Electronic Conductivity of *CaO-SiO$_2$-Al$_2$O$_3$-FeO$_x$* Slag System

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ABSTRACT A study on electronic conductivity of *CaO-SiO$_2$-Al$_2$O$_3$-FeO$_x$* slag system with Wagner polarization technique has been carried out. The experimental data shows that both free electron conductivity and electron hole conductivity are existed in the slag system. Conductivity of free electron and electron hole are related to the content of Fe^{3+} and Fe^{2+} respectively. Free electron conductivity is decreasing and electron hole conductivity is increasing while Fe^{3+} changes to Fe^{2+}. There is a maximum electronic conductivity value at a ratio of ferric ions Fe^{3+} to the total iron content. Under the experimental conditions, the electronic conductivity is in the range of $10^{-4} \sim 10^{-2}$ S·cm^{-1}.

KEY WORDS Smelt slag, Free electron, Electron hole, Electronic conductivity

1. Introduction

In the past time, because of little attention to the influence of electronic transport in the slag, research works about conductivity of the slag were mainly concentrated on ionic conductivity[1-15], so, the data of electronic conductivity is few. But the works[16-19] completed at recently years showed that reaction of metal melt with slag was controlled by the conduction of electrons in the slag under some conditions. The methods that are beneficial to electron immigrating through the ionic media between the slag bulk and the slag/gas film interface will drastically increase the reaction rate and the extent to which the reaction proceeded. So, electronic conductivity is not only important for recognizing transfer ability of ionic and electron in the slag, but also important for comprehending the electrochemical nature of the metal-slag reaction. The objective of the present work is to study the electronic conductivity of *CaO-SiO$_2$-Al$_2$O$_3$-FeO$_x$* slag system and get a determined relation between electronic conductivity and relative factors.

2. Experimental and Theories

Wagner polarization technique is usually applied on studying electrical conduction in solids exhibiting both ionic and electronic transport. It has also been employed to study the movement of electrons in molten salts[20-22]. Now, it is extended to determine the electronic conductivity of the smelting slag system in this paper.

A kind of unsymmetrical polarization cell is designed as Figure 1. One is reversible electrode and another is an inert electron conductor or blocking electrode.

A dc potential that is lower than those necessary to decompose the electrolyte is applied between two electrode. At the beginning, both ionic and electron flow, but ionic current is blocked and only electronic current flows as time going on, Then a steady state current is reached in the end.

The method has been thoroughly treated in the literature especially by Wagner[23] and Kroger[24]. The relationship of electronic current with electronic conductivity deduced by Wagner is

$$I_e = (\frac{RTA}{LF})\{\sigma_n[1 - \exp(-\frac{EF}{RT})] + \sigma_p[\exp(\frac{EF}{RT}) - 1]\} \qquad (1)$$

where I_e is steady state electronic current of polarization cell, R is gas constant, T is absolute temperature, A and L are area and thickness of the interface between slag and electrode respectively, F is faraday constant, E is the potential impressed across the cell, σ_n and σ_p are free electron conductivity and electron hole conductivity respectively.

In this paper, the following type of polarization cell is designed. The iron Fe(s) and the platinum Pt serve as a reversible electrode and a blocking electrode respectively.

$$Fe(s)\,|\,CaO+SiO_2+Al_2O_3+FeO_x\,|\,Pt$$
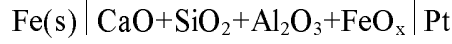
The experimental apparatus is shown in Fig 2.

An Al_2O_3 crucible with the slag materials and two electrodes are arranged in the closed reaction tube, which is heated by Mo lead furnace. The reaction tube is heated in a stream of the purified argon to keep the content of slag unchanged. When the furnace is heated to the experimental temperature, a steady voltage that is lower than those necessary to decompose the slag melts provided by 273A model potentiostat is applied across the two electrodes making the iron electrode negative and the platinum electrode positive. Simultaneously, the current through the cell is measured as a function of time with computer on line, the steady state electronic current is recorded in the end. So, conductivity of the free electron and the electronic hole can be calculated according to Eq. (1) when a series of corresponding current *vs.* potential data is recorded. The cell constant L/A is determined by measuring the AC resistance of $0.01N\ KCl$ standard solution at $20^{\circ}C$.

