

浸入式水口氧化铝结瘤堵塞机制

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摘 要: 浸入式水口(SEN)结瘤堵塞已成为中国高品质钢和高性能特殊钢质量和效率提升的关键问题, 至今仍未得到有效解决。本实验研究了 SEN 壁面和钢液中氧化铝夹杂物荷电性。结果表明: 连铸过程中 SEN 荷负电, 并随着拉坯速度的提高荷电量增大; 钢液中氧化铝夹杂物荷正电, 静电力为氧化铝夹杂物向 SEN 壁面迁移的重要驱动力; 高温模拟试验和实际工况试验均表明氧化铝夹杂物会向阴极移动并附着在 $\text{Al}_2\text{O}_3\text{-C}$ 材料上, 并随着电场强度的增大, 附着物厚度增厚。本工作揭示了 SEN 氧化铝结瘤新机理, 为后续研究提供了方向。

关键词: 浸入式水口; 氧化铝; 结瘤堵塞; 荷电; 外加电场

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连铸是钢铁生产的关键工序, 浸入式水口(SEN)是连铸安全高效顺行的核心耐火功能部件, 其与结晶器保护渣协同防止钢液氧化、赋予结晶器内钢液合理的流场和温度场、保证铸坯质量以及连铸工艺稳定^[1-3]。然而在高端轴承钢、稀土钢、汽车用钢的连铸过程中, SEN 容易与钢液中氧化铝等非金属夹杂物作用发生结瘤、堵塞^[4-5], 导致钢中大尺寸夹杂物增多, 钢坯质量恶化, 甚至使连铸中断, 造成连铸事故。为了有效抑制 SEN 结瘤, 学者们进行了大量的研究工作, 发现了以下结瘤机理: 1) 非金属夹杂物(脱氧和二次氧化产物)从钢液到 SEN 壁面的传输和沉积^[5-7]; 2) SEN 壁面耐火材料与钢液之间发生反应^[8-10]; 3) SEN 负压吸入空气导致钢液的二次氧化^[11]; 4) 温降导致的夹杂物析出^[12-13]等。基于上述考虑发展了相应的防结瘤、堵塞措施, 如: 提高钢液纯净度^[14]、改进 SEN 结构^[15-16]、施加物理场^[17-21]如吹氩^[22-23]、优化连铸工艺条件^[11]、创新内衬材料^[24-28]等。然而, SEN 结瘤堵塞问题至今仍未得到有效解决, 防止 SEN 结瘤、堵塞已成为钢铁工业研究的重点和难点问题^[7, 29], 究其原因是 SEN 结瘤堵塞机理未完全明晰。

基于双电层和摩擦荷电理论可知^[30-34], 当流体

与固体发生接触和分离时两者均会产生荷电。连铸过程中, 高流速钢液流过 SEN 产生摩擦, 同理钢液中氧化铝等夹杂物也会与其发生摩擦, 因此推测 SEN 和钢液中夹杂物会荷电。Paik 等^[30-31]曾通过微分电位分析方法, 发现在液态金属(Al、Pb、Sn 和 Hg)中, Al_2O_3 、 ZnO 、 NiO 、 Cr_2O_3 和 ZrO_2 金属氧化物荷正电荷。在 Paik 的研究基础上, Kim 等^[35]研究了液态锡中 SnO_2 、 WO_3 以及 PbO 等氧化物在静电场作用下的迁移规律, 发现在静电场力的驱动下颗粒会与金属液发生有效分离, 佐证了金属锡熔液中氧化物荷正电这一结论。然而, 关于 $\geq 1\ 500\ ^\circ\text{C}$ 的高温钢液中氧化铝夹杂物的荷电性未见研究报道; 不同于上述研究的外加氧化物, 钢液中氧化铝夹杂物并非直接引入, 而是在低氧势下熔钢中的金属[Al]与[O]反应形成。近期也有研究表明, 熔融金属中的氧化铝夹杂物的运动与外加电场存在关联性^[36-38], 电场力可能是 SEN 结瘤的重要驱动力, 然而这些研究均未涉及连铸时 SEN 及钢液中氧化铝夹杂物的荷电特性。

基于以上考虑, 开展连铸过程中 SEN 壁面和钢液中氧化铝夹杂物荷电性研究, 以进一步揭示 SEN 结瘤堵塞机理, 开发 SEN 防氧化铝结瘤新技术, 为

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解决 SEN 结瘤卡脖子技术难题提供理论与技术支撑,助力中国钢铁工业高质量发展。

1 实验

1.1 制备

主要原料为电熔白刚玉、 α -氧化铝微粉、鳞片石墨、硅粉和碳化硅等,结合剂酚醛树脂,试样由 Al_2O_3 -C 材料制备,组成如表 1 所示。

表 1 试样用 Al_2O_3 -C 材料组成

Table 1 Formulation of Al_2O_3 -C specimen w/%

Fused white corundum aggregates	Al_2O_3 micropowder ($d_{50}=5\ \mu\text{m}$)	Graphite -199	Antioxidant Si, SiC
0.5–0.2 mm	$\leq 0.2\ \text{mm}$		
40	10	25	22
			3

w is mass fraction.

