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A new model for evaluating the electrical conductivity of nonferrous slag

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Abstract: Electrical conductivity of molten slag is an important physicochemical property for designing the refining process in electric smelting furnaces. Though conductivities of many slag systems have been measured, the quantitative relationships of conductivity with slag composition and temperature are still very limited. In this article, the Arrhenius law was used to describe the experimental data of conductivities for CaO-MgO-Al_2O_3-SiO_2, CaO-Al_2O_3-SiO_2, CaO-MnO-Al_2O_3-SiO_2, as well as CaO-MgO-MnO-Al_2O_3-SiO_2 systems, and it is found that activation energy can be expressed as a linear function of the content of components, where the optical basicity of slag must be within the range of 0.58 to 0.68.

Key words: electrical conductivity; Arrhenius law; activation energy; optical basicity

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1. Introduction

In a high temperature metallurgical system, the electrical conductivity of molten slag is a very important physical property, which plays a prominent role in modeling and operating the electric smelting furnace. However, the determination of electrical conductivity is very difficult, especially in elevated temperature conditions. Therefore, it is a very significant issue to accurately estimate the conductivity both in fundamental research and industrial application.

Generally, electrical conductivity should be a function of slag composition and temperature, and this relation depends on the oxide itself. It is known that the conductivity of slag originally comes from ions that can mobilize under the electrical field. Acidic oxides, such as SiO_2, P_2O_5, and so on, always form a three-dimensional network structure, and it is difficult to form mobilizable ions when it is molten, so the conductivity of these oxides is very small. In the case of basic oxides, they can break the network structure of acidic oxides by releasing oxygen ions. Therefore, in a certain content range, the conductivity of melts will increase with increasing the content of CaO, MgO, MnO, and so on. Al_2O_3 can exhibit as a basic oxide under the condition of low basicity, and as an acidic oxide under the condition of high basicity. Al^{3+} can form AlO_4^{5-} tetrahedron, and replace the position of Si when the basicity is higher. As the valence of aluminum ions is +3, which is less than that of silicon ion when it is in the position of Si, therefore an extra cation is needed to compensate the charge balance. Furthermore, 1 mol Al_2O_3 can form 2 mol aluminum ions. Therefore, a substitution of 1 mol SiO_2 by 1 mol Al_2O_3 will greatly decrease the number of free ions and increase the tetrahedron, leading to the decrease of conductivity.

The relation between electrical conductivity and slag composition is very complex, and a small change in composition may result in a sharp decrease or increase in conductance [1]. At present, it is scarce to have a theoretical model for predicting the conductance of slag.

In recent times, Chou [2] has developed a mass triangle model to predict the physicochemical properties of the point within the composition triangle, based on the properties of the other three selected points. Several applications [2-4] have demonstrated that it is a simple, effective, and flexible method for predicting the physicochemical properties of a ternary system.

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The closer the distance of the given point to the three other selected points, the more accurate the calculation result. This model is simple and easy to use, but it may bring bigger errors when the property changes sharply in this area or the three selected points are far from the calculated point.

In order to calculate the electrical conductivity of industrial-type CaO-MgO-MnO-SiO_2 and FeO-CaO-MgO-SiO_2 slag, Jiao and Themelis have proposed a model [1], in which, electrical conductivity was assumed to be a linear function of the molar fraction of Ca^{2+}, Mg^{2+}, Mn^{2+}, and Fe^{2+}, and the influence of acidic oxide SiO_2 on conductance was negligible. Besides, the model was applicable only under the condition that the SiO_2 content of the slag was sufficiently high so that the melt was ionized, that is, CaO, MgO, and so on, exist in the melt in the form of free ions. In other words, it can only be used in the slags with low basicity. Besides, because the coefficients used in this model were obtained through a regression of a few data at a specific temperature, it was difficult to extend its application to other temperatures without introducing the consideration errors. Therefore, it is meaningful to develop a method for predicting the slag conductivity, and considering the effects of temperature and composition.

