The Impedance Analysis of Reaction Kinetics at the Interface between Molten Sn–S Alloy and ZnCl_2 –NaCl Salt

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The interfacial reaction between molten Sn–S alloy and ZnCl_2 –NaCl salt was studied by an A. C. impedance method to clarify the individual kinetic factors concerning the electrode reaction at the interface between the alloy and the salt. The total impedance between Sn–S alloy and ZnCl_2 –NaCl salt was measured.

The results obtained were successfully used to determine the individual kinetic factors on electrode reaction between the alloy and the salt, such as electrolyte resistance R_e , double-layer capacitance C_d , charge transfer resistance R_{ct} , rate constant of desulfurization reaction k_f and so on. When overpotential η equals to -85 mV, these values are as follows: $R_e = 2.93 \times 10^{-5} \Omega \text{ m}^2$, $R_{ct} = 2.47 \times 10^{-5} \Omega \text{ m}^2$, $C_d = 1.01 \text{ F m}^{-2}$, $k_f = 2.1 \times 10^{-3} \text{ s}^{-1}$.

KEY WORDS: A. C. impedance method; polarization; equivalent-circuit; double-layer capacitance; charge-transfer resistance; salt-metal interfacial reaction.

1. Introduction

The desulfurization reaction at the interface between slag and metal is one of the most important reactions in iron and steel making. It is a complicated coupling reaction consisting of several steps. The conventional method of kinetic investigation is based on experiments, which depend mainly on chemical analysis for the quenched samples.^{1–3)} Owing to the ionic nature of molten slag, the interfacial reaction kinetics can also be studied electrochemically. The A. C. impedance method is an electrochemical method, which can be used in the studies of ionic conductor, semiconductor and dielectric materials in solid or liquid state, especially suitable for systems with coupling reactions.⁴⁾ Many investigations have been done on the aqua-solution.^{5–7)} But unfortunately there only one is on the system of Pt/CaO– SiO_2 – Al_2O_3 ⁸⁾ in the field of molten metal and slag. It has not been found for the investigation of Sn–S/ ZnCl_2 –NaCl system.

The A. C. impedance method was applied to the desulfurization reaction at the interface between molten Sn–S alloy and ZnCl_2 –NaCl salt in order to obtain kinetic parameters electrochemically. The reason why ZnCl_2 –NaCl/Sn–S system was chosen for the study of the impedance was to imitate desulfurization condition in iron and steel-making process.

2. Experimental

2.1. Experimental Apparatus

The schematic diagram of the cell for impedance measurement is shown in Fig. 1. An end-closed glass tube having an inner tube in its bottom was used to contain

the Sn–S alloy and ZnCl_2 –NaCl molten salt. The Sn–S alloy was put in the inner tube. The quantity of Sn–S was selected so that the ZnCl_2 –NaCl/Sn–S interface could be located in the inner tube. This interface functioned as working electrode (WE), a platinum wire positioned in the bottom of the inner tube was used as WE lead wire, a Pt plate ($0.023 \text{ m} \times 0.009 \text{ m}$) was used as reference electrode 1 (RE1), therefore it has a small resistance and large capacitance.⁹⁾ A Zn plate ($0.23 \text{ m} \times 0.02 \text{ m}$) was inserted into the ZnCl_2 –NaCl salt as counter electrode (CE). Another reference electrode RE2 was connected with WE. The cell was shielded by a stainless steel tube, which was inserted between heating elements and the cell to prevent noise from the surroundings. All of the lead wires used were shielded and earthed. The

Fig. 1. Cell arrangement for impedance measurement.

cell was heated by a vertical electric resistance furnace. The experimental temperature was controlled at 603 ± 1 K using a programmable controller through an S-type thermocouple.