使用 Erich 强力混合机进行混料。首先将电熔白刚玉骨料在搅拌机中预混 2 min, 然后加入粉料 (Al_2O_3 细粉、石墨和抗氧化剂)继续搅拌 2 min, 之后加入无水乙醇稀释的液态树脂[质量比: $m(\text{无水乙醇}):m(\text{酚醛树脂})=1:5$], 混合 6 min。通过筛分得到造粒均匀的物料。混得的物料在烘箱中 $60\ ^\circ\text{C}$ 干燥 12~18 h。然后, 用四柱液压机压制长条状试样: $25\ \text{mm}\times 25\ \text{mm}\times 150\ \text{mm}$ 和圆柱试样 $\phi 30\ \text{mm}\times 20\ \text{mm}$; 采用等静压机制备了坩埚试样 $55\ \text{mm}$ -外径 $80\ \text{mm}$ -高度 $150\ \text{mm}$ 和内径 $20\ \text{mm}$ -外径 $34\ \text{mm}$ -高 $350\ \text{mm}$ 2 种尺寸, 成型压力为 $120\ \text{MPa}$ 。最后, 将样品在 60 、 $120\ ^\circ\text{C}$ 和 $180\ ^\circ\text{C}$ 分别干燥 6 h, 并在埋碳条件下 ($850\ ^\circ\text{C}$ 保温 6 h)热处理。

1.2 方法与表征

1.2.1 SEN 壁面荷电行为研究 首先, 在实验室条件下, 研究钢液与 SEN 摩擦荷电行为。图 1 为钢液与 Al_2O_3 -C 材料旋转摩擦荷电试验用装置示意图。碳管炉升温制度 ($15\ ^\circ\text{C}/\text{min}$ 升温至 $900\ ^\circ\text{C}$; $10\ ^\circ\text{C}/\text{min}$ 升温至 $1200\ ^\circ\text{C}$; $4\ ^\circ\text{C}/\text{min}$ 升温至 $1600\ ^\circ\text{C}$), 待升温至设定温度后 ($1600\ ^\circ\text{C}$), 控制电机高度将 Al_2O_3 -C 试样缓慢浸入钢液中, 打开电源设定电机转速, 并用数字源表记录电流。为了进一步证实连铸过程中 SEN 壁面荷电行为, 在中国某钢厂进行了 SEN 荷电的测量。图 2 为连铸现场 SEN 壁面荷电测量试验示意图。浇铸前在水口表面刻槽(深度 $\sim 5\ \text{mm}$; 宽度 $\sim 5\ \text{mm}$), 将钼丝缠入其中, 用火泥封盖, 涂覆抗氧化涂层。连铸开始, 将数字原表一端电极与钼丝相连, 另一端接地, 测试电流大小。

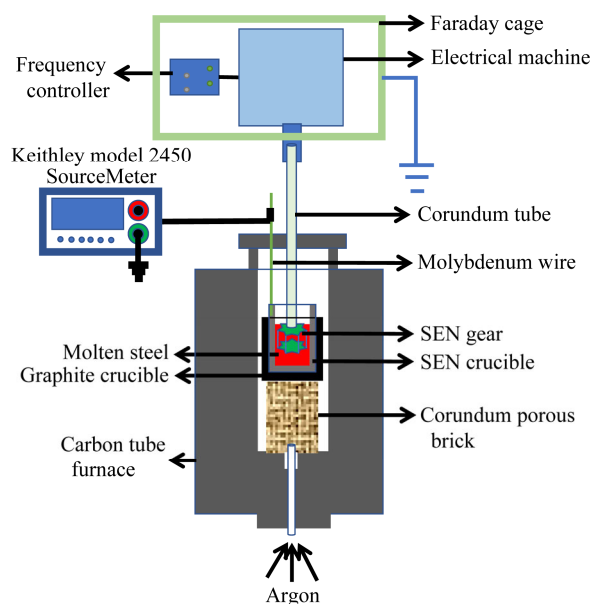


图 1 钢液与 Al_2O_3 -C 材料旋转摩擦荷电试验用装置示意图
Fig. 1 Schematic diagram of experimental device for rotating current charge experimental between molten steel and Al_2O_3 -C material

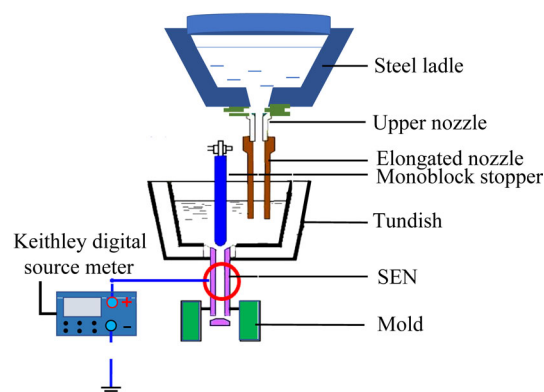


图 2 连铸现场 SEN 壁面荷电测量试验示意图
Fig. 2 Schematic diagram of SEN wall charge measurement in continuous casting site