3. Results and Discussions

Effect of temperature on electronic conductivity
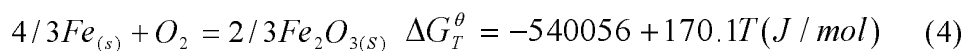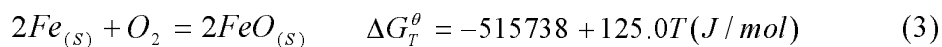
The relationships of polarization potential with steady state current at different experimental temperatures from $1330^{\circ}C$ to $1400^{\circ}C$ are shown in Fig. 3. The slag used in the experiment had 16.20%wt FeO and 18.86%wt total iron. The scatter points are experimental data and the short dot line is ideal regression curve according to Eq. (1). With the help of Eq. (1), free electronic conductivities and electron hole conductivities are calculated and listed in Table 1.

At this slag content, it can be concluded that the effect of electron hole on electronic conductivity is more pronounced and conductance due to free electrons can be neglected. The electronic hole conductivity is getting higher with the increase of temperature. An analysis of available experimental data shows that the correlation between temperature and electron hole conductivity has following logarithmic form:

$$\lg \sigma_p = 33.2 - \frac{592087}{T} \tag{2}$$

The measured steady-state current at different temperatures from $1280^{\circ}C$ to $1380^{\circ}C$ for another slag content is shown in Fig 4. The slag used in the experiment had 10.40%wt FeO and 10.70%wt total iron. Data of electronic conductivity is listed in Table 2. It can be known that both free electron conductivity and electron hole conductivity exist in this slag system. Conductivities of the electron hole and free electron are increasing and decreasing respectively with the increase of the experimental temperature.

Analyzed based on thermodynamic, for reactions:

$$2Fe_{(S)} + O_2 = 2FeO_{(S)} \qquad \Delta G_T^{\theta} = -515738 + 125.0T(J/mol) \tag{3}$$

$$4/3Fe_{(s)} + O_2 = 2/3Fe_2O_{3(S)} \quad \Delta G_T^{\theta} = -540056 + 170.1T(J/mol) \tag{4}$$

combining reactions (3) and (4), given:

$$1/3Fe_{(S)} + 1/3Fe_2O_{3(S)} = FeO_{(S)} \qquad \Delta G_T^\theta = 10659 - 20.9T \,(J/mol) \qquad (5)$$

so
$$\Delta G = \Delta G^\theta + 19.15T \lg \frac{a_{FeO}}{(a_{Fe} \cdot a_{Fe_2O_3})^{1/3}} \qquad (6)$$

$$\lg \frac{a_{FeO}}{(a_{Fe_2O_3})^{1/3}} = -\frac{556.7}{T} + 1.09 \qquad (7)$$

An analysis of Eq. (7) shows that concentration of Fe^{2+} and Fe^{3+} will increase and decrease respectively as temperature increases. It also indicates that ferrous ions Fe^{2+} is more stable than ferric ions Fe^{3+} at high temperature.

Considering the internal relation of electronic conductivity with content of Fe^{2+} and Fe^{3+} in the slag, the conduction mechanism can be explained by taking into consideration the following process:

$$Fe^{3+} = Fe^{2+} + p \qquad (8)$$

The Fe^{3+} ions will change to Fe^{2+} ions and liberate an electron hole when temperature is getting higher gradually, and the electronic conductivity mainly displays as electron hole conductivity. But in some slag systems, free electrons exist in the slag because of a lot of Fe^{3+} ions which are affected by the oxygen partial pressure of system, this is also the reason why free electron conductivities exist in some slag system at lower temperature.

Effect of iron oxide on electronic conductivity

Both Fontana[25] and Pastukhov[26] thought that conduction contributed by electrons can be represented as

$$\sigma = A \cdot P_{O_2}^m \qquad (9)$$

where P_{O2} represents the oxygen partial pressure, the coefficient A and m are dependent on temperature and composition of the slag.

Works of Engell and Vygen[27] proved that electronic conductivity satisfied the following model :

$$\sigma = b \cdot x(1-x) \qquad (10)$$

where $x = \dfrac{x_{Fe^{3+}}}{x_{Fe^{2+}} + x_{Fe^{3+}}}$, b is concentration coefficient deduced from experiments.

