A.C. Impedance Analysis of the Kinetics of Reactions between Molten Cu or Fe and $\text{CaO-Al}_2\text{O}_3$ Slag

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A chemical reaction at the interface between slag and metal can be analyzed as a kind of electrode reaction because of the ionic nature of liquid slag.

In the present work, application of an A.C. impedance method to slag-metal reaction in iron- and steel-making process was tried to clarify the individual kinetic factors concerning the electrode reactions at the interface between slag and metal. The total impedance between $\text{CaO-Al}_2\text{O}_3$ slag and Cu-S or Fe-C-S melts was measured in this paper.

The results obtained were successfully used to determine the individual factors on kinetics of the electrode reaction between slag and metal, such as solution resistance of slag, interfacial capacitance in electric double-layer, overvoltage of charge transfer, rate constant and so on.

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

1. Introduction

A chemical reaction at the interface between slag and metal can be analyzed as a kind of electrode reaction because of the ionic nature of liquid slag.

Many attempts have been made to electrochemically study the kinetics of the slag-metal reaction by means of stationary and unstationary methods. The authors tried the application of the A.C. impedance method, which is one of unstationary methods, to clarify some kinetic factors concerning the electrode reactions for the systems of $\text{Pt/Na}_2\text{O-SiO}_2$ slag^{1,2)} and $\text{Pt/Na}_2\text{O-B}_2\text{O}_3\text{-NiO}$ slag.¹⁾ It was confirmed from the work that the A.C. impedance method might be quite useful to determine the individual kinetic parameters concerning the slag-metal reactions, if the kinds of reactions occurring at slag-metal interface were reliably known. In succession, this technique was tried for the reaction between solid Pt and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag to clarify the individual kinetic factors concerning the electrode reactions at the interface between slag and metal, and to learn the oxidation-reduction reaction between solid Fe and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag as the first application for slag-metal reaction in iron- and steel-making process.^{3,4)} It was concluded that the A.C. impedance method might be also quite useful to determine the individual kinetic parameters concerning the slag-metal reactions in iron- and steel-making process.

The method was applied to desulphurization of Cu-S

or Fe-C-S melts with $\text{CaO-Al}_2\text{O}_3$ slag to make clear the reaction mechanism in this paper.

2. Principle of the Measurement on an A.C. Impedance Method

In an A.C. impedance method, the kinds of electrode reactions occurring at the interface of working electrode and electrolyte are hypocritically decided by applying a direct current overpotential between the working and the reference electrodes. Then, an A.C. overpotential of wide frequencies with amplitude less than 10 mV is overlapped on the D.C. polarization. After that, the total impedance by the A.C. polarization is measured as a function of the frequency.

The major factors affecting the total impedance, Z ($\Omega \cdot \text{m}^2$), consist of solution resistance, R_{sol} ($\Omega \cdot \text{m}^2$), resistance of charge transfer, R_c ($\Omega \cdot \text{m}^2$), and concerning diffusion, that is, Warburg impedance, Z_w ($\Omega \cdot \text{m}^2$), pre-

ceding or following chemical reaction $[X \xrightleftharpoons[k_{-p}]{k_{+p}} R]$ or

crystallization impedance, Z_R ($\Omega \cdot \text{m}^2$), and capacitance of electric double-layer, C_{dl} ($\text{F} \cdot \text{m}^{-2}$). Since the response to frequency is different by the factors affecting the total impedance, each factor in this case can be individually determined by comparing the frequency response observed with that of electrically equivalent circuits as shown in Fig. 1.

The comparison of the electrically equivalent circuit

shown in Fig. 1(a) with that of the measurements shown in Fig. 1(b) gives us Eq. (1) at high frequencies, and Eqs. (2) and (3) at low frequencies.