Sn-S mother alloy was prepared in Ar atmosphere and was added into molten Sn to obtain Sn-1mass%S alloy. ZnCl_2 (99.9 %) and NaCl (99.9 %) powders were vacuumly dried at 120°C for 36 h and 200°C 24 h respectively. The weight of the Sn-S alloy was 8 g and that of the ZnCl_2 -NaCl (ZnCl_2 : NaCl = 60 : 40 in mol%) salt was 107 g. The alloy was put in the bottom of the WE tube as shown in Fig. 1, the salt was filled along the sidewall of the cell from the opening. Then the cell was evacuated and filled with purified Ar to remove the air, this operation was repeated three times. After that the glass tube was filled with Ar and heated up to 603 K. The pressure of Ar in the glass tube was kept in 1.013×10^5 Pa. The equilibrium potential of the WE against the CE was monitored until it kept at a stable value, this value is 0.212 V when WE was as cathode. The cell reaction is:

2.2. Experimental Procedure

The four electrode cell described above was connected to a solartron 1286 potentiostat which controlled the potential between RE1 and RE2 by passing the required current through WE and CE. First the cathodic polarization curve of WE against RE1 was measured by potentiostatic method. Then the impedance between WE (RE2) and RE1 was measured by applying an A. C. signal with amplitude of 5 mV using the solartron 1255 frequency response analyser. The range of frequency sweeping is from 5 Hz to 60 kHz.

After the experiment, it was found that the thickness of the Zn plate as CE was 1×10^{-4} m thinner than that before. This phenomenon confirmed the above cell reaction (1).

3. Results and Discussions

Figure 2 shows the experimental results of polarization curve observed in the system of Sn-1mass%S/ ZnCl_2 -NaCl by means of a potentiostatic method. The values on the axis of abscissa are the overpotential which is corrected by reducing the IR drop due to electrolyte resistance of salt from the potential applied between WE against the RE1.

Figure 3 shows the impedance loci observed in the system. There are two relaxation processes in each impedance lotus.

Impedance can be expressed as a complex form:

$$Z = Z' + jZ'' \quad \dots\dots\dots(2)$$

where Z' and Z'' are the real and imaginary part of complex impedance Z respectively, they are the functions of frequency, and $j = (-1)^{1/2}$. The impedance spectra can be simulated by using some equivalent circuits. The well known Randles circuit is used to explain the

Fig. 2. Cathodic polarization curve for Sn-1mass%S/ ZnCl_2 -NaCl (ZnCl_2 : NaCl = 60 : 40 in mol%) electrode at 603 K.

Fig. 3. Complex impedance plots for Sn-1mass%S/ ZnCl_2 -NaCl (ZnCl_2 : NaCl = 60 : 40 in mol%) system at 603 K. Numbers near the data points are frequency in kHz.

Fig. 4. Randles equivalent circuit.

impedance spectrum obtained in the present work. As shown in Fig. 4, the Randles equivalent circuit is composed of four elements:

R_e : electrolyte resistance, here it stands for electrolyte resistance between RE1 and the interface of Sn-S/ ZnCl_2 -NaCl;

Table 1. Kinetic parameters for Sn-S/ZnCl₂-NaCl system at 603 K.

$-\eta / \text{mV}$	$10^5 R_e / \Omega \text{ m}^2$	$10^5 R_{ct} / \Omega \text{ m}^2$	$C_d / \text{F m}^{-2}$	$10^4 \tau / \text{s}$	$10^3 k_f / \text{s}^{-1}$
85	$2.94 \pm 7.58 \cdot 10^{-3}$	$2.47 \pm 8.68 \cdot 10^{-3}$	$1.01 \pm 1.78 \cdot 10^{-3}$	$2.97 \pm 1.33 \cdot 10^{-2}$	2.1
118	$2.93 \pm 6.18 \cdot 10^{-5}$	$1.96 \pm 6.37 \cdot 10^{-4}$	$0.95 \pm 2.33 \cdot 10^{-4}$	$2.34 \pm 3.47 \cdot 10^{-4}$	3.8
160	$2.68 \pm 2.06 \cdot 10^{-3}$	$0.95 \pm 1.00 \cdot 10^{-2}$	$0.93 \pm 8.85 \cdot 10^{-3}$	$1.68 \pm 7.75 \cdot 10^{-3}$	6.0

 Where $\tau = \delta_N^2 / D_0$.

