Applied Research on Electrical Conductivity of Slag in Metallurgical Reaction

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Abstract: Taking the deoxidization using solid electrolyte as an example, the electrochemical reaction mechanism between metal and slag was briefly introduced. The decarburizations of molten iron by CaO-SiO_2-Al_2O_3-FeO_x slag were studied through connecting metal and slag by electronic conductor and applying static electric field on the metal-slag respectively. The experimental results indicated that the electrical conductivity of slag play an important role in the electrochemical reaction between metal and slag, and any methods beneficial to the transfer of electron and/or hole between metal and slag can increase the reaction rate. The mobility of oxygen ion in slag was limited by the transfer of electron between metal and slag, so the existence of electronic conductor between metal and slag provided a shortcut for the transfer of electron and consequently increased the mobility rate of oxygen ion. Therefore, any methods that increase the transfer rate of electron between metal and slag can improve the mobility of oxygen ion in slag.

Keywords: slag, oxygen ion transport, ion conductivity, electronic conductivity, reaction between metal and slag

1. Introduction

The transport of oxygen ion in the metallurgical reaction is an electrochemical process actually. The basic principle of this process is to utilize the known battery or electrode reaction and control the metallurgical reaction. Metals such as aluminum, high purity copper, zinc, tin, nickel etc were all smelted using this method [1].

Since the seventies of the 20th century, many countries invest a large number of manpower, material resources to develop the new process of non-coke smelting, including utilizing the electrochemical method to finish metallurgical reaction. This is a revolution of iron and steel metallurgical technology. The reaction rate between carbon-containing metal and iron oxide in slag is the important parameter of this technology and thereby becomes the focal point of research. [2]. The transport mechanism of oxygen ion in the slag can not be clarified in the research of react between carbon-containing metal and slag. This promote people to t investigate the electrochemical reaction mechanism between metal and slag.

2. The Electrochemical Mechanism of Metallurgical Reaction

With the development of metallurgical industry, the studies on electrochemical mechanism of metallurgical reactions developed fastly t. Therefore, the studies on the physical chemistry properties of slag were deepened. As we have known, slag is an ion solution that composed of metal cation, silicon-oxygen anion and oxygen ion, etc. And the liquid metal is non- polar solution which has good electric conductivity. Therefore, there are electric charges exchanging in the reaction between slag and liquid metal, and is an electrochemical reaction essentially.

Taking the oxygen concentration cell shown in figure 1 as an example, when the oxygen partial pressure at the two sides of the solid electrolyte are different electrode reaction would occur at the interface of solid electrolyte and metal electrode. Consequently, different equilibrium electrode potential will established.

Anode reaction: 2O2- - 4e = O2 (p'_{O_2})

Cathode reaction: O2 (p''_{O_2}) + 4e = 2O2-

Total battery reaction: O2 (p''_{O_2}) = O2 (p'_{O_2})

The ΔG of the reaction: $\Delta G = RT\ln(p'_{O_2} / p''_{O_2})$

The relation between the EMF of the battery and partial pressure of oxygen is calculated by Nernst equation: $E = \frac{RT}{4F}\ln(p''_{O_2} / p'_{O_2})$.

R: gas constant; T: temperature; F: Faraday constant; if p''_{O_2} has already known, it could calculate the p'_{O_2} by determining E.

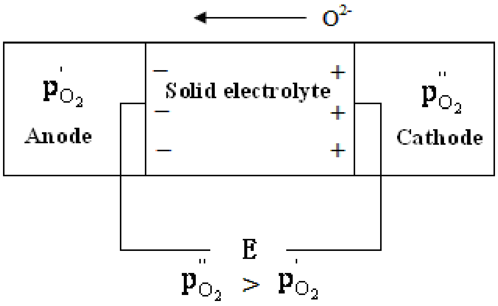

Fig.1 Schematic of oxygen battery of ZrO_2-based solid electrolyte

According to electrochemical principle, with the oxygen transporting through the solid electrolyte from high oxygen partial pressure to low oxygen partial pressure, positive charges will accumulate at the electrode interface in the high oxygen partial pressure and negative charges will accumulate at the other electrode interface in the low oxygen partial pressure. Finally, the electric field made by the accumulated charges will hinder the transfer of oxygen ion. When two electrode at both side of the solid electrolyte was connected with electron conductive material, the electron accumulated at the electrode interface in low oxygen partial pressure side would transfer to the other electode interface in the high oxygen partial pressure. And then, the electric field will disappear, and the transporting of oxygen ion could continue until the oxygen partial pressure at both side is equal.. This is the so-called short-circuited deoxidization method, its essence is still electrochemical reaction.