High frequency range:

$$\{R - (R_{\text{sol}} + R_C/2)\}^2 + (1/\omega C)^2 = (R_C/2)^2 \quad \text{.....(1)}$$

Low frequency range:

(a) In the case of high rate of preceding, or following chemical reaction, or crystallization ($k \gg \omega$)

$$1/\omega C = R - R_{\text{sol}} - R_C - m + 2\sigma^2 C_{dl} \quad \text{.....(2)}$$

Where, $m = (RT/n^2 F^2)(v^2/\bar{c}k)$.

(b) In the case of low rate of preceding, or following chemical reaction, or crystallization ($k \ll \omega$)

$$1/\omega C = R - R_{\text{sol}} - R_C + 2\sigma^2 C_{dl} \quad \text{.....(3)}$$

Where, ω ($= 2\pi f$, f : frequency (Hz)), k , n , F , $\bar{c}$, v and σ mean angular frequency (sec^{-1}), rate constant (sec^{-1}), valency, Faradaic constant ($\text{C} \cdot (\text{mole of electrons})^{-1}$), equilibrium concentration of reactant in slag ($\text{mol} \cdot \text{m}^{-3}$), stoichiometric number ($-$), and constant on the experimental condition, respectively.^{1,2,5)}

The vector locus of impedance, which is frequency response of the total impedance for electrode reaction, is shown in Fig. 2. The locus obtained at high frequencies is expressed by the semicircle of $R_C/2$ in radius, and the center of the circle exists at the position of $R_{\text{sol}} + R_C/2$ on R axis. Therefore, the Ohmic resistance of slag (R_{sol}) is obtained from the impedance at the position of an

infinite frequency, and charge-transfer resistance (R_C) is obtained by the diameter of the semicircle, respectively. At low frequencies, the information on Warburg impedance caused by mass transfer might be obtained from the extrapolated point for locus of impedance on the R axis, but it is very difficult because of the complicated shape of the locus.

In the present work, reaction or crystallization impedance is combined with diffusion, and the reaction or crystallization impedance with diffusion is redefined as Z_R . The components of resistance, R_R , and capacitance, $1/\omega C$, in Z_R are presented by Eqs. (4) and (5), respectively.

$$R_R = A[\{(\omega^2 + k^2)^{0.5} + k\}/(\omega^2 + k^2)]^{0.5} \quad \text{.....(4)}$$

$$1/\omega C_R = A[\{(\omega^2 + k^2)^{0.5} - k\}/(\omega^2 + k^2)]^{0.5} \quad \text{.....(5)}$$

Where, A and k mean term concerning diffusion composed of diffusion constant, D ($\text{m}^2 \cdot \text{sec}^{-1}$), of oxidant or reductant, and rate constant of preceding, following chemical reaction, or crystallization (sec^{-1}), respectively, and they are expressed as follows;

$$A = (1/2^{0.5})(RT/n^2 F^2)(1/c^0 D^{0.5} k_C) \quad \text{.....(6)}$$

$$c^0 = c_X^0 + c_R^0 \quad \text{.....(7)}$$

$$k_C = c_X^0/c_R^0 \quad \text{.....(8)}$$

$$k = k_{+p} + k_{-p} \quad \text{.....(9)}$$

Where c_X^0 and c_R^0 mean molarity of oxidant or reductant ($\text{mol} \cdot \text{m}^{-3}$).

Since the response for A.C. frequency is different by each factor affecting the total impedance as above-mentioned, individual factors in this case, R_{sol} , R_C , C_{dl} , A and k , can be separately determined by comparing the frequency response observed with that of electrically equivalent circuit of the electrode.³⁻⁵⁾ Two relaxation processes were observed in the impedance loci obtained in the present work. Therefore, R_{sol} , R_C and C_{dl} were evaluated from the impedance loci in high frequency range, and A and k concerning Z_R were estimated from those in low frequency range.

