STUDY ON ELECTRICAL CONDUCTIVITY OF CaO-SiO₂-Al₂O₃-FeOₓ SLAGS

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Abstract

As a fundamental study on properties of the Fe_xO-bearing slags, the total electrical conductivity and electronic/ionic properties of Fe_xO-SiO_2-CaO-Al_2O_3 slags were measured at different oxygen potentials (controlled by CO-CO_2 mixture gas) and temperatures by using four-electrode method. From experiments results, it can be seen that the total conductivity changes little as increasing the ratio of CO to CO_2 (decreasing the oxygen potential), while the electronic and ionic conductivities of all slags decreases and increases monotonously, respectively. The temperature dependences of the total electrical conductivity, electronic, and ionic conductivities follow the Arrhenius law. It was also found that with increasing CaO/Al_2O_3 ratio, the total electrical conductivity and ionic conductivity firstly decrease and then increase, while electronic conductivity firstly almost keeps constant but then increases from $CaO/Al_2O_3=1$. The minimum values of the total electrical conductivity and ionic conductivity occurs near the ratio of $CaO/Al_2O_3 = 1$, which is mainly resulted from the charge compensation effect of Al^{3+} ions.

Introduction

The electrical conductivity of molten slag is not only an important physical property that plays a prominent role in modeling and operating the electric smelting furnace and optimizing the metallurgical process, but also important for understanding the structure of molten slags[1-4]. Indeed, many studies have been conducted on investigating the electrical conductivity of molten slags. For instance, the electrical conductivities of Fe_xO-CaO-SiO_2[5-7], Fe_xO-CaO-MgO-SiO_2[8], Fe_xO-CaO-SiO_2-Al_2O_3[9], Ni_xO-CaO-SiO_2[10], and Ni_xO-CaO-MgO-SiO_2[10] slags had been measured and reported in published literatures. Because for slag systems containing the transition metal oxides, the electrical conductivity includes two parts, ionic conductance and electronic conductance, both of which are very complicated functions of temperature and composition. Consequently, the estimations for both of them will be difficult. The FeO_x containing slags are widely used and play significant roles in many pyrometallurgical processes, so more experimental studies should be done about them. The objective of this work was to study the electrical and electronic conductivity of Fe_xO-CaO-SiO_2-Al_2O_3 slags at various temperature and oxygen potentials which controlled by the ratio of CO_2/CO, which will be beneficial for modeling and operating the electric smelting furnace.

Experimental Procedure

Table 1 shows the chemical composition for each sample. Three different categories of samples were prepared. In group A, contents of FeO and SiO_2 were kept constant, while CaO

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was gradually increased. It should be pointed out that C/A is defined as the mole fraction ratio of CaO to that of Al_2O_3. For groups B and C, SiO_2 content was kept constant, while CaO content was gradually increased. Slag samples were prepared using reagent grade SiO_2, Al_2O_3, $CaCO_3$ and Fe_2O_3 powder (all reagent are analytically pure, Sinopharm Chemical Reagent Co., Ltd, China), all of which were calcined at 1273 K for 10 h in a muffle furnace to decompose any carbonate and hydroxide before use. Pure FeO was obtained by calcining Fe and Fe_2O_3 powder in CO/CO_2 atmosphere at 1373 K for 24 hours. Then about 12 g mixtures were precisely weighted according to the compositions shown in Table 1, and mixed in an agate mortar thoroughly.

Table 1. Composition of slag sample (mole percent).

	FeO	SiO_2	CaO	Al_2O_3	C/A
Group A	20	44	24	12	2
			20	16	1.25
			16	20	0.8
			12	40	0.5
Group B		55	40	5	8
			35	10	3.5
			30	15	2
			25	20	1.25
			20	25	0.8
Group C		65	30	5	6
			25	10	2.5
			20	15	4/3
			15	20	0.75

A four terminal method, which had already successfully used to measure the electrical conductivity of molten slags, was employed to accomplish the electrical conductivity measurements in this study. The descriptions of experimental principle and device have already been mentioned in our previous study[11]. During the whole heating process and the first two hours holding at the target temperature (1823K), the slag was exposed to CO_2, and the flow rate of gas was controlled by a mass flowmeter. The input gas was varied from pure CO_2 to CO_2-CO mixed gas to control the oxygen partial pressure. For group A, the experimental measurements were carried out at every 50 K interval on cooling from 1823 K, and for group B and C, the resistance measurement was carried out at every 25 K interval on cooling from 1873 K. At each temperature, the slag was kept for 2 hours before measurement for the purpose of equilibrium and uniformity of slag.