1.2.2 钢液中氧化铝夹杂物荷电行为研究 利用高温模拟试验研究了氧化铝夹杂物的荷电性, 图 3 为电场对钢液中氧化铝夹杂物运动影响研究的试验装置示意图。将 Al_2O_3 -C 材料分别作为阳极、阴极和参比样, 施加电场后观察氧化铝夹杂物在阳极、阴极的附着行为。试验中, 打开稳压直流电源, 调节输出电流值 ($10\ \text{A}$), 同时向钢液中投喂铝丝(占钢液的 0.15% , 质量分数), 静置 $10\ \text{min}$ 。最后, 使用取渣器清理钢液表面漂浮的熔渣, 将试样提出, 自然冷却后进行研究分析。另外, 还研究氧化铝的附着厚度随不同电流的变化, 过程同上, 电流强度为 0 、 5 、 $10\ \text{A}$ 和 $15\ \text{A}$ 。

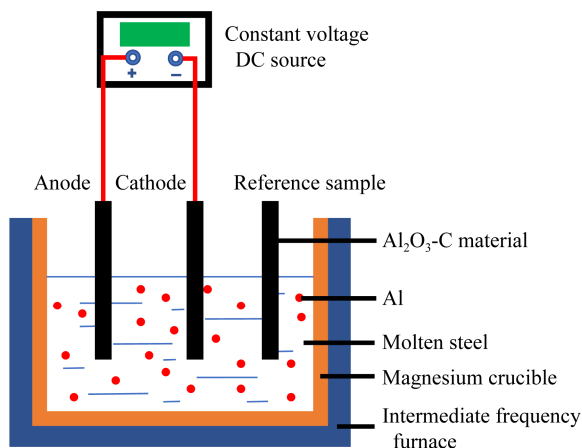


图 3 电场对钢液中氧化铝夹杂物运动影响研究的试验装置示意图

Fig. 3 Schematic diagram of experimental device for studying the effect of electric field on the movement of Al_2O_3 inclusions in molten steel

1.2.3 实际工况下外加电场对夹杂物运动的影响研究 在中国某钢厂, 采用脉冲电源进行连铸现场试验研究, 脉冲电流 110 A, 连铸 6 炉, 钢种为超低碳钢: 1) 正接试验, SEN 与电源正极相连, 整体塞棒与电源负极相连; 2) 反接试验, SEN 与电源负极相连, 整体塞棒与电源正极相连, 开浇时接通电源, 直到连铸环节结束。

1.2.4 显微结构及微区成分分析 采用 JSM-700F 型扫描电镜观察功能耐火材料氧化及侵蚀后的组织和形貌, 分辨率为 3.0 nm, 结合能谱分析仪 X-Max50 对微区成分进行分析。

2 结果与讨论

2.1 SEN 壁面荷电行为

图 4 为钢液与 $\text{Al}_2\text{O}_3\text{-C}$ 材料旋转摩擦荷电行为研究结果。当电机转速为 0 时, 电流为 -25 pA; 随着电机转速增大, 钢液与 $\text{Al}_2\text{O}_3\text{-C}$ 材料摩擦程度增大, 电流增大; 当转速达到 150 r/min 时, 电流绝对值达到最大(-400~150 pA)。这表明, 高温钢液与 $\text{Al}_2\text{O}_3\text{-C}$ 材料相对运动时 $\text{Al}_2\text{O}_3\text{-C}$ 材料荷电, 且测得的电流值正负波动, 负电高于正电。

当摩擦发生的瞬间, 因双电层分离, $\text{Al}_2\text{O}_3\text{-C}$ 材料会荷负电, 钢液荷正电。首先, $\text{Al}_2\text{O}_3\text{-C}$ 材料上的负电荷会通过源表流向大地, 电流为负值。为了中和钢液的正电荷, 会有负电荷通过源表从大地流回铝碳材料, 则源表显示的测量值为正。因此, 循环往复, 导致电流出现正负波动的现象。

图 5 为连铸过程中 SEN 荷电情况测量结果。如

图 5 所见, 连铸未开始时(拉坯速度为 0), 电压和电流值几乎为 0, 连铸开始后, 有明显的电流和电压值, 电流值为负数, 表明连铸时 SEN 荷负电。随着拉坯速度的提升, SEN 荷电量增加, 电流最大可达 70 mA。

