

Electrical conductivity of MO(MO=FeO, NiO)-containing CaO-MgO-SiO₂-Al₂O₃ slag with low basicity

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Abstract: As a fundamental study on recovery of valuable metals from nonferrous metallurgical slags, electrical conductivity values of MO(MO=FeO, NiO)-containing CaO-MgO-SiO₂-Al₂O₃ slag with a low basicity were measured at different temperatures using AC impedance spectroscopy. The result shows that the electrical conductivity increased from 1.4 S/m to 14.4 S/m with the increase of the temperature from 1 573 to 1 773 K and the content of MO which is less than 12% under the constant mass ratio of (CaO+MgO) to (SiO₂+Al₂O₃) of 0.47. Moreover, the increase magnitude of the electrical conductivity was also promoted with the increase of the content of MO. The electrical conductivity of FeO-containing slags was close to that of NiO-containing slags when the content was less than 8%; however, it was obviously larger than that of NiO-containing slags when the content was 12%. The activation energy of the electrical conductivity decreased with the increase of MO content.

Key words: FeO; NiO; molten slag; electrical conductivity; AC impedance spectroscopy

1 Introduction

Recovery of valuable elements from metallurgical slags has been paid considerable attention to the decrease of natural mineral resources for extraction of metals and the increase of the slags at our living environment. In extraction of the valuable metals from the slags, an electrical conductivity is important for understanding the structure of molten slags and optimizing the metallurgical process [1–3]. Indeed, many researches have been conducted on investigating the electrical conductivity of molten slags.

The electrical conductivities of Fe_xO-CaO-SiO₂ [4–8], Fe_xO-CaO-MgO-SiO₂ [9–10], Fe_xO-CaO-SiO₂-Al₂O₃ [11–12], Ni_xO-CaO-SiO₂ [13] and Ni_xO-CaO-MgO-SiO₂ [13] slags had been measured and reported in published literature. Normally, the electrical conductivities of those molten slags increased with the increases of temperature and contents of Fe_xO, CaO and MgO. In that, the effect of MgO on the electrical conductivity was proportional to the mass ratio of (Fe_xO+CaO) to SiO₂. In addition, KAWAHARA et al [13] reported that a dissociation of NiO into Ni²⁺ and O²⁻ was promoted after adding MgO into Ni_xO-CaO-SiO₂ slags,

which resulted in the increase of the electrical conductivity. However, no much work has been performed on investigating the electrical conductivity of MO(MO=FeO, NiO)-CaO-MgO-SiO₂-Al₂O₃ systems like nonferrous metallurgical slags [14–15]. In Fe_xO-CaO-MgO-SiO₂-Al₂O₃ slags, the electrical conductivities of 30% FeO-containing slags at different oxygen partial pressures were measured by HUNDERMARK et al [16], which shows that the electrical conductivity initially increased and then decreased with the increase of the oxygen partial pressure. The effect of the FeO content on the electrical conductivity was investigated by FONTANA et al [17], which shows the activation energy decreased with the increase of the FeO content in a range of 15%–80%. The effect of basicity on the electrical conductivity from 1 673 K to 1 873 K was studied by LUGANOV et al [18], which shows that the electrical conductivity increased with the increase of (CaO+MgO)/(SiO₂+Al₂O₃) mass ratio. However, the effect of the low FeO and NiO contents on the electrical conductivity of low basicity slag had less been reported.

In this work, the electrical conductivities of MO(MO=FeO, NiO)-CaO-MgO-SiO₂-Al₂O₃ slags with (CaO+MgO)/(SiO₂+Al₂O₃) mass ratio of 0.47 were investigated using AC impedance spectroscopy [11, 19]

in argon gas from 1 573 to 1 773 K, and the effect of FeO and NiO on the electrical conductivity in the low basicity slags was discussed as a fundamental study on extraction of valuable metals from the nonferrous metallurgical slags.

2 Experimental

Composition of experimental slags is listed in Table 1. Analytical reagent grades of MgO, Al₂O₃, SiO₂, NiO, CaCO₃ and Fe₂CO₄·2H₂O were used as raw materials to synthesize the experimental slags directly, in which CaCO₃ and Fe₂CO₄·2H₂O were used as CaO and FeO respectively for accurate weighing in experimental process. The testing temperatures were 1 573, 1 623, 1 673, 1 723 and 1 773 K, respectively.

