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外场作用下强化钢液脱氮、脱氧的研究

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Shanghai University Doctoral Dissertation (2004)

Research on Enhancement of Denitrogenization and Deoxidation from Molten Steel in Physiacal Field

Candidate: Sun Mingshan
Major: Ferro-metallurgy
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答辩委员会对论文的评语

孙铭山同学的博士学位论文"外场作用下强化钢液脱氮、脱氧的研究"探索了金属液杂质脱除的新方法，开展了施加电场促进渣金反应以脱除金属熔体中氧的研究. 论文主要创新性结果有：

利用低温等离子体对金属溶液进行精炼反应. 这是一个在文献上未见报道的新方法. 在低温等离子体的作用下，金属熔体中的杂质通过化学和物理的过程气化，排除出体系进而达到精炼的目的.

解决了以熔体作为电极时由于钢液波动造成的不稳定放电问题. 实验中采用高速开关电路，用脉冲放电形式有效抑制了液面波动形成的过电流.

论文对锡液和钢液进行了低温等离子体下的精炼实验. 结果表明在低温等离子体的作用下，金属熔体中的硫、氮可以脱到极低的程度. 论文探讨了气氛、压力以及极性对精炼效果的影响，对低温等离子体脱除熔体杂质的机理进行了分析，建立了相应的动力学模型.

论文还研究了渣金间外加电场铜液和钢液脱氧，并根据其脱氧机理，建立了相应的模型，模型计算与实验结果基本吻合. 结果表明，选择合适的渣系，渣金间外加电场对熔体脱氧有明显的效果.

孙铭山同学的博士论文选题具有创新性，有较大的学术意义和实用价值. 论文条理清晰，层次分明，实验数据翔实，分析正确，结论可信. 表明作者掌握了坚实宽广的理论基础和系统的专门知识，具备较强的独立科研能力. 作者在答辩过程中讲述条理清晰、表达清楚，回答问题正确.

答辩委员表决结果

经答辩委员会全体成员讨论和无记名投票，一致同意通过论文答辩，并建议授予孙铭山同学博士学位.

答辩委员会主席：**董元虎**

2003 年 12 月 26 日

摘 要

随着社会的进步和科技的发展，人们对钢铁材料中的有害元素氮、氧含量的要求越来越高，而传统的钢液精炼方法已不能满足这一要求，这就需要冶金科技工作者在原有的精炼基础上提出新的钢液脱氮、脱氧方法.

钢液脱氮一直是冶金界的一大难点. 一个奇特的冶金现象引起了我们的注意：暴露在非分子态（离子态或原子态）气氛下的钢液具有明显的超常规脱氮倾向. 在实验室规模的直流电弧炉内通过中空电极向钢液吹氩，钢液中的氮可以脱到较低的水平. 这个实验结果也被钢厂 15 t 电炉中空电极吹氩的工业试验所证实. 用电子束炉重熔钢和合金时脱氮效果非常明显，而在普通真空电弧炉内熔炼的合金中氮含量则变化不大. 这些试验结果说明钢液中的氮在非分子态气氛下的反应和平衡具有与分子态气氛条件下完全不同的规律，这些规律至今尚未被人们认识清楚. 因此，有必要研究在等离子体下钢液脱氮的行为，从而为钢液脱氮开辟一条新的途径.

本研究针对这一现象，提出在直流辉光等离子体下进行钢液脱氮的研究. 这样一方面真空本身可以把氮脱除，另一方面利用辉光等离子体可强化脱氮，而直流辉光等离子体有利于研究辉光等离子体脱氮的机理. 为此，我们研究了如下关键性问题.

根据直流辉光等离子体的放电特性，设计了脉冲电路控制熔体作为一极的直流辉光等离子体，并在低温熔体锡液和高温熔体钢液上进行了实验. 实验证明利用脉冲控制电路可以克服熔体作为直流辉光等离子体一极易引起电流波动这一难点，为以后进

行这一领域的研究提供了可靠的电路保证.

从理论上对直流辉光等离子体进行了解析，为实验装置的设计和实验结果的分析提供理论依据.

在低温条件下研究了直流辉光等离子体脱除熔体锡中硫的效果，结果表明：直流辉光等离子体对锡液中硫的脱除效果要比在常态下的好；非反应性气体氩直流辉光等离子体在高硫条件下对锡液中的硫有一定的脱除效果，而在低硫条件下没有去除作用；反应性气体氢直流辉光等离子体对锡液的脱硫效果是非常明显的，而 4 000 Pa 的氢直流辉光等离子体脱硫的效果明显好于 400 Pa 的；氩氢混合气体直流辉光等离子体的脱硫效果介于这二者之间，但其脱硫效果优于对应的氢分压为 400 Pa 的氢直流辉光等离子体；在极性相反（锡液为正极）时，氩直流辉光等离子体没有脱硫效果，而氢直流辉光等离子体有一定的脱除能力. 根据直流辉光等离子体的理论对实验结果进行了机理分析和解释.