The slag can act as solid electrolyte completely in the deoxidization experiment. And the rate and extent of decarbonization, deoxidization and desulfurization reactions can be controlled by adjusting the electrochemical parameters.

3. Conductivity of Slag

3.1 Ion Conductivity of slag

The conductivity of slag is closely relation to the electrochemical reaction in metallurgical processes. The electric conductivity of slag composes of ion conductivity and electronic conductivity.

The studies on the ion Conductivity of slag has been started at the beginning of 20th century.Two slag systems, FeO-SiO_2 and CaO-SiO_2-$A1_2O_3$[3], were investigated. Then, Goto K S studied the effect of the content of SiO_2 on the conductivity of the FeO-SiO_2 and FeO-CaO-MnO-$A1_2O_3$-SiO_2 systems[4~5]. Martin and Derge invetigated the relationship between the electric conductivity and composition as well as temperature[6~7].

Because the electric conductivity of slag increase with the increasing of temperature, the slag were considered to be ionic melt by the early researchers. Since 1940’s, many investigations have been carried out on the structure of slag.

It’s widely considered that most of metal oxide can release the oxygen ion and become cation, whereas oxides with high valence, such as SiO_2 and $A1_2O_3$, combine with the released oxygen ion. The electric conductivity of slag were mainly affected by the complex anions. In a certain range of concentrations, the electriconic conductivity of the slag increases with the increasing of the concentration of FeO, CaO, MnO and MgO, and decreases with the increasing concentration of SiO_2, $A1_2O_3$.

3.2 Electronic Conductivity of slag

The electricnic conductivity of the slags containing large amount of FeO, MnO, TiO_2 are usually very high, but the current efficiency and the ionic migration rate are lower. Thisproved that electronic conduction [8] exist in the slag.

The current efficiency are lower when the -concerntration of FeO are high in the slag phase because of the electronic conductance of the slag. Howeverthe current efficiency decreases obviously with the increasing -concerntration of SiO_2.

Pastukhov and Fontana[10] investigated the electrical conductivity of FeO-Fe_2O_3-SiO_2 system. They thought the electric conductivity included two parts, the ionic conductivity and the electronic conductivity. The ionic and electronic conductivities are relate to the concentration of Fe^{2+}ion and Fe^{3+}ion, and the concentration of Fe^{3+} are dependent on the oxygen partial pressure. Therefore, the total conductivity of slag could be expressed through the sum of the ionic and electronic conductivity,as follows:

$$\mathrm{K_T} = K_i + AP_{O_2}^{m} \qquad (6)$$

Where, K_T—The total electric conductivity, Ki—i electronic conduction, A—Coefficient, no relationship with the oxygen partial pressure, and only depending on the compsitoin of the slag and temperature, m—Coefficient, depending on the conditions of the lab, p_{O_2} —The oxygen partial pressure.

Engell and Vygen[11] indicated, according to the studies on the slag system of CaO-FeO-Fe_2O_3-SiO_2, the total electric conductivity could be expressed as follows:

$$\mathrm{K_T} = K_o - ax + bx(1-x) \qquad (7)$$

$$\mathrm{x} = \frac{x_{Fe^{3+}}}{x_{Fe^{2+}} + x_{Fe^{3+}}} \qquad (8)$$

Where, K_T—The total electric conductivity, Ko—Ionic conductivity, a、b—Concentration coefficient, $X_{Fe}{}^{2+}$—Concentration of Fe^{2+}in the slag phase , $X_{Fe}{}^{3+}$—Concentration of Fe^{3+}in the slag phase.

Engell and Vygen[11] considered that the first two terms in the above formula express the ionic conductivity of slag phase determined by Fe^{2+}、$Ca^{2+}$and so forth, and the third term is the ionic conductivity caused by electrons or holes.