Table 1 Chemical composition of molten slags

Type of molten slag	w/%					
	CaO	MgO	SiO ₂	Al ₂ O ₃	FeO	NiO
Based slag	25	7	58	10	0	0
4%FeO-containing slag	24	6.7	55.7	9.6	4	0
8%FeO-containing slag	23	6.4	53.4	9.2	8	0
12%FeO-containing slag	22	6.2	51	8.8	12	0
4%NiO-containing slag	24	6.7	55.7	9.6	0	4
8%NiO-containing slag	23	6.4	53.4	9.2	0	8
12%NiO-containing slag	22	6.2	51	8.8	0	12

A scheme of experimental apparatus is shown in Fig. 1. Two parallel platinum pieces (length of 40 mm, width of 10 mm, thickness of 0.5 mm) used as electrodes were connected respectively with two platinum wires ($d=1$ mm) to an electrochemical analyzer (CHI660). The platinum wires and a part of the platinum pieces were fixed into the thin corundum tubes in which some high temperature cements were used to fill for preventing the vibration and bend of the electrodes. 90 g slags with the chemical composition shown in Table 1 were set into a corundum crucible (40 mm O.D., 35 mm I.D., 100 mm H) and then placed into an electric furnace. The furnace was heated to the testing temperature (± 2 K), and then maintained for 30 min to ensure the slag melted completely. The electrodes were subsequently immersed into molten slags. High pure argon as an inert gas was continuously flushing into the furnace with a flowing rate of 1 000 mL/min to prevent oxidation of the slag in experimental process. The cell constant ($\kappa=l/S$, where l is a distance between two electrodes, 8 mm; S is an area of the electrodes immersed in molten slags, 246 mm²) measured using 0.1 mol/L KCl standard solution at 292 K, was (32.5 ± 0.1) m⁻¹.

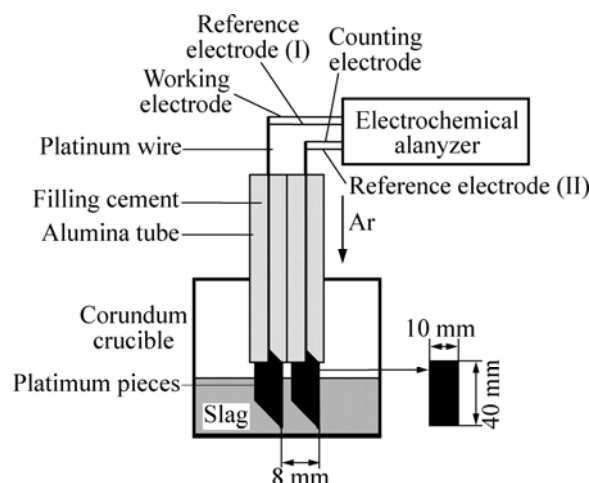


Fig. 1 Schematic diagram of experimental apparatus

The equivalent circuit for the cell is shown in Fig. 2. Total impedance (Z) can be divided into three parts: the first part impedance (Z_1) contains the apparent resistance (R_b) with the resistance of the electrodes and lead wires, the second part impedance (Z_2) contains electron-charge transfer resistance (R_{ct}) at electrode interfaces, double layer capacitance (C_{dl}) and Warburg impedance (Z_w), and the last part impedance (Z_3) contains inductance (L_e) of the lead wires.

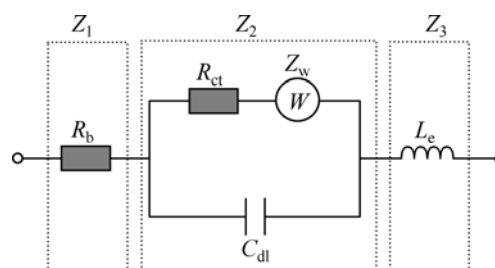


Fig. 2 Equivalent circuit for cell

The impedances of the apparent resistance, the electron-charge transfer resistance, the Warburg impedance, double layer capacitance, and the inductance of lead wires are as follows respectively:

$$Z_{R_b} = R_b \quad (1)$$

$$Z_{R_{ct}} = R_{ct} \quad (2)$$

$$\begin{aligned} Z_w &= k(j\omega)^{-1/2} = k\omega^{-1/2} \left(\cos \frac{\pi}{2} + j \sin \frac{\pi}{2} \right)^{-1/2} \\ &= k\omega^{-1/2} \left(\cos \frac{\pi}{4} - j \sin \frac{\pi}{4} \right) \end{aligned} \quad (3)$$

where k is constant.

