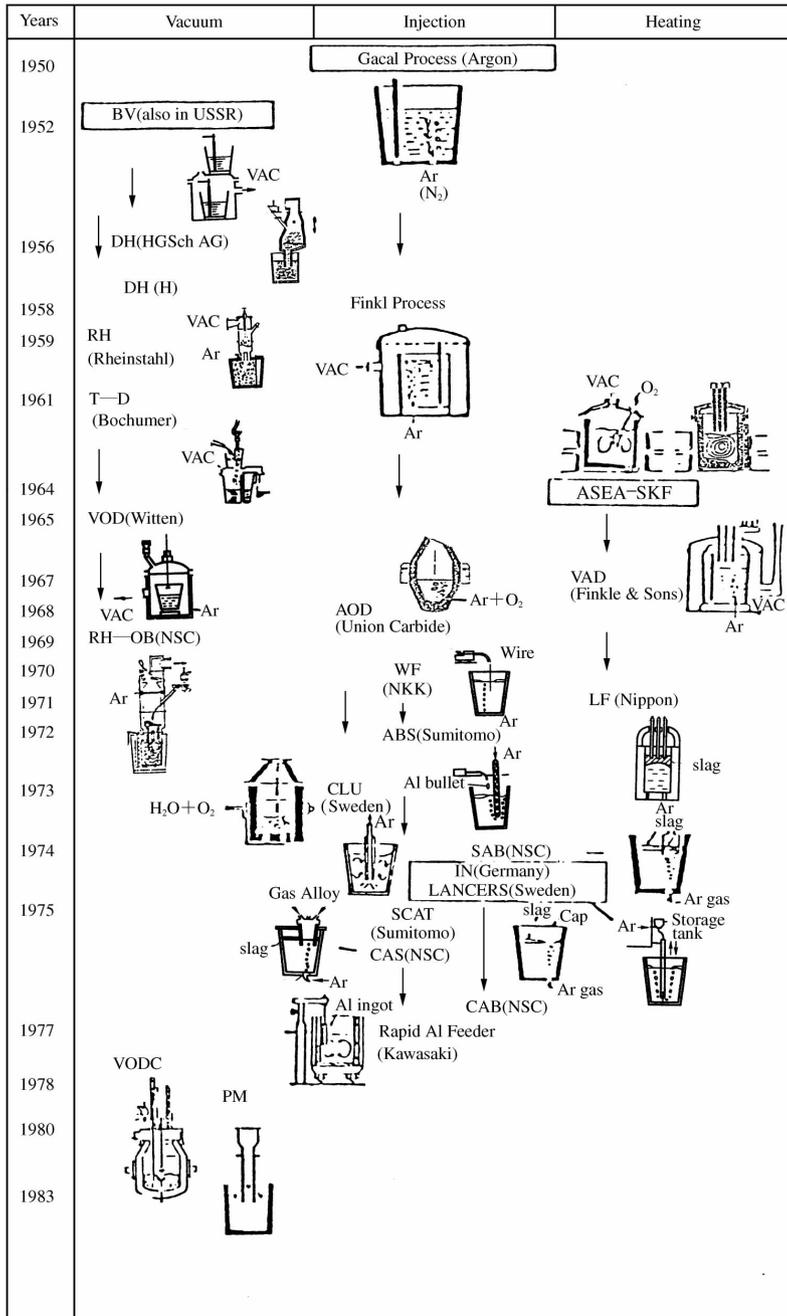


Fig. 2 Historical development of various ladle refining methods

Objective	Application module	Approach	Converter-based						Ladle-based							
			atm pressure			Vacuum			atm pressure							
			AOD	ASM		VODC			VD	VOD	(VAD) VD/LF	RH			AF	IF
Decarburization	Oxidizing	Oxygen top-blowing	●	●		●			●	—	○			—	—	—
		Oxygen injection	●	●		—			—	—	—	○		—	—	—
	CO purge-out	CO pressure reduction	○	○		●			●	●	●	●		—	—	—
Degassing	Affecting the gaseous phase	Vacuum	—	—		●			●	●	●	●		—	—	—
	Admission of external gas	Under vacuum pressure	—	—		●			●	●	●	●		—	—	—
		Under atm pressure	○	○		—			—	—	—	—		—	—	○
Deoxidation	via CO reaction	Press reduction (vacuum)	—	—		●			●	●	●	●		—	—	—
	Alloying	Injection etc	—	—		—			—	—	—	—		—	●	○
		Addition	●	●		●			●	●	●	●		●	●	●
Desulphurization	Bath-slag reaction	Ar purging with 1st slag	○	○		●			○	○	●	—		—	—	○
		Ar purging with 2nd slag	●	●		●			●	●	—	—		○	—	—
	Alloying	injection of solids	—	—		—			—	—	—	—		—	●	—
Adjustment of analysis	Alloying	Addition	●	●		●			●	●	●	●		●	●	●
	Reduction	with CO reaction (vacuum)	—	—		●			●	●	●	—		—	—	—
		with alloying agents	●	●		●			●	●	●	●		—	—	—
Temperature increase	Heating	chemical	●	●		●			—	●	—	○		—	—	—
		electric	—	—		—			—	—	●	○		—	—	●
Improvement of purity	Purge-out	Admission of external gas under reducing slag	●	●		●			●	●	●	○		○	○	○

● high potentials ○ limited potentials ○ requiring additional modules

Fig. 3 Assessment of some secondary steelmaking processes

Secondary metallurgy offers significant benefits to both the large steel producers, in the form of increased productivity, improved yield and energy savings, and to the smaller specialty steel works in the form of improved quality. For “mini-mills”, which are specialized steel-works with a production of a few hundred thousand tons/year, secondary steel making is an excellent option from productivity and quality points of view. A typical lay-out of a mini-mill is shown in Fig. 4.

This paper will describe the state-of-the art in secondary steel-making, emphasizing metallurgical considerations, and give examples of the different sys-

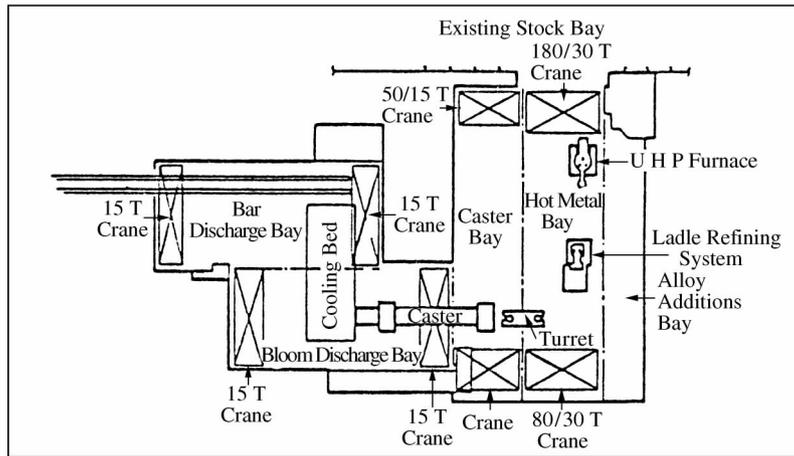


Fig. 4 Typical layout of a modern mini-steelmaking shop

tems and their characteristics.

## FUNDAMENTALS OF SECONDARY STEELMAKING

### GENERAL ASPECTS

The main metallurgical objective of secondary steelmaking is the removal from the steel of contaminants which are inherited from the raw material or picked up during processing , e. g. , C , S , P , O , N , H. The operations which are of major importance for successful refining of molten steel are identified below :

- Stirring
- Vacuum treatment
- Gas blowing
- Addition of solid reactants
- Slag refining
- Heating

The secondary steelmaking processes combine these operations in different ways , as illustrated in Fig. 5.

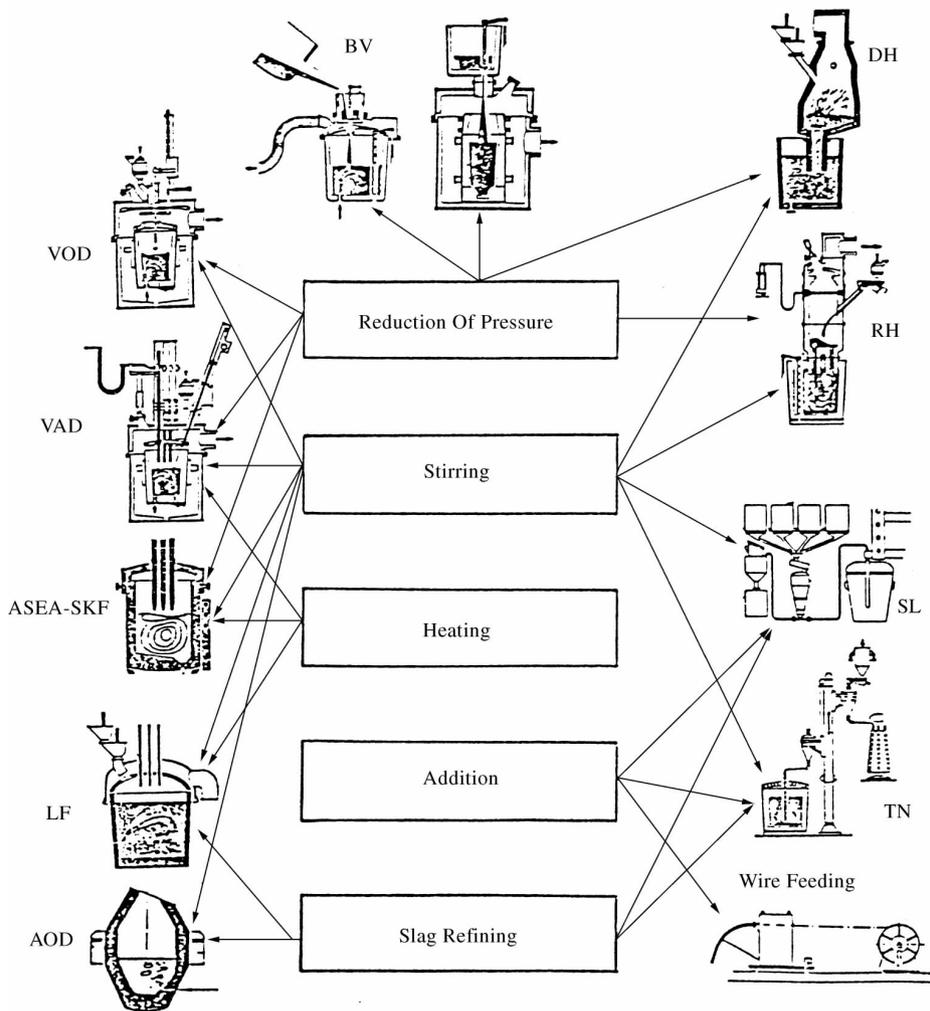


Fig. 5 Secondary steelmaking processes related to the five principal operations

## STIRRING

Stirring , mixing and convection are the true impellers for the reaction rate in most processing vessels , and are of decisive importance for the efficiency of secondary steelmaking. In the various processes different ways of stirring are practised :

- Gas stirring
- Inductive stirring
- Vacuum-driven circulation

## Gas Stirring

A gas flow for stirring the melt may be introduced into the vessel in various ways : through porous plugs , tuyeres , or lances. The specific stirring power of argon blowing into a steel ladle is related primarily to the gas flow and other parameters such as the immersion depth of lance or tuyere.

$$\dot{\epsilon} = (6.2 * 10^3 * Q * T_1) / Ml * \ln(1 + 9.68 * 10^{-3} * \rho_1 * Z) + (1 - T_0/T_1) \quad (1)$$

where :

$\dot{\epsilon}$  = stirring effect , Watt/ton of steel

T1 = temperature of molten steel , K

Q = argon gas flow rate , Nm<sup>3</sup>/min

To = argon gas temperature , K

Ml = mass of molten steel , ton

$\rho_1$  = density of molten steel , g/cm<sup>3</sup>

Z = inserted depth , cm

Different flow rates of argon are used , depending on the nature of the process. Typical values ( Nm<sup>3</sup>/min ) are<sup>[2]</sup> :

- homogenizing of temperature and of composition

0.08 - 0.13

- dissolving ladle additions

0.30 - 0.45

- slag-metal reactions ( desulph. )

0.45 - 0.90

- lance injection of powder

0.9 - 1.8

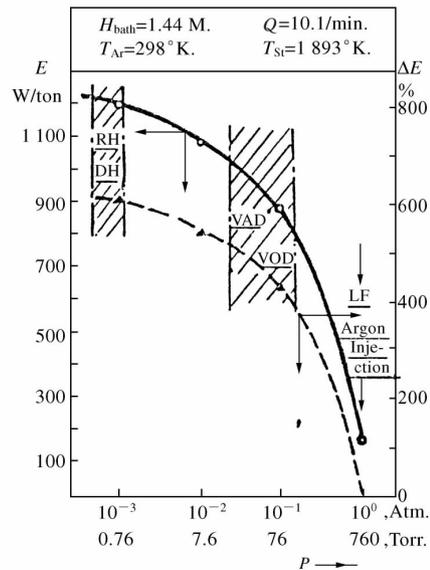


Fig. 6 Relation between gas stirring effect and the pressure over the melt

The gas stirring effect in a vacuum system is more effective , where even a moderate gas-flow gives a considerable effect. Fig. 6 indicates the stirring effect in relation to the pressure over the melt , and the working range for some common

processes.

### **Inductive Stirring**

Inductive stirring is effected by alternating electromagnetic fields in the melt. The stirring effect follows Eq 2 below. In an ASEA-SKF ladle furnace for example the stirring effect can be up to approximately 500 W/ton using straight inductors.

$$\dot{\epsilon} = 1.2 * 10^{-3} * d^2 * \rho_1 * h^{2/3} / MI \quad (2)$$

$$h = 316 * \sqrt{\mu / (r * f)} * P / S * 1 / \rho_1 \quad (2a)$$

where :

$\dot{\epsilon}$  = stirring effect , W/ton

d = ladle diameter , cm

h = swelling height of molten steel , cm

$\mu$  = permeability

f = frequency , Hz

P = supplied electric power , kW

r = resistivity , ohm-cm

S = molten steel area , cm<sup>2</sup>

$\rho_1$  = density of molten steel , g/cm<sup>3</sup>

### **Vacuum-driven Circulation**

Vacuum-driven circulation is practiced in the RH , DH and PM processes , in which the stirring is effected by pouring or pumping the melt between the vacuum vessel and the ladle. In the DH process the forces act intermittently upon the molten steel , giving a pulsating movement. The corresponding stirring energy is expressed by the equation :

$$\dot{\epsilon} = 8.35 * 10^{-6} * V^2 * m * n / MI \quad (3)$$

where :

V = average rate of exhausted steel , m/s

m = mass of sucked-up steel , kg

n = rising and falling frequency , min<sup>-1</sup>

MI = mass of molten steel , ton

## Time for Perfect Mixing

In addition to the stirring energy, the calculated time for perfect Mixing is an important indicator of mixing efficiency. In Fig. 7, the time for perfect mixing for the RH and PM processes is compared to that for argon bubbling. The relation between stirring energy density and the time for perfect mixing is illustrated in Fig. 8, which can also be expressed by the following equation :

$$\tau = \sqrt[3]{(MI/\rho)^{2/3} / \varepsilon} \quad (4)$$

where :

$\tau$  = time for perfect mixing, s

MI = mass of molten steel, ton

$\rho$  = density of molten steel, t/m<sup>3</sup>

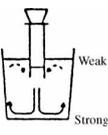
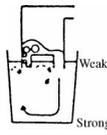
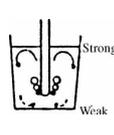
Ladle refining process		PM	RH	Ar gas bubbling
Item				
Flow pattern				
Time for perfect mixing (sec)		100 - 200	150 - 400	180 - 500
Oxygen of molten steel in tundish (ppm)	$\bar{X}$	35	34	41
	$\sigma$	8.0	8.2	15.4
Yield of aluminum added (just after addition) (%)		100	100	65
Rate of temperature drop (°C/min)		1.3 - 1.8	1.8 - 2.2	1.5 - 2.0
Running cost		2	15	1
Incidence of slivers	Low carbon	0.8	—	1
	Ultra low carbon	—	0.8	—
Inner defects of ERW pipe		0.4 - 1.1	1	1 - 1.5

Fig. 7 Metallurgical characteristics of various ladle refining processes

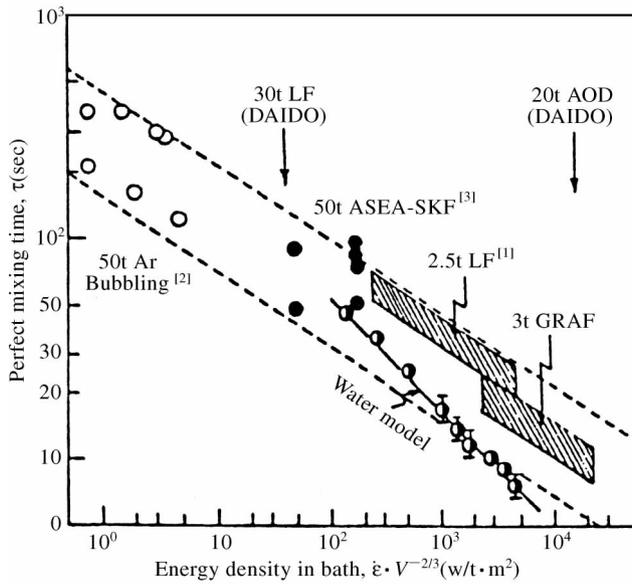


Fig. 8 Relation between time required for perfect mixing and energy density<sup>[4]</sup>

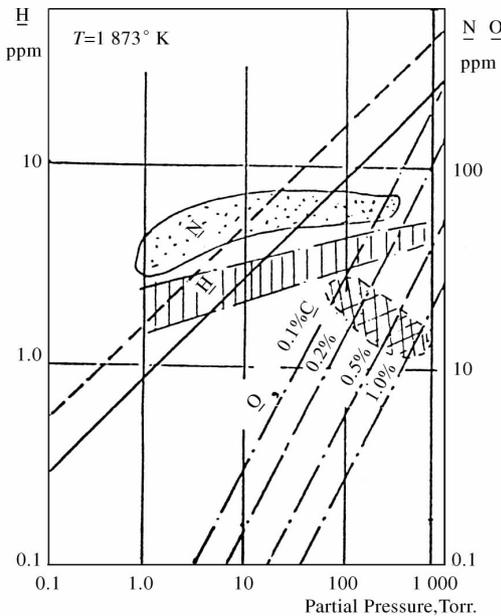


Fig. 9 Equilibrium of hydrogen , nitrogen and oxygen in iron at 1600°C as a function of partial pressure

## VACUUM OPERATIONS

According to Sievert's law the amount of gas dissolved in metal is proportional to the square root of its partial pressure. Fig. 9 illustrates the equilibrium pressure of N , H and O in carbon steel at 1600°C.

### Oxygen Removal

Oxygen dissolved in carbon steel will be removed by reducing the partial pressure of carbon monoxide formed under the carbon-oxygen equilibrium. Carbon is in fact a very efficient deoxidizer in vacuum processes , practically used in

the Vacuum-Carbon-Degassing (VCD) process, because the equilibrium oxygen content drops drastically when the pressure is reduced (Fig. 9). In practice, however, equilibrium values are rarely obtained, and we have to accept oxygen values considerably higher than predicted, although significantly lower than those obtained at atmospheric pressure.

### Nitrogen Removal

Nitrogen removal by reduced pressure presents more problems. Nitrogen activity is reduced by many elements in steel, and unsatisfactory kinetic conditions restrict the nitrogen removal. Furthermore, surface active elements such as oxygen and sulphur impede the transition of nitrogen between the liquid and the gaseous phases. This means that deoxidized and desulphurized steels are more favoured for nitrogen removal.

Good conditions for nitrogen removal also exist for unkilld steels as shown in Fig. 10. The main reason is the excellent purging effect caused by the intensive formation of CO. About 30% of nitrogen and 70% of hydrogen are removed under these conditions without the use of stirring gas.

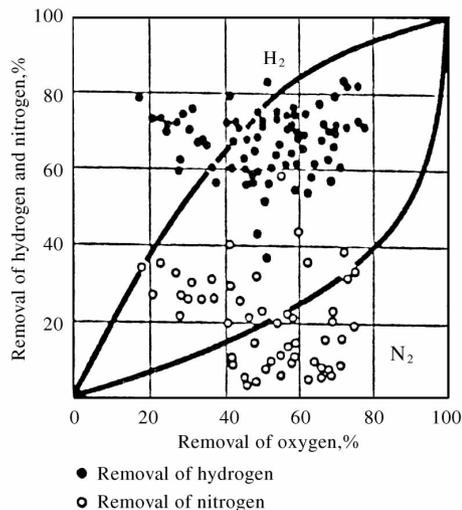


Fig. 10 Degassing effect without inert-gas purging (theoretical curves from ref 6)

### GAS BLOWING OPERATIONS

Converter refining processes for high-chromium stainless steels (VOD, AOD, CLU and RH-OB) utilize decarburization under reduced partial pressure of carbon monoxide. Modern stainless steel making largely uses an electric arc furnace (EAF) operating in sequence with one of these converter processes. As the decarburization is performed under close control of the oxidizing conditions, carbon can be removed to extremely low values without noticeable chromium

losses. The competitive oxidation of carbon and chromium during the blowing of oxygen into a steel bath can be written as follows :

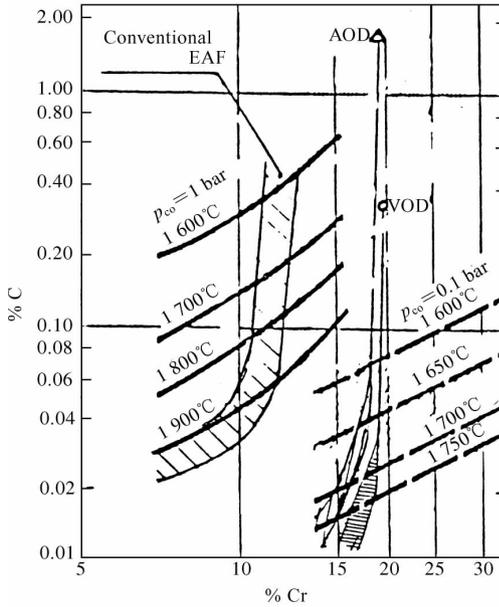
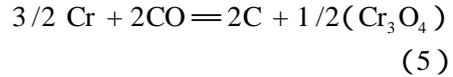


Fig. 11 Comparison of different processes for manufacture of Cr-bearing steels in terms of C-Cr pressure-temperature equilibria



In these oxygen-blown converter processes nitrogen and hydrogen are also satisfactorily removed.

The converter processes for stainless steel represent a major advance in process economy and in refining efficiency compared with the traditional refining in the arc furnace. Fig. 11 illustrates the parallel progress of decarburization and Cr-oxidation during the refining of chromium steels in the EAF and, in the VOD process, the latter giving far less Cr oxidation.

## REFINING BY ADDITION OF SOLID REACTANTS

Solid additions to molten steel are preferably immersed into the bath, which causes problems for lower density materials. In such cases lance injection or wire feeding often offer the practical solution. For the efficient reaction between the added material and the melt it is also important that the additions be rapidly dissolved and homogenized in the melt with adequate stirring. Typical yields of alloying powders added to the ladle by deep injection are given in Table 1. Injection through tuyeres under the melt surface or in the "eye" of a gas-purged ladle is used in some steel plants with good results.

**Table 1 Recoveries for trim alloying in ladle by powder injection**

Element	C	Si	Mn	Cr	Mo	Nb	V	Al	Ti	B
Recovery %	97	95	100	99	97	100	100	90	85	75

## **SLAG REFINING**

The first objective of metal-slag reactions utilized in secondary steel-making is to remove sulphur from the steel. Desulphurization is necessary because of the detrimental effect of sulphur on the mechanical properties of steel, particularly toughness and ductility. For instance, in modern linepipe manufacture the steel specifications include high values of impact toughness in the transverse direction, and correspondingly low limits on sulphur content. Modern ladle metallurgy can meet these requirements with a good margin, producing steels with 1 to 10 ppm of sulphur. This is accomplished by the application of an optimized ladle injection.

There are 3 important factors for successful desulphurization :

- optimal slag composition
- perfect deoxidation of steel and slag
- efficient stirring in the reaction vessel.

As desulphurization depends on reactions with lime (and magnesia), a high slag basicity is an obvious condition. A low oxygen content in the steel/slag system is also important because sulphur removal is based on the following equilibrium :



A common way of expressing the desulphurizing capacity of a slag is in terms of the parameter  $C'_s$  (4) :

$$C'_s = a_o \cdot (\text{S})/[\text{S}] \quad (7)$$

Fig. 12 illustrates the desulphurizing capacity in the  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  system according to Jacquemot<sup>[16]</sup>.

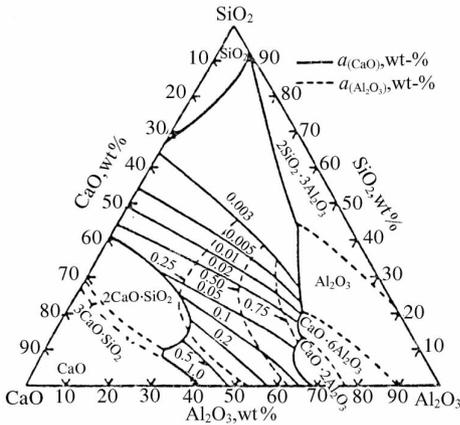


Fig. 12 Sulphide-capacity contours ( $C_s'$ , wt%) in  $Al_2O_3$ -CaO- $SiO_2$  system at  $1600^\circ C$  [3]

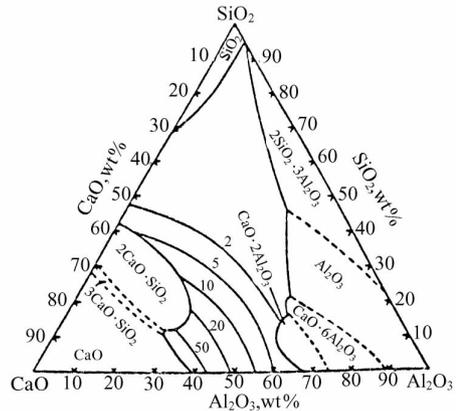
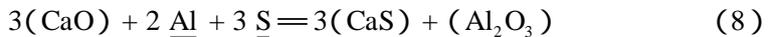


Fig. 13 Activities of CaO and  $Al_2O_3$ -CaO- $SiO_2$  system at  $1600^\circ C$  [4]

Desulphurization of an aluminum-killed steel with a lime-based slag can be expressed by the following equilibrium :



This reaction is promoted by increasing the CaO and Al activities , and is restricted by higher  $Al_2O_3$  and CaS activities. In Fig. 13 it is seen that the alumina activity is at a low level in the area where the lime activity is high , and the desulphurizing capacity , consequently , is strong.

One must be as careful about the oxygen (FeO) content in the slag as about deoxidation of the steel , or there will be a steady “leakage” of oxygen from the slag to the metal. Other sources of oxygen contamination must also be considered , such as silica refractory linings or exposure to the atmosphere. Good separation of the primary slag when tapping from the melting furnace is necessary , and the ladle lining should be basic or neutral.

Finally , secondary steelmaking slags can absorb considerable amounts of nitrogen and vapor , which can jeopardize the efficiency of slag treatments under vacuum. Therefore , dry and clean slagging constituents should be used , and after-treatment shrouding with argon is advisable to protect the steel during casting.

## HEATING

Secondary steelmaking treatments are always subject to heat losses, by heat absorption in the ladle walls, and by radiation. Moderate heat losses can normally be compensated by superheating the melt before tapping from the melting furnace. The AOD and CLU processes utilize exothermic reactions, which generate enough heat to maintain an adequate casting temperature. Other processes, however, need energy input during the treatment to compensate for losses. For 1.5% slag, 1% of alloy addition and a temperature drop of 50–80°C, it can be shown that a heat input of about 30 kWh/ton is needed. The heat transfer factor is normally about 30% to 40%, and the practical input energy needed is about 80 to 120 kWh/ton.

Heating with submerged electrodes is normally preferred, in order to minimize refractory wear in the processing vessel and to optimize the heat recovery. Low voltage/high current operation is desirable to reduce the arc length. Results from a practical study are shown in Fig. 14. To attain adequate heating power in a 250 ton ladle an electrode system with a transformer capacity of about 40 MVA is needed. To stabilize the submerged-arc heating it is necessary to control the fluctuations of the steel surface, thereby keeping the arc length to a minimum. This requirement conflicts with the need for good stirring in the vessel, and restricts, in the case of gas blow stirring, the maximum flow rate to about 0.4–0.5 m<sup>3</sup>/min at STP (Fig.

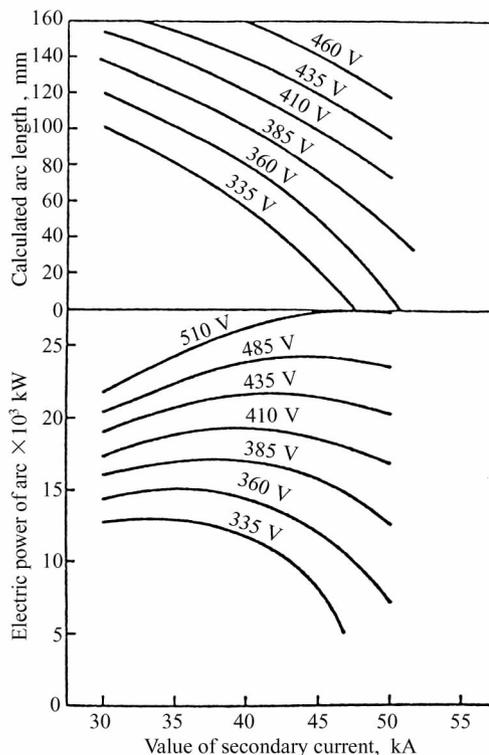


Fig. 14 Influence of voltage and current on electric power and arc lengths

15). Induction stirring , which gives a more steady turbulence of the melt , is therefore preferable in combination with submerged-arc heating.

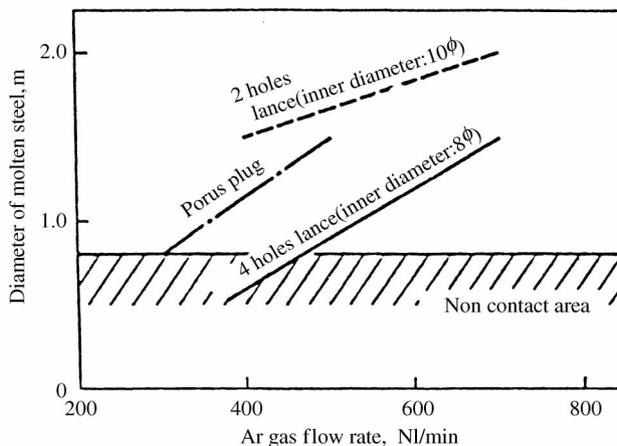


Fig. 15 Influence of argon flow rate on molten steel surface

Heating by plasma is a recently introduced technology , which holds much promise for future development. Experience indicates that submerged plasma heating is preferred , due to the optimal heat recovery.

## CONTROL OF INCLUSIONS AND RESIDUAL ELEMENTS

With adequate application of current secondary steelmaking technology we can consider the following levels of prime impurities in steel as our working standard in the production of “ clean steel ” :

carbon	< 100 ( 6 ) ppm	oxygen	< 15 ( 5 ) ppm
sulphur	< 10 ( 1 ) ppm	nitrogen	< 30 ( 14 ) ppm
phosphorus	< 50 ( 8 ) ppm	hydrogen	< 1 ( 0.2 ) ppm

The figures given in brackets represent a prediction for attainable levels in the year 2000<sup>[19]</sup>.