3. Experimentals

3.1. Experimental Apparatus

The experimental apparatus consists of a purification train for Ar, an Al_2O_3 reaction tube ($0.05^{\text{O.D.}} \times 0.04^{\text{I.D.}} \times 0.7^{\text{H}} \text{m}$), a Keramax electric resistance furnace, a potentiogalvano-stat for polarization curve measurement (input impedance: $1 \text{ M}\Omega$), a frequency response analyzer with frequency transmitter (input impedance: $1 \text{ M}\Omega$), and a digital voltmeter (input impedance $> 10 \text{ G}\Omega$). Two sets of thermocouple were used for temperature measurement. One of them, which was Pt-20%Rh-Pt-40%Rh and was inserted between a reaction tube and refractories, was connected to a program controller to maintain the furnace temperature constant, and another, Pt-Pt-13%Rh, was set just below the cell in the furnace to check the experimental temperature. The temperature studied was 1673 K.

The schematic diagram of the cell for impedance

Fig. 1. (a) Equivalent circuit diagram of an electrode reaction with the Faradaic impedance [Z_F] for charge-transfer overvoltage [R_C], Warburg impedance [Z_W], and reaction or crystallization impedance [Z_R] with consideration of the double-layer capacitance [C_{dl}] and an electrolyte resistance [R_{sol}]. R_R = Ohmic components of Z_R , C_R = capacitive components of Z_R . (b) Equivalent circuit diagram for the measurement.

Fig. 2. Frequency response of complex impedance for an electrode reaction with charge-transfer, diffusion, and reaction or crystallization rate-control.

Fig. 3. Cell arrangement for impedance measurement.

- 1: Working electrode (Liquid Cu-S or Fe-C-S)
- 2: Counter electrode (Liquid Cu-S or Fe-C-S)
- 3: Pt-Pt 13%Rh thermocouple 4: CaO-Al₂O₃ slag
- 5: Al₂O₃ reaction tube 6: Heating element
- 7: Stainless steel or Mo cylinder
- 8: Pt 20%Rh-Pt 40%Rh thermocouple
- 9: Al₂O₃ crucible 10: Al₂O₃ tube

measurement is shown in Fig. 3. The cell, of which inner diameter was 0.036 m, was made from Al₂O₃ crucible. An Al₂O₃ tube of 0.01 m inner diameter passed through a hole on the bottom of the crucible. Synthetic slag was melted in the cell, and contacted with both molten metal phase in the Al₂O₃ tube, which was a working electrode, and in the crucible, which was a counter electrode. Another Al₂O₃ outer tube pasted up the bottom of Al₂O₃ crucible so as to be duplicate tube structure, and played a role in a pedestal of the crucible. A metallic rod of 0.003 × 0.002 m, of which composition is same as that of a counter electrode, was inserted in the Al₂O₃ crucible through a channel along the outer Al₂O₃ tube and a hole drilled on the bottom of the crucible, and was made to contact with a counter electrode in the crucible. The lower parts of both the rod and the working electrode were in solid because of the temperature profile of furnace, so that they were drawn outside the reaction tube and connected with the instruments. The cell was constructed with Al₂O₃ paste.

The reason, why Cu or Fe and CaO-Al₂O₃ system were utilized as metal and slag phases in the present work, is as follows.

When the component of metal was Fe-C-S-M (*M*=Mn, Si, Al), the kinds of slag-metal reactions in iron- and steel-making process were listed up as following reactions for anodic and cathodic reactions by Ramachandran *et al.*⁶⁾

Anodic reaction:

Fig. 4. Circuit diagram for impedance measurement.

Cathodic reaction:

In the present work, the component of Fe-C-S was adopted because the number of electrode reactions was made to decrease. Therefore, the anodic reactions might be dissolution of Fe in slag shown by Eq. (10) and CO gas evolution shown by Eq. (12), and cathodic reaction might be desulphurization shown by Eq. (13). The CaO-Al₂O₃ binary was taken as slag system without SiO₂.

As a preexamination in the present work, the A.C. impedance analysis was studied to the kinetic of the reaction between molten Cu-S alloy and CaO-Al₂O₃ slag, where the number of kinds of electrode reactions was smaller than that in Fe-C-S/CaO-Al₂O₃ system. The metal and slag phases composed of Cu-1mass%S (melting point: 1378 K) and 49mass%CaO-51mass%Al₂O₃ (melting point: 1633 K). The anodic and cathodic reactions in this system might simply be oxidation of Cu and desulphurization, respectively.