$$Z_{C_{dl}} = -\frac{j}{C\omega} \quad (4)$$

$$Z_{L_e} = j\omega L_e \quad (5)$$

The first part impedance (Z_1), the second part impedance (Z_2) and the last part impedance (Z_3) are as follows:

$$Z_1 = Z_{R_b} \quad (6)$$

$$Z_2 = \frac{Z_{R_{ct}} + Z_w + Z_{C_{dl}}}{Z_{C_{dl}}(Z_{R_{ct}} + Z_w)} \quad (7)$$

$$Z_3 = Z_{L_e} \quad (8)$$

Total impedance can be expressed according to the equivalent circuit as shown in Eq. (6).

$$Z = Z' + jZ'' = Z_1 + Z_2 + Z_3 \quad (9)$$

Eq. (9) is replaced by Eqs. (1)–(8), which obtains

$$Z = R_b + \frac{R_{ct} + d - j(c + k^2 C + C\omega R_{ct}^2 + 2bR_{ct}C)}{(1 + aC)^2 + C^2\omega^2(R_{ct} + d)^2} + j\omega L_e \quad (10)$$

where

$$a = k\omega^{1/2} \sin \frac{\pi}{4}; \quad b = k\omega^{1/2} \cos \frac{\pi}{4};$$

$$c = k\omega^{-1/2} \sin \frac{\pi}{4}; \quad d = k\omega^{-1/2} \cos \frac{\pi}{4}.$$

And then Z' and Z'' in Eq. (6) can be induced as real part and imaginary part as follows:

$$Z' = R_b + \frac{R_{ct} + d}{(1 + aC)^2 + C^2\omega^2(R_{ct} + d)^2} \quad (11)$$

$$Z'' = \frac{[(1 + aC)^2\omega L_e + (R_{ct} + d)^2 C^2\omega^3 L_e - (c + k^2 C + C\omega R_{ct}^2 + 2bR_{ct}C)]}{[(1 + aC)^2 + C^2\omega^2(R_{ct} + d)^2]^{-1}} \quad (12)$$

Therefore, Z' and Z'' measured by AC impedance spectroscopy were fitted to calculate the apparent resistance (R_b) according to Eq. (11) and Eq. (12) using nonlinear least-squares. The resistance of lead wires was measured at different temperatures by AC impedance spectroscopy shown in Table 2.

Table 2 Resistances of electrodes and lead wires at different temperatures

T/K	292	1573	1623	1673	1723	1773
R_L/Ω	0.69	1.19	1.21	1.22	1.24	1.26

The resistance of molten slags (R) can be given by

$$R = R_b - R_L \quad (13)$$

And then the electrical conductivity (σ) of molten slags is calculated as follows:

$$\sigma = \kappa / R \quad (14)$$

3 Results and discussion

Figure 3 shows AC impedance spectra of base slag from 1 573 K to 1 773 K, in which points and lines were obtained from the experimental data and fitting values by Eq. (11) and Eq. (12) respectively. It is noticeable that, in high frequency region, AC impedance spectra are in the forth quadrant, which indicates L_e played a major role. Comparatively, R_{ct} , C_{dl} and Z_w played the major role in low frequency region. When AC impedance spectra intersect with the real axis ($Z''=0$), Z' equated to the impedance of the apparent resistance (R_b). Therefore, it can be considered that the resistance of molten slags decreased with the increase of temperature because the resistance of the electrodes and lead wires has a minor change from 1.19 Ω to 1.26 Ω at different temperatures.

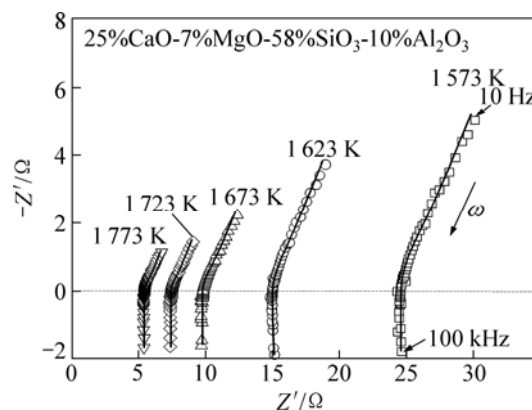


Fig. 3 AC impedance spectra of base slag at different temperatures

Figure 4 shows the AC impedance spectra of FeO-CaO-MgO-SiO₄-Al₂O₃ slags from 1 573 K to 1 773 K. The apparent resistance (R_b) was decreased with the increase of FeO content. It can be considered that the three-dimensional network structure of silicate was destroyed with increasing FeO content, thus many ions with free migration were produced in molten slags.