### CARBON CONTROL

As mentioned above , the quality requirements for steel plate for linepipe increased during the 1970's , and the severe limits on fracture toughness in the

weld heat-affected zone (HAZ) demanded a steady decrease and narrow control of carbon and sulphur contents (Fig. 16 and 17).

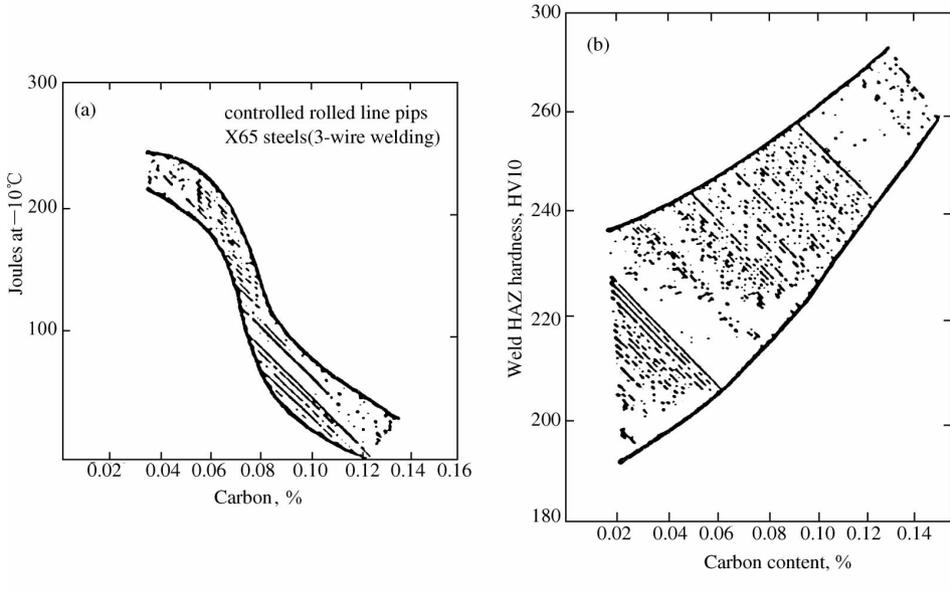


Fig. 16 Effect of carbon content on HAZ properties (a) toughness , (b) hardness

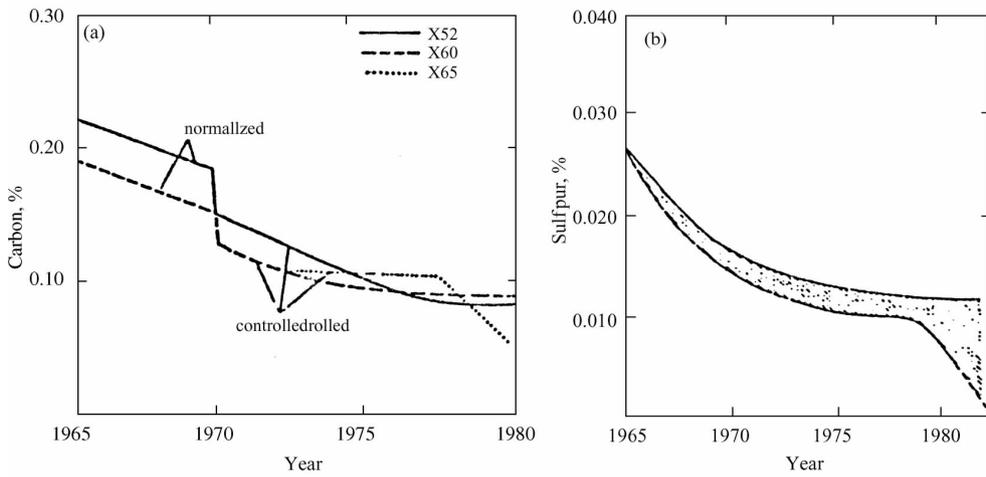


Fig. 17 Trends in composition of linepipe steel (a) carbon , (b) sulphur (X65)

By using converter processes with a combination of oxygen blowing from the top and argon blowing from the bottom , the carbon can successfully be reduced to about 0.03% . Lower values are obtainable , but at the price of in-

creased iron loss to the slag, and increased lining wear. For very low carbon contents it is necessary to use secondary steelmaking processes such as DH, RH and RH-OB.

For the decarburization reaction,  $C + O = CO$ , the equilibrium constant,  $k_c$ , is given by:

$$k_c = \% C \times a_o / p_{CO} = 0.002 (1600) \quad (9)$$

Assuming an oxygen activity ( $a_o$ ) of 0.04 and a CO partial pressure ( $p_{CO}$ ) of 0.002 bar, Eq 9 predicts a final carbon value of 1 ppm<sup>[20]</sup>. The conditions for ap-

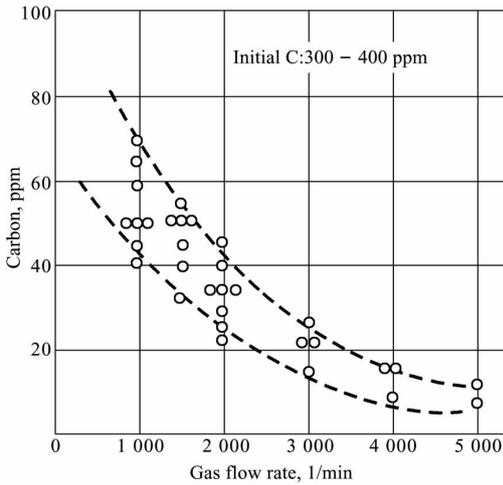


Fig. 18 Carbon content versus gas flow rate for 13 min treatment in RH process

proaching this equilibrium value in practice are good convection in the melt and rapid removal of CO by good flow of inert gas. Fig. 18 illustrates the levels of carbon which can be attained in the RH process under various gas flow rates<sup>[21]</sup>. From a practical point of view a maximum flow rate of about 2 m<sup>3</sup> per min (STP) seems realistic, and the corresponding end carbon content is of the order of 20 ppm. In some cases levels of 10 ppm carbon have been reached<sup>[22]</sup>.

Carbon removal is also important in stainless steel production. A number of new Cr-Mo steels with ultra-low carbon and nitrogen contents are now in production ("Super-ferrites"). Table 2 gives typical compositions<sup>[23]</sup>.

Table 2 Composition of "superferrites", wt%

Max. C	Cr	Mo	Ni	Others
0.015	18	2	—	Ti
0.015	28	2.5	4	Nb
0.002	26	1	—	—
0.005	28	2	—	—

These steels can only be produced by application of secondary steelmaking, the

AOD or CLU processes for steels with min C about 100 ppm , and the VOD process for even lower carbon contents. Many austenitic stainless grades are also produced with very low carbon content , primarily using AOD or CLU processes , thereby increasing their weldability and corrosion resistance considerably. Typical compositions of these low-carbon grades are listed in Table 3. Fig. 19 gives the historical trends in stainless steel process methods , and typical carbon contents. Current technology permits the economic production of commercial , low-carbon , low-nitrogen stainless steels , because of high productivity , use of less expensive raw materials ( no low-carbon ferro-alloys ) , and high metal yield. For extremely low carbon and nitrogen levels ( <50 ppm ) the oxygen refining processes alone are not sufficient , and a final , time-consuming vacuum treatment under argon blowing must be added ( Fig. 20 )<sup>[21]</sup>.

**Table 3 High-alloyed Cr-Ni-Mo stainless steels , wt%**

Max. C	Cr	Mo	Ni	Others
0.030	17.5	2.8	13	0.14 N
0.030	17.5	4.5	13.5	0.14 N
0.020	20	6.3	25	0.20 N
0.020	20	6.3	25	1.5 Cu
				0.15 N
0.020	20	6.3	18	0.7 Cu
				0.20 N
0.020	20	4.5	25	1.5 Cu
				0.08 N

## OXYGEN CONTROL

Oxygen and oxide inclusion control has to begin when the BOF or EAF is tapped. Only the minimum of primary slag , often rich in silica and FeO , should be carried into the ladle. The tolerable amount is of the order of 2–4 kg/ton. A fresh top slag on the ladle is prepared by adding lime and fluorspar during tapping , which has the following functions :

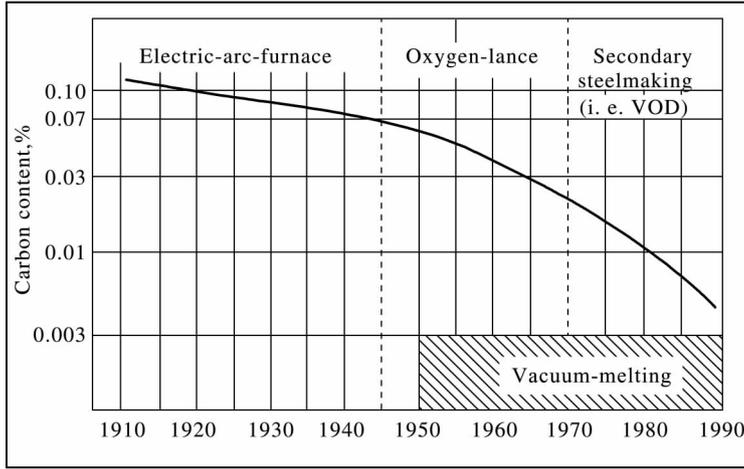


Fig. 19 Trends in carbon content and process methods for stainless steel

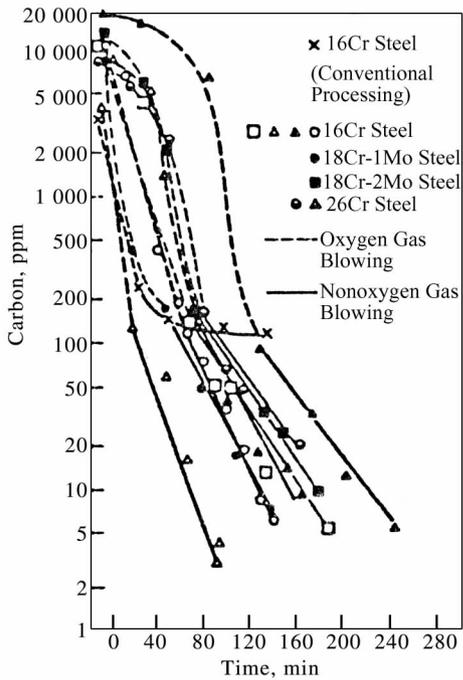


Fig. 20 Decarburization curves for various stainless steels

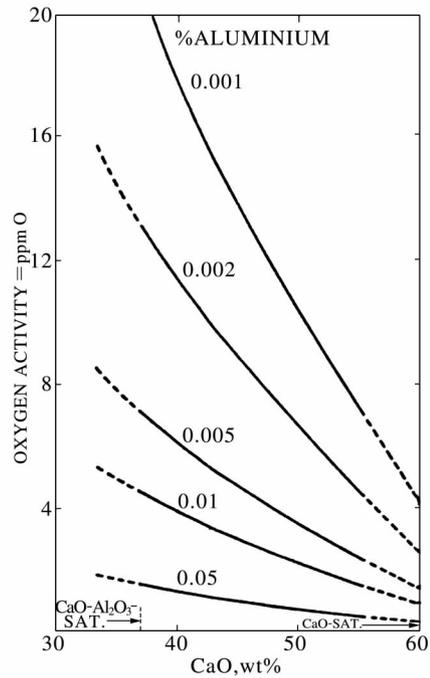


Fig. 21 Deoxidation equilibrium for Fe-Al melts and calcium aluminate melts at 1600°C<sup>[27]</sup>

– protecting the metal from reoxidation

- reducing heat loss by radiation
- being an active reagent in the desulphurization process
- absorbing oxide and sulphide inclusions from the melt.

The slag basicity should be about 3 to 5 and the slag index  $M = \text{CaO}/\text{SiO}_2 : \text{Al}_2\text{O}_3$  should be 0.25–0.35, calculated on the slag composition after ladle treatment. The oxygen activity of such a slag is very low, the activity of alumina in the lime-saturated slags not exceeding 0.001, and the oxygen activity of the steel in equilibrium with the slag, being less than  $4 \times 10^{-5}$ <sup>[26]</sup>. Most ladle treatments utilize CaO-based slags and aluminum for deoxidation. The equilibrium between Fe-Al melts and CaO-Al<sub>2</sub>O<sub>3</sub> slags plays an important role. Fig. 21 illustrates the sharp decrease of oxygen activity in the metal with increasing Al% and CaO-content in the slag<sup>[27]</sup>. In addition, the CaO-rich slags promote the formation of globular Ca-aluminates, which are far less harmful to the castability of the steel and to the properties of the end product than the dendritic alumina slag inclusions which otherwise form.

The deoxidation process normally progresses with a high reaction rate, and the growth and removal of the oxide inclusions are enhanced by stirring of the melt. Experimental and plant studies give the following expression for the rate of oxide inclusion removal<sup>[28]</sup>:

$$C_t = C_0 \exp(-Kt) \quad (10)$$

where:

$C_0$  = initial concentration of inclusions

$C_t$  = the concentration at time  $t$

$K$  = apparent removal-rate constant at a given stirring intensity.

Both the slag layer and the ladle walls are assumed to absorb inclusions, but, the ladle walls can also act as a source of reoxidation if the refractory has a higher oxygen activity than the melt. Reoxidation of steel is an obvious risk, particularly during teeming from the ladle or from the tundish. A variety of systems for teeming under protective atmosphere have been adapted for the production of clean steels, particularly for continuous casting.

Oxide inclusions can never be entirely eliminated, and thus we have to consider the shape and nature of those remaining in the steel. Control of inclusions

can be achieved by treatment of the steel with a synthetic slag , or with calcium

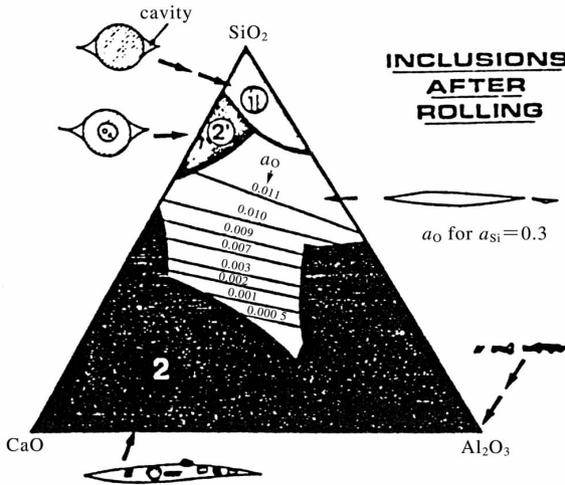


Fig. 22 Deformability of oxide inclusions at rolling temperature in the  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  system<sup>[9]</sup> (Oxygen activities in equilibrium with the oxide phase are plotted in the composition range for plastic inclusions. )

compounds. Synthetic slag treatment is frequently used to obtain deformable inclusions in wire and strip production. Inclusions of predetermined composition are stable only under close control of the oxygen activity ( Fig. 22 )<sup>[28]</sup>. Such a narrow range of oxygen activity is not easily obtained by Al or Ca additions to the steel , and it is preferable to use a synthetic slag treatment with adequate stirring.

In Si-Mn or Si-Mn-Al-killed steel , the oxygen activity is determined either by the Si-and Mn contents , or solely by the Al-content , depending on the relative amounts of these elements ( Fig. 23 )<sup>[32]</sup>. Inclusions in steels deoxidized with aluminum or silicon can be modified by lime-based powder injection or by calcium treatment. Ca-treatment is the more efficient method. Total Ca-contents needed for obtaining liquid inclusions in Al-killed steel are given in Fig. 24<sup>[33]</sup>.

Although oxide inclusions are normally regarded as harmful , they can be beneficial in certain products. For example , globular sulphide inclusions are desirable for good machinability , cold-deformable inclusions can improve the cold deformability and polishing characteristics of certain steels , and Ca-aluminates or Ca-silicates can have positive effects on the free-cutting properties.

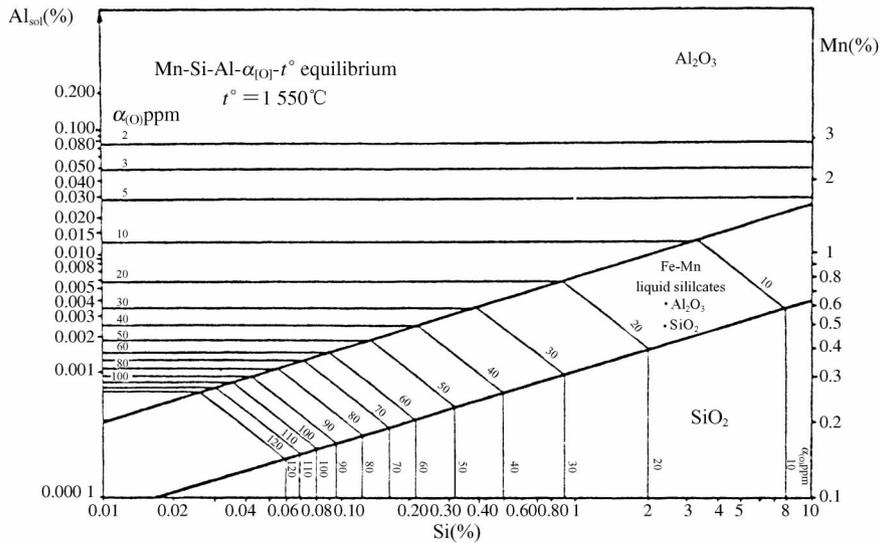


Fig. 23 Type of inclusions as a function of concentration of Mn , Si and Al

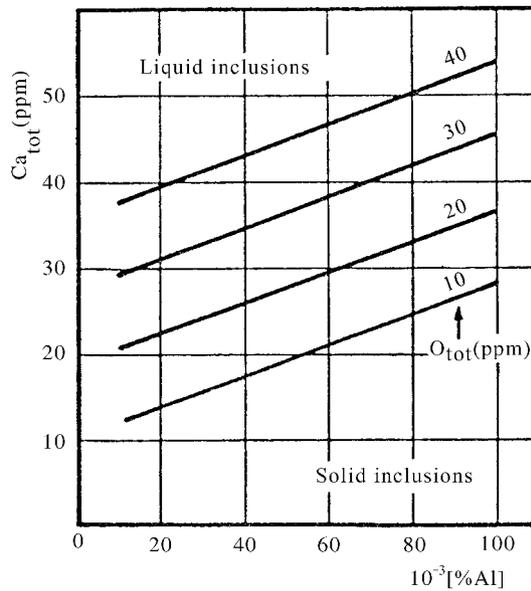


Fig. 24 Equilibrium relation between calcium and various non-metallic elements in liquid iron at 1600°C<sup>[7]</sup> (Note the high solubility product of CaO and CaS. )

Transforming the cluster-forming alumina inclusions into low-melting Ca-aluminate by CaSi in jection is another important example of inclusion modification. The alumina dendrites can cause nozzle blockage during continuous casting of Al-killed steels , while the Ca-aluminates normally do not stick to the nozzle walls , letting the steel pass freely. To eliminate nozzle blockage the Ca/Al-ratio should exceed 0.14<sup>[39]</sup> , and the oxide composition should correspond to  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  or aluminates of higher CaO-contents.

It has been suggested<sup>[35 ~ 37]</sup> that modification of inclusions can be obtained by injection of slag-forming products , or even by argon bubbling under a top-slag , but there has been no conclusive verification in practice. However , in our experience , a final injection of lime-fluorspar after CaSi-injection is recommended to counteract the formation of large Ca-oxysulphides , which may occur in Ca-saturated steel.

## **SULPHUR AND SULPHIDE INCLUSION CONTROL**

Good deoxidation is a prerequisite for sulphur removal from a steel melt. In integrated steel-works the hot metal is under reducing conditions , and desulphurization should start at this stage. There are hot metal treatments capable of reducing the sulphur content down to 0.003% . It is not likely , however , that such a level can be maintained in the BOF-plant. A final sulphur content lower than 0.010% is rarely obtained from the BOF converter. Likewise in EAF steel the minimum sulphur content is 0.010% . Thus , subsequent desulphurization is indispensable. There are two types of treatment for efficient sulphur removal :

- reaction with a synthetic top-slag under good stirring , most often argon bubbling under a  $\text{CaO-Al}_2\text{O}_3\text{-CaF}_2$  top slag
- injection of Ca-compounds or lime-based powders , or both in sequence.

In the ladle injection process , using CaSi-powder as desulphurizing agent , we find a consistent relationship between oxygen activity , the amount of CaSi added and the degree of desulphurization obtained (Fig. 25)<sup>[32]</sup>.

A basic lining and intensive stirring by the injection gas contribute to rapid desulphurization. Sulphur levels as low as 30 ppm are obtainable on a regular

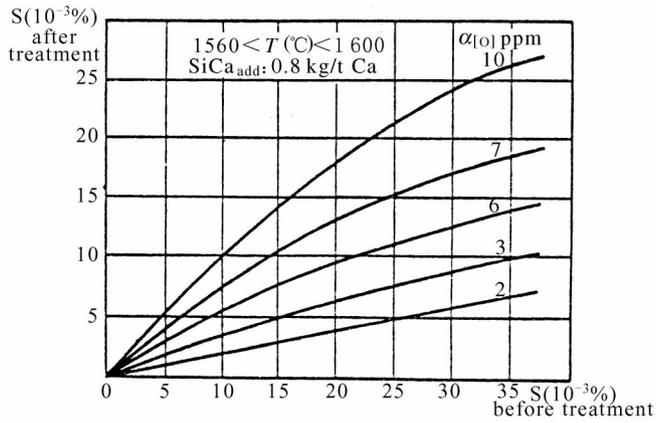


Fig. 25 Relation between degree of desulphurization and oxygen activity in liquid steel before injection of a fixed amount of CaSi

production basis.

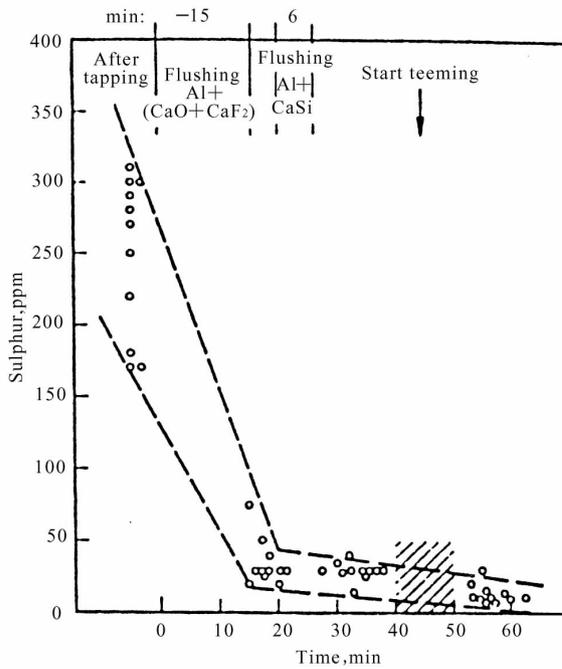


Fig. 26 Desulphurization by sequence flushing

Fig. 26 shows results obtained from full-scale production<sup>[2]</sup>, using 5 kg/ton of steel of a lime + fluorspar mix, flushing with 1 m<sup>3</sup>/min (STP) argon for about 12 min, and finally injecting 1.5 kg/ton CaSi. The SL-ULS injection process, developed by Scandinavian Lancers aims at an ultra-low sulphur content of 20 ppm max. This process is used by BSC at their Lackenby works for the productions of linepipe steel. Production results are shown in Figs. 27 and 28. The 20 ppm limit is reached by > 80% of the production with an average CaSi consumption of approximately 3 kg/ton of steel, which is 30% to 50% lower than for the standard injection procedure.

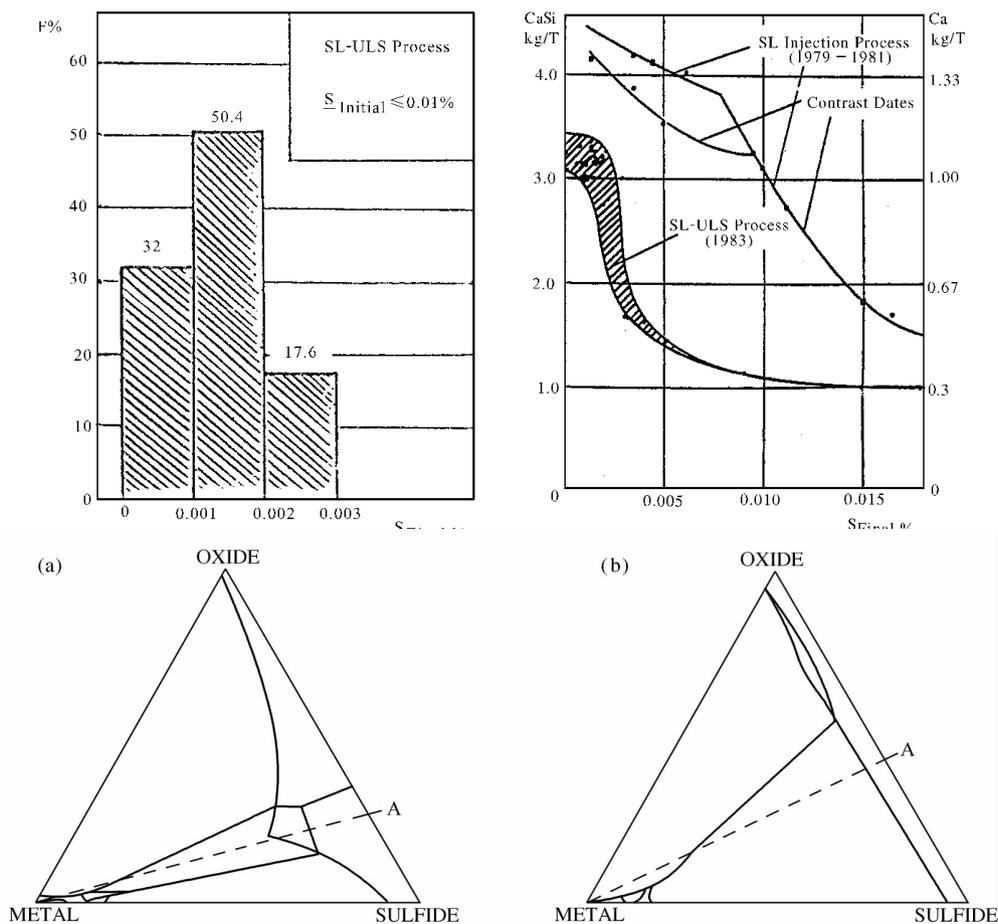


Fig. 29 Schematic solidification diagrams a) aluminum deoxidized b) aluminum and calcium deoxidized

The nature of the sulphide and oxide inclusions remaining, in small amounts in calcium-treated steels are strongly affected by the concentration of calcium (Fig. 29a, b)<sup>[38]</sup>. In Al-killed steels a low-melting-point, sulphur-rich phase, precipitates in the grain boundaries as Type-II manganese sulphide. In contrast the small amounts of oxygen and sulphur in Ca-treated steels form a eutectic melt richer in oxide, yielding globular Ca-aluminates surrounded by a Ca-sulphide coating (Fig. 30). Alumina dendrites and sulphide stringers are thereby eliminated. A recent study<sup>[40]</sup>, has shown, that sulphide inclusions in Al-killed steels are completely transformed when the quantity of soluble calcium and rare earth metals present is sufficient to react with at least 40% of the dissolved sulphur at the start of solidification (Fig. 31). Another investigation<sup>[41]</sup>, indicates how even small amounts of Ca substituting for Mn in the sulphide inclusions drastically increases their microhardness (Fig. 32).

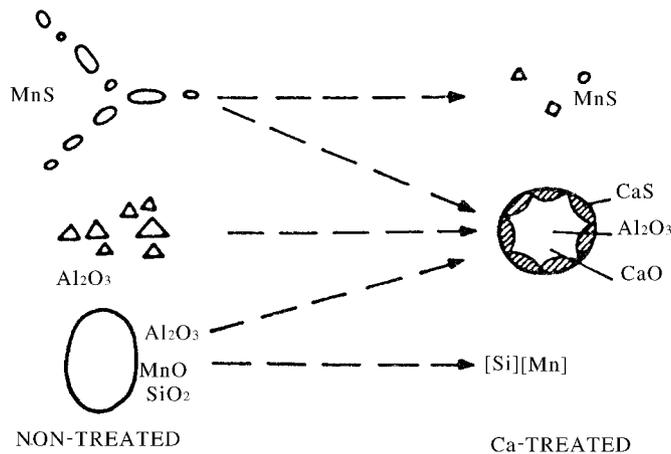


Fig. 30 Schematic representation of modification of inclusions by Ca treatment

To summarize, secondary metallurgy processes such as the SL-ULS process provide excellent control of sulphide inclusions, producing steels with extremely low sulphur content, and causing the remaining inclusions to have a shape which minimizes detrimental effects on end-product properties.

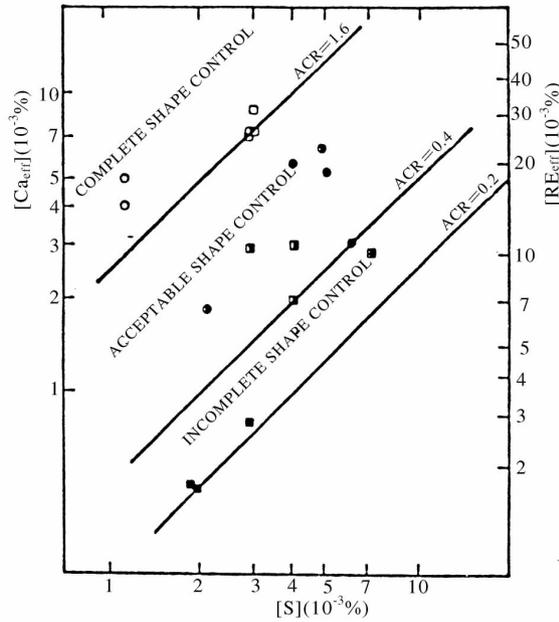


Fig. 31 Control of morphology and distribution of sulphides in HSLA steel by additions of Ca or rare earth elements

$$ACR = \frac{32 \text{ [ \% Ca}_{\text{eff}} \text{ ]}}{40 \text{ [ \% S ]}} = \frac{32 \text{ [ \% RE}_{\text{eff}} \text{ ]}}{140 \text{ [ \% S ]}}$$

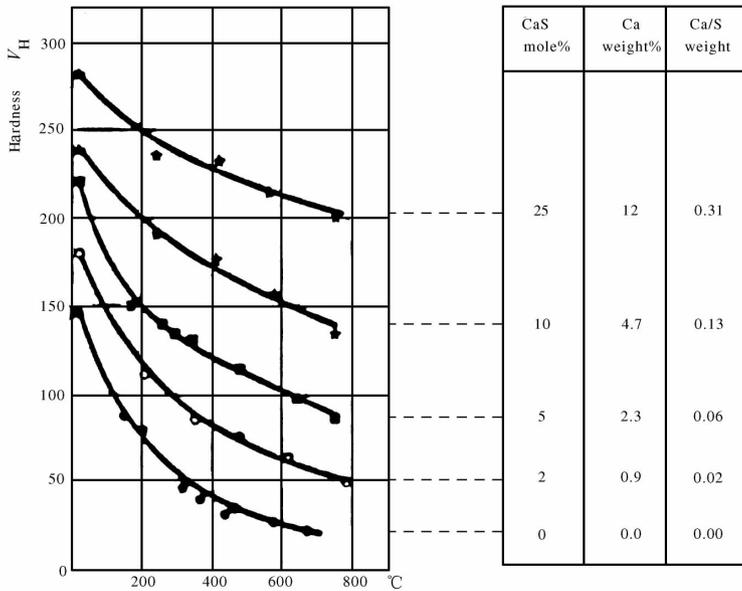


Fig. 32 Effect of temperature and sulphide composition on micro-hardness of (Ca, Mn)S solid solutions

## HYDROGEN CONTROL

The extent of hydrogen removal by various degassing processes is indicated in Fig. 33. Hydrogen contents below 2 ppm are obtainable by most of the methods. Alloyed structural steels, particularly those containing nickel, are very sensitive to hydrogen cracks ("flakes"). In large forging ingots of machine and tool steel the maximum permitted hydrogen content is usually 1.5 ppm, and at times even vacuum casting is applied. In ladle degassing considerable time and a good vacuum are needed to obtain good hydrogen removal (Fig. 34). An intensive gas agitation during the process, often induced by argon flushing, is required. The deoxidation of the steel also influences the hydrogen removal (Fig. 35)<sup>[43]</sup>.