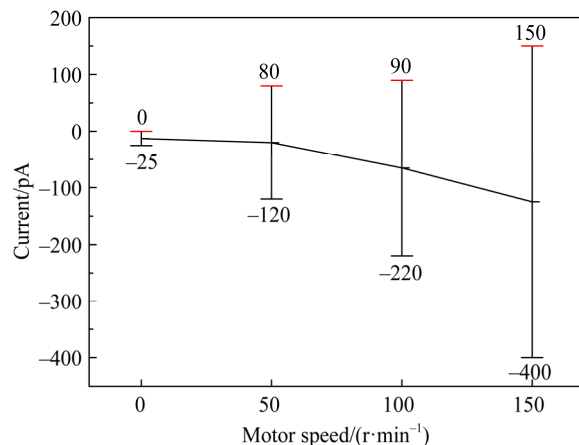
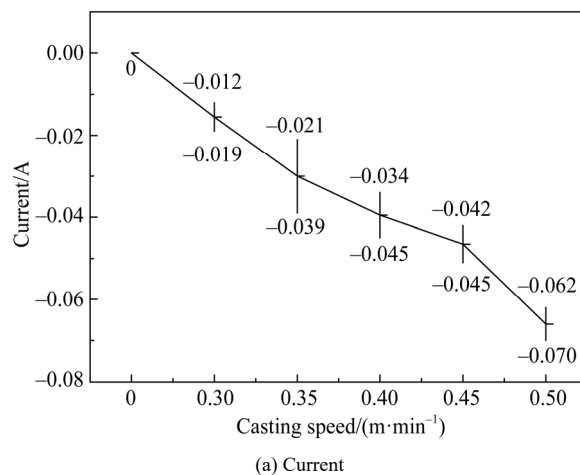
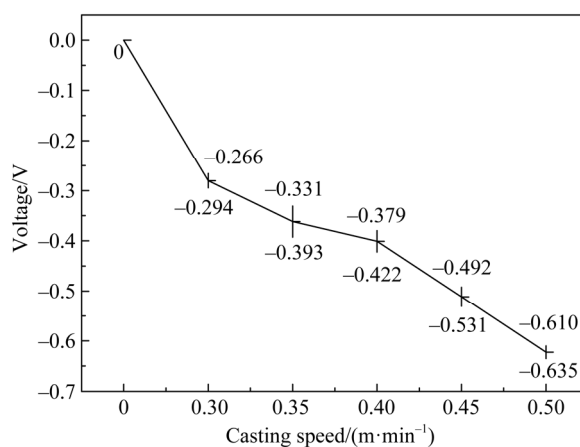


图 4 钢液以不同速度转动时铝碳材料的荷电行为

Fig. 4 Charge of $\text{Al}_2\text{O}_3\text{-C}$ materials when frictioned by molten steel at different flow rates



(a) Current



(b) Voltage

图 5 SEN 荷电行为与拉坯速度的关系

Fig. 5 Relationship between SEN charge and casting speed

2.2 SEN 壁面荷负电机理分析

1) SEN 壁面荷负电机理符合接触势差理论^[39]。不同导体内部电子密度是不同, 根据接触势差理论, 当两者接触时, 电子就会由高密度(功函数低的导体)向低密度(功函数高的导体)流动以平衡电势, 失电子的物质就会荷正电, 得电子物质荷负电, 最终在两者间形成了一个电场。因 Fe 的功函数为 4.5 eV, C 的功函数为 5.0 eV, 当钢液与 SEN 中石墨接触后, 电子会由钢液迁移至 SEN, 使 SEN 荷负电。

另外, 当 n 型半导体与金属接触时, 如果 n 型半导体的 Fermi 能级小于金属的 Fermi 能级, 金属中的电子会向 n 型半导体迁移^[39]。因为 Fe 的 Fermi 能级为 11.1 eV, Al_2O_3 的禁带宽度为 8.7 eV^[40-41], 所以 $\alpha\text{-Al}_2\text{O}_3$ 的 Fermi 能级小于 Fe 的 Fermi 能级。因此在连铸过程中, 当钢液与 SEN 中的刚玉 $\alpha\text{-Al}_2\text{O}_3$ 接触时, 电子会由钢液向 SEN 迁移, 使 SEN 荷负电。

2) SEN 壁面荷负电机理符合温差电动势理论。由温差电动势理论可知, 当温度不同的 2 种导体接触时, 电子会由温度较高的导体向温度较低的导体迁移。在连铸过程中, SEN 内部与 1 550 °C 左右的钢液接触、外部与大气接触, 所以钢液与 SEN 之间存在温差, 电子会由钢液向 SEN 迁移, 最终导致 SEN 壁面荷负电。

2.3 钢液中氧化铝夹杂物荷电行为

图 6 为高温模拟试验后试样宏观形貌照片。可以明显看出, 阴极表面上出现一层较厚的结瘤物, 参比样上结瘤物较少, 阳极表面基本没有结瘤(只在棱角处发生微弱结瘤)。图 7 阴极和参比样材料显微结构图。由图 7 可见, 阴极表面结瘤物厚度可达 1.19 mm, 参比样结瘤物厚度平均约为 0.47 mm, 阴极表面结瘤物厚度大于参比样、并远大于阳极, 表明钢液中氧化铝夹杂物向阴极迁移的趋势明显。由图 7c 和图 7d 能谱分析可见, 结瘤物主要由氧化铝和少量的 Fe 组成。因此, 可以得出连铸过程中钢液中氧化铝夹杂物荷正电, 能够在电场的作用下向阴极移动。

图 8 为不同电场强度下试验所得阴极试样显微结构图。随所施加的电流提高, 作为阴极的材料表面氧化铝结瘤厚度增加, 而作为阳极的材料, 表面几乎没有氧化铝结瘤, 更进一步说明了钢液中氧化铝夹杂物荷正电的行为。