在此基础上，在钼丝炉上进行了直流辉光等离子体钢液脱氮的实验，结果表明：在压力为 4 000 Pa 条件下，直流辉光等离子体对钢液脱氮效果要比真空脱氮的好. 氢直流辉光等离子体脱氮的效果最明显，可把钢液中的氮降到 10×10^{-6} 左右，氩氢混合直流辉光等离子体次之，氩直流辉光等离子体最差. 而在真空下钢液中的氮仅脱到 25×10^{-6} 左右. 利用等离子体的理论对直流辉光等离子体脱氮的原理进行了阐述，并从热力学上对氢直流辉光等离子体钢液脱氮和脱氧的原理进行了理论上的分析和讨论.

在真空感应炉上进行了钢液脱氮的放大实验. 先对由炉衬材料产生的氧而影响真空钢液脱氮的实验现象进行了研究，结果表明炉衬材料产生的氧降低了真空钢液脱氮的速度. 在这种条件下，钢液脱氮处于一级反应和二级反应的边缘区域. 在与真空

钢液脱氮的压力和温度相同的条件下进行的非反应性氩和反应性氢直流辉光等离子体钢液脱氮的实验结果表明：在这种条件下氩等离子体脱氮和氢等离子体脱氮效果显著，都可把钢液中的氮脱到 9×10^{-6}，基本处在同一水平级. 通过对它们的脱氮过程进行动力学分析得出：氩等离子体钢液脱氮是界面化学反应控制，而氢等离子体钢液脱氮既不是一级反应控制，也不是典型的二级反应控制，但限制环节倾向于界面化学反应为主.

在实验的基础上，对直流辉光等离子体脱除熔体杂质的机理进行了分析并建立了动力学模型.

对于钢液脱氧，近年来在浓差电池短路脱氧的基础上发展了脱氧体法，尽管该方法存在无污染、脱氧速度快等优点，但存在成本高、固体电解质大型化等缺点. 为了避免这些缺点，提出了用熔渣代替固体电解质，在渣金间外加电场来强化脱氧，这样就解决了上述问题，同时具有无需还原剂、无氧化锆管炸裂、熔渣可起到防止熔体二次氧化的作用，设备简单、成本低、可连续作业等优点. 因此，这是一种很有希望的无污染脱氧方法. 为此，进行了下面的实验研究.

选择氟铝酸钠+氧化铝渣外加电场进行了铜液脱氧的研究，实验结果表明铜液脱氧的速度随着外加电压的增加而明显加快，但是终氧含量没有明显的差别. 当使用氧化钠+氧化硅渣进行实验时，终氧含量随电压的增加没有明显的变化.

在铜液脱氧实验的基础上选择 $CaO+Al_2O_3+SiO_2$ 熔渣外加电场进行了钢液脱氧的实验，结果表明钢液中氧含量到达 80×10^{-6} 左右后再很难进一步脱除. 这可能和渣中氧离子的迁移数小以及熔渣的电化学性质等因素有关.

根据渣金间外加电场熔体脱氧的机理建立了模型并利用模

型计算的数据和实验的结果进行了对比，两者基本上相吻合.

研究表明，在直流辉光等离子体下强化钢液脱氮，可把钢液中的氮脱到很低的水平，是一种非常好的钢液深脱氮技术. 而渣金间外加电场下铜液脱氧取得明显的效果，而对钢液脱氧不显著.

关键词 直流辉光等离子体，外加电场，脱硫，脱氮，脱氧，模型

Abstract

With progressing of society and developing of science and technology, the contents of harmful elements in steel, such as nitrogen and oxygen, are desired to be lower and lower. Traditional refining methods have not been enabled to meet the demand, it requires metallurgists to propose a new denitrogenization technique and a novel deoxidation method.

It is difficult to remove nitrogen from steel in metallurgy. A peculiar phenomenon, which is an evident tendency of nitrogen removal in a non-molecule atmosphere, attracted our notice. When argon gas was blown into liquid steel in an experiment-scale DC Arc Furnace through a hollow electrode, nitrogen content in molten steel could be decreased to a lower level. The result was confirmed by the trial of argon blowing through a hollow electrode in a 15-ton arc furnace. The effectiveness of nitrogen removal is obvious when steel or alloy is remelted in an electronic beam furnace, however the nitrogen content in liquid alloy doesn't change when the alloy is remelted in a vacuum arc furnace. The results obtained from these trials demonstrated that the nitrogen behavior in molten steel under the non-molecular atmosphere was different from that under molecular atmosphere. Unfortunately, the pattern of nitrogen removal hasn't distinctly been known. So, it is necessary to investigate nitrogen removal from liquid steel in plasma, thus starting a new way for denitrogenizaion of liquid steel.

Based on the fact, the study on nitrogen removal from steel in DC glow plasma was proposed. In the plasma, nitrogen removal may be removed from steel by vacuum, on the other hand, denitrogenization may be intensified by plasma and the mechanism of nitrogen removal may be understood because DC electric field was used to generate glow plasma. A series of important results have been reached as follows.