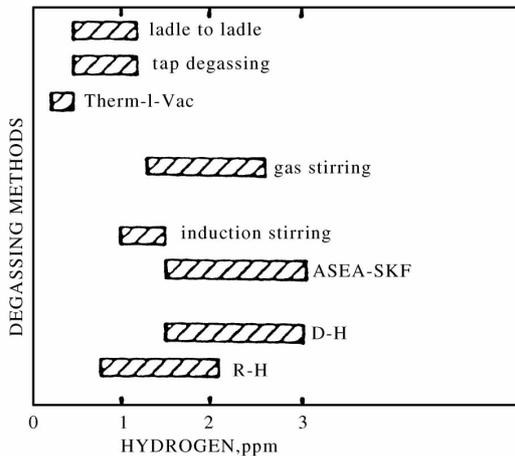


Fig. 33 Hydrogen contents obtained by various degassing methods

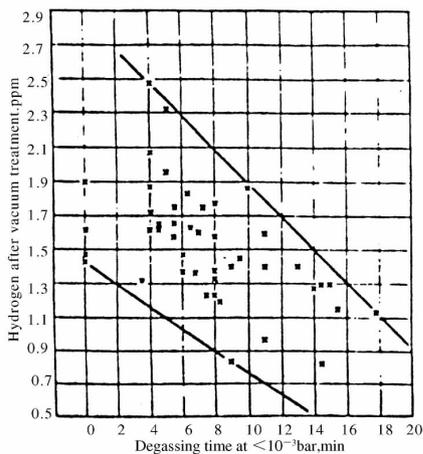


Fig. 34 Influence of degassing time on hydrogen content for ladle degassing

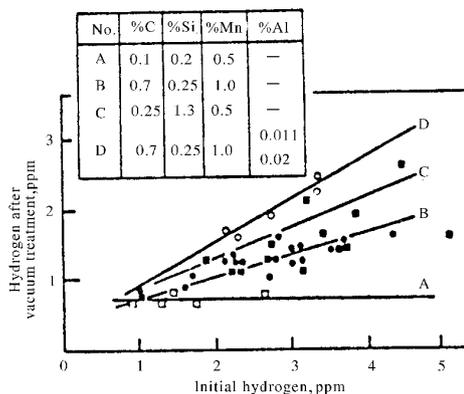


Fig. 35 Influence of the degree of deoxidation on hydrogen content for the DH process

The inverse reaction of hydrogen pick-up is unfortunately a common problem of many ladle metallurgy processes, raising the hydrogen content by about 1–1.5 ppm. The hydrogen sources are the humidity of the slag-forming additives, injection powders, ferro-alloys and even the ladle and tundish lining. Well-deoxidized steel is unfortunately strongly sensitive to hydrogen pick-up; a steel with an oxygen activity of 20 ppm has an equilibrium solubility of 20 ppm H at a water vapor pressure of 0.003 atmospheres. Also the rate of hydrogen absorption in ladle-treated steels is high, due to the very low oxygen and sulphur contents.

## NITROGEN CONTROL

Nitrogen removal by vacuum treatment is a slow-moving reaction due to the low mass transfer coefficient of this element. Thus, in practice, the only way to produce a low-nitrogen steel is avoiding all sources of nitrogen during the processing by using low-nitrogen raw materials and additives, and by avoiding re-blowing, open tapping and Al addition during secondary steel-making and teeming.

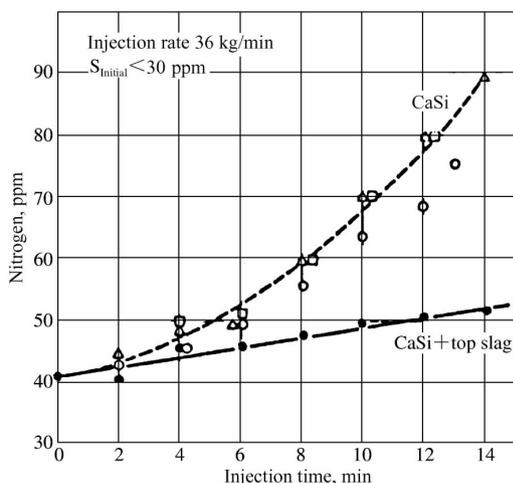


Fig. 36 Nitrogen absorption during injection of desulphurization agents [120 T dolomite-lined ladle<sup>[49]</sup>]

Nitrogen pick-up from the atmosphere generally occurs during ladle treatments. During CaSi injection, for instance, some 20 to 30 ppm of nitrogen are added to the steel. Addition of a top slag to the ladle reduces the nitrogen absorption in the steel (Fig. 36). A further advisable precaution is the use of ladle hoods to prevent the access of the surrounding atmosphere during treatment. Fig. 37 illustrates the nitrogen pick-up during the SL injection process, using a double-hood system, which efficiently reduces the nitrogen absorption by a factor of 3 to 4. Other measures taken to prevent nitrogen pick-up include the use of an iron foil covering the ladle during tapping, the tap

injection process, using a double-hood system, which efficiently reduces the nitrogen absorption by a factor of 3 to 4. Other measures taken to prevent nitrogen pick-up include the use of an iron foil covering the ladle during tapping, the tap

stream passing through the foil<sup>[46]</sup>. Large pieces of dry ice (CO<sub>2</sub>) are placed on the ladle bottom to generate a protective atmosphere over the liquid steel.

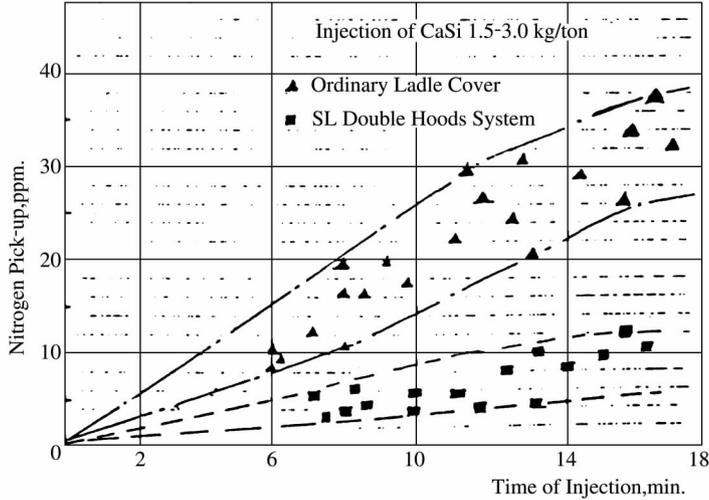


Fig. 37 Effect of double-hood system on nitrogen pick-up during injection

In the production of the extra-low interstitial-containing Cr-Mo steels, “super-ferrites”, considerable effort is necessary to achieve the extremely low nitrogen levels required. The VOD process is the one normally used, but several extra precautions must be taken<sup>[46]</sup>. The carry-over of furnace slag to the VOD treatment must be rigorously limited, the argon-oxygen process gas is injected from the top and argon blown from the bottom. Moreover, lime and fluorspar are added to form a fluid slag in the VOD. The initial carbon content should be kept at a higher level than normally used (about 1% C is recommended compared with the normal 0.3%–0.4%). With this practice 18% Cr super-ferrites are produced with total (C + N) < 150 ppm.

### CONTROL OF “TRAMP ELEMENTS”

Conventional metallurgical processes cannot remove impurities such as Cu, Sn, As, Sb from the steel, and cannot achieve dephosphorization of high-chromium or high-manganese melts. Unfortunately these tramp elements accumulate in the steel through recirculation of scrap. Table 4 indicates the limits of tramp elements in some different steel grades, and the typical contents in scrap, pig i-

ron and sponge iron. The calcium treatment of steel offers certain possibilities for removing tramp elements<sup>[48-50]</sup>. Calcium metal has a strong affinity for Sn and P, forming intermetallic phases, such as  $\text{Ca}_2\text{Sn}$  and  $\text{Ca}_3\text{P}_2$ , which can be used only in very special cases. Removing copper from steel has to date not been proven possible, and the copper level of steel production must be controlled by diluting the circulating scrap with virgin raw material.

**Table 4a Typical maximum residual limits of carbon steels**

$\Sigma (\text{Cu} + \text{Sn} + \text{Ni} + \text{Cr} + \text{Mo})$ , wt%	
• Tinplate for draw and iron cans	0.12
• Extra deep drawing quality sheet	0.14
• Drawing quality and enamelling steels	0.16
• Commercial quality sheet	0.22
• Fine wire grades	0.25
• Special bar quality	0.35
• Merchant bar quality	0.50

**Table 4b Typical residual content of selected charge materials**

$\Sigma (\text{Cu} + \text{Sn} + \text{Ni} + \text{Cr} + \text{Mo})$ , wt%	
• Direct reduced iron	0.02
• Pig iron	0.06
• No. 1 factory bundles	0.13
• Bushelling	0.13
• No. 1 heavy melting	0.20
• Shredded auto	0.51
• No. 2 heavy melting	0.73

In stainless steel production it may be possible to reduce P, As, Sb and Sn contents by calcium treatment (Fig. 38)<sup>[51]</sup>. Dephosphorizing in the AOD converter or in a ladle treatment has been studied<sup>[52,53]</sup>, as well as in the electric arc furnace<sup>[54]</sup>. A mixture of  $\text{CaF}_2 + \text{CaC}_2$  is fed to the melt and is removed after the reaction is complete. Dephosphorization of 25%–50% is obtained using 6–15 kg/ton fluorspar and 8–10 kg/ton calcium.

## PRACTICAL FEATURES OF SECONDARY STEELMAKING INSTALLATIONS

Secondary steelmaking processes are widely used today in the production of

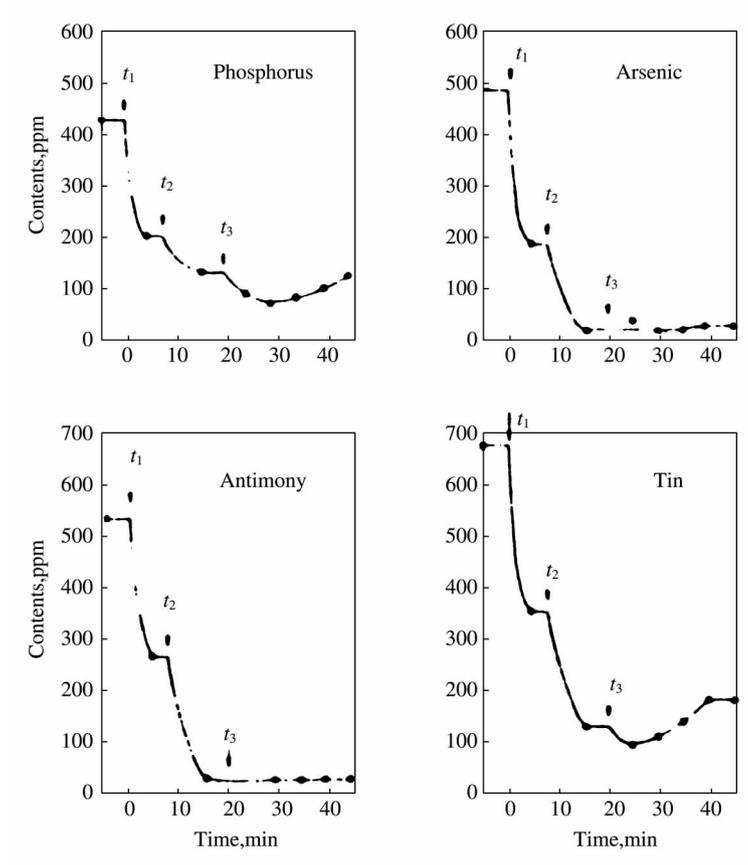


Fig. 38 Removal of phosphorus , arsenic , antimony and tin from 18 Cr-8 Ni steel by additions of Ca and a CaF<sub>2</sub> top slag

a large tonnage of a variety of steel grades to achieve high quality steels and process economy. Increased productivity is many times more important than the production of clean steels. Therefore , we consider first the productivity of the primary furnace , releasing it to the maximum possible extent from the refining processes and alloying additions , which instead should take place in the secondary steelmaking unit. A ladle heating system must be used in certain cases.

### MATERIAL HANDLING

The material handling in the steel-works will be changed , providing incentive for the installation of automated transport systems for alloying and slag-forming additives. In the case of ladle-injection refining , most materials lend

themselves to pneumatic transport from storage silos to day-bins and finally to the ladle.

The design of a ladle treatment system should be based on the following principles :

- The refining operations from tapping to casting taking place preferably in the same ladle.
- The ladle passing the number of stations needed to perform the complete treatment.
- The transportation from station to station being made on a transfer car.
- A modular design system being used to facilitate the replacement of worn-out and exposed parts of the equipment.
- Every system being provided with a ladle hood designed for the purpose of the treatment.

A ladle treatment system of this kind has been developed by Elkem/Scan-Lance , including a lance-injection station , vacuum degassing , high-power stirring inductor and ladle reheating. These optional parts can be combined to the extent needed for individual requirements.

## **PRIMARY SLAG SEPARATION**

For all of the refining processes , the slag from the primary furnace should , to the extent possible , be prevented from entering the refining vessel.

For the electric arc furnace there are 3 approaches to this problem :

- sliding gate system
- bottom tapping
- eccentric bottom tapping

At present there is widespread interest in eccentric bottom tapping.

For BOF converters a sliding gate system may also be considered. Alternatively , two other approaches are :

- swing arm with pneumatic tap-hole blocking
- re-ladling

Sliding gates and pneumatic blocking have proven to be reliable and efficient for ladle sizes < 180 tons. So far the sliding gates have a durability of some 20 heats , while the pneumatic blocking systems last for 600 to 800 heats. Lacking a

more reliable system for bigger converters , re-ladling , despite its practical disadvantages , remains a working method.

### **LADLE AND TRANSFER CAR SYSTEM**

Ladles with a basic lining are normally used. Neutral alumina-based lining is often also acceptable , but a silica lining will seriously jeopardize the refining process.

If inductive stirring is applied , the ladle should have a nonmagnetic “ window ” in the area of the magnetic field. The ladle transfer car can be combined with a built-in induction stirrer , or occasionally also with a ladle tilting system to facilitate the de-slagging operation.

### **TOP SLAG AND INSULATING POWDER ADDITION**

The refining slag addition is normally made in the preheated ladle , in the tapping launder or on the surface of the melt. An attractive alternative , or complement , for the effective distribution of top slag and insulating powders , particularly used for large ladles , is the Scanlance powder distributor , in single or twin design.

### **ALLOY ADDITION STATION**

The addition of alloying materials is preferably made in the ladle , and the use of automatic alloy feeding systems is becoming common in high productivity steel plants. The alloy feeding system includes a battery of 4-12 hoppers , vibrators , transfer alloy car or belt with an automatic weighing system , and the necessary chutes into the ladle. Provisions for preheating the bulk alloys can also be made , in order to counteract temperature drop and hydrogen pick-up in the melt.

A wire feeding system is a natural complement to ladle treatment stations , mostly used for the accurate control of oxygen activity by immersing a predetermined length of Al-wire into the steel bath. The rapid feed of the Al-wire into the melt minimizes the nitrogen pick-up. For low-silicon steels , calcium core wires may be used which also can be immersed by a wire feeding device.

## **LADLE FURNACE**

Ladle furnaces have been installed in many steel-works performing multi-station ladle refining , and they are becoming an increasingly important part of the system as the demands on the ladle refining processes increase. In most cases it is also good economy to apply ladle furnaces instead of superheating in the melting furnace. The capacity of a ladle furnace should meet the normal requirement of raising the temperature of the melt by at least 4°C per minute. Ladle furnaces are often used in combination with inductive stirring , achieving the stirring time needed for complete reaction and good homogenization.

## **INJECTION STATION**

Several ladle injection systems are used , but the most widespread is the Scandinavian Lancers system , characterized by its flexible adaptability to any steel-works layout , and by its reliable function.

For the main desulphurization the cheap lime-fluorspar powder is injected , followed by a CaSi powder injection to obtain the ultra-low sulphur levels , and for the modification of the remaining inclusions. In practice this is preferably done with the SL sequence injection technology. The reproducible production of super-clean steel with sulphur content below 15 ppm requires an injection technology well optimized by deoxidation to low-oxygen activity and by the careful control of the top slag composition ( Figs. 39 and 40 ).

Most alloying elements can be added to the steel bath by injection , for the purpose of adjusting the composition. The good stirring effect from the injection carrier gas secures the rapid dissolution and homogenization of the alloying elements. Some of these , particularly the ones with high oxygen affinity such as FeB , FeTi , FeV , FeNb , S , Te and Pb , have a low and variable yield when added by traditional methods. Injection offers big advantages for the addition of these elements , not only by increasing the recovery , but also for keeping a predictable constant yield.

Achieving accurate and reproducible temperature measurements and chemical analysis is mandatory for the sort of precision metallurgy that modern ladle treatment represents. For this purpose it is important to main-

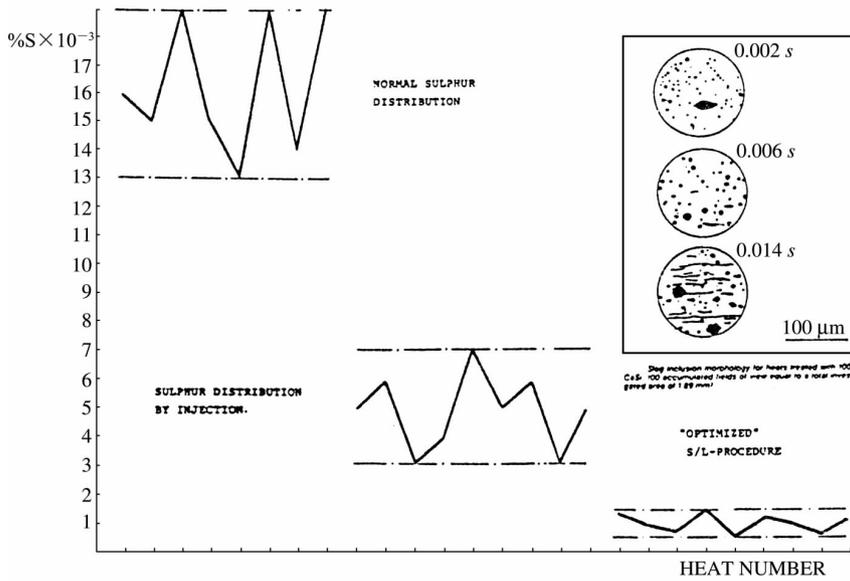


Fig. 39 Distributions of sulphur contents for different injection procedures

tain a constant depth and time of immersion when using the probe. The SL automatic depth sensing system has been developed for temperature measurement and sample collection from steel ladles (Fig. 41).

A complete view of an SL-installation in an EAF steelworks is given in Fig. 42.

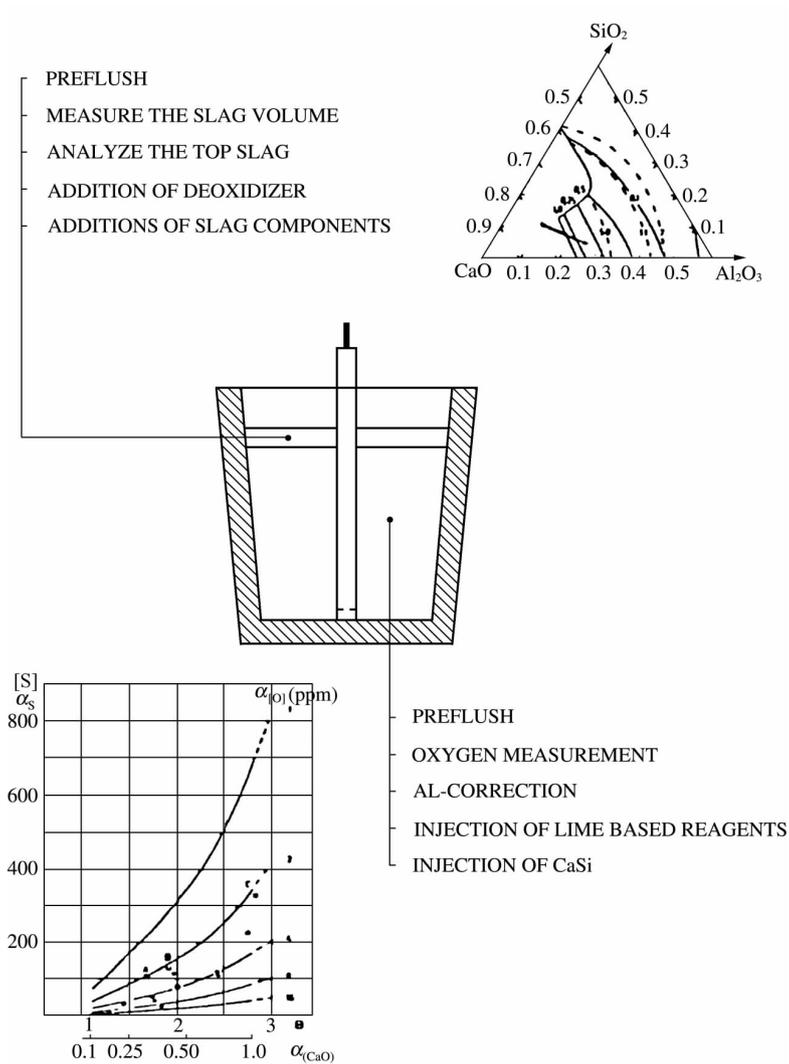


Fig. 40 Optimizing the injection procedure

## DEGASSING STATION

Steel grades sensitive to hydrogen-induced cracking or hydrogen flaking, should be degassed before casting, particularly in the case of heavy ingot casting. Often the degassing is followed by slow cooling of the ingot for diffusion annealing. The most common vacuum degassing processes have been mentioned

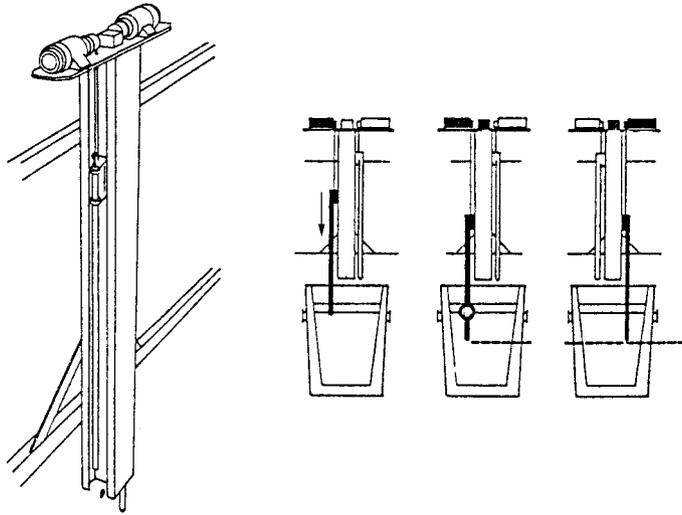
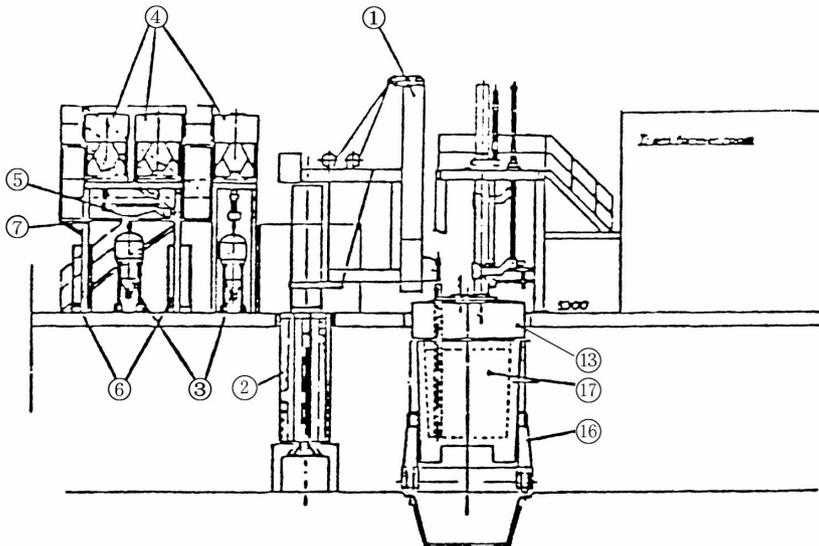


Fig. 41 Scandinavian Lancers ADS system for sampling oxygen and temperature measurement

in the earlier parts of this paper. Comparing the various methods we find that the RH process has been mostly installed for production with large ladles. Other processes, such as applying vacuum to the ladle, or using purging gas from a porous plug for stirring, are often used for small-sized ladles.



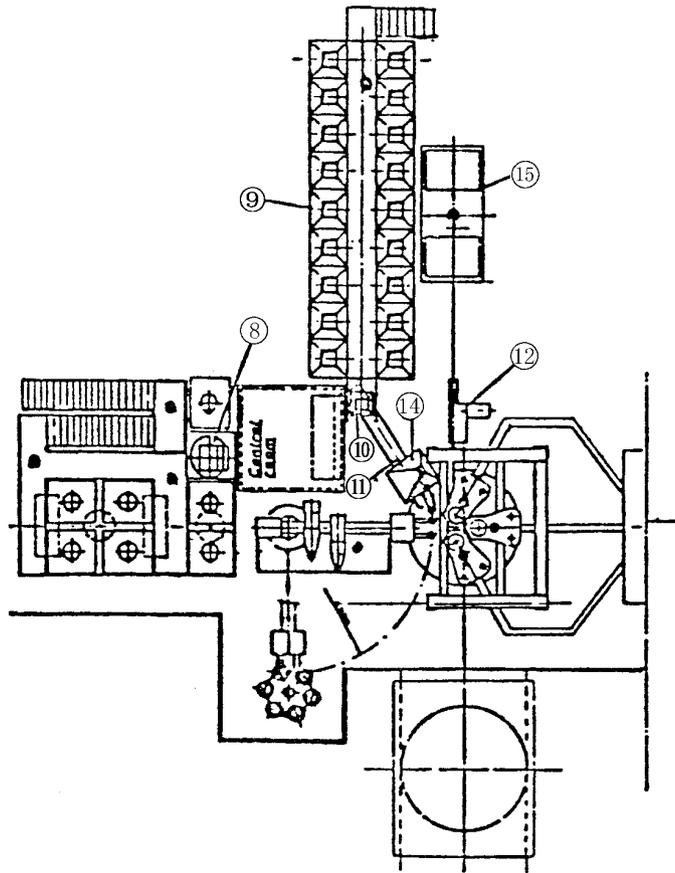


Fig.42 Complete view of an SL installation in an EAF steelworks

## References

- [ 1 ] Ohnishi , T. " Secondary steelmaking for product improvement " , *The Metals Society London* ; 15. 1 ; 1984
- [ 2 ] Turkdogan , E. T. *Arch. Eisenhutt* 54(2) : 45 ; 1983
- [ 3 ] Fujii , T. *et al. Tetsu-to-Hagane* 68 : S 270 ; 1982
- [ 4 ] Mori *et al. Tetsu-to-Hagane* 67 : 67a ; 1981
- [ 5 ] Kozakevitch , P. and Urbain , G. *Mém Sci Rev Métall* 60 ( 2 ) : 143 ; 1963
- [ 6 ] Burgmann , W. *et al. Metallurgical Plant and Technology* 4 : 34 ; 1984

- [ 7 ] Miyawak , Y. *et al.* *Nippon Kokan* Technical Report No. 39 ;1983
- [ 8 ] Guthrie , R. “Scaninject III ” *MEFOS Jernkontoret* ;19(1) :1 ;1983
- [ 9 ] Argyropoulos , S. A. *et al.* Proceedings of the I. C. H. M. T. Summer Seminar on Heat and Mass Transfer in Metallurgical Systems ;Dubrovnik , Yugoslavia :159 ;1979
- [ 10 ] Gourtsoyannis , L. *et al.* “ Physical chemistry of production or use of alloy additives ” ; Ed. J. Farrell , *TMS-AIME Warrendale* :44 ;1974
- [ 11 ] Guthrie , R. *et al.* *Can Met Quart* 15(2) :145 ;1970
- [ 12 ] Argyropoulos , S. A. Ph. D. Thesis ; *McGill University* Aug. 1981
- [ 13 ] Hou , S. and Xu , K-D *et al.* Proceedings of Shenyang Symposium on Injection Metallurgy & Secondary Refining of Steel , *Northeast Univ. of Technology Shenyang* :316 ;1984
- [ 14 ] Kor , G. J. W. *et al.* *Trans AIME* 245 :319 ;1969
- [ 15 ] Jacquemot , A. *Cent Doc Sider Inf Tech.* 34(6) :1449 ;1977
- [ 16 ] Jacquemot , A. *Cent Doc Sider Inf Tech.* 36(9) :1041 ;1979
- [ 17 ] Rein , R. H. *et al.* *Trans AIME* 233 :415 ;1965
- [ 18 ] Okamoto , S. *et al.* 7th ICVM Congress ;Tokyo ;Nov. 1982
- [ 19 ] Kawakami , K. *Trans ISIJ* 24 :754 ;1984
- [ 20 ] Scheel , R. *et al.* “ Secondary steelmaking for product improvement ” *The Metals Society* London ;6.1 ;1984
- [ 21 ] Ueda , A. *et al.* *Trans ISIJ* 22 :8 ;1982
- [ 22 ] Sumida , N. *et al.* *Kawasaki Steel Tech Rep.* 69 ;1983
- [ 23 ] Wessling. W. *et al.* *Krupp Stahl AG* 11/82 :4 ;1982
- [ 24 ] Kraatz , D. *et al.* “ Secondary steelmaking for product improvement ” *The Metals Society* London ;4.1 ;1984
- [ 25 ] Iwaoka , S. *et al.* in “ Stainless steel '77 ” ; *Climax Molybdenum Co.* New York :139 ;1978
- [ 26 ] Usui , T. *et al.* “ Scaninject II ” *MEFOS Jernkontoret* ;12 :1 ;1980
- [ 27 ] Turkdogan , E. T. *Arch Eisenhutt* 54(1) :1 ;1983
- [ 28 ] Sandberg , H. *et al.* *Jernkont. Ann* 155(5) :201 ;1971
- [ 29 ] Lindskog , N. and Kjellberg , B. *Scand J Metall* 6(2) :522 ;1977
- [ 30 ] Loscher , W. *et al.* “ Schlacken in der metallurgie ” ;Eds. K. Koch and D. Janke , *Verlag Stahleisenk Dusseldorf* ;1984
- [ 31 ] Bernard , G. *et al.* *Rev Met CII* 78(5) :421 ;1981
- [ 32 ] Carlens , J. P. “ Aluminum , deoxidation and desulfurisation control in ladle metallurgy for billet and slab casters by means of the oxygen activity measurement with the celox oxygen probe ” *Electro-Nite N. V. Houthalen* Brussels
- [ 33 ] Riboud , P. V. *et al.* “ Secondary steelmaking for product improvement ” *The Metals Society* London ;7.1 ;1984

