

李正邦 著

电渣冶金 原理及应用

冶金工业出版社

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北 京
冶 金 工 业 出 版 社
1996

图书在版编目 (CIP) 数据

电渣冶金原理及应用/李正邦著. -北京:冶金工业出版社, 1996.12

ISBN 7-5024-2001-0

I. 电… II. 李… III. 电渣熔炼 IV. TF141

中国版本图书馆 CIP 数据核字 (96) 第 23790 号

出版人 卿启云 (北京沙滩嵩祝院北巷 39 号, 邮编 100009)

北京市社科印刷厂印刷; 冶金工业出版社发行; 各地新华书店经销

1996 年 12 月第 1 版, 1996 年 12 月第 1 次印刷

850mm×1168mm 1/32; 8.75 印张; 235 千字; 270 页; 1-1000 册

15.00 元

序 言

电渣重熔是提纯钢及合金的一门重要技术，其原理在半个世纪前已经提出，60年代在苏联和美国发展成工业生产方法。我国亦及时积极开发，解决了早期的轴承钢及其后的其他合金钢以至高温合金等新型材料的质量问题和工业生产问题。为了生产特殊异形产品，还开发了电渣重熔与（精密）铸造相结合的电渣熔铸工艺。

本书作者李正邦教授是我国最早从事这一领域研究开发的工作者之一。30余年来，他在电渣设备的设计、建设、投产，电渣过程的机理，新工艺、新产品的研究开发和实施等方面，都做了具有创新性的工作，对这一门技术在我国的成长和发展，满足国民经济建设和国防建设中的需要，以及对专业人才的培养等方面，做出了重要贡献。本书汇集了作者先后发表的一部分有代表性的文章，是电渣冶金方面一本很有意义的参考文集。相信它将受到本专业及各方有关人员的欢迎，对我国电渣技术的更大进步和发展有所裨益。

特为序。

邵象华

1996年11月8日

前 言

当前正处于世纪之交，在这个划时代的时刻，由于高新技术进入产业，引发了“第三次产业革命”、“第四次浪潮”，出现了一系列令人瞩目的新动向。新材料是高新技术发展的基础，因此材料制备科学倍受重视。金属材料面临高分子材料和硅酸盐材料激烈竞争，但金属材料仍在发展，在市场中占有相当的比率。1990～1995年欧共体先进材料计划（简称EURAM）的84个重点项目中，新金属材料研制经费占45%，1995年在世界新材料贸易中新型金属材料占交易额的47%。

金属材料的发展战略是：提高金属纯净度、控制凝固组织，以保证质量及性能，发展近终成形实现毛坯精化。现行生产工艺中只有在水冷结晶器中的重熔精炼才兼具提高金属纯净度和控制凝固组织的双重功能。重熔精炼成熟工艺有四种：电渣重熔、真空电弧重熔、电子束重熔和等离子重熔。就目前生产应用而言，电渣重熔金属材料产量居第一，它的年产量超过后三种重熔方法产量的总和。而唯有电渣熔铸独具提高金属纯净度、控制凝固组织及近终成形达到毛坯精化三重功能，因此美国材料咨询局给总统的报告称“电渣熔铸是跨世纪的技术”。

人们研究电渣冶金发展史，可以追溯到美国霍普金斯（R. K. Hopkins）于1940年所取得的“电铸锭法”专利（美国专利号No 2191479），但由于独家封闭性生产，技术落后，成分不均匀，特别是理论研究的落后——霍普金斯及其同事长期误认为电渣过程是“埋弧过程”，所以未获推广。现代电渣冶金技术起源于乌克兰巴顿电焊研究院，在电渣焊的基础上开发出电渣重熔技术。1958年，苏联德聂泊尔特钢厂P909型工业电渣炉（0.5t）建成，苏联电渣重熔起步比美国、联邦德国、日本、奥地利、英国等早7年。

1965年后,由于航空航天工业的发展、动力设备大型化、海洋开发及军备竞赛等的需要,电渣重熔钢生产空前兴隆,各国特殊钢厂纷纷建设电渣炉,加强了对于电渣工艺及理论研究,一批电渣技术开发中心形成,这些中心常常受到国防工业部门及尖端产业的支持。