2.4 钢液中氧化铝夹杂物荷正电机理

氧化铝夹杂物分散在钢液中, 不停的做无规则运动, 由双电层和摩擦荷电理论可知钢液中氧化铝夹杂物荷电。

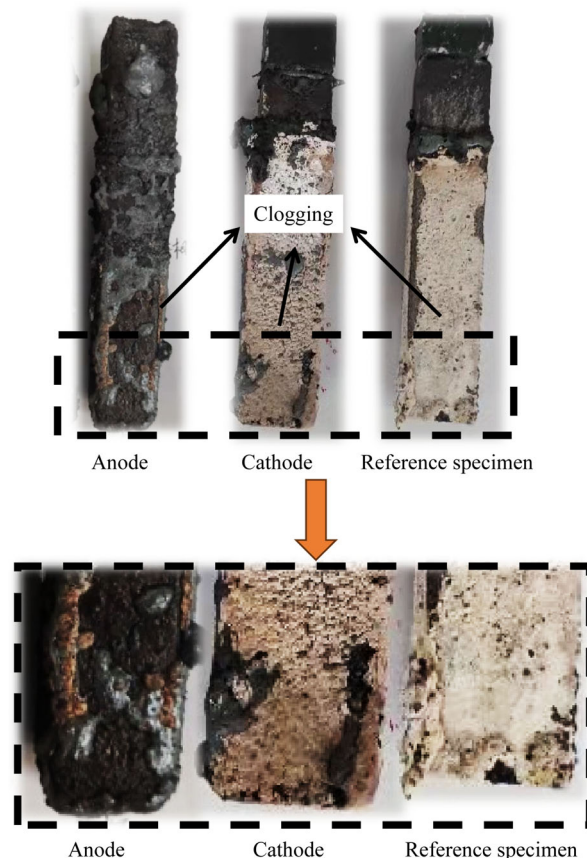


图 6 试验后电极宏观形貌照片

Fig. 6 Macrographs of electrode after experiment

事实上, 在晶体中由于热振动能量的涨落, 有许多原子会脱离正常点阵位置, 在较高温度下, 一些原子会跃迁至晶体外, 晶体中存在一定数量空阵点(空位)和间隙原子(或离子)。 $\alpha\text{-Al}_2\text{O}_3$ 是典型的离子晶体, 晶体中存在各种缺陷(V_O^{2+} , V_Al^{3+} , O_i^{2+} , Al_i^{3+})。 $\alpha\text{-Al}_2\text{O}_3$ 晶体结构存在畸变(见表 2, 表明晶体中存在缺陷), O-O 之间存在较大排斥力, O 离子有向八面体外移动的趋势。

常秋香等^[39]通过第一性原理计算了温度对 $\alpha\text{-Al}_2\text{O}_3$ 晶体中点缺陷振动熵的影响, 指出随温度的升高 V_O 的振动熵增大, 温度越高 V_O 越有利于产生(如图 9 所示); 通过计算不同 Fermi 能级、高温低氧分压下的各种点缺陷的形成能, 发现在高温低氧分压下, 最稳定的缺陷是 V_O^{2+} , 这与 Matsunaga 等^[40]的热力学计算结果相一致。在高温下, 氧化铝夹杂物中点缺陷主要为氧空位, 从而说明了高温低氧分压的熔钢条件下氧化铝夹杂物荷正电的本征特性。