2. Model

2.1. Introduction of optical basicity

Basicity is an important property of slag, which can give the information of the relative content of basic oxide and acidic oxide. There have been many types of definitions about basicity, such as $\frac{\%(\mathrm{CaO})}{\%(\mathrm{SiO_2})}$, $\frac{\%(\mathrm{CaO})}{\%(\mathrm{SiO_2})+\%(\mathrm{Al_2O_3})}$ and so on. In recent times, Duffy and Ingram proposed an optical basicity [5], which can also be used to measure the basicity of slag. Meanwhile, the value of optical basicity of an individual oxide can also be calculated easily from Pauling electronegativity. The value of optical basicity for a multicomponent slag can be expressed as follows [6]:

$$\Lambda = \frac{\sum x_i n_i \Lambda_i}{\sum x_i n_i} \qquad (1)$$

where x_i and Λ_i are the mole fraction and optical basicity of component i, respectively; n_i is the number of oxygen atoms in the molecule, for example, 2 for SiO_2, 3 for Al_2O_3. Optical basicity is used as a constraint condition in the authors' model, in this article.

2.2. Relation between conductivity and temperature

Considering that ion conductance is related to a thermal activation process, the relationship between electrical conductivity and temperature can be described by the Arrhenius law:

$$k = A\exp(-E/RT) \qquad (2)$$

where k, A, E, R, T are the electrical conductivity of slag, constant, activation energy, gas constant, and thermodynamic temperature, respectively.

Because both basic oxide and acidic oxide can affect the value of conductivity, it is assumed that the activation energy E is the weight summation of the containing oxides by mole fraction:

$$E = \sum x_i E_i \qquad (3)$$

where x_i is the mole fraction of component i, and E_i can be seen as the contribution of activation energy of component i to the total system. The higher the value of E_i, the greater the effect of temperature on conductivity. It has been found that the slag with a higher SiO_2 and Al_2O_3 content causes lower conductivity and is more sensitive to temperature [1], therefore it is expected that $E_{\mathrm{Al_2O_3}}$ and $E_{\mathrm{SiO_2}}$ may possess a large value.

2.3. Conductivity of slag containing MnO, CaO, MgO, SiO_2, and Al_2O_3

CaO, MgO, MnO, Al_2O_3, and SiO_2 are the common oxides existing in high temperature metallurgical slag, and many investigations have been done in molten slag containing these oxides, such as CaO-MgO-Al_2O_3-SiO_2 [7-9], CaO-Al_2O_3-SiO_2 [7], CaO-MgO-MnO-Al_2O_3-SiO_2 [10], CaO-MnO-Al_2O_3-SiO_2 [11], CaO-MgO-MnO-SiO_2 [10], and so on. Because the relationship among composition, temperature, and electrical conductivity of slag is complex, the present study does not attempt to give a universal expression that could be used for all the above slag systems. Every model must have its application range, and the following equations can only be used for a certain content and temperature range. Applying Eqs. (2) and (3) to the four slag systems mentioned above, and regressing the undetermined parameters based on the available experimental data, the optimized parameters have been obtained and are now listed in Table 1. The ranges of content and temperature suitable for this model are listed in Table 2. It must be kept in mind that it will bring great errors if the ranges go out of the ones mentioned in the table.

Table 1. Values of model parameters for different systems

System	A / ($\Omega^{-1}\cdot cm^{-1}$)	E_i / ($J\cdot mol^{-1}$)				
		CaO	MgO	MnO	SiO_2	Al_2O_3
$CaO-Al_2O_3-SiO_2$	7947	108088	—	—	197061	250324
$CaO-MgO-Al_2O_3-SiO_2$	2354	69319	81313	—	203587	205834
$CaO-MnO-Al_2O_3-SiO_2$	1430	93461	—	59805	136180	216344
$CaO-MgO-MnO-Al_2O_3-SiO_2$	333.4	84929	115500	35939	130973	158386

Table 2. Application range of composition content and temperature

System	Composition range / mol%					Temperature range / °C
	CaO	MgO	MnO	SiO_2	Al_2O_3	
$CaO-Al_2O_3-SiO_2$	0.32-0.56	—	—	0.31-0.6	0.03-0.25	1350-1550
$CaO-MgO-Al_2O_3-SiO_2$	0.26-0.51	0-0.29	—	0.34-0.62	0.02-0.17	1350-1600
$CaO-MnO-Al_2O_3-SiO_2$	0.1-0.36	—	0.28-0.58	0.27-0.43	0.02-0.19	1050-1600
$CaO-MgO-MnO-Al_2O_3-SiO_2$	0.05-0.22	0.02-0.08	0.26-0.56	0-0.38	0.1-0.3	1500

3. Results

3.1. $CaO-MgO-Al_2O_3-SiO_2$ system

Several investigators have measured and studied the conductance of this system. A comparison of the conductivity between the measured value and the calculation result predicted by this model is given in Fig. 1, from which it can be seen that they are in a good agreement. The mean deviation Δ can be calculated as follows:

$$\Delta = \frac{1}{N} \times \sum_{i=1}^{N} \frac{\left|\kappa_{i,\mathrm{mea}} - \kappa_{i,\mathrm{cal}}\right|}{\kappa_{i,\mathrm{mea}}} \times 100\% \quad (4)$$

where $\kappa_{i,\mathrm{cal}}$ and $\kappa_{i,\mathrm{mea}}$ are the estimated and measured conductivities, respectively, and N represents the number of the samples. The mean deviation Δ between the calculated value and the experimental data is 13.6%.