Figure 5 shows the AC impedance spectra of NiO-CaO-MgO-SiO₄-Al₂O₃ slags from 1 573 K to 1 773 K. The apparent resistance decreased with the increase of NiO content, which has a similar trend in the case of adding FeO.

The electrical conductivities of molten slags was calculated by Eq. (13) and Eq. (14), and were shown in Table 3. The electrical conductivity increased from 1.4 S/m to 14.4 S/m with the increases of the temperature and MO content, which is close to that in previous measurements for similar slag.

Figure 6 shows the plot of electrical conductivity of molten slags as a function of MO content. The increase of electrical conductivity was promoted with the increase

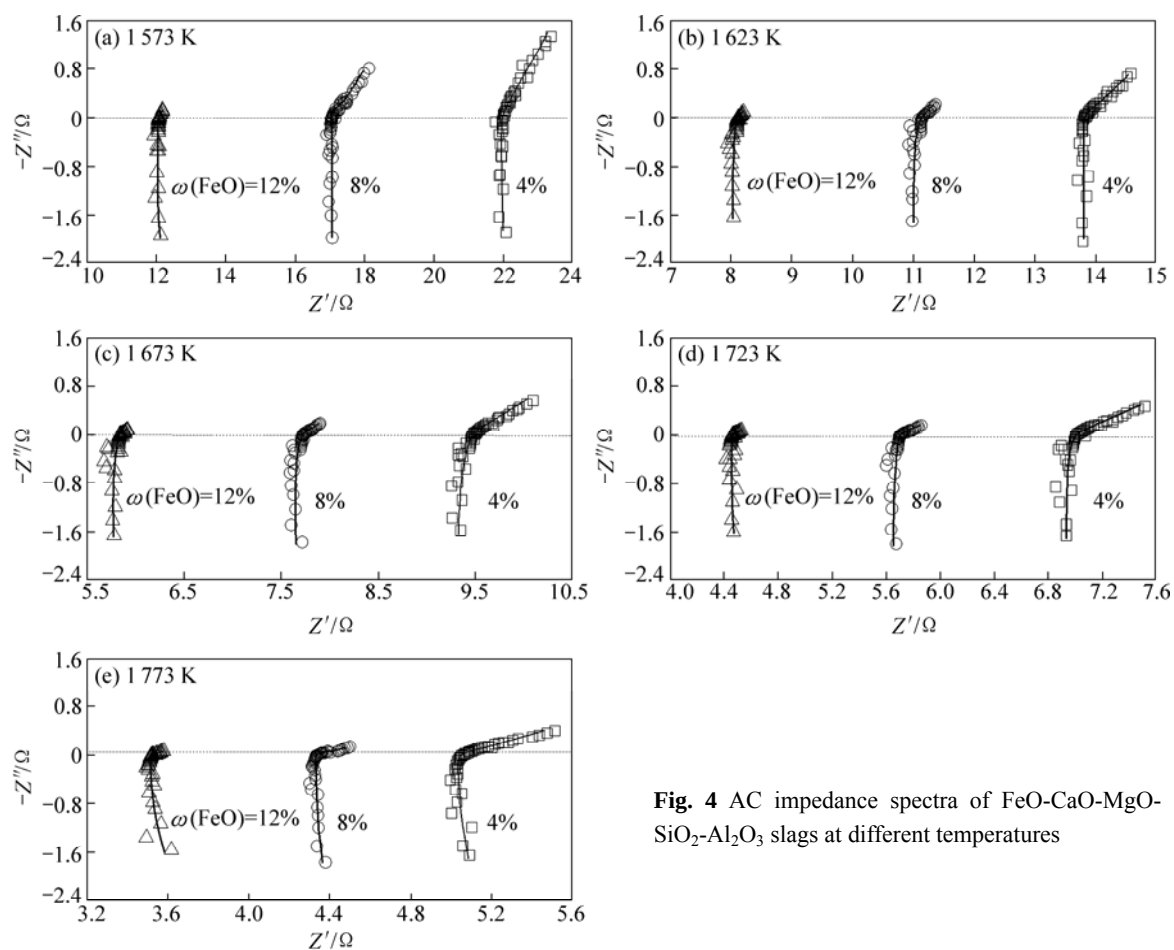


Fig. 4 AC impedance spectra of FeO-CaO-MgO-SiO₂-Al₂O₃ slags at different temperatures