根据有关资料推算,世界电渣钢生产能力超过120万t/a。生产的品种有:优质钢琴丝钢、高强马氏体特殊钢、航空及仪表用轴承钢、工具钢、模具钢、耐热不锈钢、冷轧轧辊用钢、高温合金、精密合金、耐蚀合金、电热合金钢等400多个品种。近年电渣重熔的品种进一步扩大到有色金属领域,Al、Cu、Ti、Mo、Co、Ag等合金都应用电渣重熔技术。

世界上最大的电渣炉是德国萨尔钢厂220t电渣炉。最大的板坯电渣炉是前苏联70t电渣炉。电渣焊所焊接最大断面达10m²。世界上最大的电渣车间是前苏联德聂泊尔特钢厂车间,年生产能力超过10万t。

从学科上划分,电渣冶金属于冶金领域,特种冶金学科。由于各国致力于发展电渣冶金,又开拓出不少新分支,包括电渣重熔、电渣熔铸、电渣浇注、电渣转注、电渣热封顶、电渣自熔模、电渣离心浇注、电渣直接还原、电渣焊等。

电渣冶金之所以能如此迅速发展,是由于它在技术经济上具有一系列优越性:

(1) 金属质量优良。金属纯净度高,组织致密,成分均匀,表面光洁。

(2) 生产灵活。电渣冶金不仅可以生产圆锭、方锭、扁锭,而且能生产空心管及异形铸件,实现毛坯精化。

(3) 工艺稳定。质量及性能再现性高,可将电炉母炉号为一批抽检。

(4) 经济合理。设备相对简单,操作方便,生产费用低于其他重熔精炼工艺,金属成材率高。

(5) 过程可控性好。对产品化学成分、夹杂物性质及形态、结

晶方向、枝晶间距、显微偏析、碳化物颗粒度均可不同程度予以控制。可控制参量少，外围检测准确，便于实现微机闭环控制。

20 世纪 60 年代后期至 70 年代，欧美各国发展电渣重熔技术均引进苏联技术，美国引进苏联 Y436C (M) 型电渣炉技术，法国建立电渣炉的硬件及软件全部由苏联引进，日本由苏联引进了 $\Theta\Pi\Pi-40$ 型 40t 板坯电渣炉技术。而我国发展电渣重熔是出于军工材料的需要，早在 1958 年我国冶金工作者在电渣焊的基础上开发出电渣重熔技术，1959 年在衡阳冶金机械厂炼出高速钢，1960 年 8 月 25 日重庆特殊钢厂建成工业电渣炉，炼出 1t 钢锭。目前国内所有特殊钢厂都建立了电渣重熔车间，全国有工业电渣炉 (2~10t) 86 台，年生产能力 10 万 t，小型电渣炉星罗棋布，遍及全国，从结晶器消耗推算产量近 3 万 t/a。我国电渣冶金技术在上处于领先地位，有独到之处，表现在：

(1) 电渣炉炉型上。1960 年重庆特殊钢厂建立的电渣炉采用双电极送进机构交替工作，连铸抽锭方案。设备可使用铸造电极 (长度 $L < 2m$)，抽锭可扩大锭重，节省结晶器费用。该设备采用液渣启动、液位检测、抽锭速度控制、二次冷却，均属创新。这一设备结构公诸于世后国外纷纷仿制，奥地利著名专家霍茨格鲁伯 (M. Holzgruber) 1988 年设计 10t 电渣炉就是在消化吸收我国经验的基础上设计而成的。

(2) 电渣熔铸方面。1969 年在美国匹兹堡召开的“第二届国际电渣会议”上，苏联首次展示电渣熔铸产品照片，引起同行兴趣。其实早在 1967 年我国电渣工作者就开始开发电渣熔铸，先后研制成轧辊、模块、曲轴、火炮、飞机起落架及航空发动机涡轮轮盘，特别是涡喷八发动机涡轮轮盘的定型生产，是世界航空史上的创举，在苏联展示照片时，我国熔铸火炮管已制成 122 榴弹炮并发射。