Although the function expressions of above two conduction mechanisms are different, the fact both proved is that the electronic conductivity is dependent on concentration ratio of Fe^{3+} and Fe^{2+} in the slag. Since the concentration of Fe^{3+} is function of oxygen partial pressure of system in nature, but it is more directly to explain this phenomena in the model of Engell and Vygen. The experimental results of the electronic conductivities under the different content of iron oxide and temperatures are listed in Table 3.

The effect of the content of ferric ions on electronic conductivity is illustrated in Fig 5. The x-axis is the mole ratio of ferric ions to the total iron content and y-axis is electronic conductivity. It can be seen that electronic conductivity has a maximum value at one content of Fe^{3+} in the slag. Changing tendencies of electronic conductivity along with the ratio of ferric ions to the total iron content is similar to the results of model as predicted by Engell and Vygen[27].

Effect of electronic conductivity on electrical conductivity

Studies on conductivity of $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}FeO\text{-}Fe_2O_3$ slag system[28] show that the

content of FeO in the slag varying from 0.01 to 0.05 mole at 1300 to 1500°C, the electrical conductivity is in the range of 0.1 to 0.4 S·cm^{-1}. The experimental data of present work indicates electronic conductivity is in the range of 10^{-4} to 10^{-2} S·cm^{-1}. The comparison of conductivity data of ionic and electron shows that conduction due to free electron and/or electronic hole can be neglected. But the results of works[7-12] on FeO-SiO_2, FeO-CaO, FeO-CaO-SiO_2 and FeO-MnO-SiO_2 slag systems prove that the effect of electronic conductivity on slag conductivity can not be neglected as the concentration of iron oxide is in the range of 0.2 to 0.5 mole. On the other side, the electronic conductivity is one of the important factors judging transfer ability of free electron and/or electron hole. Works to examine electronic transport in PbO-SiO_2 melt have been carried out by U. Paul [16,17], the results showed that the oxidation rate is moderate increased with additions of a transition metal oxide such as Fe_2O_3 to the melt. However, when gas/slag and slag/metal interfaces were shorted circuited by Ir wire, a much higher increase in the oxidation rate was noticed. Other researchers[18, 19] had observed the same experimental phenomena. It is postulated that reaction of metal melt with slag will be controlled by electronic transport in the slag.

4. Conclusions

Based on experimental data, the following conclusions can be drawn:

The electronic conductivity of the slag is the sum of free electron and electron hole conductivity. Free electron conductivity and electron hole conductivity are most likely associated with Fe^{3+} and Fe^{2+} in the slag respectively. The electron hole conductivity is increasing and the free electron conductivity is decreasing subsequently as ferric ion Fe^{3+} change to ferrous ions Fe^{2+}. Under the condition of this experiment, the range of electronic conductivity is from 10^{-4} to 10^{-2} S·cm^{-1}. However, as the fact has been noted by electrochemical studies on metal-slag reaction that rate-controlling step is electronic transport. Therefore, studies on electronic conduction and mechanism of electron transfer will be got more attention.

5. Acknowledgement

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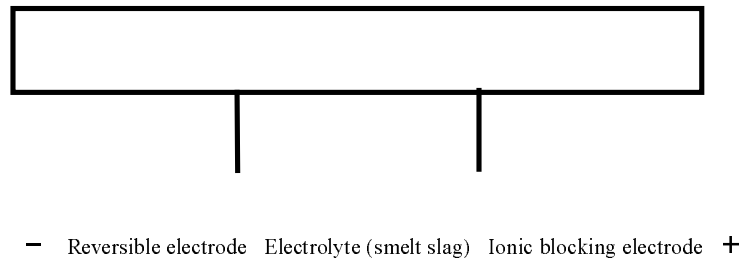[28] M. Kato and S. Minowa: *Trans. Iron Steel Inst., Japan.* 1969, 9, p.39-46.