2.5 钢厂连铸条件外加电场对夹杂物运动的影响

图 10 为正接试验后试样的宏观形貌照片。由图 10 可见, 与电源正极相连的 SEN 出钢口堵塞情况明显弱于未加电场的参比 SEN, 而与电源负极相

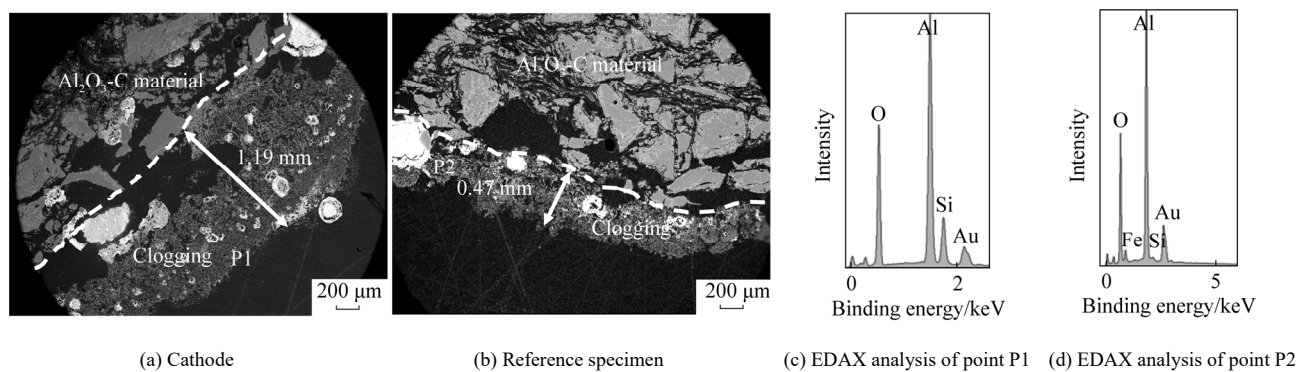


图 7 阴极和参比样材料显微结构图

Fig. 7 Microstructure diagram of cathode and reference material

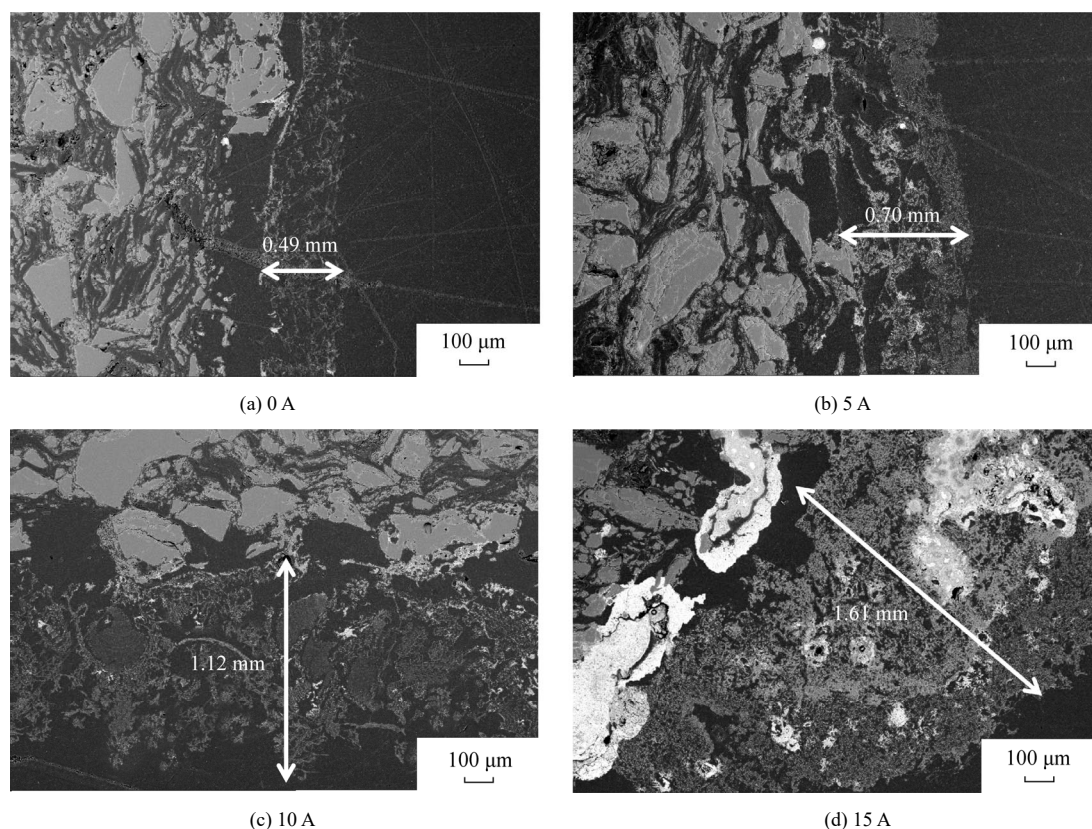


图 8 不同电场强度下试验所得阴极试样显微结构

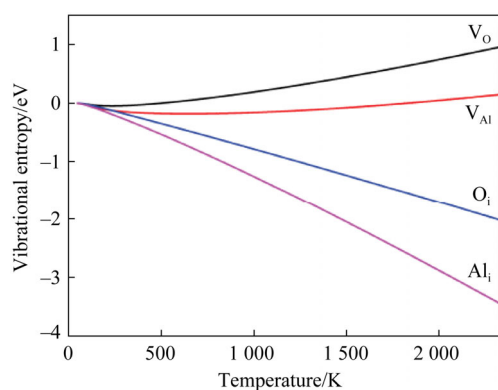
Fig. 8 Microstructure of cathode specimens under different electric field strength

表 2 α - Al_2O_3 晶体的键长及键布居数Table 2 Bond length and bond population of α - Al_2O_3 crystal

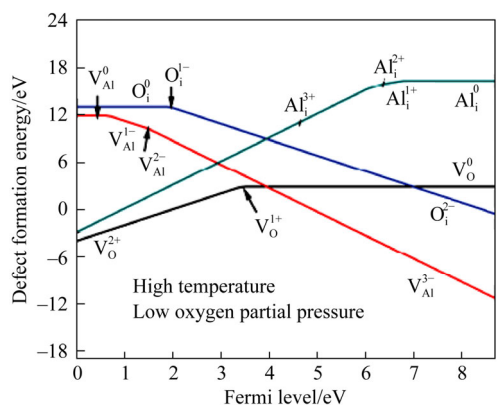
Atomic bond	Bond population	Bond length/nm
O—Al	0.35	0.185 6
O—Al	0.26	0.196 9
O—O	-0.17	0.252 2
O—O	-0.16	0.261 9
Al—Al	-0.49	0.265 0
O—O	-0.10	0.272 5
Al—Al	-0.62	0.279 0

连的 Al_2O_3 -C 电极表面附着层较厚。对两者 SEN 的内腔进行观察, 可以看出, 与电源正极相连的 SEN 内腔几乎没有发生结瘤, 而参比 SEN 内腔的氧化铝结瘤程度较高。图 11 为参比 SEN 内腔结瘤物断口的形貌分析。由图 11 可见, 结瘤物主要由 α - Al_2O_3 、 β - Al_2O_3 和 Fe 组成。