All the measurements were recorded using a CHI 660a electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.). The resistance was found to be independent of the frequency, over the range 0.5 kHz to 100 kHz. All of the measurements were carried out at 20 kHz.

Results and Discussion

1. Influence of temperature on electrical conductivity

It is widely accepted that the temperature dependence of electrical conductivity can be expressed by the Arrhenius law as:

$$\sigma = A \exp(-E/RT) \tag{1}$$

where σ is electrical conductivity, $\Omega^{-1}cm^{-1}$; A is pre-exponent factor; E is activation energy, J/(mol·K); R is the gas constant, 8.314 J/(mol·K); T is the absolute temperature, K. Figures 1 to 3 show the change of electrical conductivity as a function of temperature for group A slags, at $CO/CO_2 = 0.2$. It can be seen from these figures, that the electrical conductivity increases by increasing the temperature, furthermore, the temperature dependence of electrical conductivity obeyed the Arrhenius law very well.
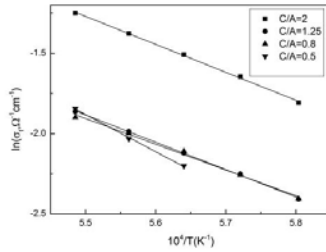
Figure 1. Arrhenius plot of total electrical conductivity for group A slags when $CO/CO_2 = 0.2$.
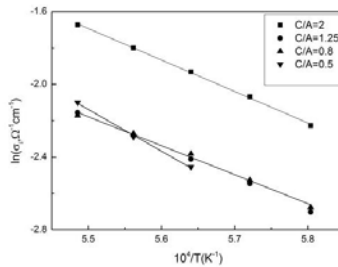
Figure 2. Arrhenius plot of the ionic conductivity for group A slags when $CO/CO_2 = 0.2$.
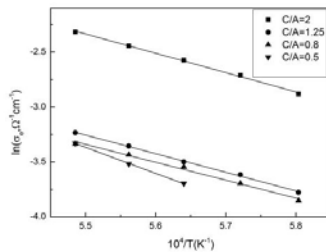
Figure 3. Arrhenius plot of the electronic conductivity for group A slags when $CO/CO_2 = 0.2$.

2. Influence of equilibrium oxygen potential on electrical conductivity

The total electrical conductivity for group A slags at 1823 K as a function of CO/CO_2 ratio is shown in Figure 4. As can be noted, the total conductivity changes little in the oxygen potential range of the present study.
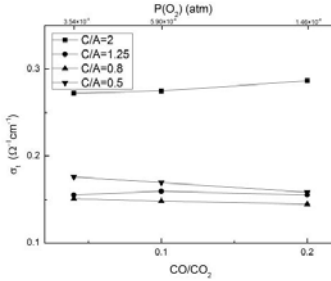

Figure 4. The total electrical conductivity of group A
slags for different CO/CO_2 ratio at 1823 K.

The ionic conductivity for group A slags at 1823 K as a function of equilibrium CO/CO_2 is shown in Figure 5. It is evident from figure 5 that the ionic conductivity of all group A slags increases with increasing the ratio of CO/CO_2. From Eq. (2), it can be known that more and more ferric ion will replace ferrous ion with decreasing the CO/CO_2 ratio (or increasing the oxygen potential). According to conclusions of Fontana et al.[12], ferrous ion is the only iron ion that significantly contributes to the ionic conduction in iron-oxide-containing melts. The tendency of the ferric ion toward covalent binding with oxygen is strong enough to stimulate the formation of highly covalent anions (FeO_4^{5-} or $Fe_2O_5^{4-}$) instead of an isolated Fe^{3+} cation, which will lead to greatly reduced mobility compared with ferrous ion. Therefore, the ionic conductivity of all slags increases with increasing the ratio of CO/CO_2.
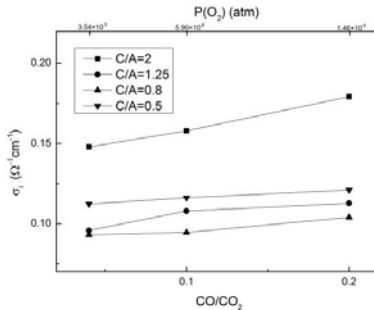
$$4FeO_4^{5-} = 4Fe^{2+} + O_2 + 14O^{2-}$$

(2)

Figure 5. The ionic conductivity of group A slags for
different CO/CO_2 ratio at 1823 K.