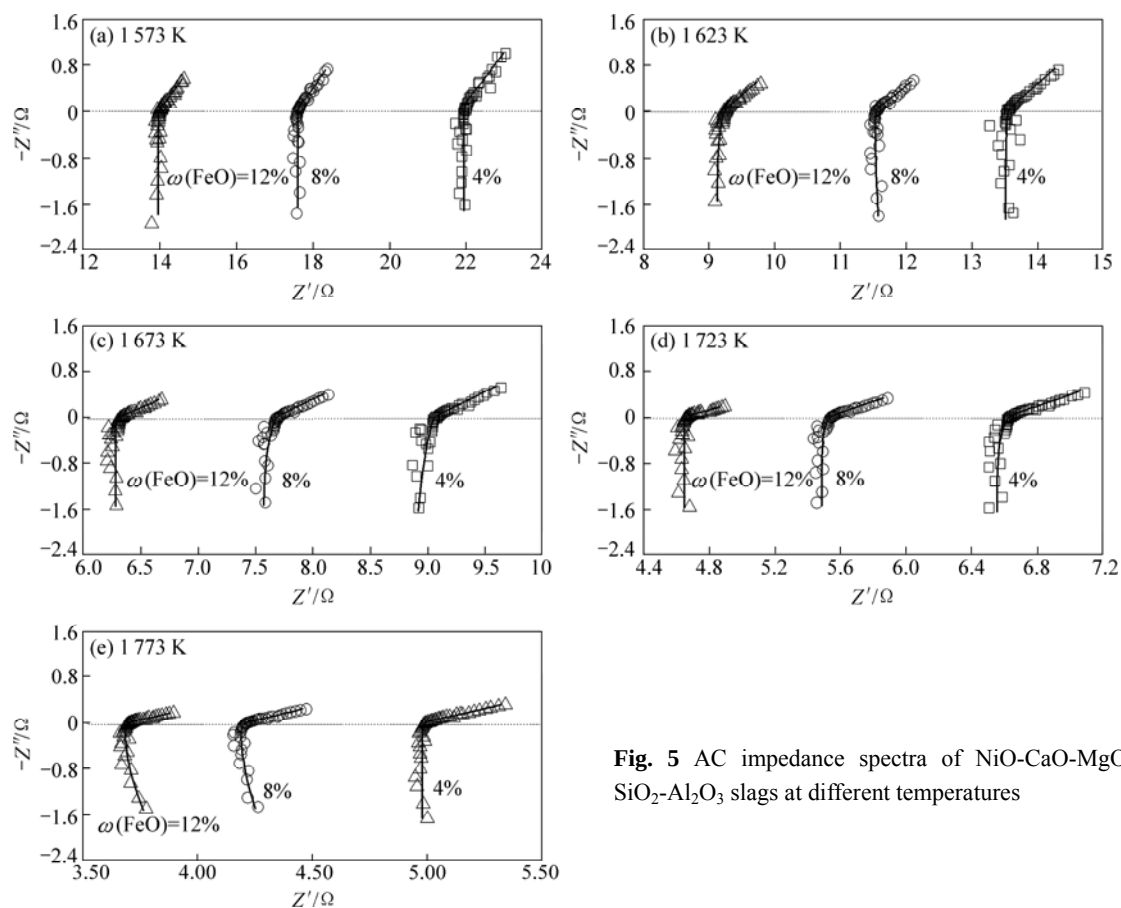
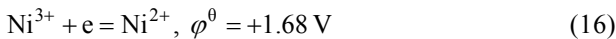


Fig. 5 AC impedance spectra of NiO-CaO-MgO-SiO₂-Al₂O₃ slags at different temperatures