- [34] Faulring, G. M. *et al.* *J. I. & S. M.* 14 ;1980
- [35] Saxena, S. K. *et al.* "Steelmaking proc." 61 :561 ;1978
- [36] Tivelius, B. *et al.* "Symposium on ladle treatment of carbon steel" *McMaster University* 3 ;1979
- [37] Meredith, J. G. "Scaninject II" *MEFOS Jernkontoret* ;32 ;1980
- [38] Hilty, D. C. *et al.* *I. & S. M.* May 1975 ;June 1975
- [39] Tahtinen, K. *et al.* "Scaninject II" *MEFOS Jernkontoret* ;24 ;1980
- [40] Iida, Y. *et al.* "Scaninject III" *MEFOS Jernkontoret* ;1 :1 ;1983
- [41] Leung, C. H. *et al.* *Met Trans.* 12A :987 ;1981
- [42] Usui, T. *et al.* "Scaninject II" *MEFOS Jernkontoret* ;1980
- [43] Motte, J. P. *et al.* *Rev Metall CIT* 15 ;Jan. 1981
- [44] Richter, H. *et al.* *Radex-Rundschau* 480 ;1981
- [45] Abe, Y. *et al.* *Tetsu-to-Hagane* 68 :91 ;1982
- [46] Hasegawa, M. *et al.* "Secondary steelmaking for product improvement" *The Metals Society London* ;19.1 ;1984
- [47] Brown, J. W. *et al.* "Seminar on the economic problems related to the creation of steel plants using direct reduction" ;May 16-20, 1983, Nordwijerhout, NL *EEC Steel Committee Report R. 30* ;1983
- [48] Engell, H. -J. *et al.* *Stahl u. Eisen* 104(9) :443 ;1984
- [49] Thielmann, R. *et al.* *Thyssen Edelst Tech* 8(1) :3 ;1982
- [50] Nakamura, Y. *et al.* *I. S. I. J.* 35 ;1976
- [51] Bode H. *et al.* *Stahl u. Eisen* 103(5) :211 ;1983
- [52] Kaneko, K. *et al.* "Proc of the Third International Iron and Steel Congress" *ASM Metals Park* :583 ;1979
- [53] Katayama, H. *et al.* *Trans I. S. I. J.* 19(10) :635 ;1979
- [54] Yongxi Q. *et al.* "Sino-Japan symposium on steelmaking" ;1981

## 氮对钙处理 16Mn 钢机械性能的影响及机理探讨<sup>\* 1</sup>

\* 本文合作者：许珞萍、顾洪涛、刘平、章忻宝. 原发表于《特殊钢》(增刊), 134 ~ 140 (1984) **摘要** 对喷粉处理的 16Mn 钢进行了机械性能测试、电子探针、能谱分

析,并与未经喷粉处理的同炉钢进行了比较,结果说明,经喷粉处理后氮含量虽有提高,但由于钢中氮化铝夹杂为氮化钙所替代,大颗粒夹杂减少,并造成夹杂变性,使喷粉钢(与未喷粉钢相比)的抗拉强度、屈服强度和延伸率均无变化,而抗时效性能、冲击值均有明显提高,各向异性也大大改善。在试验的氮含量范围内( $[N]=62 \sim 97 \text{ ppm}$ ),氮含量对喷粉处理钢的脆性转折温度无影响。

## 1 前言

16Mn钢是低合金钢中使用量最大的一个钢种。采用钢包喷钙处理方法,可使16Mn钢的机械性能得到明显改善。但是,国内、外的实践均表明,在钙处理过程中,由于钢中氧、硫等表面活性元素的急剧减少,钢液面裸露严重,因此喷吹处理后的钢液含氮量普遍有不同程度的增加。根据鞍钢二炼钢52炉次的统计,平炉16Mn钢110吨钢包的钢液喷钙前平均含氮量38.3 ppm,喷后增氮至53.3 ppm,增氮量为15 ppm<sup>[1]</sup>。上钢三厂电炉车间电炉冶炼的16Mn钢24个炉次的统计,在16~21吨钢包中,钢水喷钙前平均含氮量54 ppm,喷吹后增氮至68 ppm,增氮量为14 ppm<sup>[2]</sup>。

按照一般规则,氮的增加会使低碳钢产生应变时效现象,引起脆性,而且氮也是导致钢产生兰脆的主要原因。对于氮含量高的钢,在250~550℃区间内加热,将出现冲击值的明显下降。基于上述情况,尽管钙处理后16Mn钢的常规机械性能有明显改善,部分用户对钢中氮的增加仍持疑虑态度。因此,对钙处理钢中氮含量增加所产生的影响及其机理的研究,显得十分必要。

本试验以鞍钢二炼钢及上钢三厂大生产中所取喷钙处理16Mn钢钢板试样为依据,对其常规机械性能、时效敏感性、低温冲击性能及断口形貌进行了研究。为突出氮的影响,在其他化学成分基本一致的情况下,有意选取氮含量较高的炉号,并在电炉16Mn钢中将氮含量的区间拉大(62~97 ppm)。

## 2 氮对钙处理16Mn钢常规机械性能的影响

关于氮对钙处理16Mn钢常规机械性能的影响,从两个方面进行了研究。首先是对喷吹工艺条件相似、氮含量不同的总共120炉钢的常规机械性能进行多元逐步回归分析,以便找出影响常规机械性能的主要因素,及查明氮的影响。其次是取七炉典型试样,进行对比分析。

## 2.1 大生产统计数据的微机多元回归分析

取鞍钢二炼钢喷钙处理的 45 炉平炉 16Mn 钢钢板,及上钢三厂电炉车间喷钙处理的 75 炉电炉 16Mn 钢钢板,就其常规机械性能和钢中化学成分的关系,进行微机多元逐步回归分析,得到有显著相关系数的回归方程如表 1 所示。

表 1 对钙处理 16Mn 钢常规机械性能有显著相关性的回归方程

炉种	炉数	氮含量范围(ppm)	回 归 方 程	相关系数
平炉	45	43 ~ 82	$\sigma_b = 14.37 \times \underline{\text{Si}}\% + 51.83$ $\sigma_s = \text{平均值}$ $\delta\% = -24.97 \times \underline{\text{Mn}}\% - 192.78 \times \underline{\text{C}}\% + 97.10$	0.373 $3.58 \times 10^{-7}$ 0.697
电炉	75	46 ~ 93	$\sigma_b = -61.77 \times \underline{\text{Ca}}\% + 27.39 \times \underline{\text{Si}}\% + 47.78$ $\sigma_s = 11.48 \times \underline{\text{Si}}\% + 33.72$ $\delta\% = \text{平均值}$ $a_K^{20} = -794.53 \times \underline{\text{O}}\% \times 10^{-3} + 28.115$ $a_K^{-40} = -987.33 \times \underline{\text{O}}\% \times 10^{-3} + 19.82$	0.555 0.343 $-3.58 \times 10^{-7}$ 0.228 0.366

从表 1 所列回归方程可看出,16Mn 钢中硅及钙的含量对强度指标  $\sigma_b$  及  $\sigma_s$  有影响,而碳和锰的含量则影响其延伸率,氧含量对不同温度下的冲击韧性有较明显的影响。氮含量的波动范围尽管很大,但对钢的常规机械性能却未显示出任何影响。

## 2.2 氮含量对典型试验炉号 16Mn 钢钢板常规机械性能的影响

考虑到大生产统计数据,由于生产时间、某些工艺条件及不可控制因素的限制,可能离散度较大,难以显示某单一因素的影响。为此,在生产条件下,选取其他化学成分比较一致、冶炼时间接近、工艺条件相对稳定的两炉平炉 16Mn 钢钢板(其中 1 号及 2 号试样为同炉冶炼 16Mn 钢,仅有喷钙及不喷钙的差别)、四炉电炉 16Mn 钢钢板,进行典型试验,试样状况如表 2 所示。

表 2 典型试验用的 16Mn 钢钢板

炉 种	编 号	厚 度(mm)	工 艺	氮含量(ppm)
-----	-----	---------	-----	----------

平 炉	1	6	不喷钙	58
	2		喷钙处理	76
	3			84
电 炉	4	14	喷钙处理	62
	5			68
	6			76
	7			97

从图 1 及图 2 可以看出,当氮含量在62 ~ 97 ppm范围内波动,未发现其对钙处理电炉16Mn钢常规机械性能的影响. 钙处理对常规机械性能的改善,较突出地表现在钢材各向异性的改善. 图 3 表明钙处理16Mn钢的各向冲击值(0°、30°、60°、90°)尽管因喷钙处理后氮提高18 ~ 24 ppm,仍获得极好的各向同性. 数值均比未处理的提高,其中横向冲击值大约可提高100%以上. 图 4 为氮对电炉16Mn钢各向冲击值的影响. 其中5#、6#的各向冲击值差别不大,差值范围分别在4.2%及15%之间,7#试样中含氮量高达97 ppm各向冲击值差别较大,差值范围达到32%. 表明在氮含量极高时(如接近或超过100 ppm),会削弱钙处理的某些效果.

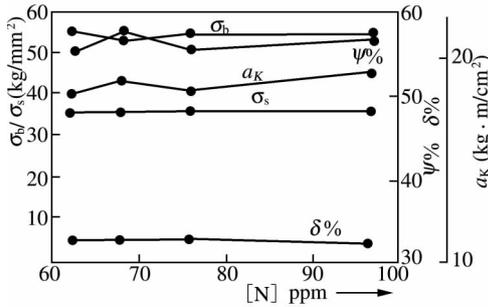


图 1 16Mn 钢常温机械性能与氮含量的关系

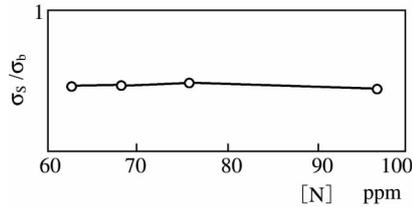


图 2 16Mn 钢屈服比与氮含量的关系

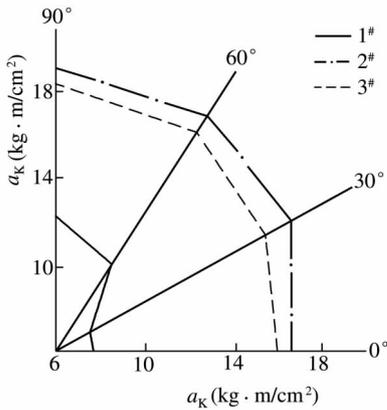


图3 平炉钙处理和未经钙处理的16Mn钢各向冲击值(U型)

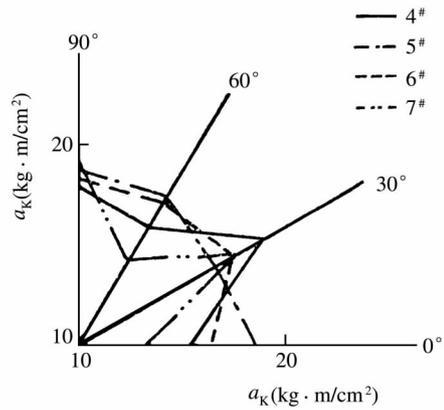


图4 氮含量对16Mn钢各向冲击值(V型)的影响

### 3 氮对钙处理16Mn钢时效敏感性的影响

在一般低合金钢中,氮含量控制得较为严格,认为最好不要超过80 ppm.主要原因是考虑到过饱和固溶的氮,在时效过程中以氮化物( $Fe_4N$ )的形式呈弥散状态析出,加剧了时效敏感性<sup>[3]</sup>.如图5所示,未经钙处理的1#试样,在100 °C以上的温度进行时效三小时就出现 $a_K$ 值的明显下降(由12.6公斤·米/厘米<sup>2</sup>下降至8公斤·米/厘米<sup>2</sup>).而经过钙处理的2#、3#钢,尽管氮含量要高18~26 ppm,都已接近或超过80 ppm,但其时效脆性温度却推迟到400 °C以上,从而大大降低了该钢种的时效敏感性,这对焊接件无疑十分有利.

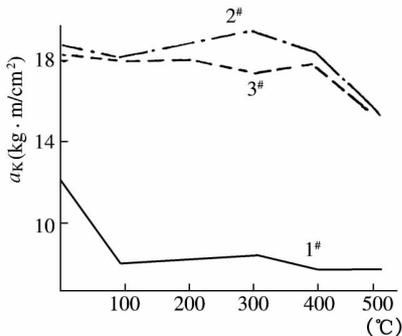


图5 平炉钙处理和未经钙处理的16Mn钢 $a_K$ 值与时效温度的关系

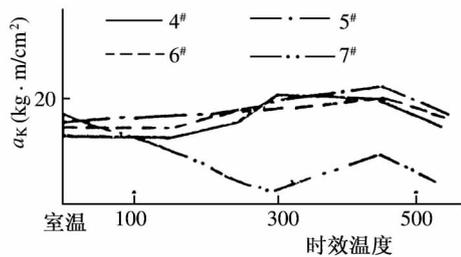


图6 电炉钙处理16Mn钢不同含氮量时 $a_K$ 值与时效温度的关系

图 6 给出了电炉钙处理 16Mn 钢的  $a_K$  值与时效温度间的关系. 可见, 除了含氮量高达 97 ppm 的样品以外, 其余三个样品(含氮量为 62 ~ 76 ppm)时效温度高达 450 时  $a_K$  值仍不下降.

#### 4 氮对 16Mn 钢低温冲击性能的影响

喷钙处理后氮含量增加对 16Mn 钢低温冲击值的影响见图 7、图 8. 尽管喷钙处理后增氮情况及最终氮含量不同, 但它们都有相似的转折规律, 其脆性转折温度范围基本都在  $-13 \sim -26$  范围以内, 见图 9. 4# 钢板脆性转折温度最高, 为  $-13 \sim -17$ , 5# 钢板脆性转折温度最低为  $-24 \sim -26$ , 6#、7# 钢板则居中.

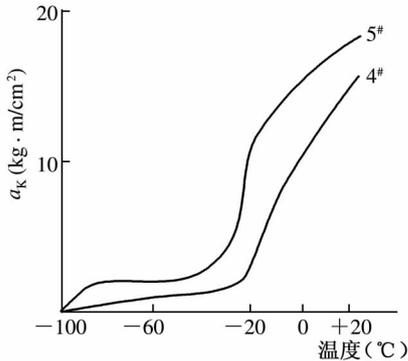


图 7 电炉钙处理 16Mn 钢  $a_K$  值与冲击温度的关系

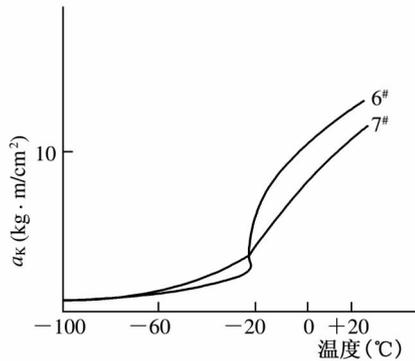


图 8 电炉喷钙处理 16Mn 钢  $a_K$  值与冲击温度的关系

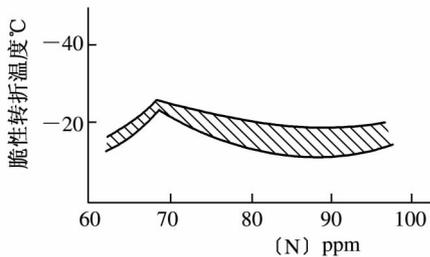


图 9 电炉钙处理 16Mn 钢氮含量对脆性转折温度的影响

这说明氮含量增至 97 ppm 的钙处理 16Mn 钢, 其脆性转折温度仍无明显变化. 这一点亦从断口形貌方面得到证实, 用 JCSA733 扫描电镜对 16Mn 钢板 -15 冲击断口进行扫描, 不同氮含量的钢板断口上, 均出现类似的准解理和少量韧窝的断口形貌.

## 5 氮对钙处理 16Mn 钢机械性能影响的机理探讨

在本试验的氮含量范围内( $N = 58 \sim 97$  ppm),未发现氮对钙处理 16Mn 钢的机械性能、时效敏感性、低温冲击时的脆性转折温度以及断口形貌有明显的不利影响.对比氮在未经钙处理钢中的行为,两者具有很大的差异,为此对氮在钙处理 16Mn 钢中存在的形式及其对钢性能影响的机理进行一些理论分析与探讨.

如所周知,氮和碳一样,降低  $A_3$  点,并在  $590^\circ\text{C}$  及氮含量为 2.35% 处发生  $\gamma \rightarrow \alpha + \text{Fe}_4\text{N}$  ( $\gamma'$ ) 的布氏体共析转变.氮在  $\alpha$  铁中的溶解度在布氏体共析转变温度  $590^\circ\text{C}$  时最大,约 0.10%;随着温度的下降,其溶解度也急剧降低,在  $400^\circ\text{C}$ 、 $300^\circ\text{C}$ 、 $200^\circ\text{C}$  和  $100^\circ\text{C}$  时分别为 0.02%、0.01%、0.005% 及 0.001%,因此,随着温度的降低氮的过饱和度急增.含氮铁素体钢从高温快冷后回火或在室温停留较长时间,从过饱和的  $\alpha$  固溶体中析出弥散分布的超显微氮化物组织将使钢产生时效脆性.

对于钙处理后的 16Mn 钢,钢中溶解有一定数量的钙,而钙是一个十分强烈的氮化物形成元素,因此钢中溶解的氮以什么形式析出、什么温度析出、是否导致钢产生时效脆性,很有探讨必要.

### 5.1 喷钙处理 16Mn 钢中氮化物的析出条件的热力学分析

典型的喷钙处理 16Mn 钢,具有下列化学成分:

元素	C	Mn	Si	P
%	0.16	1.4	0.25	$\leq 0.015$
元素	S	Al	Ca	
%	$\leq 0.010$	0.025	0.0040	

其中有可能形成氮化物的是铝及钙,现分别计算它们的析出温度及生成条件.

氮化铝的生成反应为



根据 Darken L. S. 给出的公认的热力学数据为<sup>[4]</sup>

$$\lg k_{\text{AlN}} = -\frac{7400}{T} + 1.95 \quad (2)$$

考虑到 16Mn 钢中各组元素的相互作用系数后,可求得铝及氮的活度系数分别为

$$\begin{aligned} \lg f_{\text{Al}} &= e_{\text{Al}}^{\text{Al}} \times [\% \text{Al}] + e_{\text{Al}}^{\text{C}} \times [\% \text{C}] + e_{\text{Al}}^{\text{Ca}} \times [\% \text{Ca}] \\ &\quad + e_{\text{Al}}^{\text{N}} \times [\% \text{N}] + e_{\text{Al}}^{\text{S}} \times [\% \text{S}] + e_{\text{Al}}^{\text{Si}} \times [\% \text{Si}] \\ &= 0.045 \times 0.025 + 0.091 \times 0.16 + (-0.047) \times 0.004 \\ &\quad + (-0.058) \times 0.007 + 0.03 \times 0.010 + 0.0056 \times 0.25 \\ &= 0.01679 \quad f_{\text{Al}} = 1.039 \end{aligned}$$

$$\begin{aligned} \lg f_{\text{N}} &= e_{\text{N}}^{\text{Al}} \times [\% \text{Al}] + e_{\text{N}}^{\text{C}} [\% \text{C}] + e_{\text{N}}^{\text{Mn}} \times [\% \text{Mn}] + e_{\text{N}}^{\text{P}} \\ &\quad \times [\% \text{P}] + e_{\text{N}}^{\text{S}} \times [\% \text{S}] + e_{\text{N}}^{\text{Si}} \times [\% \text{Si}] \\ &= -0.028 \times 0.025 + 0.13 \times 0.16 + (-0.02) \\ &\quad \times 1.4 + 0.045 \times 0.015 + 0.007 \times 0.01 + 0.047 \\ &\quad \times 0.25 = 0.004595 \quad f_{\text{N}} = 1.01 \end{aligned}$$

从(2)式可求得 AIN 形成温度为

$$T = \frac{-7400}{\lg \alpha_{\text{Al}} \cdot \alpha_{\text{N}} - 1.95} \quad (3)$$

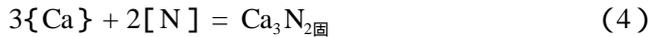
将不同的 16Mn 钢喷钙处理后铝及氮含量乘以活度系数代入(3)式,就可得到相应条件下的 AIN 析出温度,如表 3 所示.通常喷钙处理后钢中铝含量为 0.015% ~ 0.035%,氮含量为 0.005% ~ 0.009%,故 AIN 的析出温度应在 945 ~ 1084 之间.

表 3 喷钙 16Mn 钢中 AIN 析出温度

[% Al]	[% N]	AIN 析出温度
--------	-------	----------

0.015	0.003	902
	0.005	945
	0.007	975
	0.009	998
0.025	0.003	945
	0.005	991
	0.007	1 023
	0.009	1 048
0.035	0.003	975
	0.005	1 024
	0.007	1 058
	0.009	1 084
0.05	0.003	1 009
	0.005	1 060
	0.007	1 096
	0.009	1 124

氮化钙的生成反应为<sup>[5]</sup>



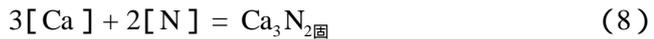
$$\Delta F_4^0 = -219\,500 + 117.55T \quad (5)$$

同时再考虑钙在钢中的溶解,有<sup>[6]</sup>



$$\Delta F_6^0 = -9\,430 + 11.8T \quad (7)$$

(4)式减3×(6)式,可得



$$\Delta F_8^0 = -191\,210 + 82.15T \quad (9)$$

考虑到实际钢中反应是在指定态下进行的,因此判断氮化钙能否析出及其温度,应看 $\Delta F_8$ :

$$\Delta F_8 = \Delta F_8^0 + RT \ln \frac{\alpha_{\text{Ca}_3\text{N}_2}}{\alpha_{[\text{a}]}^3 \cdot \alpha_{[\text{N}]}^2} \quad (10)$$

整理(10)式可得出指定态下 $\text{Ca}_3\text{N}_2$ 的析出温度为

$$T = \frac{191\,210}{82.15 + R \ln \frac{1}{\alpha_{[Ca]}^3 \cdot \alpha_{[N]}^2}} \quad (11)$$

在 16Mn 钢中钙的活度系数为

$$\begin{aligned} \lg f_{Ca} &= e_{Ca}^{Al} \times [\% Al] + e_{Ca}^C \times [C\%] + e_{Ca}^{Ca} \\ &\quad \times [\% Ca] + e_{Ca}^{Si} \times [\% Si] \\ &= (-0.072) \times 0.025 + (-0.34) \times 0.16 \\ &\quad + (-0.002) \times 0.004 \\ &\quad + (-0.097) \times 0.25 \\ &= -0.0805 \quad f_{Ca} = 0.83 \end{aligned}$$

将不同的 16Mn 喷钙后实际钙及氮含量乘以活度系数入后,代入(11)式,可得到  $Ca_3N_2$  的析出温度,如表 4 所示.通常钙处理后钢中含钙在 0.004% ~ 0.008% 之间,含氮在 0.005% ~ 0.009% 之间,相应的  $Ca_3N_2$  析出温度应在 1116 ~ 1186 范围.将上述两种氮化物析出条件作成图 10,由图可见  $Ca_3N_2$  将在比 AlN 高 100 左右的温度析出.较高温度下氮化物的析出,减少了固溶的氮含量,使钢继续冷却后的氮的过饱和度大大减少,从而改善了氮对低碳钢时效脆性的不良影响.

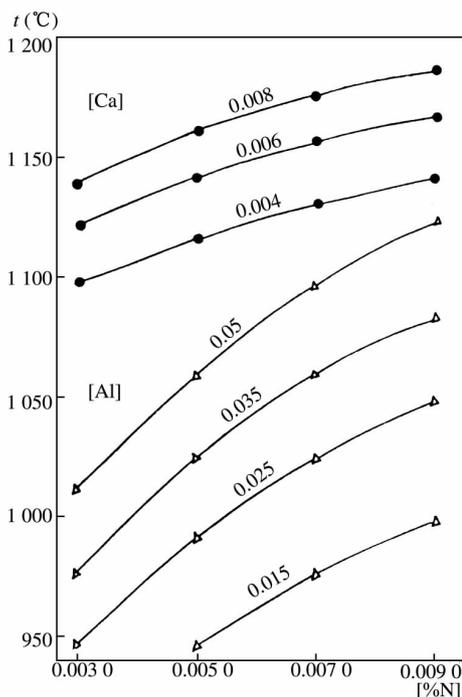


图 10 氮化钙及氮化铝的生成温度  
(曲线所列数字为 [Ca] 或 [Al] 的百分含量)

表 4 喷钙 16Mn 钢中氮化钙析出温度

[ % Ca ]	[ % N ]	Ca <sub>3</sub> N <sub>2</sub> 析出温度( )
0.004	0.003	1 096
	0.005	1 116
	0.007	1 130
	0.009	1 141
0.006	0.003	1 120
	0.005	1 141
	0.007	1 156
	0.009	1 167
0.008	0.003	1 138
	0.005	1 160
	0.007	1 175
	0.009	1 186

## 5.2 喷钙 16Mn 钢中实际氮化物形貌的检验

采用 IMS-300 离子探针检查钢中显微氮化物夹杂物时,观察到了氮化钙夹杂物存在,其离子像如图 11 所示,直接证实了上述热力学分析的可靠性。但是当增氮量过高,如 4<sup>#</sup> 钢板达到 97 ppm 时,由于钢中溶解钙数量的限制,不可能结合析出所有的氮,其基体中固溶的氮含量仍偏高,在人工时效时其析出显著,而原先以弥散分布析出的较多的氮化物,随温度之升高及保持时间的延长,也会出现一定的集聚,从而使  $a_k$  值下降。

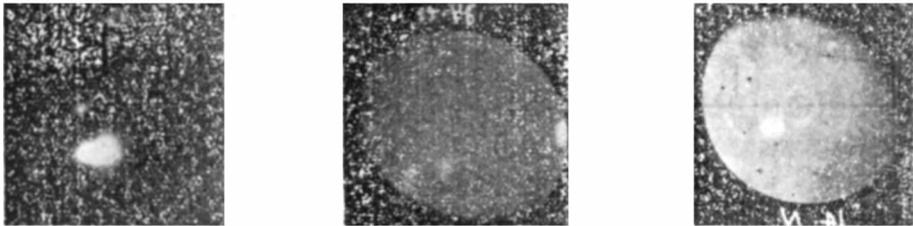


图 11 离子探针测得元素富集离子像 120 ×

上述看法在断口俄歇能谱测试的谱线图上得到证实,见图 12、13 及 14。图 12 是同一试样四个点的四组谱线都出现了 [S] 峰和 [N] 峰,两组有 [Ca] 峰,而两组则不出现钙峰。由此可见,该试样中的钙主要以硫化钙及氮化钙形式存在,而不固溶于基体中。

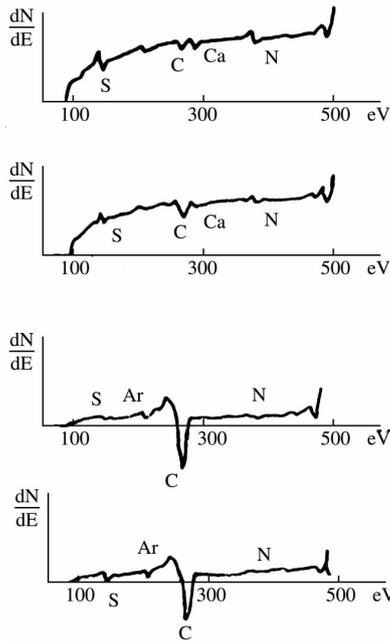


图 12 平炉喷钙处理 16Mn 钢断口 AES 谱线图

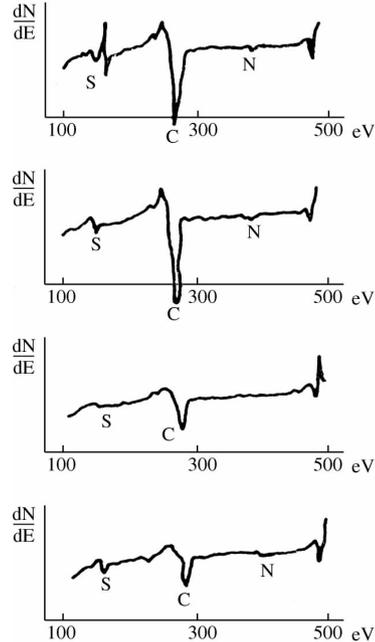


图 13 平炉未经钙处理 16Mn 钢断口 AES 谱线图

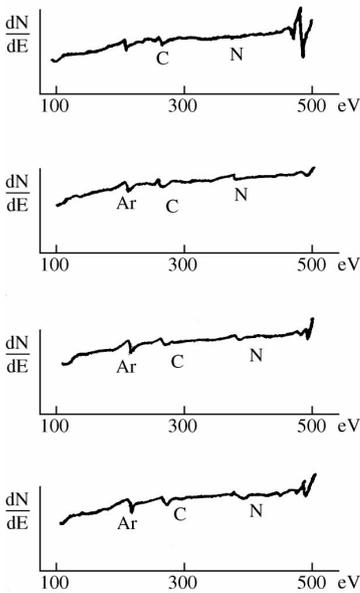


图 14 平炉喷钙处理 16Mn 钢 200 时效后断口 AES 谱线图

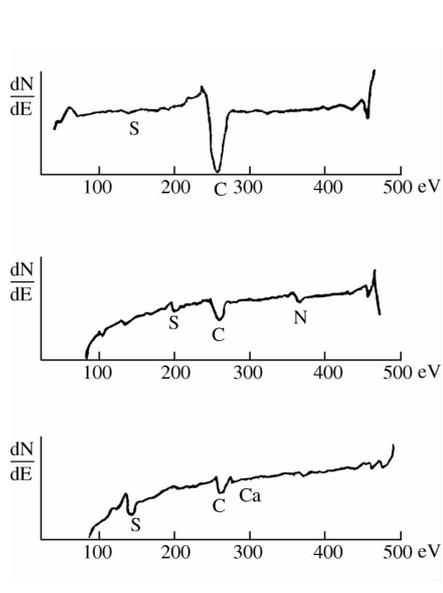


图 15 平炉喷钙处理 16Mn 钢 550 时效后断口 AES 谱线图

图 13、14 及 15 的俄歇能谱谱线,说明了氮化物弥散析出温度与钙处理的关系.图 13 为未经钙处理的平炉 16Mn 钢钢板(1<sup>#</sup>试样)AES 谱线.在四组谱线中,前两组为未时效的钢板断口,都出现了[N]峰,说明此时氮主要以固溶形式存在于基体中.后两组为经 200 时效的断口,一组有[N]峰,而另一组则不出现[N]峰,表明未经钙处理的 16Mn 钢,虽然氮含量较低(58 ppm),在 200 时效后,已有部分固溶的氮呈氮化物析出,这与前述氮对时效敏感性试验的数据,互为印证.