According to discharging characteristics of DC glow plasma, a pulse controlled circuit was designed to control the circuit of DC glow plasma with melt as a polar and used it to make experiment in molten tin and liquid steel. The results showed that the pulse controlled circuit was feasible to control DC glow plasma with melt as a polar, thus resolving the difficulty of current fluctuation when melt was a polar and providing a reliable circuit for studying on the field in future.

The DC glow plasma was theoretically explained and a basis was provided for the experimental design and theoretical analysis.

Desulfurization of molten tin in DC glow plasma was examined. The results indicted that the effectiveness of sulfur removal from molten tin in DC glow plasma was better than that in normal state. A certain amount of sulfur could be removed in non-reactive argon gas DC glow plasma when the sulfur content was high, and the desufurizaion did not take place when the sulfur content was low in molten tin. In the reactive hydrogen gas DC glow plasma it had remarkable desufurization effectiveness. The sulfur removal effectiveness of hydrogen DC glow plasma at a pressure of 4 000 Pa was better than that at a pressure of 400 Pa. The desulfurization

power of DC glow plasma of argon and hydrogen was between that of hydrogen DC glow plasma and that of argon DC glow plasma, but, better than that of hydrogen DC glow plasma at a hydrogen pressure of 400 Pa. While polarity was changed (the melt was anode), the argon DC glow plasma hadn't desulfurzated and the hydrogen DC glow plasma had desulferization power. Based on the theory on DC glow plasma, the experimental results were discussed and the removal of other elements from melt was considered.

Further the dinitrogenization of molten steel was investigated in DC glow plasma on a molybdenum wire furnace under the pressure of 4 000 Pa. The experiment results showed that the denitrogenization effectiveness in DC glow plasma was better than that in vacuum. The denitrogenization effectiveness of hydrogen DC glow plasma was the best in different kinds of DC glow plasmas and could make the nitrogen content of steel decrease to 10×10^{-4}mass% or so, better for argon and hydrogen DC glow plasma, and the worst for argon DC glow plasma. While in vacuum the nitrogen content in molten steel could be decreased to 25×10^{-4}mass%. Finally, nitrogen removal from liquid steel was theoretically discussed based on the theory about plasma. Especially, denitrogenization and deoxidation. in hydrogen DC glow plasma were thermodynamically explained.

The scale-up experiment was made in a vacuum induction furnace. First, the influence of oxygen from refractory lining on denitrogenization in vacuum was investigated. The results showed that the denitrogenization rate of molten steel was lowered because of the influence of oxygen from refractory lining. On the conditions, the

denitrogenization of liquid steel was controlled by both one-order reaction and two-order reaction. On basis of the experiment in vacuum, the denitrogenization of molten steel in DC glow plasma was carried out. The results indicted that both the argon and hydrogen DC glow plasma could all make the nitrogen content in molten steel decrease to about 9×10^{-4}mass %. The kinetics of denitrogenization of melt steel was discussed and it was found that the limited step was the interface chemical reaction in an argon DC glow plasma, while the controlled step was neither one-order reaction nor two-order reaction in a hydrogen DC glow plasma, and preferred the interface chemical reaction, which were explained from reaction mechanism.

From experimental results mentioned above, the mechanism of impurity removal from melt in DC glow plasma was analyzed and a kinetic model was developed.

For deoxidaion of molten steel, a new unpolluted technique, which is based on a short circuit method with solid electrolyte used as oxygen ion permeable membrane, has been developed in recent years. Although the method has many advantages such as non-pollution, quick deoxidation rate and so on, it has some shortcomings of expensive cost and difficulties of producing large solid electrolyte and other. To avoid these troubles, using slag to replace solid electrolyte with an electric field applied between slag and melt was proposed. It doesn't need reducing agent, hasn't the problem of explosion of zirconia tube, the slag can prevent secondary oxidition, and has the merits of simple equipment and low

cost. So, it would be promising deoxidation method and its study was conducted.

Choosing sodium fluoaluminate + alumina as slag, the deoxidation experiment of the molten copper with an electric field applied between the metal and slag was performed. The experimental results showed that the deoxidation rate increased with an increase in voltage. However, final oxygen content reached almost same. When sodium oxide + solica were used as slag, the final oxygen content of liquid copper was not changed with an increase of voltage.

Taking lime+aluminia+silica as slag, the deoxidation experiment of the molten steel with an electric field applied between liquid steel and slag was also made. The experimental results indicted that the oxygen content was decreased about 80×10^{-4} mass %, then was not be able to reduced further. Probably it would be due to the small transport number of oxygen ion in the slag and the electrochemical property of the slag.

On the basis of the deoxidation mechanism with an electric field applied between slag and melt, a model was developed and used to simulate the process of the experiment. The data obtained by the model were essentially agreement with the experimental result.

The present studies showed that DC glow plasma made the nitrogen content of molten steel decease to a lower level than that at the normal state. It is a good method of denitrogenization. The deoxidatin effectiveness of molten copper with an electric field

applied between liquid steel and slag was good, and the deoxidation of liquid steel was not well.

Key words DC glow plasma, electric field, desulfurizaion denitrogenization, deoxidation, kinetic model