The effect of the CO/CO_2 ratio on electronic conductivity for group A slags at 1823 K is shown in Figure 6. As can be noted, the electronic conductivity decreases with increasing the ratio of CO to CO_2. According to the above results, it can be known that the ionic conductivity of all slags increases with increasing the ratio of CO to CO_2, which leads to the little change of total conductivity as shown in Figure 7
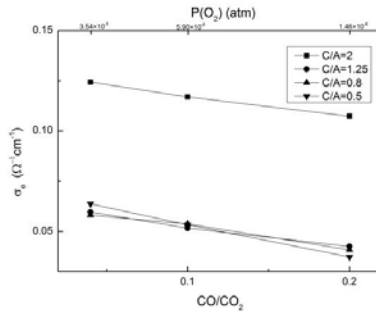

Figure 6. The electronic conductivity of group A slags
for different CO/CO_2 ratio at 1823 K.

3. Influence of the ratio of CaO/Al_2O_3 on electrical conductivity

The total electrical conductivity and electronic/ionic conductivity for group A slags with different ratios of CaO/Al_2O_3 at fixed FeO and SiO_2 contents under the atmosphere of CO/CO_2=0.2 at 1823 K are shown in Figure 7. As can be noted, by increasing CaO/Al_2O_3 ratio, the total electrical conductivity and ionic conductivity firstly decrease and then increase, while electronic conductivity firstly almost keeps constant but then increases from CaO/Al_2O_3=1. The minimum values of the total electrical conductivity and ionic conductivity occurs near the ratio of CaO/Al_2O_3 = 1. The electrical conductivity for group B and C slags with different ratios of CaO/Al_2O_3 at fixed SiO_2 content at 1873 K are shown in Figure 8 and Figure 9, respectively. As the CaO/Al_2O_3 ratio increases, the electrical conductivity will decrease firstly and then increase. In other words, the electrical conductivity exhibits a minimum value with the change of CaO/Al_2O_3 ratio, which occurs near the ratio of CaO/Al_2O_3 equal to 1.
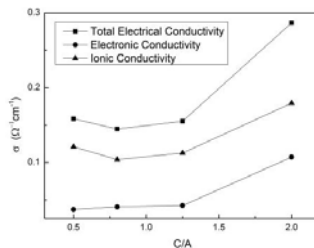

Figure 7. The total electrical, electronic and ionic conductivities of group A
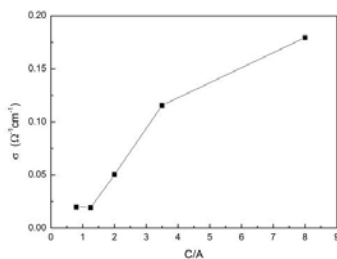slags for different CaO/Al_2O_3 ratio at 1823 K when CO/CO_2 = 0.2.

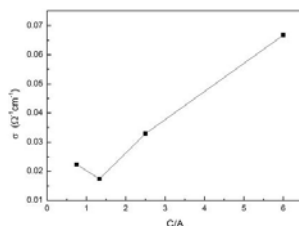Figure 8. The electrical conductivity of group B slags for the different CaO/Al_2O_3 ratio at 1873 K.

Figure 9. The electrical conductivity of group C slags for the different CaO/Al_2O_3 ratio at 1873 K.