图 14 为喷钙处理的平炉 16Mn 钢,经 200 时效后,四组谱线均有[N]峰出现,表明此时氮仍固溶于基体中.这种情况一直维持到 550 时,才有部分氮化物析出(见图 15 的三组 AES 谱线图).说明喷钙后的 16Mn 钢时效推迟到了较高的温度.

## 6 结论

(1) 16Mn 钢经钢包喷吹 Ca-Si 粉处理后,增氮量在一定限度内(最终含氮量小于 97 ppm),未发现其对常规机械性能及屈强比有明显影响.

(2) 16Mn 钢机械性能的各向异性,主要反应在冲击值上.通过喷钙处理后其冲击值各向异性有非常显著的改善.

(3) 16Mn 钢喷钙处理后,尽管氮含量较高,但其时效敏感性反而比不喷钙的、氮含量较低的钢小.后者在 100 以上时效处理,就因弥散析出而引起  $a_k$  值的显著下降(约达 50%).喷钙 16Mn 钢的时效敏感温度区推迟到 300 ~ 400 ,且其  $a_k$  的绝对值,均较对应温度下的、未经钙处理的钢高出 1 倍左右.

(4) 喷钙处理的 16Mn 钢,含氮量在 < 97 ppm 时,其脆性转折温度都在 - 13 ~ - 26 之间.氮含量的波动对其脆性转折温度影响不大.

(5) 对于喷钙处理后,氮含量增加未引起冲击韧性值及时效敏感性明显变坏的机理,进行了讨论.热力学计算表明,当钢中存在一定数量钙时,可在较高温度下析出点状氮化钙夹杂,使固溶于基体中的氮含量相对减少,从而减轻了氮对冲击韧性及时效敏感性的不良作用.钙处理钢中生成  $Ca_3N_2$  夹杂物的理论分析,在实物离子探针图像及俄歇能谱谱线图上得到了直接的证实.

## 参考文献

- [ 1 ] 顾洪涛：硕士学位论文，上海工业大学，1984
- [ 2 ] 上钢三厂熊宗禹等：电炉钢包喷射冶金新工艺的应用. 特殊钢，1984 年增刊
- [ 3 ] 北京钢铁研究总院：合金钢手册，上册第一分册
- [ 4 ] Darken ,L. S. et al. :J. Metal ,1951 ,Vol. 3 ,p. 1174
- [ 5 ] B. B. 阿维林：金属中的氮，冶金工业出版社，1983 p. 9
- [ 6 ] 魏寿昆编著：冶金过程热力学，上海科技出版社，1980 p. 16

# 向铁水喷吹 CaO 系粉剂的 脱硫动力学研究<sup>\* 1</sup>

## 1 概述

近年来,铁水预处理已成为钢铁生产的一个重要环节,其原因在于使高炉、转炉高效操作及节省能源、材料消耗.同时也是由于工业部门已对钢材质量提出了更高的要求,其中铁水脱硫预处理得到了最广泛的应用.在处理方法上则主要有搅拌法及喷吹法两大类,后者因设备简单、效果稳定而被更多的钢铁厂所采用.

目前各国采用的主要铁水预处理脱硫喷吹粉剂见表 1.

表 1 各国铁水炉外喷粉脱硫简况

铁水脱硫粉剂种类	喷入量 kg/t 铁水	脱硫率 $\Delta[S]/[S]$	国名
CaC <sub>2</sub> 100%	3 ~ 4	85% ~ 90%	美国 <sup>[1]</sup>
CaC <sub>2</sub> + CaO 2%	4 ~ 5	80% ~ 85%	联邦德国
CaC <sub>2</sub> + CaCO <sub>3</sub> + C 56% + 29% + 15%	5 ~ 7	70% ~ 85%	日本 <sup>[2]</sup>
CaO + CaF <sub>2</sub> + CaCO <sub>3</sub> + C 55% + 5% + 25% + 15%	8 ~ 10	70%	日本 <sup>[3]</sup>

\* 本文合作者:干勇.原发表于《第二届全国炼钢理论冶金反应动力学学术讨论会论文集》,重庆,136 ~ 150(1982)

(续 表)

铁水脱硫粉剂种类	喷入量 kg/t 铁水	脱硫率 $\Delta[S]/[S]$	国 名
CaO + Al 5%	6 ~ 7	80%	日 本 <sup>[4]</sup>
CaO + Mg 98.5% + 1.5%	5 ~ 7	80%	美 国 <sup>[5]</sup>
CaO + Mg(1 ~ 2) (CaCN + Al)	5 ~ 7 4 ~ 6	80%	英 国
CaCl <sub>2</sub> + CaO 70% + 30%		70%	日 本 <sup>[6]</sup>

喷吹法中最初得到稳定应用的是 CaC<sub>2</sub> 粉剂,但由于 CaC<sub>2</sub> 生产过程能耗高及贮运、保管中的困难,增加了其操作成本,故近年来对 CaO 系脱硫剂的研究逐步增多。CaO 脱硫剂从热力学来看具有极高的脱硫潜力,如当铁水成分为 4% C、0.8% Mn、0.7% Si 及 1 300 ~ 1 350 ℃ 时,与固体 CaO 相平衡的铁水中 [S] 应  $\leq 0.001\%$ 。但是由于存在某些动力障碍,采用 CaO 系脱硫粉剂时,一般脱硫率为 30% ~ 50%,CaO 利用率  $\leq 5\%$ ,故难以在生产上稳定使用。为此各国研究工作者相对对 CaO 系脱硫过程的动力学进行研究,同时在工艺方法上采用各种添加剂、助剂,来提高其脱硫效率与 CaO 利用率。

上海工业大学与宝山钢铁厂合作研制了本质上属于 CaO 系的 CCCA 脱硫剂,并取得良好脱硫效果,见表 2 及图 1。

表 2 CCCA 与各种脱硫剂效果比较

粉剂类别	炉数	粉 剂 配 方	铁水平均温降( )	粉剂吹入量 (kg/t 铁水)	CaO 平均利用率(%)	脱硫率平均 $\Delta[S]/[S]\%$
		CaO		10	2.6	38
		CaC <sub>2</sub> <sup>[3]</sup> (100%)		3 ~ 4	32.0	80 ~ 90
II	2	CaO + CaF <sub>2</sub> + CaCO <sub>3</sub> + C + Al	30	10	13.0	70
III	3	CaO + CaF <sub>2</sub> + Al	45	10	13.0	80
IV	2	CaO + C + CaF <sub>2</sub> + CaCO <sub>3</sub>	45	10	12.0	65
V	1	Al <sub>2</sub> O <sub>3</sub> + CaO(机械混合)	55	15	3.5	30
VI	1	Al <sub>2</sub> O <sub>3</sub> + CaO(预熔)	50	15.0	6.0	78
CCCA	16		50	10.0	17.0	75 ~ 90

本研究采用脱硫粉剂压块浸泡法,研究铁水中硫向CaO系脱硫相扩散机构及脱硫的速率现象,从而阐明CCCA脱硫剂中各组元的作用及其最佳配比.

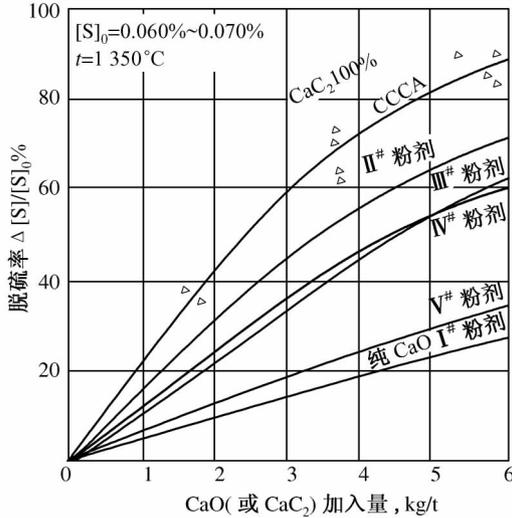


图1 CaO加入量与脱硫率的关系

## 2 试验方法及主要结果

### 2.1 浸泡试验

将250~400目的CaO、CaF<sub>2</sub>粉,分别以90/10和95/5的比例拌匀,也有个别粉剂中配入6%的铝粉,然后在压力机上压成 $\phi 18 \times 30$ 的圆柱形浸泡压块,并在马弗炉内烧结固化.试验时将它们分别浸入含铝及不含铝的铁水中,受泡时间及铁水成分见表3,试验过程示意图见图2.浸泡开始前除尽铁水面浮渣,并调节功率使铁水温度保持恒定.

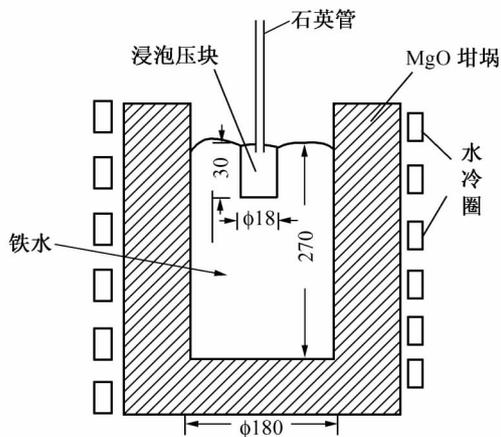


图2 浸泡试验示意图

表3 CCCA 粉炉压块浸泡时间

铁水成分(%)				浸泡压块		浸泡时间(分)				
S	Si	C	Al	CaO	CaF <sub>2</sub>	1	3	5	8	15
0.112	0.64		0.05	90%	10%	1	3	5	8	15
0.086	0.76	3.74	0	90%	10%	1	3	5	8	15
0.112	0.64		0.05	95%	5%	1	3	5	8	15
0.086	0.76	3.74	0	95%	5%	1	3	5	8	15

将不同浸泡时间的试块取出后 清除表面粘结物 并在  $\frac{1}{2}$  高度处切取横截面

试片 然后在上海硅酸盐研究所磨制成光片和超薄片. 其中部分试片作岩相观察, 分析其物相. 其余大部分试片表面真空喷镀 200~350A 的碳膜, 然后作电子探针分析, 以确定试块表面脱硫反应层的组成. 脱硫层生产速度及硫在 CaO—CaF<sub>2</sub> 试块中的传质行为 即经由电子束微区分析仪(EPMA)作 K<sub>α</sub> 线、面扫描, 及定量、定性分析元素在试块表面及内层的分布, 从而阐明 CaO 系脱硫粉剂与铁水间硫转移的动力学.

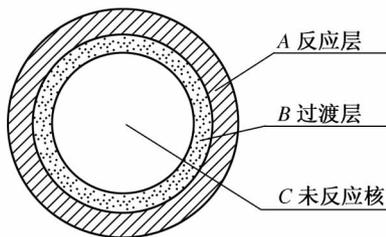


图3 浸泡块的断面模式图

## 2.2 岩相鉴定结果

切开后的浸泡块横断面的基本模式为: 最外层为反应层(A), 中间为过渡层(B), 中心部分为未反应核(C). 其各层厚度及主要物相组成, 则因铁液组成及浸泡时间而异. 根据岩相鉴定, 如表4及图4所示.

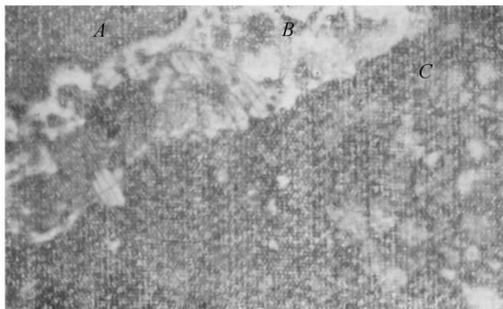
表4 浸泡块横断面的岩相鉴定结果(浸泡8分钟)

部 位	95% CaO + 5% CaF <sub>2</sub>	89% CaO + 5% CaF <sub>2</sub> + 6% Al
宽度 μ	140 ~ 280 (多数为 200)	300 ~ 800
A 物相组成	主要物相: <ul style="list-style-type: none"> <li>CaO · Fe<sub>2</sub>O<sub>3</sub> 2CaO · Fe<sub>2</sub>O<sub>3</sub> 40% ~ 50%</li> <li>3CaO · 2SiO<sub>2</sub> 2CaO · SiO<sub>2</sub> 35% ~ 40%</li> <li>Fe<sub>3</sub>O<sub>4</sub> 1% ~ 2%</li> <li>Fe 3% ~ 5%</li> </ul> 分散相: CaS 3CaO · 2SiO <sub>2</sub> , CaF <sub>2</sub>	主要物相: <ul style="list-style-type: none"> <li>4CaO · Fe<sub>2</sub>O<sub>3</sub> · Al<sub>2</sub>O<sub>3</sub> 40% ~ 50%</li> <li>2CaO · Al<sub>2</sub>O<sub>3</sub> · SiO<sub>2</sub> 30% ~ 35%</li> <li>3CaO · SiO<sub>2</sub> α-2CaO · SiO<sub>2</sub> 10% ~ 15%</li> <li>Fe<sub>3</sub>O<sub>4</sub> Fe 2% ~ 5%</li> </ul> 分散相: CaS

(续 表)

部 位		95% CaO + 5% CaF <sub>2</sub>	89% CaO + 5% CaF <sub>2</sub> + 6% Al
B	宽度 $\mu$	100 ~ 350	300 ~ 500(分别达 1 000)
	物相组成	主要物相: 充填在 CaO 晶粒间隙中的 CaO · Fe <sub>2</sub> O <sub>3</sub> 分散相: 极少量 CaS	主要物相: 充填在 CaO 晶粒间隙的 CaO · Fe <sub>2</sub> O <sub>3</sub> · Al <sub>2</sub> O <sub>3</sub> · 2CaO · Al <sub>2</sub> O <sub>3</sub> · SiO <sub>2</sub> (约 10% ~ 20%) 分散相: 少量 CaS
C	宽度 $\mu$	从 B 层内至中心	从 B 层内至中心
	物相组成	CaO, CaF <sub>2</sub>	CaO 85% ~ 90% CaF <sub>2</sub> , 11CaO · 7Al <sub>2</sub> O <sub>3</sub> · CaF <sub>2</sub> 5% ~ 10%

由浸泡块的岩相分析可知, 脱硫主要是在反应层进行, 而含硫的浸泡块反应层厚度 要比不含 Al 的增加 2 倍, 这和它形成了熔点低、硫容量大的铁铝酸四钙及黄长石( $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ )有关. 相反在不含铝时, 主要物相中有近一半的硅钙石( $3\text{CaO} \cdot 2\text{SiO}_2$ )及  $\alpha'$ -正硅酸钙( $2\text{CaO} \cdot \text{SiO}_2$ ), 它们的熔点高, 致密, 对于硫的传质有限制作用.



(a) 不含铝浸泡块中的物相结构: A 反应层; B 过渡层; C 未反应核(反射光  $100 \times$ );



(b) 含铝浸泡块中的物相结构: A 反应层; B 过渡层; C 未反应核(单偏光  $100 \times$ );

图 4 浸泡块横断面的岩相图片

### 2.3 电子探针(EPMA)分析结果

铁液中含铝及不含铝时, 浸泡试样的  $K_{\alpha}$  面扫描结果见图 5. 由图片可明显看出, 浸入不含铝铁水的浸泡块, 表面层富集有 Si、Ca, 但 S 很少. 而浸入含铝铁水的试块, 表面富集有 Al、Ca, 且有一定量的硫.

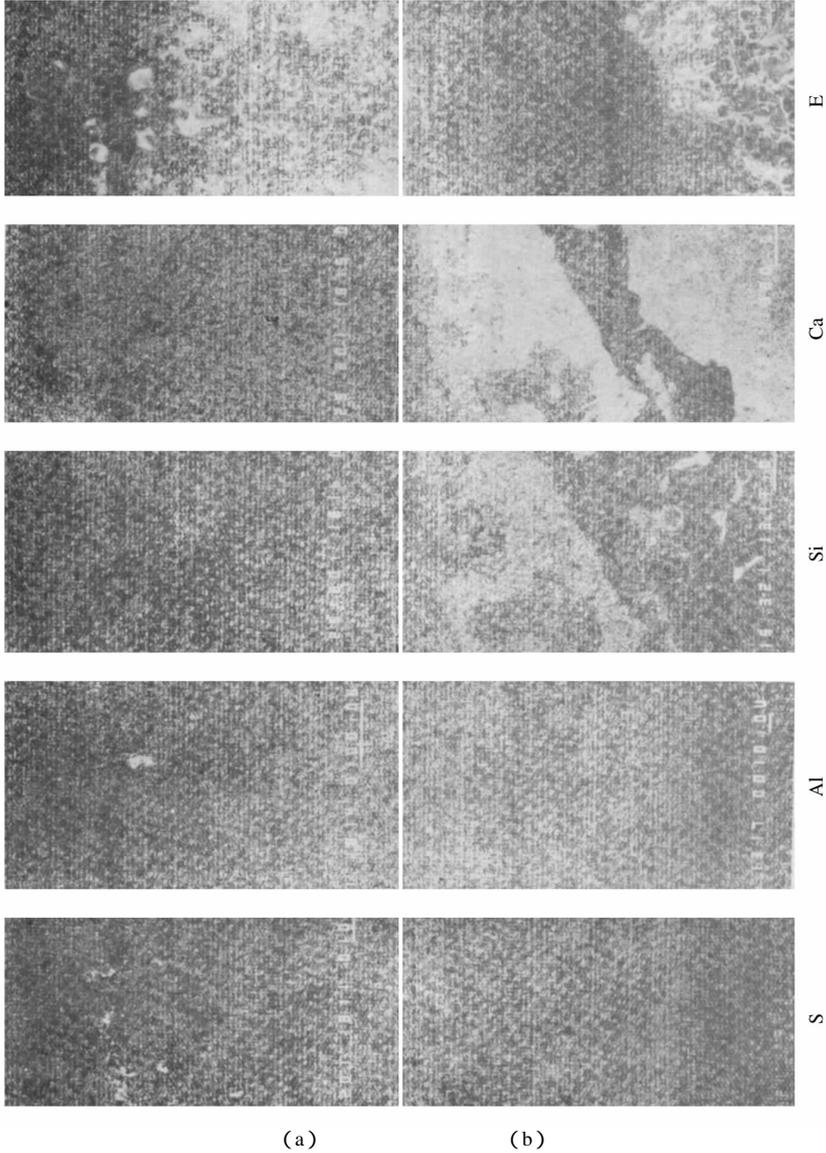


图 5 铁液含铝和不含铝浸块表面生成物比较(EPMA  $K_{\alpha}$  面扫描)

(a) 加 Al 0.05% ; (b) 不加 Al

从图 5 的  $K_{\alpha}$  线扫描,可清楚地看到 硫的扩散因硅钙石及硅酸钙的生成而受阻.

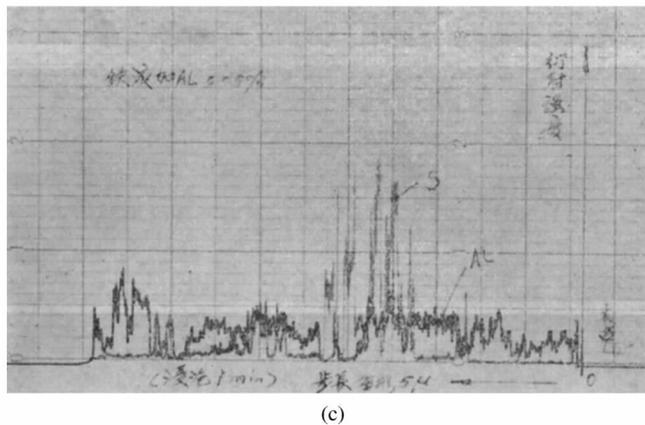
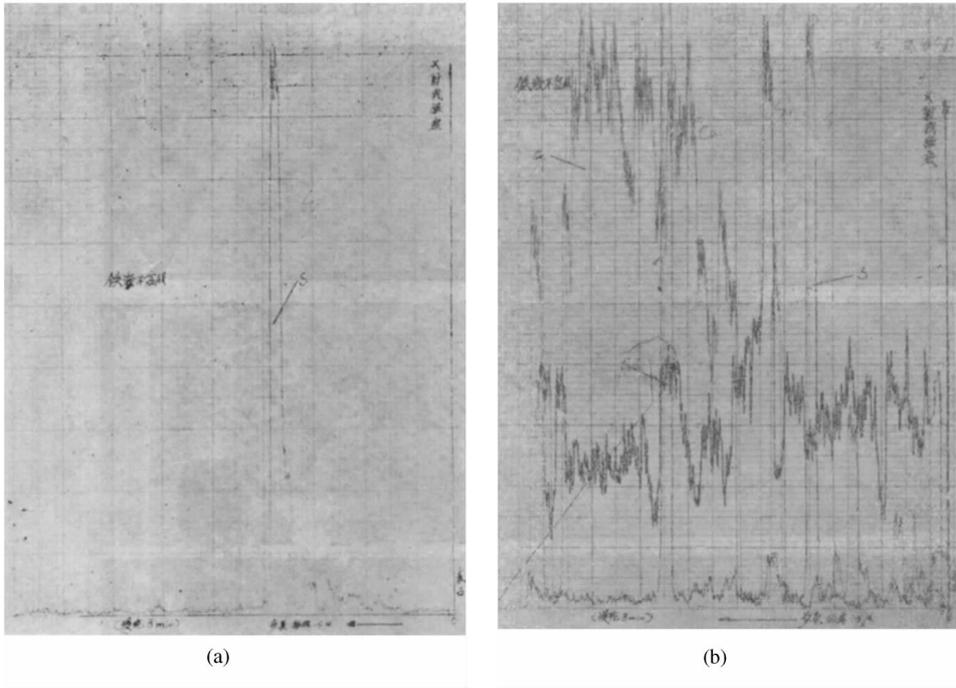


图 6 铁液含铝及不含铝时浸块由表面向中心的元素分布(EP-MA  $K_{\alpha}$  线扫描,铁液含硫 [% S] = 0.086%)

(a) 硅酸钙层阻挡硫扩散的情形: 只作 S 的扫描;(b) 硅酸钙层阻挡硫扩散的情形: S、Si、Ca 同时扫描;(c) 硅酸钙被抑制后硫一分钟扩散层厚度 ([% S] = 0.086)

对各种不同的浸泡时间的试块上切片,采用  $K_a$  线扫描法求其平均脱硫生成物厚度,发现它与时间的  $2/3$  次方成正比,见图 7。

$$\delta = K' \tau_v^{2/3} \quad (1)$$

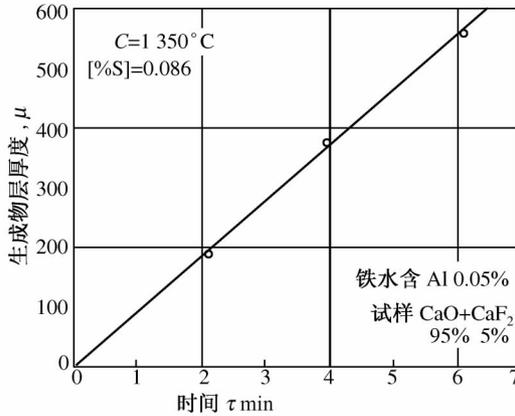


图 7 脱硫生成物厚度与浸泡时间的关系

式中  $\tau_v$  为浸泡时间, min;  $\delta$  为脱硫生成物厚度,  $\mu$ ;  $K'$  为生成速度常数, 它取决于铁液及浸泡块成分, 以及铁水温度. 在 1350 °C 铁液含铝 0.05%,  $[S] = 0.086\%$ , 浸泡块组成为 95% CaO + 5% CaF<sub>2</sub> 时,  $K' = 92.5$ . 而不含铝时,  $K' = 71.4$ . 浸泡块含有 10% CaF<sub>2</sub> 时,  $K'$  显著提高为 175. 这在二次电子象及面扫描的对照图中可清楚地看到, 是由于硫向浸泡块内的扩散, 沿着 CaO<sub>2</sub>CaF<sub>2</sub> 共晶相进行的.

### 3 讨论

喷吹 CCCA 系脱硫剂使铁水脱硫的反应, 属于固液反应. 其反应机构为:

- (1) CaCO<sub>3</sub> 粒子分解成 CaO 粒子;
- (2) 铁液中硫通过液体侧边界层扩散到 CaO 粒子表面;
- (3) 在 CaO-铁液界面上发生脱硫的化学反应;
- (4) 脱硫生成物在固体石灰中的扩散;
- (5) 反应生成的 O<sup>2-</sup> 向铁液中扩散.

高温下的化学反应速度很快, 不可能是限制性环节. 反应生成的 O<sup>2-</sup> 由于是在生铁液中, 将很快因与  $[C]$ 、 $[Si]$ 、 $[Al]$  等组元作用而消耗, 也不会成为反应的障碍, 故仅对 (1)、(2)、(4) 三个步骤进行讨论.

### 3.1 喷吹入铁液的 CaCO<sub>3</sub> 分解速度

高温下 CaCO<sub>3</sub> 分解反应速度很快,而限制性环节是粉粒中热的传输速度.由热传导方程的球坐标表达式可知:

$$\frac{\partial \Delta U}{\partial \tau} = \frac{D}{r} \cdot \frac{a^2 (r \Delta U)}{ar^2} \quad (2)$$

式中:  $\Delta U$  - 温差, ;  $D$  - 粉粒热扩散系数, mm<sup>2</sup>/s ;  $r$  - 球坐标 ;  $a$  - 粒子半径, mm ;  $\tau$  - 时间, s ;

并设  $t_M$  - 铁水温度 ;  $t_p^0$  - 粉粒初始温度, ;  $t_p^c$  - 粉粒中心被加热后的温度. 且知  $\Delta U_{\tau \rightarrow 0, r \rightarrow c} = t_M - t_p^0 = \Delta U_0$ , 而  $\Delta U_{\tau \rightarrow 0, r \rightarrow a} = 0$ , 则解方程(2)可得

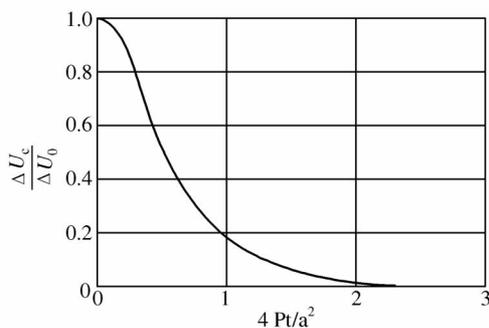
$$\frac{\Delta U}{\Delta U_0} = \frac{2}{\pi} \frac{\alpha}{\gamma} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \exp\left(-\frac{n^2 \pi^2 D \tau}{a^2}\right) \sin \frac{n \pi \gamma}{a}$$

设  $\gamma \rightarrow 0$ , 铁液与粉粒中心温差为  $\Delta U_c = t_M - t_p^c$ , 即可求得

$$\begin{aligned} \frac{\Delta U_c}{\Delta U_0} &= \lim_{\gamma \rightarrow 0} \frac{\Delta U}{\Delta U_0} = 2 \sum_{n=1}^{\infty} (-1)^{n+1} \exp\left(-\frac{n^2 \pi^2}{4} \cdot \frac{4D\tau}{a^2}\right) \\ &= f\left(\frac{4D\tau}{a^2}\right) \end{aligned} \quad (3)$$

将热扩散过程温度变化与  $\frac{4D\tau}{a^2}$  的关系作图,如图 8 所示.

CaCO<sub>3</sub> 在 900 分解,故设  $t_p^c = 900$  ;  $t_p^0 = 20$  ;  $t_M = 1350$  则  $\frac{\Delta U_c}{\Delta U_0} =$



$$\frac{t_M - t_p^c}{t_M - t_p^0} = 0.338.$$

查图 8 得

$$\frac{4D\tau}{a^2} = 0.89 \quad (4)$$

这里

$$D = \frac{K}{C_p \cdot \rho_p} \quad (5)$$

图 8 热扩散过程中的温度变化(方程式 3 的图解) 其中,  $K$  为导热率, W/(m · K) ;  $\rho_p$

为粉粒密度  $\text{kg/m}^3$  ;  $C_p$  为粉粒比热  $\text{kcal/kg} \cdot ^\circ\text{C}$  .

对于  $\text{CaCO}_3$  粉粒而言<sup>[8]</sup> ,  $K = 1.26 \sim 1.33 \text{ W}/(\text{m} \cdot \text{K})$  ,  $\rho_p = 2500 \text{ kg}/\text{m}^3$  ,  $C_p = 0.90 \text{ kcal}/\text{kg} \cdot ^\circ\text{C}$  . 则得  $D = 0.5 \text{ mm}^2/\text{s}$  . 如粉粒直径为  $d$  (mm) 代入(4)式可得  $\text{CaCO}_3$  传热所需时间为

$$\tau = 0.89a^2/4D = 0.098d^2 \quad (6)$$

不同粒度时  $\text{CaCO}_3$  粉粒在铁水中加热达到分解温度所需时间 ,可由图 9 及表 5 所示. 它实质上也就是  $\text{CaCO}_3$  的分解时间.

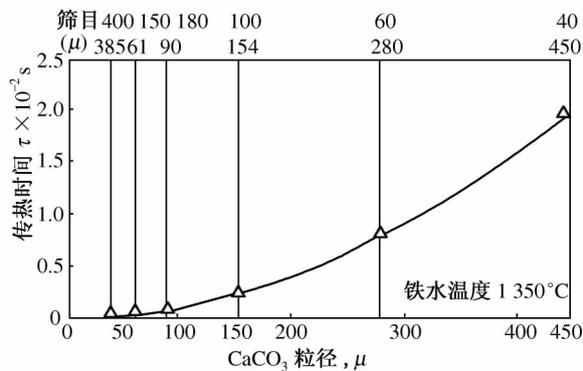


图 9  $\text{CaCO}_3$  粒子在铁液(1350 )中达到分解温度所需时间与粒度的关系

表 5  $\text{CaCO}_3$  在铁液中(1350 )的分解时间

筛 目	20 目	40 目	100 目	180 目	250 目	400 目
粒径 $d$ , mm	0.9	0.45	0.154	0.09	0.061	0.038 5
分解时间 $\tau$ , s	0.08	0.02	0.002 3	0.000 8	0.000 4	0.000 15

由此可见 如果  $\text{CaCO}_3$  粒径小于 1 mm 则所需分解时间  $< 0.1 \text{ s}$  相对于粉粒在铁水中的逗留时间来说 ,是极短的. 因此它不可能是喷粉脱硫的限制性环节.