- Reversible electrode   Electrolyte (smelt slag)   Ionic blocking electrode   +

Fig.1 Principle illustration of Wagner polarization technique

Gas

Reaction Tube

Electrode

Crucible

Slag

273 A model
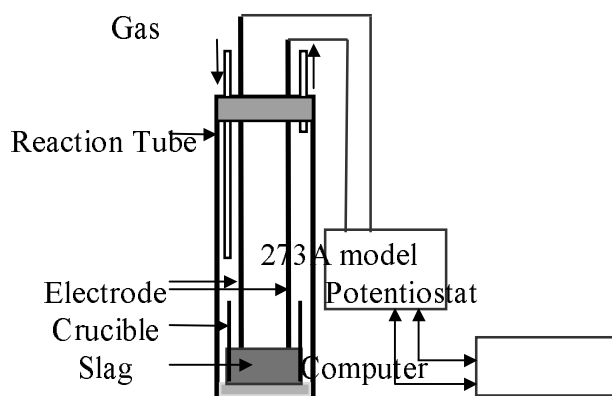Potentiostat

Computer

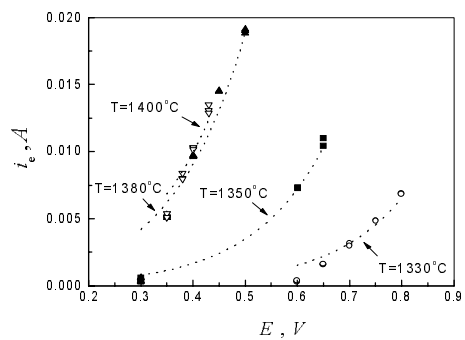Fig.2 Schematic diagram of the experimental apparatus

Fig.3 Steady-state electronic current *vs.*
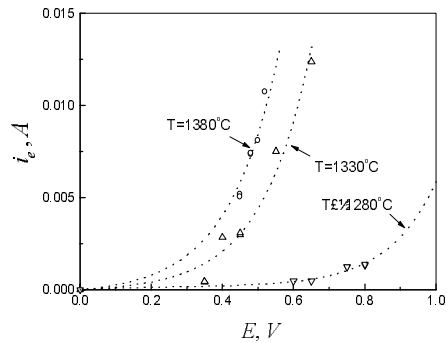polarization potential at different temperatures

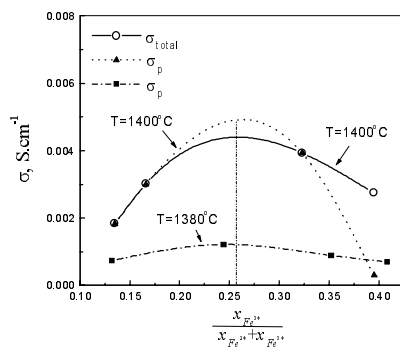Fig.4 Current *vs.* potential at different temperatures

Fig.5 The relations of σ with different
ratio of Fe^{3+} to the total iron content

Table 1. Calculations of electronic conductivities using Eq. (1) under different temperatures

Temperature	σ_n	σ_p
°C	S·cm^{-1}	S·cm^{-1}
1330	0	1.242×10^{-4}
1350	0	6.135×10^{-4}
1380	0	3.494×10^{-3}
1400	0	3.928×10^{-3}

Table 2. Calculations of electronic conductivity using Eq. (1) under different temperature

Temperature	σ_n	σ_p
°C	S·cm^{-1}	S·cm^{-1}
1280	7.950×10^{-4}	1.615×10^{-5}
1330	1.924×10^{-5}	8.773×10^{-4}
1380	0	1.220×10^{-3}

Table 3. Electronic conductivities under the different content of iron oxide and temperatures

Temperature	TFe	FeO	$\dfrac{x_{Fe^{3+}}}{x_{Fe^{2+}}+x_{Fe^{3+}}}$	σ	
				σ_n	σ_p
°C	%wt	%wt		S·cm^{-1}	S·cm^{-1}
1400	18.60	16.20	0.323	0	3.928×10^{-3}
1400	10.80	11.90	0.135	0	1.835×10^{-3}
1400	9.89	10.61	0.166	0	3.001×10^{-3}
1400	9.44	7.35	0.395	2.441×10^{-3}	2.976×10^{-4}
1380	9.93	11.08	0.132	0	7.362×10^{-4}
1380	10.70	10.40	0.244	0	1.220×10^{-3}
1380	11.20	9.31	0.354	1.532×10^{-3}	8.891×10^{-4}
1380	12.25	9.32	0.408	3.051×10^{-2}	7.046×10^{-4}