Regarding the most important difference between the two empirical formulas, Pastukhov and Fontana considered the ionic conductivity of slag phase as a constant, but the Engell and Vygen thoughtit as a variable. The concerntration of Fe^{2+}in the slag phase decrease with the concerntation of Fe^{3+} increasing, and this will affect the value of the ionic conductivity Therefore, it is reasonable that the ionic conductivity of slag is variable.

4. Appliied studies of Slag Conductivity

4.1 Decarbonization of liquid iron containing carbon by CaO-SiO_2-Al_2O_3-FeOx slag through connecting metal and slag by electronic conductor

Reaction rate and extent of decarbonization under connecting metal and slag by electronic conductor were investigated. The metals with different carbon content were weighed according to the experimental requirement, and then put into high pure Al_2O_3 crucible. The crucible was then put in the even hot zone of the furnace, heated in high pure argon. Slag was added when the metal had been melted completely. CaO/SiO_2:/Al_2O_3 ratio in the slag is 50/30/20, and the content of iron oxide was also determined according to the experiment requirement. metal was sampled at each time interval, then carbon content was analyzed.

The experiment with and without electronic conductors connecting slag and metal were carried out. . Experimental equipment is shown as Fig.2, the equipments for the two experiment are almost the same. The only difference is that the molybdenum ceramic slice (electronic conductor) was placed in the metal and slag layer. ,

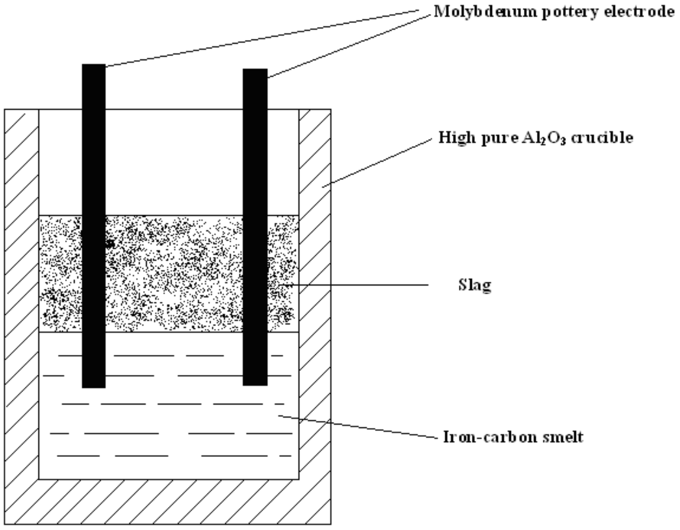

Fig.2. The schematic diagram of decarbonization experiment

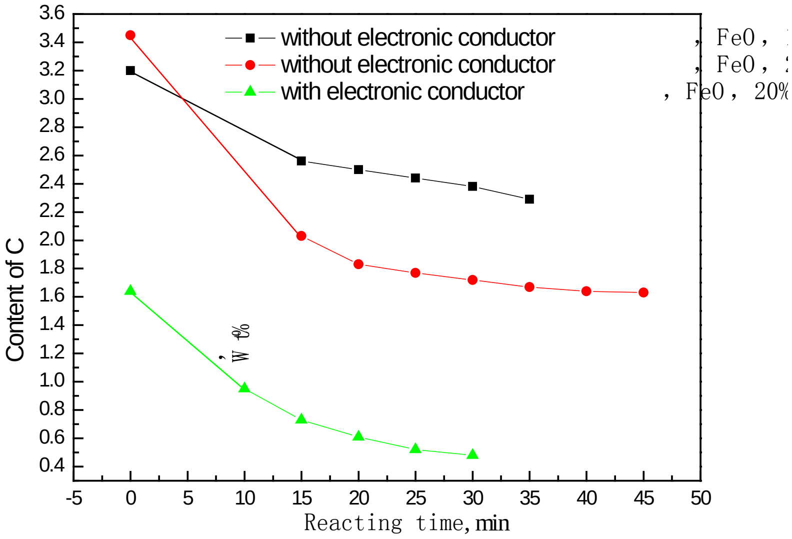

Fig.3. The relation between carbon concentration and reaction time

in various situations

As shown in Fig.3, reaction rate and extent of decarbonization were influenced obviously by the electronic conductor. Carbon content decreased from 3.4% to 1.7% within 45 minutes in the condition of without electronic conductor. Howerer, carbon content decreased from 1.64% to 0.4% within 30min when electronic conductor was applied, and carbon content would become much lower if the reacting time was prolonged. Therefore, it can be deduced that, when the electronic conductor was added between slag and metal, positive charges and negative charges accumulated at the interface of slag and metal melt were eliminated, then the electric field which hindering the transfer of oxygen ion was also eliminated. Consequently, the reaction could continue going on, and even carbon can be removed to a much lower content.