(3) 探明电渣重熔机理。长期以来，国外学者认为电渣重熔去除钢中夹杂物的原因是夹杂物自金属熔池浮升，而我国冶金工作者经系统工作证明，电渣重熔去除非金属夹杂物主要发生在电

极端头，反应是炉渣对夹杂的吸附和溶解。这一理论为国际同行承认，在专著中引用。美国、前苏联、英国、日本核心期刊全文转载。

(4) 降低电耗方面。电耗高、生产率低是世界各国电渣重熔普遍的问题，我国冶金工作者研究出，电导率高的氟渣配合大填充比重熔，利用渣凝固过程的选择结晶形成绝缘渣皮，使本溪特钢电耗由 $1775\text{kW} \cdot \text{h}/\text{t}$ 降至 $936\text{kW} \cdot \text{h}/\text{t}$ 。在全国推广这一工艺原则，1983~1993 年十年节电 $133.90\text{GW} \cdot \text{h}$ 。

(5) 控制模型研究方面。我国冶金工作者首先将热传递模型与凝固模型关联。应用此模型重熔出优质大断面高速钢，碳化物不均度达世界名牌 Isodics 水平。采取在两相区取微分元方法，推导出计算局部凝固时间 LST 的简化公式，代入验证工艺迅速，满足生产实际需要。

38 年来，我国电渣冶金经历了启蒙阶段、发展阶段，已进入成熟阶段，拥有相当生产能力，形成了一支强大的技术队伍，在技术上对世界电渣冶金的发展做出了一定贡献。

本书在作者 74 篇论文中，选择 19 篇，部分地反映了作者对我国电渣冶金发展所做的贡献，供读者阅读参考。

本书的出版要感谢我的老师邵象华院士作序，林功文教授、张家雯教授及车向前高工校正。

李正邦

1996 年 9 月 27 日，中秋

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MECHANISM OF OXIDE INCLUSIONS REMOVAL IN THE ESR PROCESS

1 INTRODUCTION

The purification of metal in ESR process, especially with respect to removal of nonmetallic inclusions, has been well established. However, about its mechanism various researchers are holding different view points. It has been stated by Latash^[1] and Madono^[2] that the principle of removing inclusions in ESR process is through physical floating of non-metallic inclusions from molten metal pool to slag bath. According to the Stokes' Law they calculated floating velocity of the inclusion. Garevsky and Schult^[3] have suggested that removal of inclusions takes place mainly at the stage of droplets falling through the slag bath. Even Gammal^[4] and Hasegawa^[5] have further thinned droplets by changing the frequency of electric current. Early in 1961 the author^[6] had suggested that removal of inclusion occurred mainly at the stage of formation of droplets or at the electrode tip. This conclusion was based upon quantitative determination by metallography. Mitchell^[7] had also reached a similar conclusion through metallographic studies. However, these methods are not sufficiently accurate because metal samples under the condition of quick cooling could contain excess oxygen.

Inclusion removal in ESR process is by absorption into the slag. The mechanism of absorption is related to interfacial phe-

nomenon or dissolution or electro-chemistry or chemical reactions. No final conclusion has yet been reached on exact mechanisms. Some metallurgists^[8,9,10] believe that the metal cleaning during electroslag remelting occurs because inclusions are absorbed and dissolved in the slag. Factors directly affecting cleaning depend on the components and composition of the slag and the type and size of inclusions.

It is known that the type, composition and size of inclusions in steel often depend on the deoxidization system used in steel-making. This research deals with the mechanism of inclusion removal in ESR. This paper presents the experiments conducted in three parts:

(1) Measurement of reaction time and the interfacing area between metal and slag in the following three sites: electrode tip, molten droplets and molten metal pool. Metal samples taken from three stages are annealed for 3 hours to cancel the defects of experimental methods cited in literature^[1,6] and analyzed for change of oxygen and sulfur in metal. A high sensitivity indicator is used for studying the behavior of oxide inclusions $Zr^{95}O_2$ considered as representative during electroslag refining.