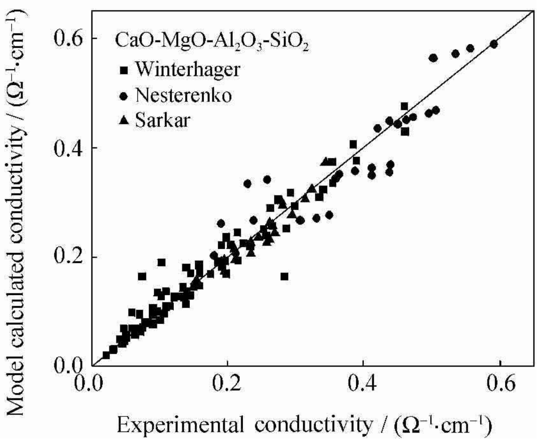

Fig. 1. Comparison between the estimated and measured values for the $CaO-MgO-Al_2O_3-SiO_2$ system.

It should be pointed out that parameters are regressed only with Winterhager's [7], Sarkar's [7-8], and part of Nesterenko's [9] experimental data, while the other part of Nesterenko's data and Adachi's [7] result are not adopted. It is found that only when the optical basicity value is in the range of 0.68-0.78, the present model can work, whereas, in the case of high and low optical basicity, the model is not applicable. It is probably due to the reason that the law in different optical basicity regions is different. It has been pointed out that if the SiO_2 content is sufficiently high for the melt to be ionized, electrical conductivity can be expressed as a linear function of the molar fraction of Ca^{2+}, Mg^{2+}, and other cations [1], which just corresponds to the case of low optical basicity. Based on this assumption, Jiao and Themelis successfully developed the conductance model for the $CaO-MgO-MnO-SiO_2$ system [1]. If one calculates the optical basicity value of the composition dots of the $CaO-MgO-MnO-SiO_2$ system used in Jiao's model, one will find that the optical basicity of all the composition dots are less than 0.58.

3.2. $CaO-Al_2O_3-SiO_2$ system

Electrical conductivity of the $CaO-Al_2O_3-SiO_2$ system is also estimated by the present model. The experimental data are from Winterhager [7]. Fig. 2 shows that the model calculated conductivity values agree well with the measured ones. The mean deviation Δ is 11.7%. Considering the optical basicity of the selected composition dots, it can be found that the values of all the measured dots are in the range of 0.58-0.68.

3.3. $CaO-MnO-Al_2O_3-SiO_2$ system

Conductivities of 17 composition dots in the $CaO-MnO-Al_2O_3-SiO_2$ system have been measured by

Chubinidze [11] at 12 different temperatures. Fig. 3 shows the comparison between the calculated conductivity values and experimental data.

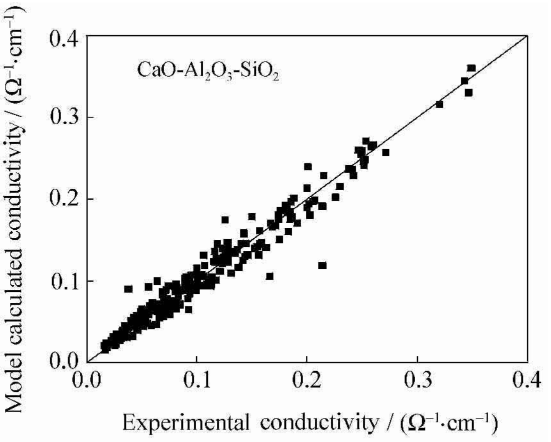

Fig. 2. Comparison between the estimated and measured values for the CaO-Al_2O_3-SiO_2 system.