### 3.2 喷吹 CCCA 脱硫剂时的速度表达式

关于喷吹  $\text{CaO}$  系脱硫剂时 ,反应的限制性环节存在不同的看法. Oeters 等<sup>[9]</sup>认为 1300 下 ,铁水含硫  $< 0.040\%$  时 ,石灰粒子在铁水中逗留时间内形成的反应层比较薄 ,这时硫通过铁水侧液体边界层的扩散 ,是反应的限制性环节. 脱硫速度可由下式表示 :

$$\frac{d[\% S]_c}{dt} = - K[S]_c \quad (7)$$

式中 K 是表观速度常数。

$$K = \frac{3B}{\bar{r}} \cdot \frac{\rho_{Fe}}{\rho_{CaO}} \cdot \frac{D_s}{\delta} \cdot t_v \quad (8)$$

其中 B 为喷吹速度  $\text{kg CaO/t} \cdot \text{min}$ 。  $\rho_{Fe}$ 、 $\rho_{CaO}$  分别为铁水及 CaO 的密度  $\bar{r}$  是石灰的平均半径  $D_s$  是铁水中硫的扩散系数  $\delta$  是边界层厚度  $t_v$  是石灰粒子在铁水中的逗留时间。

在铁水含硫高时,石灰粒子在铁水中逗留时含形成一层较厚的反应层,而硫通过反应层的扩散将成为限制环节,川合<sup>[10]</sup>等由此认为固相传质是限制性环节,并由此导出脱硫速度表达式为

$$\frac{d[\% S]_t}{dt} = - 300 \frac{\beta}{\bar{r}} \cdot \frac{C_s}{\rho_{CaO}} (2V_{CaS} \cdot t_v K_R)^{1/2} \quad (9)$$

式中  $C_s$  是 CaS 中的含硫量,  $V_{CaS}$  是 CaS 的 mol 体积,  $K_R$  是反应层长大的表观速度常数。

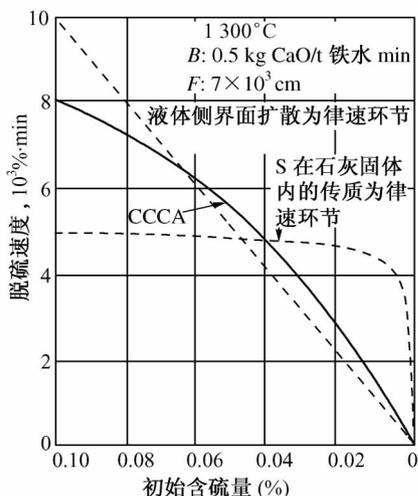


图 10 脱硫速度与  $[\% S]$  的关系

综合以上两种观点作图(图 10),可知低硫区液体边界层扩散是限制环节,此时脱硫速度与硫含量呈直线关系。而高硫量时,由于固相扩散是限制环节,脱硫速度与硫含量的  $1/2$  次方成正比,且实验点与此理论计算曲线基本吻合。

关于喷吹 CCCA 脱硫剂的脱硫速度公式,可推导如下:

如设在喷吹脱硫过程中,铁液内悬浮的氧化钙粒子数  $n$  为定值,则

$$n = \frac{\dot{W}_{CaO}}{4/3 \cdot \pi \bar{r}^3 \cdot \rho_{CaO}} \cdot \tau_v \quad (10)$$

式中  $\dot{W}_{CaO}$  为每分钟喷入的 CaO 量  $\rho_{CaO}$  为 CaO 密度。

以  $j_t$  表示每分钟每颗 CaO 结合的硫含量,则瞬时脱硫速度为

$$\frac{d[\% S]}{dt} = 100 \cdot n \cdot j_t / W_{Fe} \quad (11)$$

将(10)式代入(11)式可得

$$\frac{d[\% S]}{dt} = j_t \cdot \tau_v \cdot \frac{100 \dot{W}_{CaO}}{W_{Fe} \cdot 4/3 \cdot \pi \cdot r^3 \cdot \rho_{CaO}} \quad (12)$$

每个粉粒在铁液中整个逗留时间内,所吸收的硫为

$$\int_0^{\tau} j_t dt = \bar{j}_t \cdot \tau = -4\pi r^2 \cdot C_s^* \delta_{\tau} \quad (13)$$

式中  $\delta_{\tau}$  为逗留时间形成的反应层厚度, cm.  $C_s^*$  为脱硫生成物层中硫的浓度.

从(1)式可得

$$\bar{j}_t \cdot \tau = -4\pi r^2 C_s^* K \tau_v^{2/3} \quad (14)$$

将(14)式代入(12)式可得

$$\frac{d[\% S]}{dt} = \frac{300 \dot{W}_{CaO} \cdot C_s^*}{W_{Fe} \cdot r \rho_{CaO}} \cdot \tau_v^{2/3} \cdot K \quad (15)$$

式(15)即为喷吹 CCCA 粉剂时的脱硫速度表达式,如制成图线,则固相与液相侧传质在限制环节之间(见图 10). 它可使固相侧控制速度的转化硫含量范围由 0.07% ~ 0.08% 降至 0.05% 以下. 造成 CCCA 粉剂这种特点的原因,在于表层生成的  $CaO-Al_2O_3-CaF_2-Fe_2O_3$  及  $CaS$  的低熔点反应层. 曾将浸泡块表面反应层刮下来的粉末压成小块,测定其熔点为 1340 ~ 1375, 故它在铁水温度下应属于半熔融状态,正好介于液相与固相传质之间.

### 3.3 较好的脱硫剂组成

#### 3.3.1 $CaCO_3$ 含量

采用  $CaCO_3$  取代  $CaO$  可明显改善粉剂流动性,见图 11. 采用  $CaCO_3$  的另一作用是在其分解时产生气体,使  $Ar$  气气泡炸裂,粉体进入铁液,且此时生成的为多孔、活性  $CaO$ . 由于这两个原因,在 CCCA 粉剂中提高  $CaCO_3$  与  $CaO$  的比率,有助于改善  $CaO$  利用率,如图 12 所示. 但过分提高此比率,而 C 粉用量一定时,还原气氛将无法保持,势必导致氧化钙利用率的下降,如图 10 虚线所示. 同时在工艺上也还要考虑大量吹入  $CaCO_3$  引起的温降与喷溅问题.

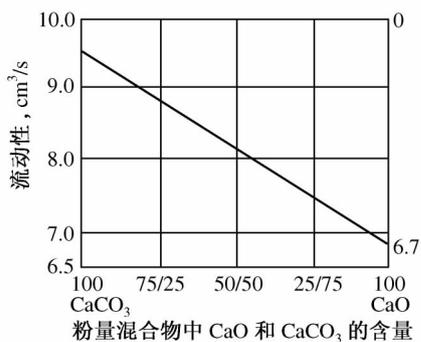


图 11 CaO + CaCO<sub>3</sub> 粉剂流动性  
(0.15 ~ 0.25 mm)

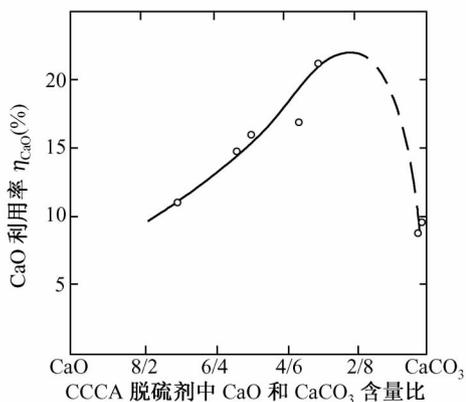


图 12 CaO/CaCO<sub>3</sub> 与  
 $\eta_{CaO}$  的关系

### 3.3.2 碳粉配入量

由于较大量 CaCO<sub>3</sub> 的使用,它释放出大量 CO<sub>2</sub> 气体,故还原气氛的控制极为重要.若按理论计算,50% CaCO<sub>3</sub> 时,相应碳粉配入量应为 6%,但实际试验表明,碳粉配入量应为 15% 左右,方能保证喷吹过程铁水含碳量基本不变,而脱硫率达到 75% ~ 90%,见图 13.这显然是由于 C 粉因密度、粒度、表面张力等不同,难以在粉气流股中与 CaCO<sub>3</sub> 同时作用有关,而高温下碳粉的烧损也比较大.

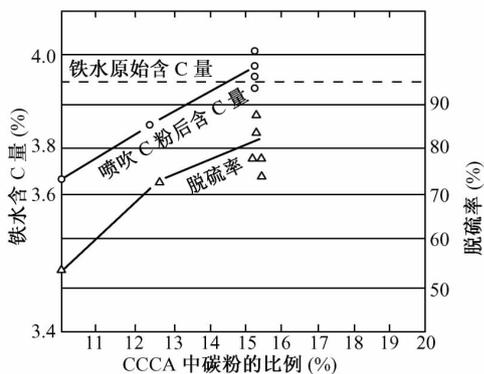


图 13 CCCA 中碳粉比例的影响

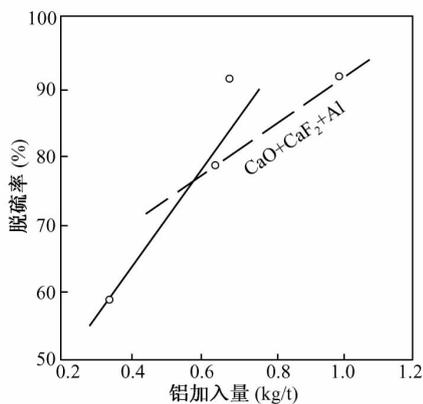


图 14 加铝量对  $\eta_s$  的影响

### 3.3.3 活性剂铝的作用

鉴于前述铝在 CaO 系脱硫中的作用, 试验了不同加铝量对 CCCA 脱硫剂及 CaO—CaF<sub>2</sub> 脱硫剂脱硫率的影响, 见图 14. 此外, 对铁水中残留 [% Al] 与初始的 [% Si] 之比对脱硫率的影响进行分析, 发现当此比值 > 0.05 时,  $\eta_s$  可达到 60% 以上. 随着 [% Al]/[% Si] 值的提高,  $\eta_s$  作线性变化, 见图 15. 当铁水初始含硅量为 0.5% ~ 0.8% 时, 为使  $\eta_s = 75\% \sim 90\%$ , 加铝量应为:

$$A_{\text{add}} \% = (0.01 \sim 0.03)[\% \text{ Si}]_0 + (0.4 \sim 1.2)\Delta[\% \text{ S}] \quad (16)$$

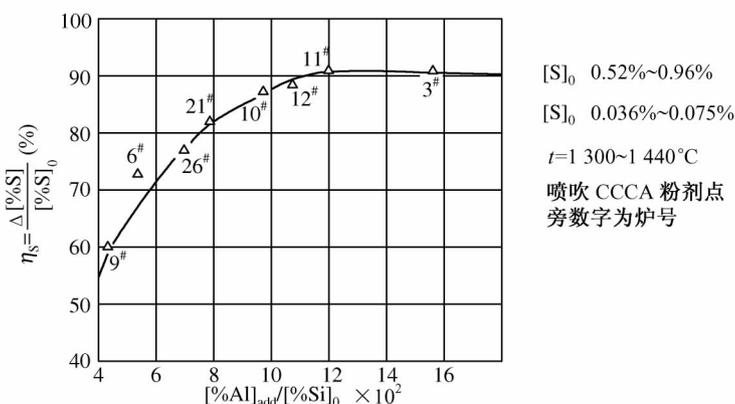


图 15 铁水中 [Al]<sub>add</sub> 与 [% Si]<sub>0</sub> 之比对  $\eta_s$  的影响

## 4 结论

(1) 借助于电子探针微区分析法及岩相分析法, 证实了喷吹 CaO 基脱硫粉剂时, 脱硫速度的限制环节因硫含量而不同, 高硫时是硫在固相中的传质, 低硫时是硫在液体边界层的扩散.

(2) 改善 CaO 基脱硫动力学条件的途径, 在于利用 CaCO<sub>3</sub> 形成活性 CaO, 加入碳粉保持还原气氛, 采用助剂 CaF<sub>2</sub> 及活性剂 Al, 使之在 CaO 表面形成半熔融状态的、高硫容量的反应层, 从而打破固相传质的障碍, 并由 CO 气体搅拌粉剂与铁水界面, 加速液相边界层的扩散.

(3) 为了避免生成  $n\text{CaO} \cdot m\text{SiO}_2$ , 妨碍硫向粉剂的扩散, 加 Al 量与初始含硅量有定量比率关系.

## 参 考 文 献

- [ 1 ] Heastest ,H. P. et al. ,Operational aspects of the injection process for desulphurization of the hot metal Iron and steel Eng. 1975 :10
- [ 2 ] 山中启允门. 吹入式溶铁脱硫剂的开发《铁と钢》,1979 ,65(4) :79 - SIS2
- [ 3 ] 山田纯夫门. 生石灰脱硫剂的开发《铁と钢》,1979(4)
- [ 4 ] 满尾利晴门. 溶铁の生石灰脱硫におよぼす诸要因の影響《铁と钢》,1980 ,66 :80 - S225
- [ 5 ] Kandler et al. ,Desulphurization of an iron melt US 4139369 ,C21c -07/02
- [ 6 ] 井山博文门. 用 CaCl-CaO 熔剂使铁水同时脱磷、脱硫 Scaninject II ,1980
- [ 7 ] 徐匡迪 ,干勇 ,李炳源 ,包学新 ,达世全 ,丁山. CCCA 铁水预处理脱硫剂研究 ,1981 年中国金属学会炉外精炼学术年会论文
- [ 8 ] J. P. Holman. 《热传递学》杨春钦译 ,1966
- [ 9 ] Oeters F. Kiretik der Entsehuiefelung Von Koheisen Schmslzen mit Kalk und Erdgas. Arch Eison ,1973(10) :727
- [ 10 ] 川合保治. 固体石灰による溶铁の脱硫速度に関する基础的研究 ,《铁と钢》,1975 ,61 (1) :29 -35

# RH-IJ 钢包中的环流特性与搅拌效率<sup>\* 1</sup>

**摘要** 应用双相流理论发展了物理和数学模型,获得了 RH 装置中的钢液环流特性,以及几何结构因素对它的影响.发现了从 RH 下降管流出的液流发生周期性的摆动,而当水平移动至某一距离时,这种现象能被消除.此时,能得到最小的混合均匀时间,同时下降管液流的扩张角约为  $18^\circ$ .

进一步的水模拟试验表明,在 RH 钢包中喷吹气-粉时,喷枪有一个最佳的几何位置,对于 RH-IJ 装置中喷枪的最佳几何位置也作了测定,它与气泡流扩张角计算的结果相吻合.

## 1 前言

RH 真空循环脱气过程和喷粉工艺都是钢包冶金中有效的钢液精炼技术. RH 与喷吹若能以最佳方式组合可获得良好的冶金效果,即不仅可脱氢、脱氮,还可脱氧、脱硫.而这一切都在很大程度上取决于钢包中流体的流动状态.

本研究工作提供了 RH-IJ 钢包中的环流特性与混合搅拌效率.发展了一种双相流模型,以获得 RH 装置中钢液的环流速度,以及几何结构参数对它的影响.此计算结果已被水模拟实验及工业装置的实测值所证实.进一步的水模拟试验提供了喷粉枪在 RH 钢包中的最佳几何位置,大致为  $h = 0.80 \sim 0.90H$ ,而  $r = 0.72 \sim 0.86R$ (上升管一侧).

而对于 RH-IJ 联合装置而言,喷枪的最佳位置是  $h/H = 0.21 \sim 0.23$ (上

\* 本文合作者:樊养颐、李维平.原发表于《特殊钢》(5) 30~37(1982)

升管以下). 这一点与气泡流股的扩张角计算相符合.

## 2 RH 装置中的环流速度计算

RH 装置中的环流速度对于获得良好的冶金效果是一个最重要的因素. 这一点已被许多研究者所证实<sup>[1,2]</sup>, 它取决于提升气吹入量、吹气深度、上升管与下降管的直径等.

在 RH 装置中, 循环流动的驱动力是上升管中吹入的气体. 如果把通过上升管—真空室—下降管的钢液循环流动看作是一维流动, 那么在这种情况下, 其一维流动方程可给出如下:

$$\Delta P_F = \Delta P_f + \Delta P_a + \Delta P_g = \Delta P_T \quad (1)$$

这里  $\Delta P_F$  是吹入的提升气气泡浮力所产生的压差 ( $N/m^2$ )  $\Delta P_f$  是摩擦压力损失 ( $N/m^2$ )  $\Delta P_a$  是流体加速压力损失 ( $N/m^2$ )  $\Delta P_g$  是重力压力损失 ( $N/m^2$ )  $\Delta P_T$  是总的压力损失 ( $N/m^2$ ).

RH 装置的环流特性可描述为

$$G_L = f \left[ Q_{gr} \cdot D_U \cdot D_d \left( = \frac{D_U^2}{D_d^2} \right) \cdot h \right] \quad (2)$$

式中,  $Q_{gr}$  是提升气吹入量 ( $l/min$ )  $D_U$ 、 $D_d$  是上升管与下降管的直径 ( $m$ )  $h$  是提升气吹入深度 ( $m$ ).

方程(2)的数值解存在若干困难, 诸如: 1) 上升管的气泡与钢液之度差 2) 当提高  $Q_{gr}$  的数值时, 提间存在着速升气泡的浮升效率将从 1 变到 0, 而非定值 3) 上升管中双相流的摩擦力难以计算.

运用双相流理论中 Hughmark 真实含气率关系式<sup>[3]</sup>和 Baroczy 的阻力关系式, 可以解决以上的困难. 再在式(1)中代入阿基米德浮力定律、理想气体方程和水力学中的压力损失关系式, 通过计算机可获得(1)式的数值解, 如图 1、图 2 及图 3. 此计算结果被 120 kg 水模拟实验所证实, 并与工业装置上的放射性物质的测定值相吻合<sup>[4]</sup>(见图 4). 此计算结果的精度比早先的研究工作<sup>[5]</sup>要高.

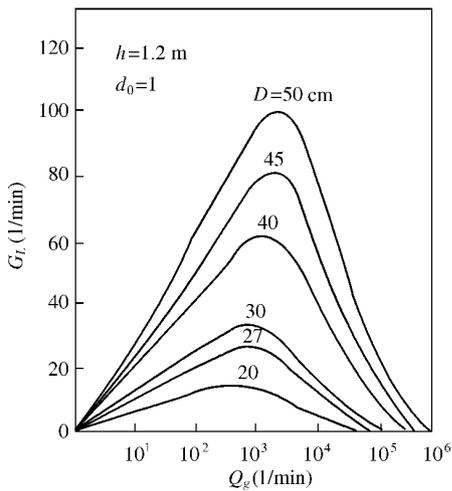


图1 管径对装置环流特性的影响

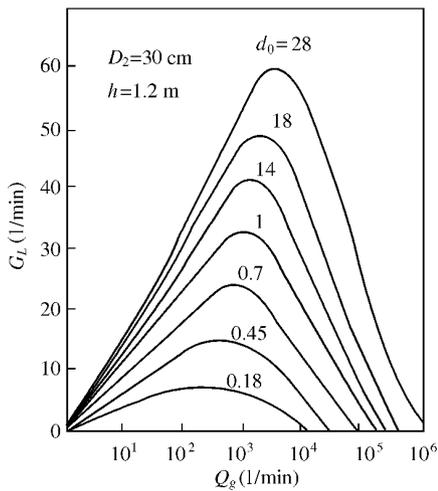


图2  $d_0$ 对装置环流特性的影响

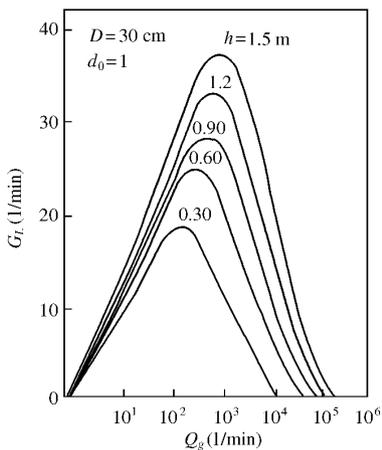


图3 吹气深度对装置环流特性的影响

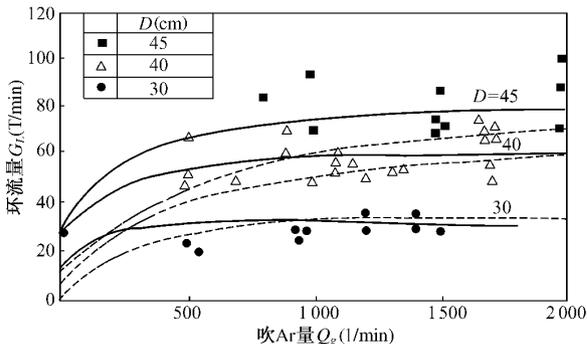


图4 计算结果与实测结果及渡边计算结果的比较

实线 本文计算结果 实验点 金同位素测定值；  
虚线 按渡边的计算结果

### 3 试验

图5 为实验室模型装置的系统图,其几何尺寸为大冶钢厂 100 t RH 装置的 1/5。模型钢包的直径为480(底)~563 mm(液面),高为580 mm(至液面),模型真空室直径为 243 mm,管径为 42~52 mm。

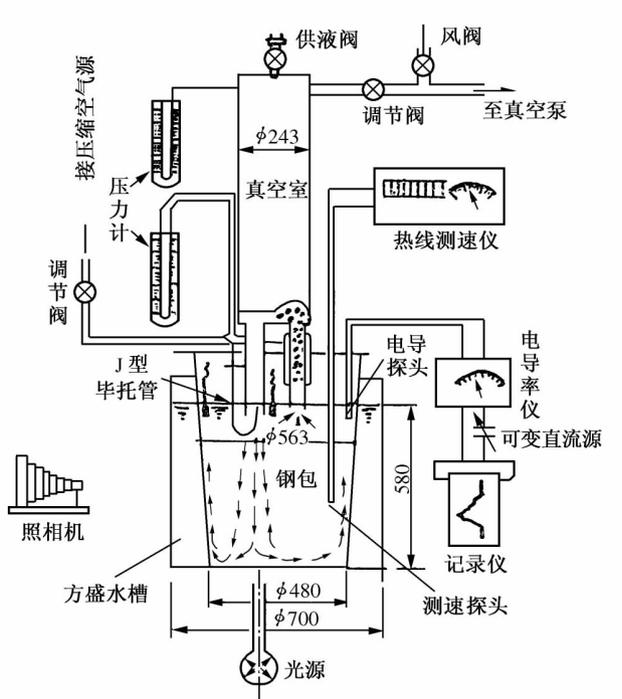


图5 RH-II水模拟装置及测试系统简图

真空室压力和提升气流量均可调节. 由于钢包的环流特性和混合效率都取决于从下降管流出的流体流速. 根据相似原理应保持模型及工业装置的下降管流体流动的费鲁德准数  $F_r$  相等. 由此, 可决定模型装置的下降管流速应为

$$\begin{aligned} U_{L,d2} &= (D_2/D_1)^{1/2} \cdot U_{L,d1} \\ &= 0.53 \text{ m/s} \end{aligned} \quad (3)$$

这里  $U_{L,d2}$  和  $U_{L,d1}$  是水模型和 100 t RH 装置下降管的流速,  $D_2$  和  $D_1$  是水模型和 100 t RH 装置下降管的直径. 喷枪结构也是按 1/5, 将 100 t 喷吹系统缩小, 并使模型和实物喷气的修正费鲁德数  $F'_r$  相等. 由此出发, 模型吹气量可给出如下:

$$\begin{aligned} F'_r &= \rho_g \cdot U_{gi}^2 / (\rho_L - \rho_g) g \cdot L \\ Q_{gi2} &= M_L^2 \cdot U_{gi2} \frac{U_{gi1}}{U_{gi2}} \approx 960 \text{ l/h} \end{aligned} \quad (4)$$

这里,  $Q_{gi2}$  和  $Q_{gi1}$  分别是模型和工业装置的吹气量,  $U_{gi2}$  和  $U_{gi1}$  分别为两者喷

枪出口的气流速度  $M_L$  是几何尺寸之比率。

下降管流体的速度采用特殊的 J 型毕托管测定,并用溢流法及高速摄影法校正。RH 和 RH-IJ 钢包中流体的流态摄影采用聚苯乙烯粒子作示踪剂,片光源宽度为 0.8 ~ 1.0 cm。该系统的混合特性的研究是靠真空室中滴入 NaCl 溶液进行的。有两支电导率探头分别插在不同的位置,一支安置在下降管之下,而另一支放在近包壁的水面(上升管外侧)。混合均匀时间定义为,两探头测得电导率之差值小于 5% 时,此混匀时间记为  $\tau_{0.95}$ 。

从下降管流出的流股中的速度分布,用热线风速仪及照相法测定。

获得如下试验结果:

### 3.1 RH 装置的环流速度

图 6 描述了环流速度与提升气吹入速度,不同上升、下降管径间的关系。由图 6 可清楚地看出,出气速度与环流速度之间的关系为对数函数。

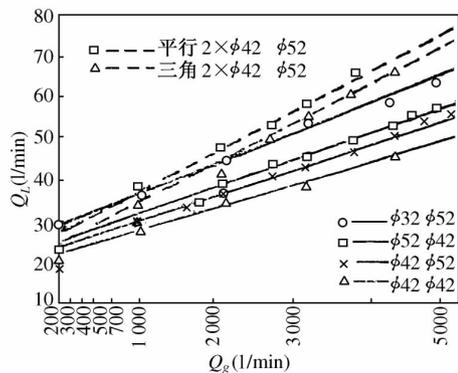


图 6 装置腿径不同时的环流特性

### 3.2 RH 钢包中的流体流动现象

采用照相法研究了 RH 钢包中流体的流动现象。当大量照片被仔细分析后,发现了从下降管流出的液流是周期性摆动的(见图 7)。而当真空室的下降管向钢包中心水平位移时,此现象可消除,获得基本是垂直向下的液流。图 8 ~ 10 表示了真空室不同位移量时,对下降管液流的影响。

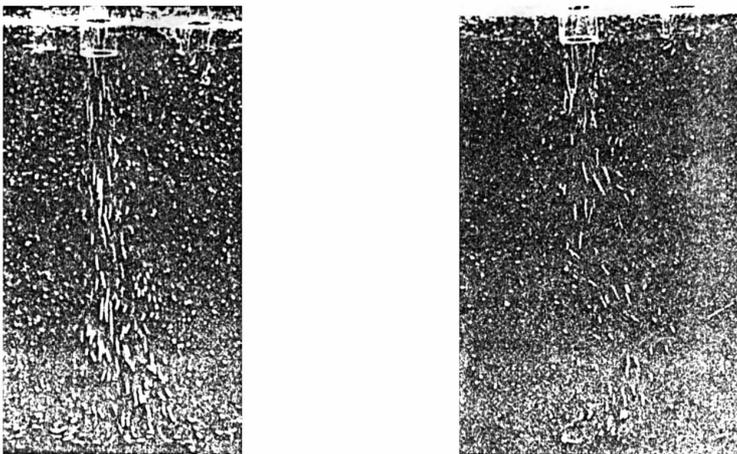


图 7 下降管流的摆动现象

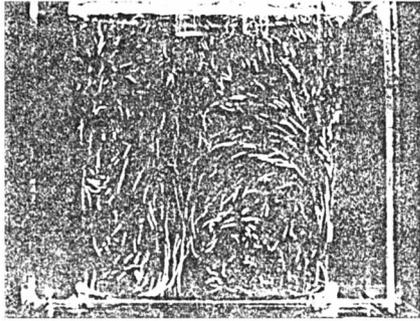


图8 下降管流在正常位量的摆动

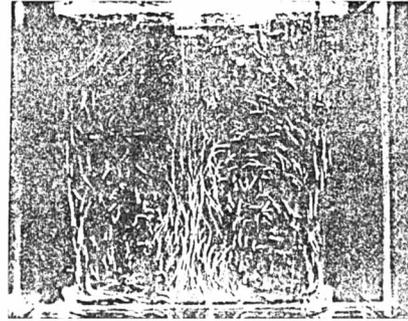
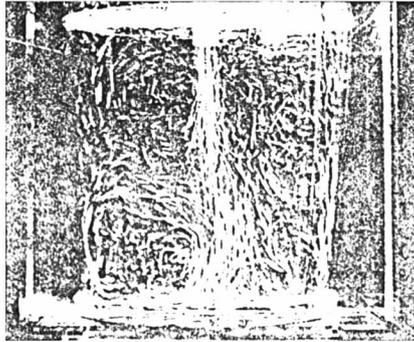


图9 真空室横移率为 0.15 时下降流无摆动现象



10 真空室位移为 0.22 时下降流发生摆动

不同水平位移率对流股摆动及混均时间的影响列于表 1 及表 2.

表 1 流股摆动与水平位移率的关系

横 移 率	0	0.075	0.15	0.22
有无摆动	有	有	无	有

表 2 不同横移率下的混均时间

横 移 率	- 0.1	0	+ 0.15	+ 0.30
$\tau_{0.95}$ , sec	68.3	63	58	57

表列结果表明,最小混均时间恰好是在横移率为 0.15 和流股周期性摆动现象被消灭的时候.

在此条件下测定了下降管流出流股的扩张角及其速度分布,图 11 为采

用热线风速仪测定的结果. 其中流股中心的最大速度是离下降管出口距离的函数, 如(5)式所示:

$$U_{J \cdot \max} = a - bh_{Li} \quad (5)$$

这里  $U_{J \cdot \max}$  是流股中心的最大速度,  $a$  和  $b$  是常数,  $h_{Li}$  是离下降管口的距离.

由于下降管流出液流的抽引作用, 流股四周的液体被不断卷入, 所以 RH 钢包的环流量将与 RH 装置不同. 根据理想自由紊流理论计算的结果表明, RH 装置的环流量是  $D_d^2$  的函数, 而 RH 钢包中的环流量, 则是  $D_d^{1/2}$  及钢包中熔池深度的函数.

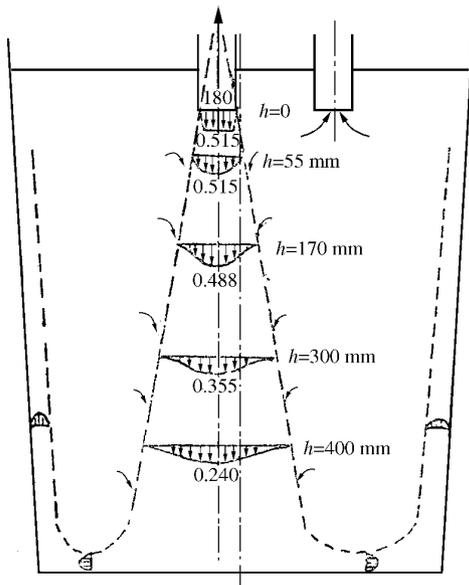


图 11 下降管流中的速度分布及流股扩张 ( $\eta = +0.15$ )

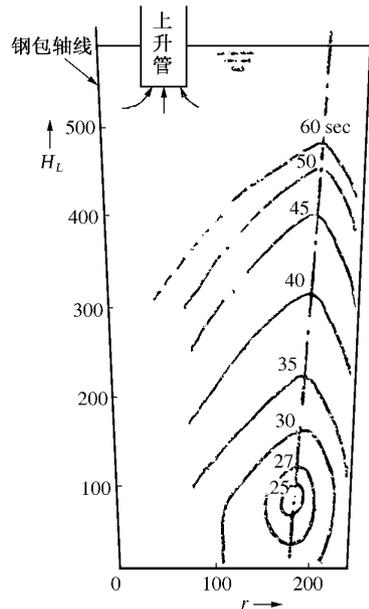


图 12 不同几何位置时 RH-IJ 中的混匀时间

### 3.3 RH 钢包和 RH-IJ 装置中喷枪的最佳位置

图 12 表示了不同喷枪位置喷吹时测定的 RH 钢包中的等混均时间曲线. 从图 12 可以看出, 喷枪的最佳垂直位置大约为  $h = (0.80 - 0.90)H_L$ , 这里  $h$  是喷枪浸入深度,  $H_L$  是钢包中熔池总深度. 而喷枪的最佳水平位置为  $r = (0.72 - 0.86)R$ , 这里  $R$  是钢包半径, 而  $r$  是喷枪水平位置与钢包中心的距离.