(2) Examination of the mechanism of absorption and dissolution of inclusions in the ESR process: consumable electrodes of ZGCr15 bearing steel of high cleanliness were prepared using different types and quantities of deoxidization agents to refine the melt. Accurate quantitative and qualitative analysis of inclusions and size and amount of inclusions before and after electroslag remelting were determined. The influence of the composition of original inclusions in the consumable electrode and their behavior during ESR were studied.

(3) Experimental confirmation was also obtained through

performance of industrial scale electroslag refining of ZGCr15 bearing steel electrodes.

2 EXPERIMENTAL PROCEDURES AND RESULTS

Melting installations: 50kg electrode slag furnace, 100kV • A transformer.

Remelting technology: consumable electrode $\phi 50\text{mm} \times 1700\text{mm}^2$, ZGCr15 steel; slag CaF_2 70% + Al_2O_3 30%; current 2000 A, Voltage 31 V; cooling water temperature $< 45^\circ\text{C}$; ignition with liquid slag.

Electrode materials melting: Bearing steel was primary melted in an induction furnace. Final deoxidization was with Al 1kg/t for conventional test and radioactivity indicator Zr^{95} for radioactive test. 1.5g of deoxidizing agent Zr^{95} was added into 8kg of steel forming Zr^{95}O_2 ; then the steel was cast into an electrode.

3 TESTING PROCEDURES AND RESULTS

The refining during the three stages was compared and droplet transferring frequency (drops/s) was measured by SC-1 oscilloscope. Combined with the value of melting rate (g/s) droplet weight and metal-slag contacting specific area (mm^2/g) were evaluated.

Under protection of argon atmosphere, electrode was rapidly withdrawn from the melt and, the specific area (mm^2/g) of the liquid metal film on the electrode tip based on the value of droplet falling frequency, the time of droplet formation (s) are evaluated. Geometry of the metal pool was determined by sulfur printing method.

Droplet falling velocity w (cm/s) was calculated based on the following formula:

$$g(\rho_1 - \rho_2) \frac{\pi d^3}{6} - \varepsilon \frac{\pi d^2}{4} \rho_2 \frac{w^2}{2} = \rho_1 \frac{\pi d^3}{6} \frac{dw}{dt} \dots\dots (1)$$

where g —gravity acceleration;

ρ_1 —density of metal;

ρ_2 —density of slag;

d —diameter of droplet;

w —falling velocity of droplet;

ε —coefficient of resistance.

Results of measurements and calculations are shown in Table 1.

Table 1 Comparison of Smelting Conditions

part	contacting area between metal — slag/ mm ²	weight of metal and slag	specific area/ (mm ² /g)	Reacting time/s
electrode melting tip	2780	3.15	880	0.257
molten droplets	272	3.15	86.4	0.113
metal pool	11300	2400	4.6	198

Comparison of refining efficiency during the three stages: Quantitative determination of inclusions was made by microscopic examination of inclusions at 100 \times . Oxygen content in metal was analyzed by means of vacuum fusion method. The results are shown in Table 2.

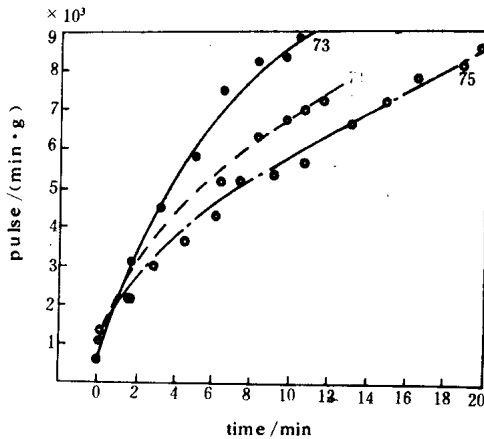
Measurement of oxide inclusion $Zr^{95}O_2$ absorption in slag samples have been taken at definite intervals after the start of remelting by the intensity of radioactivity. The variation of $Zr^{95}O_2$ contained in slag with the progress of remelting is shown in Figure 1.