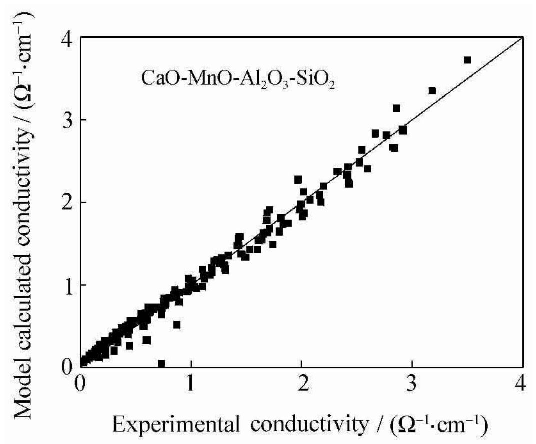

Fig. 3. Comparison between the estimated and measured values for the CaO-MnO-Al_2O_3-SiO_2 system.

It can be concluded that the model works well for evaluating the conductivity of the CaO-MnO-Al_2O_3-SiO_2 system. The mean deviation, Δ, is 15.7%, for this system. The optical basicity values of the measured composition dots are also in the range of 0.58-0.68.

3.4. CaO-MgO-MnO-Al_2O_3-SiO_2 system

Segers *et al.* [10] measured the conductivity of 25 composition dots in the CaO-MgO-MnO-Al_2O_3-SiO_2 system at 1500°C. The conductivity values of these dots were also estimated by the present model. From Fig. 4, it can be concluded that the estimated values agree well with the measured ones, with a mean deviation Δ =12.3%. The optical basicity values of these 25 dots are also in the range of 0.58-0.68.

4. Discussion

From Table 1, it can be seen that the E_i values of CaO and MgO in different systems are almost equal to each other, which can give an indication that basic oxides CaO and MgO have a similar behavior to the conductivity of slag. This can be proved by the following experimental results. Electrical conductivities of CaO and MgO at a temperature just above the melting point are 40 $\Omega^{-1}\cdot cm^{-1}$ (2580°C) and 35 $\Omega^{-1}\cdot cm^{-1}$ (2800°C) [12]; in the binary molten slag system CaO-SiO_2 and MgO-SiO_2, the values of conductivity are very close, at the same content of SiO_2 [13].

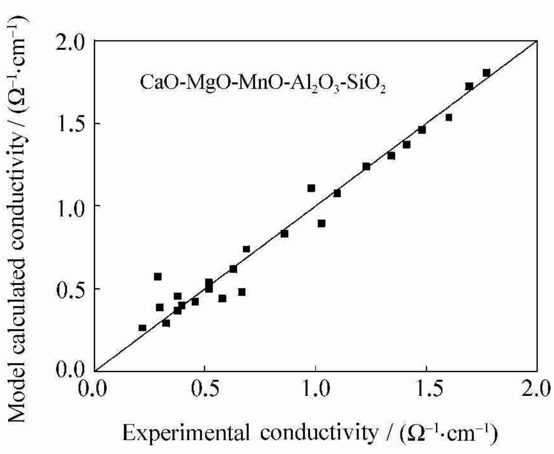

Fig. 4. Comparison between the estimated and measured values for the CaO-MgO-MnO-Al_2O_3-SiO_2 system.

As discussed earlier, Al_2O_3 may have a big influence on decreasing the conductance of molten slag in a certain content range. Substituting SiO_2 by the same mole Al_2O_3 may lead to the decrease in conductivity, and this can also be seen from the optimized parameter values of the model (Table 1), in which the value of E_{SiO_2} is smaller than that of Al_2O_3.

The present model works well in the content and temperature range specified in Table 2. When the composition or temperature is out of the specified range, it may bring error in the conductivity calculation. But even if within the content and temperature ranges of the model, a big deviation could still generate between the calculated and actual values. In this article, optical basicity is used to constrain the application range of the model, and the range of 0.58-0.68 is suggested. The slags with a high (>0.68) and low (<0.58) optical basicity value may obey different laws, which will be discussed in the authors' future articles.

5. Conclusions

(1) Different components have different influences on electrical conductivity. Generally, conductivity of molten slag will increase with increasing basic oxide content, and decrease with an increase in acidic oxide content, in a certain content range. CaO and MgO

have a similar behavior, while Al_2O_3 has a greater influence on conductance than SiO_2.

(2) The relation among electrical conductivity, composition content, and temperature can be expressed by the Arrhenius law, where the activation energy is a linear function of the content (mol%) of all components in the system.

(3) In order to minimize the error, the model should be used within or close to the specific content and temperature range. Meanwhile optical basicity is also used to constrain the application range to the range of 0.58-0.68, which is suggested.

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