一个很好的设想是将 RH 和喷吹过程结合起来,运用气泡搅拌模型并配合水模拟研究,发现当喷枪处于上升管以下喷气或气粉时,钢液的混合效率获得明显的改进(见图 13)。在此情况下,一个重要的参数是喷枪的深度。图 14 显示了在 RH-IJ 系统中,喷枪浸入深度与钢包熔池深度之比( $h/H$ )在 0.23 时有一个转折点。这一点可解释为环流速度与喷枪浸入深度之间的关系并非单调增长(见图 15)。而此过程的一个必要条件是,从喷枪出来的气泡流股能完全地上浮进入上升管。

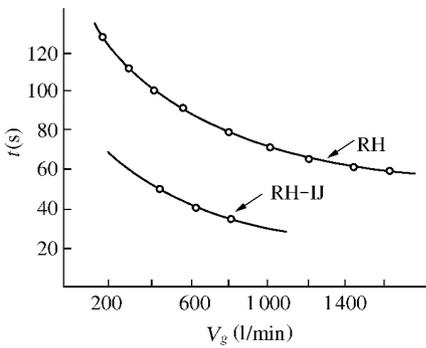


图 13 RH 及 RH-IJ 的混匀时间对比

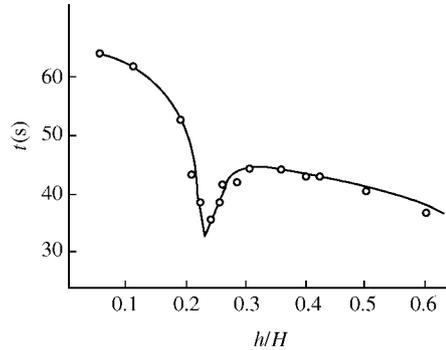


图 14 RH-IJ 中不同喷枪深度时的混匀时间

气泡流股的半径的理论计算式如下:

$$r_{b-j} = C(h + h_0) \left\{ 2 \ln \left[ - \frac{P_{atm} \cdot T \cdot V_g \cdot \ln(1 - Z/Z^*)}{2\pi C^2 (h + h_0)^2 U_m^2 \cdot \bar{U}_L \cdot \rho_L \cdot 298} - 1 \right] \right\}^{0.5} \quad (6)$$

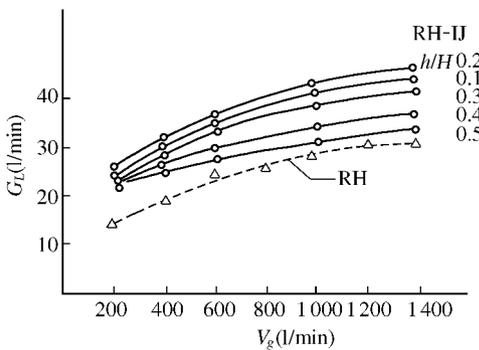


图 15 不同喷枪深度时 RH-IJ 装置中的环流量

这里  $C$  是扩张系数,约为  $0.05^{[6]}$ ,  $h$  是喷枪离上升管的距离,  $h_0$  是气泡流股的穿透深度,  $P_{atm}$  是真空室的压力,  $T$  是系统的温度,  $U_m$  是气泡流的最大速度,  $\bar{U}_L$  是气泡流的浮升速度,  $\rho_L$  是液体的密度。而

$$Z^* = h + P_{atm} / \rho_L \cdot g$$

另一方面,得到了实验结果的回归方程:

$$Q_L = 19.9 + 0.018V_g + 66(h/H)$$

$$- 0.015V_g(h/H) - 142(h/H)^2 \quad (7)$$

这里,  $Q_L$  是环流量(l/min),  $V_g$  是提升气吹入量. 将(7)式求偏导数, 可得

$$\frac{\partial Q_L}{\partial(h/H)} = - 284(h/H) + 66 - 0.015V_g \quad (8)$$

因此, 当  $\frac{\partial Q_L}{\partial(h/H)} = 0$  时, 可得到的最佳位置为

$$\left(\frac{h}{H}\right)_{opt} = \frac{66 - 0.015V_g}{284} \quad (9)$$

当  $V_g = 200 \sim 600$  l/h 时, 喷枪插入深度的最佳位置应为:  $(h/H) = 0.20 \sim 0.23$ .

如果将  $V_g = 600$  l/h 和  $(h/H) = 0.20$  代入理论计算式(6), 就会得到  $r$  的值, 正好为  $\frac{1}{2}D_U$ . 这意味着这是气泡流股能完全地上浮进入上升管的最大喷枪插入深度. 此时, 由于全部的气泡流股都用于驱动环流, 所以可以获得最大的搅拌效率.

## 4 结论

(1) 发展了双相流模型, 从而得到了 RH 装置中钢液的环流速度, 以及几何结构参数对它的影响.

(2) 从 RH 下降管流出的流股, 有周期性摆动现象. 而当真空室水平位移至  $0.15R$  时, 这个现象可消除.

(3) 在 RH 钢包中喷枪的最佳位置大致为,  $h = 0.80 \sim 0.90H$  和  $r = 0.72 \sim 0.86R$ , 即在上升管一侧.

(4) 在 RH-IJ 装置中喷枪的最佳位置在上升管下面,  $(h/H) = 0.2 \sim 0.3$  处. 在此情况下, 由于有最大搅拌效率而可获得最短混均时间.

## 参 考 文 献

- [ 1 ] H. Mass, P. Huofer: Vacuum, Vol. 19, No. 4, pp. 199-203
- [ 2 ] Nakanishi et al.: Ironmaking and Steelmaking, 1975, No. 2, pp. 115-123

- [ 3 ] Hughmark , G. A. : Chem. Eng. Progr. 1962 , Vol. 58 , p. 62
- [ 4 ] 佐田则夫等 : 《铁と钢》 , 1980 , Vol. 66 , No. 4 , pp. S80-S130
- [ 5 ] 渡边秀夫等 : 《铁と钢》 , 1968 , Vol. 54 , No. 13 , p. 1327
- [ 6 ] Hsiao Tse-Chiang : Scand. J. Metall. 1980 , Vol. 19 , No. 3

## 氩搅拌钢包水模拟<sup>\* 1</sup>

**摘要** 用塑料粒子作示踪剂,观察了通过安装在钢包模型底部距中心为0, R/2, 2/3R处的透气砖吹入氩气时的流态. 发现在这三种吹氩位置下,流态有本质的区别,后两种情况下的流态,不能用二维流动的数学模型来描述. 加入饱和 NaCl 溶液并测量其电导率的变化,可确定每种情况下溶液均匀化所需时间. 采用自制的热线风速仪,测定了三种流态下的速度场. 分析了流态和均匀化时间的关系,以及因吹氩位置而引起的流态的不同作用. 对于氩搅拌的工艺效果而言,吹氩位置有着决定性的作用.

### 导 言

将氩气通过喷枪或设置在钢包底部的透气砖吹入钢液,可使钢液以一定形式运动,从而改善温度及成分的均匀情况,减少钢中气体含量,促进夹杂物上浮. 由于钢包吹氩的工艺和设备简单,因此被广泛采用.

一般认为钢包吹氩可降低钢中氧、氢含量,减少夹杂物沾污度,但其效果波动较大. 而在使钢液成分和温度均匀、改善流动性,和降低轧废率等方面,则比较稳定一致<sup>[1, 2]</sup>. 显然,如能将钢包吹氩工艺和其他炉外精炼手段相结合(如 FinKL-VAD、VOD 或 LF 等),则可望取得更好的效果.

对钢包吹氩的热力学,目前已有较好的了解<sup>[2~4]</sup>. 然而,由于氩搅拌钢包中流场的复杂性,对于这一工艺的动力学还了解得很不够,这势必会影响此工艺效果的稳定性. 近十年来,国外曾对此进行了一些工作<sup>[5, 6]</sup>,国内也作过

\* 本文合作者: 顾洪涛、谢宇、左跃、张晓兵、张家武. 原发表于《上海工业大学学报》, (2)78~89(1981)

初步尝试<sup>[7,8]</sup>。70年代后期,国外有关学者在氩搅拌钢包的数学模型方面发表了不少详尽的报告<sup>[9~15]</sup>。纵观文献资料所述,氩搅拌钢包的流体力学研究现状可归纳为:

(1) 对于二维流场已经作出比较严密的数学模型,计算结果与水模型中的实测值能定量一致。文献[14]中报道了用数学模型直接预测6吨钢包中示踪剂分散情况,取得了与实测值比较一致的结果。但是所选用的K-W方程组计算相当复杂,其中紊流粘度表达式<sup>[15]</sup>与通过透气砖吹氩的实际情况差别较大,一定程度上会影响该方法的实际应用。

(2) 由于实际流场的不稳定性,气-液两相区(“气泡柱”区)与液相区的交界面模糊、多变(严格地说,无固定分界面),液体自由表面也因吹气而不断波动,因此上述数学模型中的边界条件在实际上难以满足。

(3) 特别应该指出的是,实际生产中使用的钢包都是截锥体形的,氩气也并不是在钢包底部中心导入。因此,这样得到的流场应是三维的,前述文献所得到的二维流场的统制方程组,误差较大。

为此,有必要对与实际情况更一致的三维流场进行研究。作为第一步,首先在水模拟上观察,比较了二维与三维流场流态的异同,实测了相应的均匀化时间和流体中速度的分布,为进一步深入研究三维流场的数学模型奠定基础。

## 1 试验过程与装置

### 1.1 概述

本试验采用水模拟法,在一个与生产实际中所用钢包几何相似的有机玻璃容器中,研究了在二维、三维流态条件下,吹氩点几何位置和氩气流量对混合均匀时间、流场特征的影响,并自制了热线风速仪,测定了上述不同流态下,钢包中流体内的速度分布。

钢包模型的尺寸及吹氩系统如图1所示。

### 1.2 流态摄影与观察

在钢包中加入直径为2 mm左右、密度为 $1.025 \text{ g/cm}^3$ 的塑料粒子,摄下不同吹氩位置、不同氩气流量下中心截面上塑料粒子运动轨迹,以此研究流体的流态。为了减小圆弧形包壁产生的折射影响,在钢包外套上一个边长为

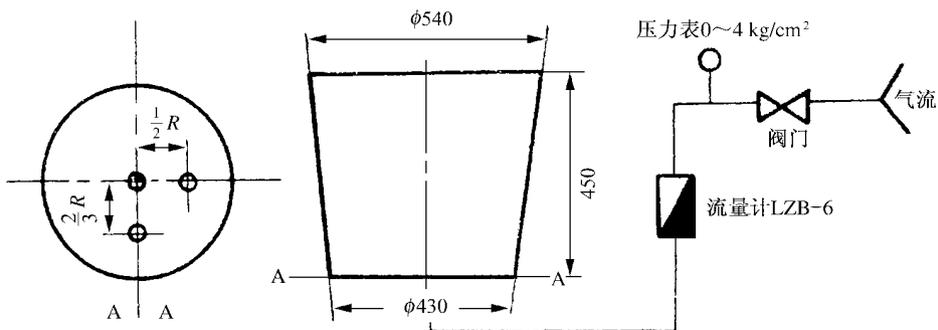


图1 钢包模型和吹氩系统图

0.7 m的正方形有机玻璃容器,摄影时外层容器也注满光密度相同的水.光源采用220 V、1300 W的卤钨灯,外面罩上铝皮灯罩,使光束通过0.8 cm的狭缝投下,由此得到一束宽约为1 cm左右、透过整个钢包中心截面的平行光.为了得到尽可能清晰的照片,采用活性炭净水器处理,以增加水的透明度.流态摄影装置见图2.摄影时相机距钢包中心约1.8 m,摄得的典型照片如图3~5.照片中白色线条为塑料粒子在1秒钟内走过的轨迹,白色带是气泡上升的两相区(气泡柱区).

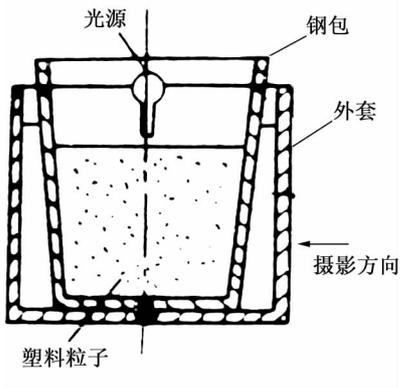


图2 流态摄影装置



图3 中心喷吹时的流态照片  
(因对称,照片取1/2,上部有明显环流)

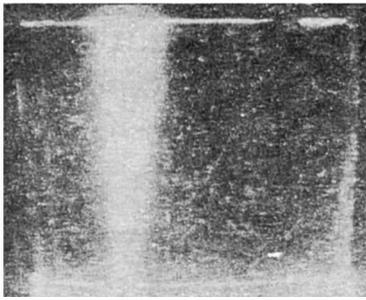


图4 R/2 喷吹时,平面摄影的流场紊乱

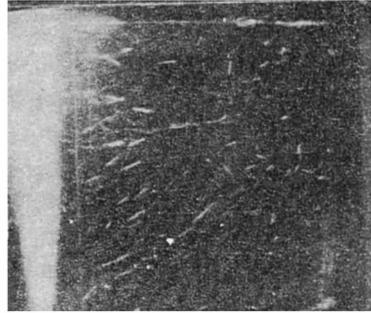


图5 2/3R 喷吹时,有较大回流,并被“气泡柱”区吸引、上升

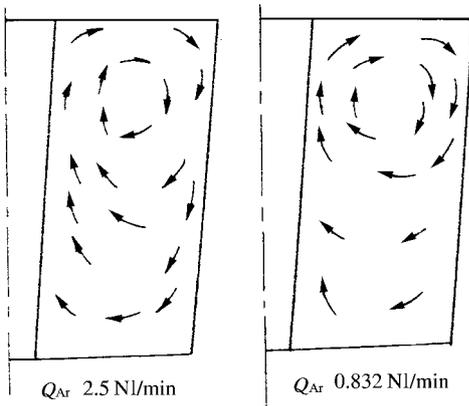


图6 不同流量中心喷吹时的流态示意图

照片反映了经过吹气点和钢包中心,并和底部垂直的平面上的流动状态.中心喷吹时,流场基本上是二维的,因此通过摄影就可以反映流态.然而当 R/2 和 2/3R 喷吹时,流场是三维的,为了更清楚地反映其流态,在不同角度摄影和观察,再根据照片复叠法,画出三种情况下的流态图,如图 6~8 所示.

可以看到,在不同位置喷吹时,流态有着质的区别:

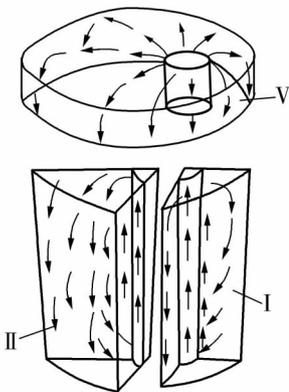


图7 R/2 喷吹流态示意图  
(III与I对称,IV与II对称,未画出)

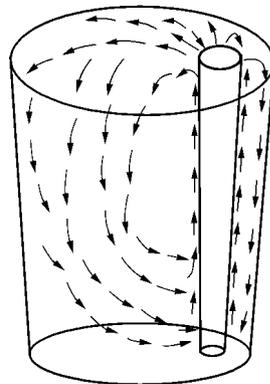


图8 2/3R 喷吹流态示意图

(1) 中心喷吹时,在光束区撒下示踪粒子,发现粒子基本上在光束平面上运动,可见流场基本上是平面的。具体流态见图 6,其上部环流区高度由氩气流量为 0.832 NI/min 时的 0.4H,增至氩流量为 2.5 NI/min 时的 0.6H。

(2) R/2 喷吹时的流态见图 7,这是一个很复杂的流场,大致可划分成五个区域。上部 V 区是近水面的高度很小的圆柱区,该区内液体以气泡涌出点为中心,向四壁呈放射状流动。在 V 区以下的流体依两个“零速度面”,可划分成四个相对独立的回流区域。“气泡柱区”明显地向钢包中心倾斜,V 区高度随流量增大而增大,从 0.832 NI/min 的约 0.12H,增至 2.5 NI/min 的约 0.2H。I、III 区随流量增大而扩大(流体自壁横向滑动更为明显)。II、IV 区中近气柱区的上升部分亦随流量增大而范围扩大,由 0.832 NI/min 时的 0.3R 厚,增至 2.5 NI/min 时的 0.6R 厚。

(3) 2/3R 喷吹时,流场不很复杂,近气柱区液体上升,离气柱区较远处,液体下降,再经过水面和包底形环流。同时,在钢包下半部有明显的横向流动,上升区随流量增大而增大,两相区周期性向侧壁倾倒。

在小流量喷吹时,比重为  $1.025 \text{ g/cm}^3$  的示踪粒子在底部有局部沉积的现象,说明包底存在着若干“滞流区”(见图 9 及图 10 中白色部分)。



图 9 R/2 喷吹时底部滞流区照片

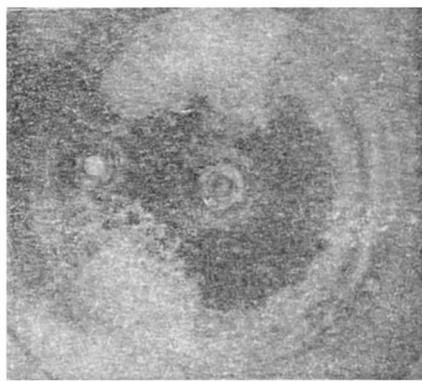


图 10 2/3R 喷吹时底部滞流区照片

### 1.3 均匀化时间测定

试验装置如图 11 所示,将饱和 NaCl 溶液通过虹吸管加入钢包底部,采用两支铂黑电导率探头,一个置于近水面处,另一个置于钢包底部;虹吸管及底部电导率探头,尽可能置于“滞流区”两侧(见图 12)。实测得电导率随时间变化,通过电导率仪的毫伏信号输出,用自动平衡仪加以

记录,如图 13 所示.从溶液加入起,到两测点电导率一致时止,即为均匀化时间.

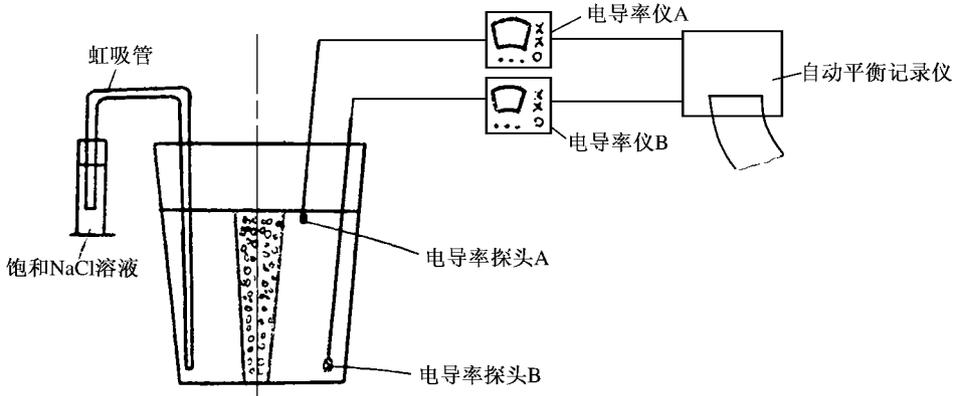


图 11 氩搅拌混合均匀化时间测定装置图

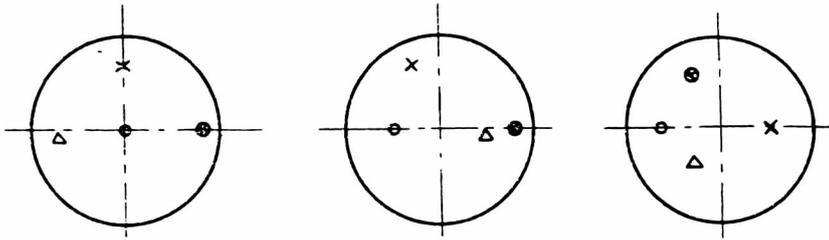


图 12 钢包中不同吹氩点时的测量点及 NaCl 注入点

△ NaCl 溶液加入点 ; × 短探头位置 ; ⊙ 长探头位置 ; ○ 吹氩点

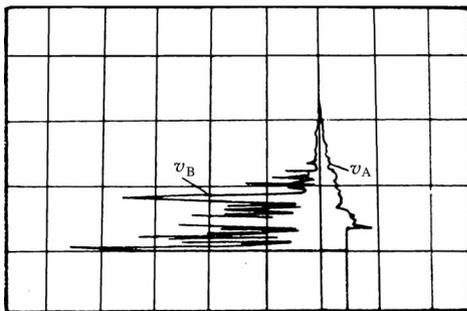


图 13 典型的电导率随时间变化的曲线

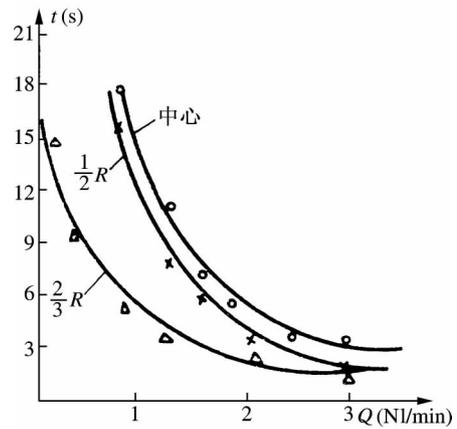


图 14 均匀化时间与吹氩强度的关系

不同位置吹氩时,氩气流量与均匀化时间的关系如图 14 所示.经回归分析后可得流量与均匀化时间的关系,如表 1 所示.

表 1 均匀化时间与氩气流量的数学关系式

位 置	线 性 方 程	相 关 系 数
中心	$t = 15.4 Q^{-1.47}$	0.998
R/2	$t = 10.7 Q^{-1.51}$	0.990
2/3R	$t = 4.57 Q^{-0.818}$	0.997

可以看到,小流量喷吹时,吹氩位置对均匀化时间影响很大,吹氩位置偏离中心时,均匀化时间明显缩短,而大流量喷吹时,位置的影响就不那么明显了.

另外,曾作过不同起始浓度下加入溶液的试验,结果证明,在起始浓度不大时,起始浓度与均匀化时间无关,后者仅与加入的剂量有关,故本试验采用了固定加入剂量连续测定法.还做过加入溶液后,不搅拌的对比试验,结果虽经 45 分钟以上,两侧点的电导率仍相差很远,因此静止溶液中浓差扩散的影响,亦可以认为是很小的,在氩气搅拌的均匀时间中,未加考虑.

#### 1.4 用热线风速仪测定速度场

对于流体中微区速度的测量,广泛应用热线风速仪<sup>[16,17]</sup>,本试验采用了自制的热线风速仪(原理图见图 15),对不同流量、不同吹氩位置时的速度场进行了测定.热线风速仪的探头用经过绝缘处理的  $\phi 12 \mu\text{m}$  钨丝制成,将探头作为电桥的一臂接入电路,测量时探头置于流场内欲测部位,当流体速度大时,对流散热增加,影响到探头温度,使热线电阻值变化,这样就导致不平衡电桥有毫伏信号输出.探头预先在已知流速的稳定流场中进行标定,其流速-毫伏关系如图 16 所示.将测量时记录下的毫伏信号与标定曲线比较,即可得相应的流速.利用旋转探头所得毫伏值的不同,还能大致判断流体的运动方向.测定结果见图 17、18、19.

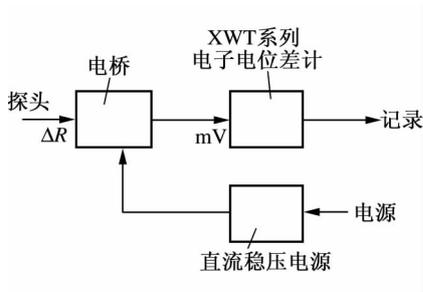


图 15 热线风速仪原理图

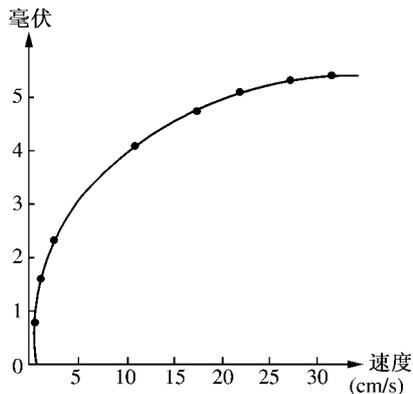


图 16 标定的热线探头流速-毫伏关系曲线

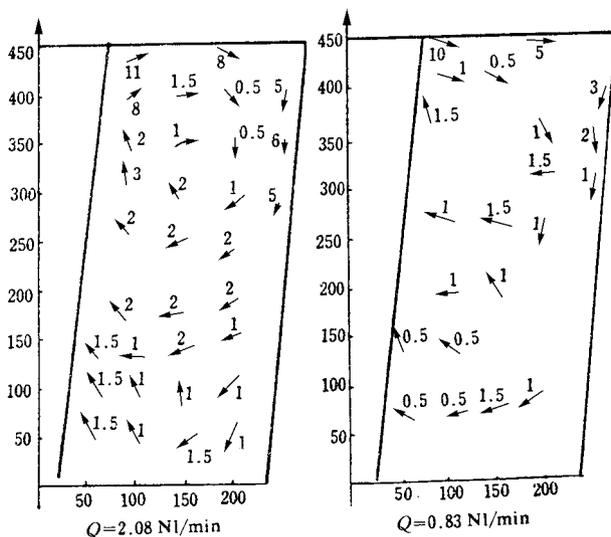


图 17 中心喷吹时的流速分布图(单位: cm/sec)

运用热线风速仪实测流体中的速度场后发现：① 钢包内流场并不是稳定的，在以稳定的气流量喷吹相当长时间后，包内某些点的速度、方向还会有无规则变化，特别在近自由表面、壁、气柱等界面处，尤其容易出现。② 各点的速度都具有脉动特性，脉动范围可达到最大值的 1/3 左右。因此，可进一步推断，在此系统中大范围内的传质是靠形成环流完成，而局部区域内的传质，则是通过紊流形式进行的。

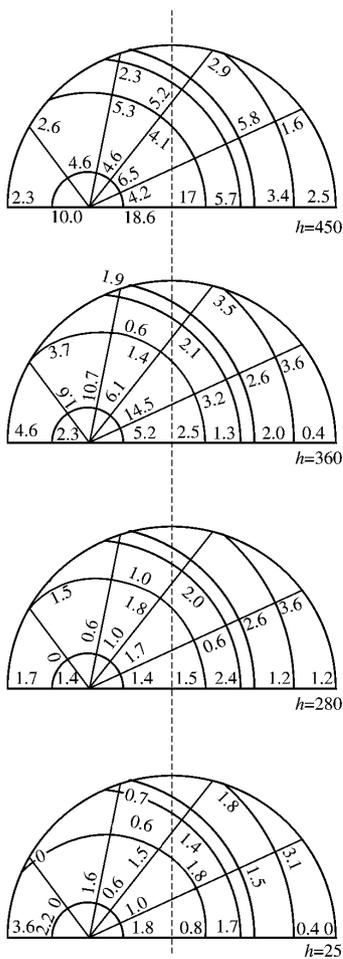


图 18 R/2 喷吹时的速度分布  
 $Q = 0.83 \text{ Nl/min, cm/sec}$

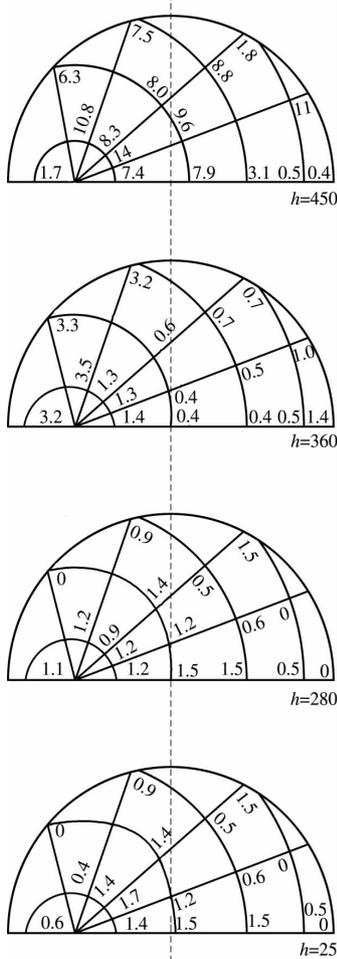


图 19 2/3R 喷吹时的速度分布  
 $Q = 0.83 \text{ Nl/min, cm/sec}$

## 2 讨论

### 2.1 流态

通过大量照片及试验中的观察,发现氩气在钢包中导入的位置,决定了钢包中的流态,而氩气流量的大小,对流态无根本性的影响.因此选择恰当的吹氩位置,就能用最少量的氩气,在最短的时间内,对钢液进行充分的搅拌.这对实际生产无疑是有指导意义的.

中心吹氩时,流场是平面型的,相邻平面间质量的传递主要靠紊流进行,势必影响均匀化时间.在 $R/2$ 喷吹时,整个钢包分成在一定范围内摆动的五个流动区域,而 $2/3R$ 喷吹时,整个钢包形成了两个互相对称的环流区域,在大范围内进行质量的对流传递,能使均匀化时间明显缩短,这一点已为实验事实所证明.

同时,试验中发现,喷吹点不在中心时气泡柱区不断摆动. $R/2$ 喷吹时,从包壁而来的横向液流,使其明显地向钢包中心倾倒.而在 $3/2R$ 喷吹时,气泡区近壁一侧除了紧贴气泡流有一极薄的上升区域以外,主要是形成了一股沿壁而下的高速流束,由于速度大、静压小,再加上另一侧液体中、下部的横向流动的综合作用,产生了附壁效应,使气泡区明显地向侧壁倾倒,并在一定的范围内不断摆动,即使在长时间保持氩气流量稳定时,亦是如此.

从测速中还可发现,在每一种流态时,钢包的某些部位都存在流速极慢的“滞流区”.它们存在于钢包下部(中心喷吹时)、近底部( $R/2$ 或 $3/2R$ 喷吹时),以及环流所形成的“眼”中.对比各种流量和各种不同喷吹位置的照片和速度分布图,可明显地看到,流动区域划分得较多,“滞流区”也越小.同时,由于三维流场的相对不稳定性,环流“眼”的位置经常飘移(底部例外).这些都是三维流场比二维流场(中心喷吹)完成均匀化时间较短的重要原因.增大氩气流量可明显地增大气泡区、水面、侧壁及环流部分的流体速度,但对“滞流区”大小的影响并不很大.这也说明了为什么吹氩位置对均匀化时间的影响要比吹氩流量的影响大.

## 2.2 从能量利用率看吹氩位置的影响

由图 14 可见,吹氩流量对均匀化时间的影响曲线有明显的“拐点”,并随着吹氩位置向侧壁移动,“拐点”也向小流量方向移动.即当流量小时,流量的变化对均匀化时间的影响很大,而当流量达到某一临界流量后(拐点),再增大流量,作用就不明显了.且在大流量时,吹氩位置的影响也不大了.上述种种现象,均反映了不同情况下氩气泡能量利用率的程度.