Table 3 Electrical conductivities measured and comparison with previous data

Source	Composition of slag	Electrical conductivity/($\text{S}\cdot\text{m}^{-1}$)				
		1 573 K	1 623 K	1 673 K	1 723 K	1 773 K
Present study	Base slag	1.4	2.3	3.8	5.3	7.8
	4%FeO-containing slag	1.6	2.6	4.0	5.7	8.6
	8%FeO-containing slag	2.0	3.3	5.1	7.4	10.6
	12%FeO-containing slag	3.0	4.7	7.2	10.1	14.4
	4%NiO-containing slag	1.6	2.6	4.2	6.1	8.8
	8%NiO-containing slag	2.0	3.2	5.2	7.6	11.0
	12%NiO-containing slag	2.5	4.1	6.4	9.5	13.4
Ref. [4]	C/S=0.58; 8.32% Fe_xO	3.5	—	7.6	—	—
	C/S=0.65; 17.78% Fe_xO	6.5	—	11.6	—	—
Ref. [7]	C/S=0.3; 10% FeO	—	—	—	7.0	8.4
	C/S=0.6; 10% FeO	—	—	—	17.0	22.6
	C/S=0.3; 20% FeO	—	—	—	13.1	14.9
Ref. [18]	(C+M)/(S+A)=0.48	—	2.2	3.2	4.6	6.5
	(C+M)/(S+A)=0.57	—	3.4	5.0	7.2	10.1
Ref. [18]	(C+M)/(S+A)=0.4; 7.4% FeO	—	—	2.4	—	4.5
	(C+M)/(S+A)=0.54; 6.7% FeO	—	—	3.2	—	5.6

of MO content. The electrical conductivity of FeO-containing slags was close to that of NiO-containing slags when the content was less than 8%; however, it was obviously larger than that of NiO-containing slags when the content was 12%. The electrode reactions at standard state are



where φ^{θ} is standard electrode potentials, in which the standard potential of Fe^{2+} formed from Fe^{3+} is lower than that of Ni^{2+} formed from Ni^{3+} . So Fe^{2+} is easier to lose an electron than Ni^{2+} , which indicates that Fe^{2+} is more beneficial to increase the electronic conductivity in

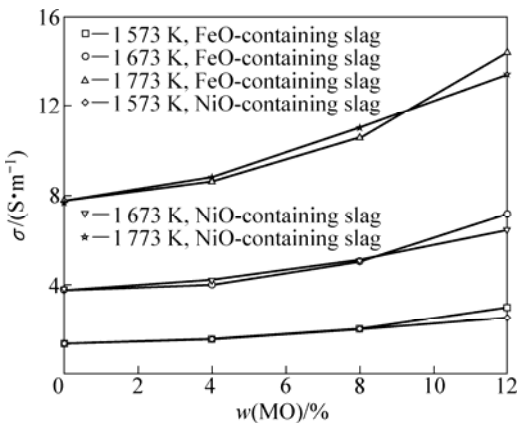


Fig. 6 Electrical conductivity as function of MO content

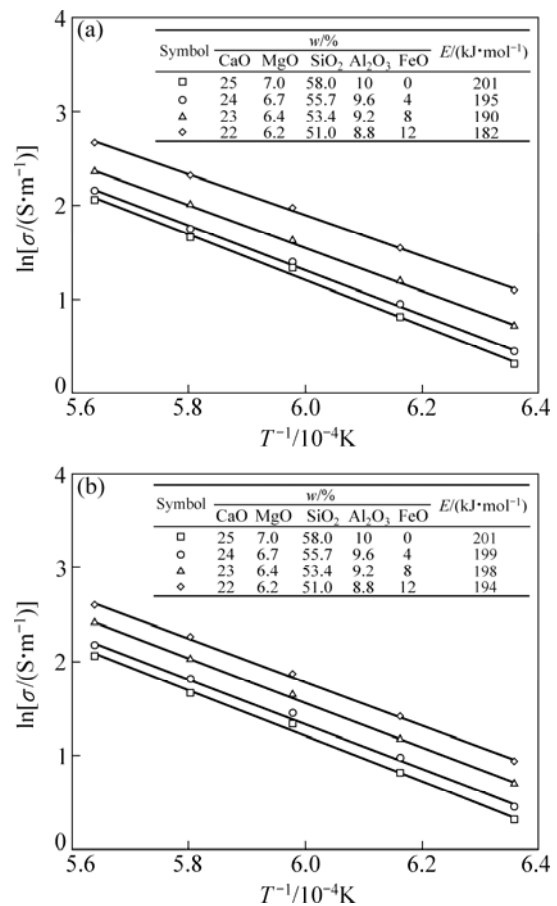


Fig. 7 Arrhenius plot of electrical conductivity: (a) FeO-CaO-MgO-SiO₂-Al₂O₃ slags; (b) NiO-CaO-MgO-SiO₂-Al₂O₃ slags

molten slags. Therefore, the electrical conductivity of FeO-containing slags was larger than that of NiO-containing slags when MO content was enough high, e.g. 12%.