LU Xiong-gang[12] have made studies on the electrochemical reaction between carbon-containing -iron and iron oxide of slag, and set up the model of reacting (as shown in Fig.4). They considered that the oxygen ion in slag diffusing to react interface(slag boundary-gas film interface) form a static electric field. When the driving force of diffusion attributed to oxygen pontentail gradient is equal to that caused by static electic field, , the diffusion of oxygen ion would stop. If electron conductor was used to connect the metal and slag, the electron could transfer easily from reacting interface to the slag , and the electric field in the slag boundary layer become weak or even be eliminated. Then the diffusion of the oxygen ion would continue, and the decarbonization reaction continue going on until the thermodynamic equilibrim.

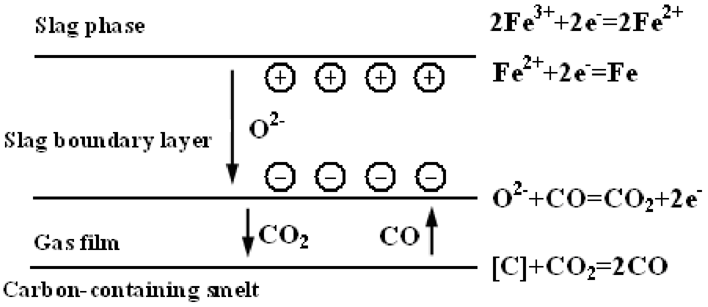

Fig.4 Reaction model of Fe-C droplet with FeO in slag

As shown in Fig.3, that reaction of removing carbon was strongly influenced by the content of FeO in the slag. The higher FeO content wss in the slag,the faster and completer the decarbonization rate was. When the FeO conten in the slag was increased, the oxygen ion conductivity can be improved and the decarbonization reacted with higher speed. This implied that the electronic conductivity of the slag played an essential role in removing carbon. Because iron are present in slag with different valence states, the molten slag has high electronic conductivity. The main reason is the equilibrium reaction between different valence, such as $Fe^{2+} = Fe^{3+} + e$, would produce a considerable amount of free electron or electronic hole. Therefore, the slag has high electronic conductivity, consequently increase the decarbonization reaction rate.

4.2 Experimental studies on deoxidization withstatic electric field

The new unpolluted deoxidization method with voltage applied between metal and slag had been also studied. This unpolluted deoxidization study was carried out in the 500Kg multifunction furnace with the stable DC voltage which was applied between CaO-Al_2O_3-MgO-FeOx slag and metal.

The experimental equipment is shown in Fig.5. 350～400Kg ultra-low carbon steel was put into 500Kg multifunction furnace, then 10～20Kg pre-melt slag was added after the steel had been melted. Utilizing Heraeus apparatus was used to detect oxygen content after slag had been melted. Then the anode electrode was lowered and make it contact with slag but not contact with molten steel. The bottom blowing system was opend, and DC voltage was applied .