图 12 为负接试验后试样的宏观形貌照片。由图 12 可见, 与电源负极相连的 SEN 内腔结瘤程度明显高于未加电场的参比 SEN, 而与电源正极相连的 Al_2O_3 -C 电极表面未见明显结瘤。



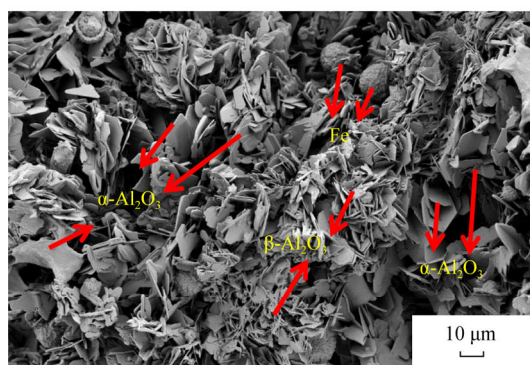
(a) Effect of temperature on the vibration entropy of point defects



(b) Defect formation energy at different Fermi levels, high temperature, and low oxygen partial pressure

图 9 氧空位形成机理

Fig. 9 Formation mechanism of oxygen vacancy



(a) Fracture microstructure of clogging

图 11 参比 SEN 内腔结瘤物断口显微结构

Fig. 11 Fracture microstructure of inner cavity clogging of reference SEN

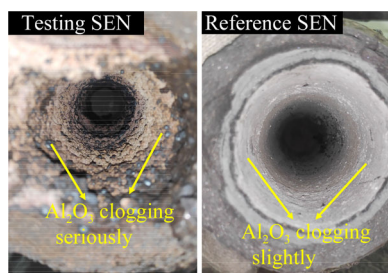


图 12 负接所得试样宏观形貌照片

Fig. 12 Macroscopic photos of the specimens obtained by reverse polarity

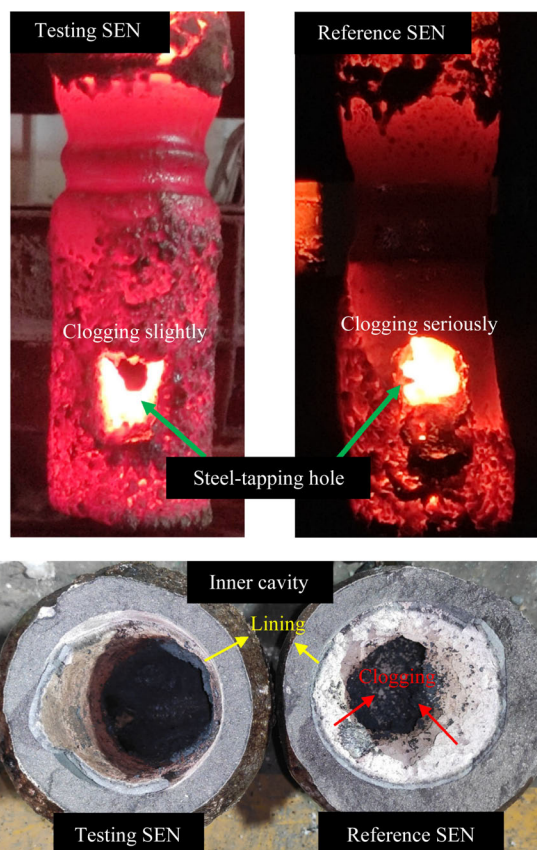
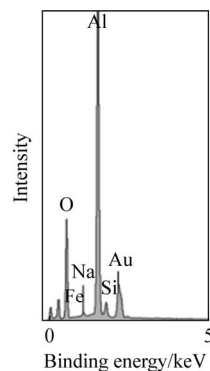
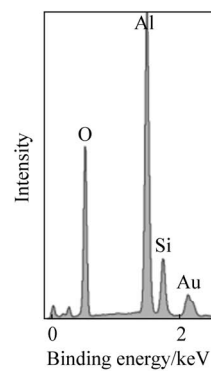


图 10 正接试验后试样宏观形貌照片

Fig. 10 Macroscopic photos of the specimens obtained by straight polarity



(b) EDAX analysis of point 1



(c) EDAX analysis of point 2

3 结论

从电化学角度研究了 SEN 结瘤机理, 基于高温模拟试验、实际工况测试和现场验证, 对 SEN 壁面带电特征、钢液中氧化铝夹杂物荷电行为及其在电场下的运动行为进行了深入探究, 并通过双电层和摩擦荷电理论、离子晶体中的点缺陷理论以及第一性原理解释了钢液中氧化铝夹杂物荷电机理, 结论如下:

1) 连铸过程中 SEN 荷负电, 并随着拉坯速度的提高荷电量增大;

2) 钢液中氧化铝夹杂物荷正电, 静电力为氧化铝夹杂物向 SEN 壁面迁移的重要驱动力;

3) 高温模拟试验和实际工况试验均表明氧化铝夹杂物会向阴极移动并附着在 $\text{Al}_2\text{O}_3\text{-C}$ 材料上, 并随着电场强度的增大, 附着物厚度增厚。