Figure 7 shows a plot of logarithm of the electrical conductivity as a function of reciprocal of temperature, where E as the activation energy of the electrical conductivity was obtained according to an Arrhenius-type relation shown in Eq. (17),

$$\ln \sigma = \ln A - \frac{E}{RT} \quad (17)$$

where A and R is the pre-exponential factor and the gas constant, respectively.

The activation energy of the electrical conductivity decreased with the increase of MO content, which has a good agreement with the results from previous researchers shown in Fig. 8. The activation energy was higher than that of LU et al [11] because the basicity of molten slags in present work was lower, and it could be also explained by the experimental results of SARKAR [20] that the activation energy of the electrical conductivity decreased with the increase of the basicities. Moreover, the activation energy of FeO-containing slags was lower than that of NiO-containing slags, and the activation energy of FeO-containing slags decreased larger than that of NiO-containing slags with the increase of the content.

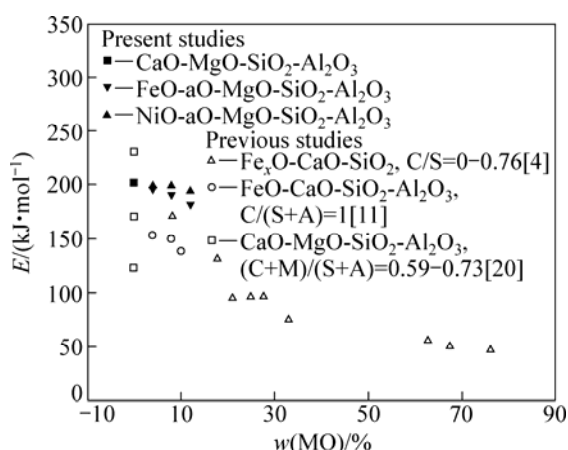


Fig. 8 Activation energy as function of MO content

4 Conclusions

1) The electrical conductivities of MO(MO=FeO, NiO)-CaO-MgO-Al₂O₃-SiO₂ slags with (CaO+MgO)/(SiO₂+Al₂O₃) mass ratio of 0.47 and MO content of 0–12%, were measured by AC impedance spectroscopy from 1 573 K to 1 773 K.

2) The Z' and Z'' calculated from equivalent circuit are well consistent with the experimental results obtained by AC impedance spectra, and the electrical

conductivities of molten slags increased from 1.4 S/m to 14.4 S/m with the increases of temperature and MO content.

3) The increase of the electrical conductivity was promoted with the increase of MO content in the low basicity slags, but the electrical conductivity of FeO-containing slags was close to that of NiO-containing slags when the content was less than 8%; it was obviously larger than that of NiO-containing slags when the content was 12%.

4) Activation energies of the electrical conductivity decreased with the increase of MO content, and the activation energy of FeO-containing slags decreased larger than that of NiO-containing slags with the further increase of MO content.

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含 $\text{MO}(\text{MO}=\text{FeO}, \text{NiO})$ 的低碱度 $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ 熔渣电导率

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摘 要: 作为有色冶金渣中有价金属回收基础, 利用电化学交流阻抗谱法, 测定低碱度 $\text{MO}(\text{MO}=\text{FeO}, \text{NiO})\text{-CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ 五元熔渣体系的电导率。结果表明: 随着熔渣体系温度的升高和 MO 浓度的增大, 熔渣电导率增大。在 1 573~1 773 K 下, $(\text{CaO}+\text{MgO})$ 与 $(\text{SiO}_2+\text{Al}_2\text{O}_3)$ 质量比为 0.47, 当 MO 浓度小于 12% 时, 熔渣电导率为 1.4~14.4 S/m。随着熔渣中 MO 浓度的增大, 熔渣电导率增大的幅度增加。当熔渣中 FeO 和 NiO 浓度小于 8% 时, 两种熔渣的电导率相差不大; 当浓度达到 12% 时, 含 FeO 的熔渣电导率明显大于含 NiO 的熔渣电导率。随着 MO 浓度的增加, 电导活化能降低。

关键词: FeO ; NiO ; 熔渣; 电导率; 交流阻抗

(Edited by YANG Hua)