Fig. 5. Overpotential dependence of R_e and R_{ct} for Sn-1mass%S/ZnCl₂-NaCl (ZnCl₂:NaCl=60:40 in mol%) system at 603 K.

Fig. 6. Overpotential dependence of C_d for Sn-1mass%S/ZnCl₂-NaCl (ZnCl₂:NaCl=60:40 in mol%) system at 603 K.

R_{ct} : charge transfer resistance of reaction: $[S] + 2e = S^{2-}$;

C_d : double layer capacitance;

Warburg impedance: diffusion resistance. In the case of finite diffusion layer, it can be expressed as⁹⁾:

$$Z(\omega) = R_{ct} \{ 1 + (k_f \tau \delta_N (j\omega/D_0)^{1/2}) / (j\omega D_0)^{1/2} \} \dots (3)$$

δ_N and D_0 are thickness of Nernst' layer and diffusion coefficient of S in molten Sn. Equation (3) can also be expressed as

$$Z(\omega) - R_{ct} = R^* (1 + x^2/6) / (1 + x^2/2) \dots (4)$$

where $R^* = R_{ct} k_f \delta_N / D_0$, $x = \delta_N (j\omega/D_0)^{1/2}$, k_f is rate con-

Fig. 7. Overpotential dependence of k_f and τ for the reaction $[S] + 2e = (S^{2-})$ in Sn-1mass%S/ZnCl₂-NaCl (ZnCl₂:NaCl=60:40 in mol%) system at 603 K.

stant of desulfurization reaction.

The LEVM impedance analyzing program was used for the complex nonlinear least square fitting. The values of the circuit parameters obtained are listed in **Table 1** along with relative standard deviation. Generally, the diffusion coefficient of sulfur in liquid metal is about $10^{-9} \text{ m}^2 \text{ s}^{-1}$,¹⁰⁾ δ_N can be calculated from $\tau = \delta_N^2 / D_0$ and so can k_f from R^* . These results are also listed in **Table 1**. **Figures 5, 6 and 7** show the overpotential dependence of the individual kinetic factors in this system. R_{ct} and C_d increase with the increasing of the overpotential, k_f decreases with that. Electrolyte resistance in ZnCl₂-NaCl (ZnCl₂:NaCl=60:40 mol%) system at 603 K is about 0.25 Ω . The conductivity of the electrolyte can be calculated using the cell constant determined by standard KCl aqueous solution, is $1.4 \times 10^{-2} \Omega^{-1} \text{ m}^{-1}$. It is in good agreement with the value of $2.0 \times 10^{-2} \Omega^{-1} \text{ m}^{-1}$ (773 K) in Ref. 11). According to kinetic theories for heterogeneous reaction, rate constant of diffusion process $k_D = D_0 A / \delta_N V$, A and V are the area of WE and electrolyte volume respectively. In this experiment, $A = 7.9 \times 10^{-5} \text{ m}^2$, $V = 7.9 \times 10^{-7} \text{ m}^3$, D_0 is about $10^{-9} \text{ m}^2 \text{ s}^{-1}$ and δ_N about $0.5 \times 10^{-6} \text{ m}$, then k_D is about 0.2 and $k_D \gg k_f$, therefore the rate control step of desulfurization reaction in this system is electrochemical reaction process.

4. Conclusions

A. C. impedance method was used to investigate the interfacial reaction between molten Sn-1mass%S alloy and ZnCl₂-NaCl (ZnCl₂:NaCl=60:40 mol%) salt. Randles circuit was used to simulate the system. Elec-

trolyte resistance R_e , charge transfer resistance R_{ct} , double-layer capacitance C_d , and rate constant of desulfurization reaction k_f concerning this system were obtained by complex nonlinear least square fitting to the parameters of the equivalent circuit. Following could be concluded:

(1) A. C. impedance method is very useful for the study of interfacial reaction in the salt/metal system.

(2) The rate constant of the reaction: $[S] + 2e = (S^{2-})$ in Sn-1mass%S/ZnCl₂-NaCl system was obtained as $k_f = 2.1 \times 10^{-3} s^{-1}$ in the case of $\eta = -85$ mV.

(3) The rate controlling step in this system is electrochemical reaction process.

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