For the Al_2O_3 bearing molten slag, when there are several basic oxides, there is a strict order for cations when charge compensating the Al^{3+} ions. In the present system, there are two basic oxides. The priority order for charge-compensation of Al^{3+} ions fulfills $Ca^{2+} > Fe^{2+}$.[13] In other words, when there is enough Ca^{2+}, Fe^{2+} with a lower priority will not be used to charge compensate the Al^{3+} ion. Intuitively, Ca^{2+} mainly contributes ionic conductivity, while Fe^{2+}/Fe^{3+} influence both electronic and ionic conductivities. In $FeO-CaO-Al_2O_3-SiO_2$ system, there are two types of Ca^{2+} cations: One compensates Al^{3+} ion and the other forms nonbridging oxygen. Figure 10 shows the schematic diagrams. The transport ability of the former type of cation is much weaker than that of the latter type of cation. In the case of $x(CaO) < x(Al_2O_3)$, as increasing CaO content the degree of polymerization is enhanced which decreases ionic conductivity. Whereas, the increase of concentration of metal cations will have little influence on ionic/electrical conductivity because in this case most of the new added Ca^{2+} ion are used for charge compensators of Al^{3+} and have little mobile ability. In the case of $x(CaO) > x(Al_2O_3)$, with the addition of CaO content, the degree of polymerization decreases and the concentration of metal cations increases, both of which will enhance the ionic conductivity.[14,15] Therefore, there should be a minimum value for ionic conductivity near the ratio of $CaO/Al_2O_3 = 1$.
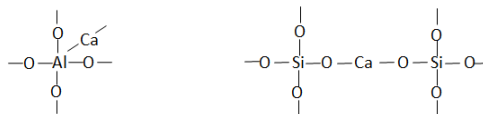
Figure 10. The schematic diagrams of tow type of Ca^{2+} ions.

However, it has been pointed out that the electronic conductivity is determined by the concentration product of Fe^{2+} and Fe^{3+} ions.[7] Therefore, the electronic conductivity will increase when the concentration of Fe^{3+} ion increases. It is known to us that the ratio of Fe^{3+} ion to total Fe ion is affected by temperature, oxygen potential and the basicity of the slag. When temperature and oxygen potential are kept constant, the proportion of Fe^{3+} ion increases as increasing the basicity, which can be seen easily from Eq. (3). In Eq. (3), O^{2-} expresses the free oxygen ion. In the case of $x(CaO) < x(Al_2O_3)$, almost all the CaO all used for charge compensation, the concentration of free oxygen ion O^{2-} doesn't have an equivalent increase as increasing CaO/Al_2O_3 ratio. Consequently, there is little change of Fe^{3+} ion concentration, so the electronic conductivity almost keeps constant. However, when $x(CaO) > x(Al_2O_3)$, all the Al^{3+} ions are get compensation, so there will be an large increase of free oxygen ion as increasing CaO/Al_2O_3 ratio. Based on Eq. (3), the concentration of Fe^{3+} ion (highly covalent anion such as FeO_4^{5-} is always formed instead of an isolated Fe^{3+} cation) will also increase which enhances the electronic conductivity.

According to the above analyses, as increasing CaO/Al_2O_3 ratio, the ionic conductivity first decreases and then increases, while the electronic conductivity firstly almost keeps constant and then increases from $CaO/Al_2O_3 = 1$. Therefore, the total electrical conductivity also firstly decreases and then increases with the change of CaO/Al_2O_3 ratio, with the minimum value occurring near $CaO/Al_2O_3 = 1$. For $CaO-SiO_2-Al_2O_3$ slags, the minimum value of electrical conductivity near $CaO/Al_2O_3 = 1$ is also resulted from the charge compensation effect of Al^{3+} ions.

Conclusions

The electrical conductivity of $Fe_xO-SiO_2-CaO-Al_2O_3$ slags was measured by a four-terminal technique. The results show that the temperature dependences of ionic, electronic and total conductivity for different compositions obey the Arrhenius law. The experimental results show that the total conductivity changes little as increasing the ratio of CO to CO_2, while the electronic and ionic conductivities of all slags decreases and increases monotonously, respectively. With increasing CaO/Al_2O_3 ratio, the total electrical conductivity and ionic conductivity firstly decrease and then increase, while electronic conductivity firstly almost keeps constant but then increases from $CaO/Al_2O_3=1$. The minimum values of the total electrical conductivity and ionic conductivity occurs near the ratio of $CaO/Al_2O_3 = 1$, which is resulted from the charge compensation effect of Al^{3+} ion.

Acknowledgements

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