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Mechanism of Alumina Clogging on Submerged Entry Nozzle

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Extended Abstract

Introduction In the continuous casting of aluminum-killed steel, alumina (Al_2O_3) clogging frequently forms on the submerged entry nozzle (SEN) inner wall, causing SEN clogging. SEN clogging has several negative influences, i.e., flow field instability, reduced continuous casting efficiency, deteriorated billet quality, decreased quality of produced steel, and even interruption of continuous casting. The SEN clogging problem in the continuous casting of aluminum-killed steels has attracted much attention in metallurgy and refractory materials. Although many anti-clogging measures are proposed, the SEN clogging problem has not been solved yet. The main reason is that the mechanism of SEN clogging is still unclear. The clogging of SEN is mainly caused by the movement and adhesion of inclusions in molten steel to the SEN wall. It is thus necessary to clarify the mechanism of SEN clogging, especially force condition of inclusions in molten steel. Recent studies indicate that there is a correlation between the movement of oxide inclusions in molten metal and an applied electric field. The movement of inclusions under the action of electric field force is an important factor in SEN clogging. An effective way to solve SEN clogging problem is to analyze the effect of inclusions in refractory materials and molten steel from the perspective of electric field. In this paper, the charge of Al_2O_3 inclusions in SEN wall and molten steel during continuous casting was investigated to reveal the mechanism of SEN clogging and blockage, and to develop a technology for preventing alumina clogging in SEN. This work can provide a theoretical and technical support for solving the technical problems of SEN clogging in iron and steel industry.

Methods The powerful mixers (Erich Co., Germany) were used for mixing. The blast drying oven was used to control the volatile matter of the material. The samples were prepared by four-column hydraulic press and isostatic press. The samples were heat treated under the condition of carbon embedded (i.e., 850 °C for 6 h). The wall charge of SEN in the continuous casting process was measured by a digital source meter. The charging properties of Al_2O_3 inclusions was determined based on the movement law of Al_2O_3 inclusions under the action of external electric field. The correctness of the experimental results was verified by applying a reverse electric field on the continuous casting site. The microstructure and morphology of the refractory were determined by a model JSM-700 F scanning electron microscope with a resolution of 3.0 nm, and the micro-area composition was analyzed by a model X-Max50 energy spectrum analyzer.

Results and discussion The results of rotating flow experiment indicate that the SEN material is charged when rubbing with the molten steel. The experiments in the continuous casting site show that the SEN wall is negatively charged during the continuous casting process. There are three main reasons: 1) since the work function of Fe is 4.5 eV less than that of C is 5.0 eV, when the molten steel contacts with graphite in SEN, the electrons will migrate from the molten steel to SEN, making SEN negatively charged; 2) because the Fermi level of Fe (11.1 eV) is more than that of Al_2O_3 (8.7 eV), the electrons will migrate from the molten steel to SEN when the molten steel contacts with the corundum Al_2O_3 in SEN, making SEN negatively charged; 3) When the two conductors with different temperatures are in contact, the electrons will migrate from the conductor with a higher temperature to the conductor with a lower temperature. In the continuous casting process, the temperature of the SEN is less than that of molten steel, and the electrons will migrate from the molten steel to the SEN, eventually leading to the negative charge on the SEN wall.

Al_2O_3 inclusions in molten steel move and adhere to the negative electrode under the action of electric field. This indicates that Al_2O_3 inclusions in molten steel are positively charged. The main reason is that in the continuous casting process, the molten steel is under high temperature and low oxygen conditions, and the oxygen vacancy in the defects of Al_2O_3 formed by the reaction of [Al] and

[O] in the molten steel has the lowest energy.

The effect of applied electric field on the SEN nodulation was carried out in the continuous casting site. The results show that the degree of nodulation in the inner cavity of SEN connected to the negative electrode of the power supply is higher than that of the reference SEN without electric field, while there is a slight nodulation in the inner wall of SEN connected to the positive electrode of the power supply. This further indicates that the SEN wall is negatively charged in the continuous casting process, and the Al_2O_3 inclusions in the molten steel are positively charged. SEN clogging can be effectively prevented *via* applying an external reverse electric field.

Conclusions The clogging mechanism of SEN was analyzed based on the perspective of electrochemistry. In high-temperature simulation tests, actual working condition test and field verification, the charging characteristics of SEN wall surface, the charging behavior of Al_2O_3 inclusions in molten steel and their motion behavior under electric field were explored. The charging mechanism of alumina inclusions in molten steel was explained by double electric layer and friction charging theory, point defect theory in ion crystal and first-principle.

The SEN was negatively charged in continuous casting, and the charge increased with the increase of casting speed. The Al_2O_3 inclusions in molten steel were positively charged, and the electrostatic force was an important driving force for the migration of Al_2O_3 inclusions to the SEN wall. The high-temperature simulation test and the actual working condition test both showed that the Al_2O_3 inclusions could move to the cathode and adhered to the Al_2O_3 -C material, and the thickness of the attachment increased with the increase of the electric field strength.

Keywords submerged entry nozzle; aluminum oxide; clogging; charged; external electric field