Table 2 Comparison of Refining Efficiency

items part	quantitative determination of inclusions by metallo- graphic method			oxygen content in metal		sulfur content in metal	
	No. of samples	No. of samples	con- tent/%	No. of samples	con- tent/%	No. of samples	con- tent/%
primary electrode	3	30	0.01830	3	0.0063	3	0.032
electrode tip droplet	3	30	0.00590	2*	0.0033	3*	0.013
droplet in slag bath	6	60	0.00434	6	0.0024	6	0.010
metal pool	6	60	0.00411	6	0.0021	6	0.009

* Samples from electrode tip served as quantitative determination of oxygen and sulfur contents are taken from the droplets just falling off with a small spoon. Samples for metallographic determination are the droplets having not yet fallen. By corroding electrode tip with abenhoffer agent, the melting area is in appearance. Samples of inclusions for metallographic quantitative determination are annealed under temperature 1050 °C.

Inclusions were separated by electrolysis method; then ra-



**Figure 1 Variation of Radioactivity Intensity
in Slag With Sampling Time**

radioactivity was measured so as to study the variation of oxide inclusions $Zr^{95}O_2$ in metal during different remelting stages. The results are shown in Table 3 and Figure 2.

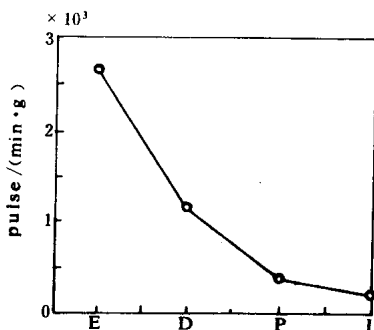


Figure 2 Variation of Specific Radioactivity During Remelting Stages

E—original electrode; D—electrode tip droplets; P—metal pool; I—ingot

In the next set of experiments the, bearing steel was smelted in the induction furnace. Final deoxidization system included Al 0.5kg/t; Al 1kg/t; Al 1.5kg/t; Ca-Si 1kg/t; Ca 1kg/t; Ca-Mn-Si 7kg/t; AMS 10kg/t; Mn 1kg/t; Ce-La 0.5kg/t.

4 ANALYSIS OF INCLUSION

Qualitative Analysis of Inclusions: The inclusions were observed by polarized light using dark and bright fields in the metallograph mode MNM-8 with sample magnification of 500×.

Quantitative analysis of inclusions: The diameters of inclusions were measured by ocular gauge with microscope magnification of 115×.

Electrolysis of inclusions; Micro-analysis of the residual inclusions were made after cleaning the nonmetallic inclusions and residual carbide with copper ammonia salt and potassium man-

ganate solutions. The data of the qualitative tests of inclusions before and after electroslag remelting, quantitative analysis with electrolytic and metallographic methods as well as the average value of gas content in the liquid steel are listed in Table 4 and 5.

Table3 Radioactivity Measurement of Inclusions Separated by Electrolysis

part items measured	original electrode	electrode tip droplets	metal pool	remelting ingot		
				upper part	middle part	bottom part
weight of metal electro-lysed/g	20. 9119	5. 7921	5. 6205	21. 414	21. 4477	21. 4392
total weight of precipitates/g	1. 675	0. 4073	0. 1212	2. 4473	2. 4859	2. 4675
measured weight of ppt/g	0. 0386	0. 0323	0. 0297	0. 0388	0. 0402	0. 0378
radioactivity in- tensity of ppt. measured/ (pulse/min)	1275	525	559	97	91	88
specific intensi- ty of radioactiv- ity/ (pulse/min • g)	2650	1174	405	285	264	268

Industrial scale experiments were conducted in an ESR fur-
nace of the following characteristics;

ESR furnace capacity 500kg

Transformer capacity 240kV • A

Melting method electrode changing and continuous with-
drawing ingot Electrode size $85 \times 85 \text{ mm}^2$, Steel ZGCr15

Mould inner diameter 240mm