在本试验中,氩气泡在浮力作用下上升,推动流体而做功,同时因上升时水静压减少,体积膨胀而做功(在实际钢包吹氩时,还有气泡因热膨胀而做功).在流量小时,氩气泡所做的功主要用于推动流体运动,在钢包形成环流.在流量增大超过临界值时,相当一部分能量消耗于流体表面隆起及翻动,即因液-气界面能量交换而损失.同时,氩气泡以越来越大的速度逸入大气,也

带走了相当一部分动能,因此,尽管总能量增大,但用于推动流体环流的那部分,增加并不明显。至于三条曲线的不同,则反映了吹氩位置对能量利用率的影响。显然,吹氩位置偏离中心,对于在钢包中形成环流是有利的。

必须指出,本试验所进行的水模拟,在传质和传热方面,都难以与高温下的钢包情况相似,只有在动量传递方面,可作近似的比拟。故上述均匀化时间的数字关系,必须经过热模拟校验,方可作出定量比较。但是,吹氩位置的影响及吹氩量有一临界值这两点,则可肯定是定性准确的。

### 2.3 速度场

对于测得的速度分布,有几种情况值得注意。

(1) 在流量为  $0.832 \text{ NI/min}$ ,  $R/2$  喷吹的速度图上(图 18),有一个纵切面( $108^\circ$ 面)上,各点速度均较相邻面为低,这显然是一个流区分界面。流区过多、分界面增多,低速度面也就多,它使得  $R/2$  喷吹所需均匀化时间比  $2/3R$  要长一些。

(2) 在相同流量情况下,  $2/3R$  喷吹的速度分布比其他两种喷吹时要来得均匀。在  $Q = 0.832 \text{ NI/min}$  时,将三种位置喷吹情况下测得的各点速度进行统计,结果见表 2。  $2/3R$  喷吹时流体中  $v = 1 \sim 3 \text{ cm/sec}$  的点,要比其他两种情况多 15% 左右。

表 2 吹氩位置对速度分布的影响

吹氩位置	总测点数	$v = 1 \sim 3 \text{ cm/sec}$ 的点数	占总测点 %
中心	45	26	58
$1/2R$	120	72	60
$2/3R$	102	75	74

(3) 热线风速仪在稳定的一维流场(标定)中,精度及重现性较好,但在二维、三维流场中波动较大,所得结果只是该点速度的平均值。

(4) 二维流动时的速度图是矢量图,三维流动是标量图。后者应该用其他物理量,例如物质通量来更确切地表示流态,及其与均匀化时间的关系。

## 3 结论

(1) 吹氩工艺参数,对吹氩搅拌均匀化效果有明显的影响:

1) 吹氩位置对流动形态有决定性影响,对速度分布也有很大影响.在距中心 $2/3R$ 处喷吹,完成均匀化的时间最短,距中心 $1/2R$ 处喷吹,均匀化时间较长,中心喷吹时,均匀化时间最长.

2) 在小流量时,流量增大,均匀化时间缩短,但超过某临界值时,流量的影响就不明显,这一临界值,随吹氩点向包壁移动而减小.

(2) 用热线风速仪能测定水模拟中速度的分布.因探头对流动方向很敏感,在一个紊流场中,这显然会影响测定的精度,但另一方面,却可利用来判断流动的方向.

(3) 吹氩位置偏离中心时,流体具有三维流动的特征,用速度场来表示,有其不便之处,可以考虑用与动量传递和质量传递都有密切关系的物理量,例如物质通量来表示之.

(4) 为了更好地模拟钢包中实际氩搅拌情况,应进一步考虑各相似准数的不同,对模拟效果的影响,并进行热状态下的试验,进行对比.

(5) 进一步开发三维流场的统制方程组及其解法,用三维流场中的物质传输方程来计算均匀化时间,无疑是这一领域研究的最终目标.

## 参 考 文 献

- [ 1 ] 全国钢水吹氩会议资料,1974年3月,北京
- [ 2 ] 太原钢铁公司:《钢包吹氩总结》,(载于《冶金部特钢第一届铸锭专业会议资料汇编》)
- [ 3 ] 北京钢铁设计院:《国外炉外精炼概况》
- [ 4 ] 上海工业大学:《特殊钢炉外精炼的技术基础》,1978
- [ 5 ] K. Nakanish, J. Szekely : Trans. I. S. I. J. , Vol. 15 , p. 523 , 1975
- [ 6 ] J. Szekely , Shigeo Asai ; Trans. I. S. I. J. , Vol. 15 , p. 270 , 1975
- [ 7 ] 袁以中,李文梁等:钢包吹氩水力学模型试验,《新金属材料》,No. 10, 1974
- [ 8 ] 吴士白:钢包吹氩的模型试验,上海工业大学冶金工程系炼钢76级毕业论文
- [ 9 ] J. Szekely , H. J. Wang and K. M. Miser : Metall. Trans. , Vol. 7B , p. 287 , 1976
- [ 10 ] J. Szekely , S. Asai and C. W. Chang : International Iron and Steel Congress , Vol. IV , 5 - 2 - 2 - 1 , 1974
- [ 11 ] J. Szekely , A. H. Drlawari , *et al.* : Metall. Trans. , Vol. 10B , p. 33 , 1979
- [ 12 ] J. Szekely , *et al.* : Trans. I. S. I. J. , Vol. 15 , p. 276 , 1975
- [ 13 ] J. Szekely , *et al.* : Ironmaking and Steelmaking , Vol. 6 , p. 285 , 1979
- [ 14 ] J. Szekely : Scaninject II , 1980. 6

- [ 15 ] D. B. Spalding , *et al.* : Appl. Math Modelling , No. 2 , p. 146 ,1978
- [ 16 ] D. D. Ernest : Measure System , ( Application and Design )
- [ 17 ] P. Bradshaw : An Introduction to Turbulence and Its Measurement

## Warer Modelling of Argon Stirring Ladle

**Abstract** In a ladle model , by using plastic particles as tracers , the fluid flow regimes agitated by introducing argon gas stream through porous plug placed at the center ,  $R/2$  from the center , and  $2/3R$  from the center of the ladle bottom were observed. It is found that the fluid flow regimes are essentially different in each of these three cases , and the regimes in the two latter cases can not be described by means of the mathematical model for the two-dimensional flow. Adding a saturated NaCl solution and measuring the variations of the electrical conductivity , we can determine the time taken for solution homogenization in each case. Using a hot-wire anemometer , the velocity field of the three fluid flow regimes was determined. The relationship between fluid flow regime and homogenization time , and the different effect on the fluid flow regime caused by the location where argon is introduced are analysed. The argon-introduced location has a decisive effect on the result of argon-stirring technology.

表3 轴承钢喷粉脱氧试验结果汇总(25 kg 中频炉)

方 案	炉号	取样 时间	样号	钢液化学成分(%)							
				C	Mn	Si	P	S	Cr	Al	
I	高 Fe-Si 4.0 g/kg No. 2 渣 10 g/kg	4	喷 前	14	0.88	0.27	0.27	0.010	0.054	1.56	≤0.02
			喷毕 0'								
			3'								
			6'								
	高 Fe-Si 3.5 g/kg No. 2 渣 10 g/kg	1	化渣 喷前	1	0.58	0.27	痕迹	0.011	0.017	1.40	≤0.02
			喷毕 0'	2	0.54	0.28	0.20	0.010	0.015	"	"
			3'	3	0.54	"	"	0.011	0.014	"	"
			6'	4	0.52	"	0.18	0.009	0.012	"	"
	高 Fe-Si 3.4 g/kg No. 3 渣 6 g/kg	6	喷前	22	0.80	0.25	0.30	0.013	0.056	1.54	≤0.02
			喷后 0'	23	0.80	"	0.29	0.011	0.051	"	"
3'			24	0.79	"	"	0.010	0.050	1.53	"	
6'			25	0.79	"	"	0.009	0.052	"	"	
II	高 Fe-Si 3.2 g/kg No. 3 渣 10 g/kg	2	喷前	6	0.58	0.24	0.29	0.008	0.013	1.40	≤0.02
			喷后 0'	7	"	0.25	0.24	0.010	0.014	1.35	"
			3'	8	"	0.25	0.23	0.008	"	"	"
			6'	9	"	0.24	0.22	0.007	0.013	"	"
	高 Fe-Si 3.5 g/kg No. 3 渣(机 械混合) 6 g/kg	7	喷前	26	0.87	0.27	0.43	0.010	0.019	1.50	≤0.02
			喷后 1'								
			3'	27	0.86	"	"	"	0.018	"	"
			6'	28	0.85	"	0.42	0.011	0.017	1.49	"
			9'	29	0.81	"	"	0.010	0.013	"	"

(续 表)

温度	浓 差 定 氧				脱氧 率 %	$\Sigma[\text{O}]$ (ppm)	$f_{\text{Si}}$	$\alpha_{\text{Si}}$	平衡 $\alpha_{\text{SiO}_2}$	平衡 $\alpha_{[\text{O}]}$ (ppm)		
	E(mV)	$\alpha_{\text{O}}$ (ppm)	$f_{\text{O}}$	$[\text{O}]_f$ (ppm)						$\alpha_{\text{SiO}_2}$ =1	$\alpha_{\text{SiO}_2}$ =0.1	$\alpha_{\text{SiO}_2}$ =0.01
1 555	20	26		43								
1 505	- 150	1.25		3.1		22		0.43	0.002	27.0		2.7
	- 135	1.8		3.0								
1 535	- 20	12.5	0.60	20.3	95	19.5/40	0.6	0.43				
	- 25	11.5		19.2		24		0.43	0.115	36.9	11.7	
	- 20	12.5		20.8				0.42	0.094	37.6	11.9	
								0.43	0.115	36.9	11.7	
1 555	120	105		141.9								
1 565	60	50		67.6		46						
1 545	- 30	11.5	0.74	15.5	77	44	1.3	0.26	0.047	52.8		5.3
	30	28		37.8		34		0.26	0.281	52.8	16.7	
	10	21		28.4		31		0.23	0.143	55.6	17.6	
1 605						65		0.20				
1 650	0	41		66.1				0.45				
1 455	- 30	4.7	0.62	7.6	89	39	1.5	0.44	0.098	15.0		1.5
	- 25	7.6		12.3		31/64		"	0.257	15.0	4.7	
1 520	- 20	11		17.7		31		"	0.124	31.3	9.9	
1 620	10	38		55.1								
	25	47		68.1		47		0.41				
1 520	- 100	3.2	0.69	4.6	93	43	1.4	0.34	0.008	35.6		3.6
	35	14		34.8		39		0.32	0.435	36.4	11.5	
	10	17		24.6		47		0.31	0.209	37.2	5.4	
1 580	- 8	13		18.8		48		0.25	0.100	41.1	13.5	
	- 7.5											
1 505	50	27		46.6								
1 490	- 40	6.2	0.58	10.7	77	26	1.6	0.69	0.121	17.8		1.8
	- 60	4.8		8.3		23		0.69	0.073	17.8	5.6	
1 540	- 40	9.7		16.7		23		0.67	0.095	31.4	3.1	
1 565	- 35	12.5		21.6		22		0.67	0.096	40.4	12.8	

对轴承钢熔池, O 的活度系数  $f_o$  波动在 0.58 ~ 0.74.

(2) 一俟喷入低  $\text{SiO}_2$  活度渣后, 钢中溶解氧急剧降低, 在喷毕时达最低值, 获得  $\alpha_{[O]} = 1.25 \sim 6.2 \text{ ppm}$  或  $[O] = 2.1 \sim 10 \text{ ppm}$  的低氧水平. 这与低活度渣脱氧理论相符. 唯有炉号 1 较高, 由喷前这炉钢液 Si 为痕迹知, Fe-Si 尚未进入钢液, 故喷粉时钢中无足够 Si 向低活度渣粉扩散, 等 Fe-Si 均匀化后渣粉也喷得差不多了, 故喷毕  $\alpha_{[O]}$  比其他四炉高些.

从脱氧率看波动在 77% ~ 95%, 机械混合渣粉的脱氧效果稍低, 但成绩仍令人注意. 两种渣粉的脱氧水平无显著差别, 渣量的改变, 也没带来显著差别, 文献[7]在 200 t 钢包的结果认为渣粉量 2 kg/t 就足够了.

(3) 喷毕至浇注 10' 内, 由于喷入渣粉基本上浮至表面渣, 此时钢中氧力图 and 表面渣及氧化性炉气平衡, 使钢中溶解氧略有上升, 但稳定在  $\alpha_{[O]} = 11 \sim 13 \text{ ppm}$  或  $[O] = 17.7 \sim 20.8 \text{ ppm}$ , 只有炉号 1 因钢中 Si 不低, 回升较高. 由于表面渣仍为低  $\alpha_{\text{SiO}_2}$ , 炉衬氧位低, 故只要表面渣覆盖好, 避免接触氧化性炉气, 钢中氧仍大大低于按 Si 沉淀脱氧的平衡值:  $\alpha_{[O]} = 31.3 \sim 55.6 \text{ ppm}$ .

(4) 由于感应搅拌以及低活度渣吸收夹杂的能力, 钢中  $\Sigma [O]$  很低, 为 22 ~ 48 ppm, 钢锭总氧量 26 ~ 51 ppm, 由于炉号 1 成品 Si 为 0.12%, 故  $\Sigma [O]$  较高.

(5) 假定实测的  $\alpha_{[O]}$  与渣平衡, 可以算得平衡的  $\alpha_{\text{SiO}_2}$ , 其值在喷毕时为 0.002 ~ 0.121, 浇注前为 0.096 ~ 0.143, 这说明比原始渣粉  $\alpha_{\text{SiO}_2}$  活度高. 这是因为脱氧产物  $\text{SiO}_2$  不断生成之故.

(6) 喷粉前后钢液化学成分变化: C、Mn、Cr 是稳定的, Si、S 略有下降, 二炉 S 高者系 FeS 带入, 供夹杂变性研究之用. 喷粉后钢液降温 15 ~ 100°C, 降温大的原因是钢水量少, Ar 吹入量大.

以上为轴承钢喷粉脱氧结果及热力学方面的初步分析. 下面对动力学问题——两种渣粉在钢液中行为及脱氧机构与速度作深入一步讨论和计算.

### 3 喷低 $\text{SiO}_2$ 活度渣的硅脱氧的机构与速度

渣粉粒度的选择最好使粉粒不注入钢液(避免混渣夹杂物), 而在 Ar 气泡表面融化形成一层液体渣膜, 以使钢中 Si 和 O 向渣膜扩散, 生成  $\text{SiO}_2$  活

度低的脱氧产物,这样喷入的渣粉和脱氧产物均随 Ar 气泡排出钢液而不沾污钢液,这种 Si 脱氧机构见图 4,这可收到扩散脱氧不沾污钢液的效果,而又比表面渣扩散脱氧法速度快,因为喷粉脱氧时物料的比表面积比熔池—表面渣比表面积大几个数量级,且有 Ar 气搅拌,增大了扩散传质系数。

因此动力学问题的关键在于能否形成符合上述条件的液渣,为此首先考察所喷渣粉在钢液中的力学和热学行为。

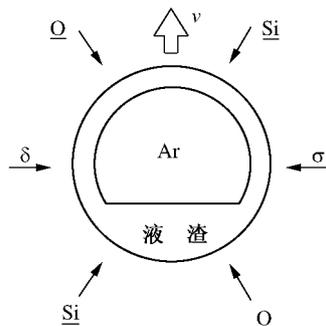


图 4 Si 脱氧机构示意图

### 3.1 粉粒注入钢液的临界速度

关于粉粒突破气泡进入钢液所需的最低速度的计算,已有若干文献<sup>[8,9]</sup>讨论。

按物理学的牛顿运动第二定律,粉粒在金属液中运动的微分方程式为

$$m_{\text{粉}} \frac{dv}{d\tau} = -F_s - F_{\sigma} - F_A = -KS_{\text{粉}} \rho_m \frac{v^2}{2} - 2\pi r_{\text{粉}} \sigma - \frac{4}{3}\pi r_{\text{粉}}^3 g(\rho_m - \rho_{\text{粉}}) \quad (8)$$

式中： $m_{\text{粉}}$ ——粉粒的质量 kg；

$v$ ——粉粒的瞬时速度 m/s；

$\tau$ ——时间 s；

$F_s$ ——粉粒在钢液内运动阻力；

$F_{\sigma}$ ——由于粉粒和钢液的表面张力产生的阻力；

$F_A$ ——粉粒在钢液受到的浮力；

$K$ ——阻力系数,为 1.3；

$\rho_{\text{粉}} \rho_m$ ——分别为粉粒及钢液密度  $\text{kg}/\text{m}^3$ ；

$r_{\text{粉}} S_{\text{粉}}$ ——粉粒半径 m 及粉粒最大横截面积  $\text{m}^2$ ；

$\sigma$ ——表面张力 N/m；

$g$ ——重力加速度  $9.8 \text{ m}/\text{s}^2$ 。

将式 8 积分可得粉粒行程、速度与时间的关系,若认为粉粒行程为  $2r_{\text{粉}}$  时  $v = 0$ ,则可得粉粒注入钢液所需临界速度为

$$v_{\text{临}} = \sqrt{\frac{8\sigma}{d_{\text{粉}} \rho_m} \left( \exp \frac{3\rho_m}{2\rho_{\text{粉}}} - 1 \right)} \quad (9)$$

取  $\rho_m = 7000 \text{ kg/m}^3$   $\rho_{\text{粉}} = 2990 \text{ kg/m}^3$  (对 No. 2 渣粉) 及  $3370 \text{ kg/m}^3$  (对 No. 3 渣粉)  $\sigma = 1.2 \text{ N/m}$  (按上限计) 代入式 9 则得

$$\text{对 No. 2 渣粉} \quad v_{\text{临}} = 0.211 d_{\text{粉}}^{-\frac{1}{2}} \quad (10)$$

$$\text{对 No. 3 渣粉} \quad v_{\text{临}} = 0.172 d_{\text{粉}}^{-\frac{1}{2}} \quad (11)$$

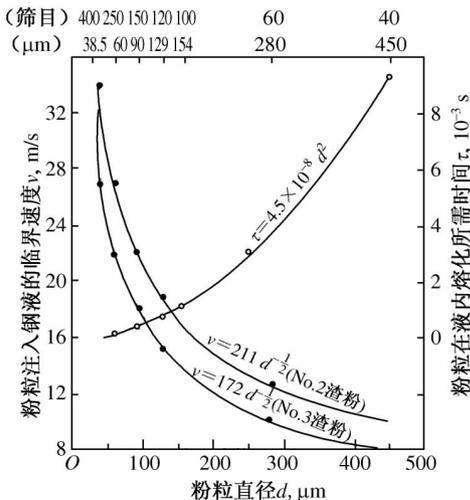


图 5 两种渣粉射入钢水的临界速度和在钢水中被熔融所需的时间

两种渣粉各种粒度分布下的注入钢液的临界速度见图 5。由图可见, 即使对最大的粉粒,  $d_{\text{粉}} = 450 \mu\text{m}$ , 亦需  $8 \text{ m/s}$  的速度才能进入钢液内部。

另一方面看一看粉粒所能达到的实际速度。

关于粉粒在气粉流中速度, 据水力学实验及高速摄影研究<sup>[10]</sup>, 大致可估计为纯气流速的一半。在五炉钢喷吹时, 由 Ar 气平均流量为  $960 \text{ L/h}$ , 可算得  $\phi 5 \sim 5.5 \text{ mm}$  石英管的口处 Ar 气平均流速为  $12 \text{ m/s}$ , 因此可粗略认为粉粒在石英管出口处为  $6 \text{ m/s}$  和现场观察甚符。

粉粒注入钢液前和钢液碰撞还要损失其速度, 按动能守恒定律可推得<sup>[11]</sup>;

$$\frac{v_{\text{碰撞前}}}{v_{\text{碰撞后}}} = \sqrt{2 + \frac{\rho_m}{2\rho_{\text{粉}}}} \quad (12)$$

其比值大致为 1.7, 因此所喷粉粒和钢液碰撞后减速至  $3.5 \text{ m/s}$ , 小于渣粉注入钢液所需的临界速度。

从上述计算可知, 所喷渣粉在所有粒度分布范围内全部不能进入钢液, 而这也为激冷钢液的金相观察没有出现原先所担心的混渣夹杂物所证实。

### 3.2 所喷渣粉在钢液的熔化时间

设渣粉为球状, 钢液为  $1600$ , 渣粉从  $20$  加热到高于熔点的温度  $1400$ 。

球的热传导方程的解为

$$\theta = \frac{t_m - t'_{\text{粉}}}{t_m - t_{\text{粉}}} = \sum_{n=1}^{\infty} \frac{2(-1)^{n+1}}{n\pi \frac{r}{r'}} \sin\left(\frac{n\pi r'}{r}\right) \cdot \exp\left(-\frac{n^2 \pi^2 a_{\text{粉}} \tau}{r^2}\right) \quad (13)$$

式中： $t'_{\text{粉}}, t_{\text{粉}}$ ——粉粒加热后温度及原始温度， $^{\circ}\text{C}$ ；  
 $r', r$ ——粉粒的瞬时半径和原始半径， $\mu\text{m}$ ；  
 $t$ ——加热时间， $\text{h}$ 。

$$a_{\text{粉}} = \frac{\lambda}{C_p \cdot \rho}, \quad \text{粉粒的导温系数 } \text{m}^2/\text{h}$$

这样求得  $\theta = 0.126$  对  $r'/r = 0.9$ ，由式 13 的图解<sup>[12]</sup>，可得

$$\frac{a_{\text{粉}} \cdot \tau}{r_{\text{粉}}^2} = 0.07$$

取粉料的热容  $C_p = 0.215 \text{ kcal/kg} \cdot ^{\circ}\text{C}$ ，导热系数  $\lambda = 1.03 \text{ kcal/kg} \cdot ^{\circ}\text{C} \cdot \text{h}$ ，

代入  $\frac{a_{\text{粉}} \cdot \tau}{r_{\text{粉}}^2} = 0.07$  则得  $\tau = 50r^2$ ，经变换单位得

$$\tau = 4.5 \times 10^{-8} d^2 \quad (14)$$

式中： $\tau$ ——熔化 10% 直径(27% 体积)所需时间， $\text{s}$ ；  
 $d$ ——粉粒原始直径， $\mu\text{m}$ 。

所用渣粉各种粒度的熔化时间亦见图 5，由图可见，粉粒在所有粒度分布范围内的熔化时间，其数量级为  $10^{-3} \text{ s}$ ，这也为熔化试验所证实。

将 5.0157 g 的圆柱形 No. 2 渣压块浸入 1600 轴承钢液，即发现迅速熔化 3 s 后取出称重为 4.9443 g，求得平均熔化速度为 0.0238 g/s，而算术平均径为 0.0198 cm 的一个渣粉重 0.000122 g，按此熔化速度则熔化时间为  $5 \times 10^{-4} \text{ s}$ ，考虑到渣块的熔化速度前小后大，因此可以认为熔化时间大致为  $10^{-3} \text{ s}$ 。

另一方面，气泡在钢液内的滞留时间，可根据气泡上浮速度及在钢液内行程而得，由于气泡先向下运动至停止再上浮，其总时间  $\gg 10^{-3} \text{ s}$ 。

因此可以认为渣粉在接触钢液的一瞬间，即熔化，而成液膜状态存在于 Ar 气泡的表面。渣膜厚度根据气泡大小、数量及喷粉量曾经算得，平均为 2.4  $\mu\text{m}$ ，相当于扩散反应的浓度边界及厚度，而大大发挥低  $\text{SiO}_2$  活度渣的精

炼作用. 可以推知脱氧速度将是很快的.

### 3.3 扩散脱氧反应速度

根据以上对两种渣粉在钢液中力学和热学行为的计算分析, 可知在 Ar 气泡和钢的界面上造成了熔融的  $a_{\text{SiO}_2} = 10^{-3}$  的渣, 而钢中 Si 和 O 向液渣扩散. 根据图 4 的脱氧模型, 可以计算喷粉期的脱氧速度.

因扩散反应为一级反应, 故速度方程式的积分式为

$$\ln \frac{\alpha_{[\text{O}]}}{\alpha_{[\text{O}]_{\text{喷前}}}} = -k\tau \quad (15)$$

假定喷入粉量 W 随喷粉时间  $\tau$  均匀增加, 则式 15 亦可写为

$$\ln \frac{\alpha_{[\text{O}]}}{\alpha_{[\text{O}]_{\text{喷前}}}} = -k'W \quad (16)$$

式中:  $\alpha_{[\text{O}]}$ ——喷粉过程的瞬时氧活度, ppm;

$\alpha_{[\text{O}]_{\text{喷前}}}$ ——Si 脱氧后、喷粉前的氧活度, ppm;

k——反应速度常数,  $\text{s}^{-1}$ ;

k'——反应速度常数, kg/g;

$\tau$ ——喷粉及吹氩进行的时间, s;

W——瞬时喷入的总粉量, g/kg.

这样, 根据实验结果算得脱氧速度常数 k 值见表 4, 脱氧速度方程式见表 5.

表 4 脱氧反应速度常数

方案	渣粉	炉号	$\alpha_{[\text{O}]}$ (ppm)		$\ln \frac{\alpha_{[\text{O}]_{\text{后}}}}{\alpha_{[\text{O}]_{\text{前}}}}$	t(s)	k ( $\text{s}^{-1}$ )
			喷前	喷后			
I	No. 2	4	26	1.25	- 3.03	45	0.067
		1	50	11.5	- 1.47	113	0.013
II	No. 3	6	41	4.7	- 2.17	40	0.054
		2	47	3.2	- 2.69	95	0.028
		7	27	6.2	- 1.47	60	0.025

表 5 脱氧速度方程式

方案	炉号	$\frac{\alpha_{[\text{O}]}}{\alpha_{[\text{O}]_{\text{喷前}}}} = f(\tau)$	$\frac{\alpha_{[\text{O}]}}{\alpha_{[\text{O}]_{\text{喷前}}}} = f(W)$

I	4	$\alpha_{[O]}/\alpha_{[O]}^{\text{喷前}} = \exp(-0.067\tau)$	$\alpha_{[O]}/\alpha_{[O]}^{\text{喷前}} = \exp(-0.3015W)$
	1	$\alpha_{[O]}/\alpha_{[O]}^{\text{喷前}} = \exp(-0.013\tau)$	$\alpha_{[O]}/\alpha_{[O]}^{\text{喷前}} = \exp(-0.1469W)$
II	6	$\alpha_{[O]}/\alpha_{[O]}^{\text{喷前}} = \exp(-0.054\tau)$	$\alpha_{[O]}/\alpha_{[O]}^{\text{喷前}} = \exp(-0.36W)$
	2	$\alpha_{[O]}/\alpha_{[O]}^{\text{喷前}} = \exp(-0.028\tau)$	$\alpha_{[O]}/\alpha_{[O]}^{\text{喷前}} = \exp(-0.266W)$
	7	$\alpha_{[O]}/\alpha_{[O]}^{\text{喷前}} = \exp(-0.025\tau)$	$\alpha_{[O]}/\alpha_{[O]}^{\text{喷前}} = \exp(-0.25W)$

喷粉期相对氧含量随喷入粉量的变化见图 6. 图中虚线为 Sandberg<sup>[13]</sup> 在 7 kg 高频炉对不锈钢熔池的实测值的回归曲线. 由图可见, 喷粉期氧含量的变化趋势和 Sandberg 的实测曲线形状一致, 这进一步证明了扩散机理. 同时由图 6 可见, 方案 1、2 无显著差别, 而炉号 1 结果稍差, 原因在上面已指出. 就喷入渣量看, 喷 6 g/kg 者 (炉号 6、7) 稍差于喷 10 g/kg (炉号 2、4). 机械混合渣 (炉号 7) 比预熔渣稍差. 但这 5 炉结果均优于 Sandberg 的结果, 而且喷机械混合渣效果之降低不像 Sandberg 那样明显.

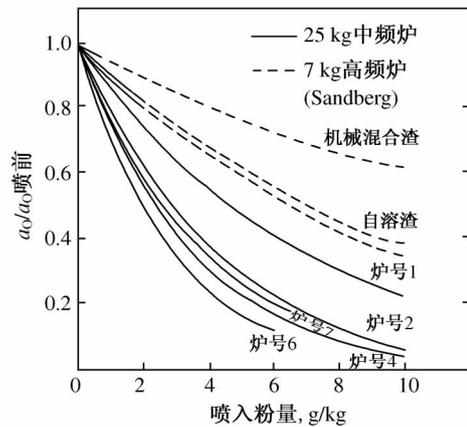


图 6 喷粉期相对氧含量变化

## 结 论

在轴承钢钢液中, 采用喷低  $\text{SiO}_2$  活度渣粉的硅脱氧, 在脱氧方面能达到以下目的:

(1) 钢中氧能降得很低. 热力学计算表明, 当 Si 脱氧产物的活度很低时, 和 Si 平衡的氧量能降低到 1~2 ppm.

(2) 脱氧速度快、效率高. 由于 Ar 的搅拌作用和渣粉的极大比表面积, 加快了 Si 和 O 向渣粉的扩散传质, 使钢中 [O] 在 1'~2' 内从 50 ppm 降至 5 ppm, 脱氧率 90%.

(3) 不沾污钢液. 渣粉的喷射冶金特性计算表明: 渣粉和脱氧产物不注入钢液而随 Ar 气泡排出.

(4) 无二次氧化之忧. 只要面渣覆盖好, Si 脱氧不像 Al 脱氧那样易被空气二次氧化, 而且随钢液凝固降温, 由于 Si-O 平衡的移动, [O] 能进一步降低.

(5) 不像真空脱氧那样, 受耐材分解的影响, 因为耐材在常压的氧位低

于钢液的氧位。

(6) 由于(4)、(5) 因此脱氧后钢液的氧量能保持稳定, < 15 ppm.

(7) 由于不用 Al 作终脱氧, 故能为消除 B 类夹杂及消除 Ca-Al 系的 D 类夹杂创造条件, 但带来少量 C 类夹杂。

本法粉料廉价来源广, 设备简单, 在经济上可取。如配合其他手段, 如真空处理、电磁搅拌, 可炼出优质轴承钢。可以这样说, 这种脱氧方法糅合了三种传统脱氧方法的长处, 而避免其各自的短处, 值得在大生产中采用。对这种脱氧的理论, 值得进一步深入探讨。

## 参 考 文 献

- [ 1 ] E. T. Turkdogan : Deoxidation of steel. JISI No. 1 (1972) , 21-26
- [ 2 ] H. Sandberg : Deoxidation of steel by injection of slags with low SiO<sub>2</sub> activity. Scaninject I , 1977 , pp. 10-11
- [ 3 ] 曲英 : 炼钢学原理. 1980 , p. 135
- [ 4 ] John F. Elliott : Thermochemistry for Steelmaking , Vol. II , 1963 , p. 59
- [ 5 ] 同[3] , p. 67
- [ 6 ] Д. Я. Поволочкий : Раскисление ст али , Издат ельст во Мет аллургия (Москва) , 1972 , СТР16
- [ 7 ] 饭田义治 : 硅镇静钢喷粉脱氧. 铁と钢 65 卷 8 号(1979) , 1159 - 1166
- [ 8 ] R. J. O'Malley , C. E. Dremann and D. Apelian : Alloying of molten aluminum by manganese powder injection. J of Metals , Vol. 31 , No. 2 (1979) , 14-19
- [ 9 ] М. Ф. Сидоренко : Теория и Практ ика Продувки Мет алла Порошками. Москва , Мет аллургия , 1978
- [ 10 ] T. A. Engh. K. Larsen and K. Venas : Penetration of particle-gas jets into liquids. Iron-making and Steelmaking , Vol. 6 , No. 6 (1979) , 268-273
- [ 11 ] 同[9] , СТР15
- [ 12 ] Тайч Н. Ю : Технология Нагрева Ст али. М. Мет аллургиздат , 1962 , СТР567
- [ 13 ] 同[2] pp. 10 - 17