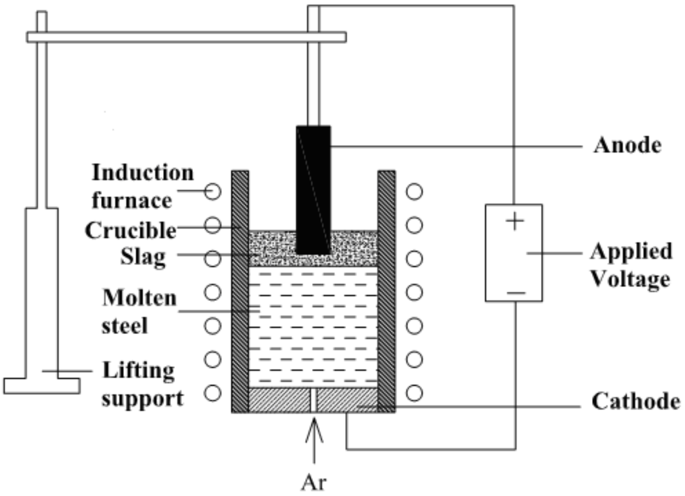

Fig.5. Schematic of experiment equipment

Table 1 The experimental condition and results of deoxidization experiments

No.	Mass of steel, Kg	Mass of slag, Kg	Experimental condition	Oxygen concentration mass fraction, 10^{-6}		Rate of deoxidization 10^{-6}×min^{-1}
				Initial	Final	
Exper.No.1	350	0	Without carbon anode without slag and voltage	864	973	-3.63
Exper.No.2	375	10	Without carbon anode and voltage with slag	885	841	1.47
Exper.No.3	380	10	Without voltage with slag and carbon anode	860	757	3.43
Exper.No.4	370	12	1～2V, 3～5A	802	354	11.20 (reaction time,40min)

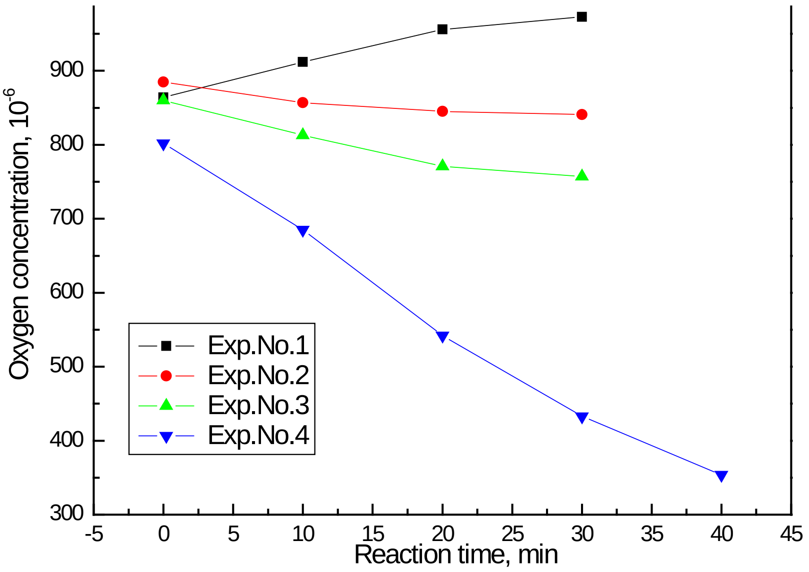

Fig.5. The relation between oxygen concentration and reaction time

in molten steel with different situation

The experiment result was shown in Table 1 also and presented in Fig.5. It could be found that when no slag was added and no DC voltage was applied, the oxygen content in liquid iron increased from the initial 864×10^{-6} to in 30min. . The increase of oxygen may come form the gas phase and liner of the furnace. When after slag was added, oxygen content in liquid iron decreased from initial 885×10^{-6} to 864×10^{-6}, the deoxidization rate was 1.47×10^{-6}·min^{-1}. When the pre-melt slag was added and DC voltage was applied, the oxygen content in liquid iron decreased from initial 860×10-6 to 757×10^{-6}, the deoxidization rate was 3.43×10^{-6}·min^{-1}. This indicated that the electric double layer formed between the slag and metal interface was destroyed after the DC voltage was applied through the graphite anode. Then the transfer of oxygen from liquid iron to the slag was improved after DC voltage was applied. The deoxidization rate with DC voltage applied was faster than that without DC voltage applied. The oxygen concentration in liquid iron can decrease from 802×10^{-6} to 354×10^{-6} rapidly in 40min with1～2V, 3～5A stable DC voltage applied, and the deoxidization rate reached 11.2×10^{-6}·min^{-1}.

5. Epilogue

With the detailed study on the steel-making progress, people paid more attention to the essence of electrochemistry. The electrical conductibility of the slag has been applied in many ways, such as decarbonization, deoxidization, desulfurization in the process of steel making gradually. Ion conductibility of the slag and electronic conductibility of the slag are playing an important role gradually in the interaction between metal and slag.

Any methods benefical for the transfer of electron and hole between metal and slag will accelerate the reaction rate. Thus, the research onthe transprot mechanism and the electrical conductivity of the slag phase will attract more attention.

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