Anodic reaction

Cathodic reaction

On the other hand, the metal and slag phases composed of Fe-3.7mass%C-0.1mass%S (melting point: 1403 K) and 49mass%CaO-51mass%Al₂O₃ in Fe-C-S/CaO-Al₂O₃ system. The anodic and cathodic reactions in this system might be above-mentioned.

Since the interfacial ratio of a working electrode for a counter electrode was so small like as 1/10 that the results obtained were directly concerned with a single electrode reaction on the working electrode.

The schematic circuit diagram of the instruments for impedance measurement is shown in Fig. 4. A potentiostat-galvanostat, an impedance analyzer and a digital voltmeter were connected in parallel with the working and the counter electrodes. The kinds of electrode reactions occurring at the interface of working

electrode and electrolyte were hypocritically decided by supplying a D.C. overpotential between the working and the counter electrodes. The D.C. polarization curve was measured by monitoring the D.C. overpotential between the electrodes with the digital voltmeter on the experimental condition. Next, the frequency response for total impedance was measured in the range from 5 to 100 kHz by overlapping the sinusoidal A.C. overpotential with amplitude of 1×10^{-3} V on the constant D.C. overpotential between the same electrodes. Blocking capacitors were set in the circuit as shown in Fig. 4 for D.C. streaming from the potentiostat into the impedance analyzer. Viewed from the angle of impedance analyzer, the cell, potentiostat and digital voltmeter were connected in parallel with the analyzer, so that all of them were objects of impedance measurement. Therefore, resistance and coils were set in the circuit as shown in Fig. 4 for blocking A.C. stream from the impedance analyzer to them. A stainless steel or molybdenum cylinder earthed to a ground was inserted between heating elements and the cell to prevent noise from the surroundings. All of the lead wires used were shielded and earthed.

3.2. Experimental Procedure

The master metals and slags used were prepared as follows.

Cu-S alloy was made by premelting Cu drops of 4 N purity and Cu-25mass%S powder, which was fired with chemical reagent grade Cu and S powder, in a graphite crucible by means of a high frequency induction furnace, and pouring itself into warmed cast-iron split molds with 0.01 and 0.035 m of inner diameter. The working electrode was turned from the Cu-S rod with 0.01 m of diameter. An iron bar with 0.005 m of diameter was screwed-in the bottom of working electrode, $0.009^D \times 0.145^L$ m (0.086 kg), and was drawn outside the reaction tube. The counter electrode was turned from Cu-S rod with 0.035 m of diameter into the shape of crucible with a center hole of 0.0155 m diameter, of which weight was 0.245 kg. This corresponded to the depth of 0.04 m in the Al_2O_3 crucible when the electrode was in melt.

Fe-C-S electrodes were prepared in the same procedure from electrolytic iron and FeS powder made in laboratory. However, the weight of counter electrode was 0.235 kg in this system, so that the depth of counter electrode in Al_2O_3 crucible was the same as that in Cu-S system at experimental temperature.

The slag was prepared by premelting the mixtures of chemical reagent grade CaCO_3 and Al_2O_3 powder in a Pt crucible with Keramax electric resistance furnace and quenching themselves. The weight of slag used in an experiment was 0.042 kg, which corresponded 0.015 m of depth in the cell at the experimental temperature.

These metal and slag were set in the cell in a reaction tube. They were heated up to their melting points under an Ar atmosphere. The reaction tube was evacuated during and after the melt-down period, so that residual gas in slag phase was released and the slag could contact smoothly with the metal phases. Since the melting temperature of slag was higher than those of metals, the

temperature was once increased up to 1703 K and decreased to the experimental temperature after recognition of the melt-down of slag. After that, Ar was introduced into the reaction tube again, and the mixed potential of the working electrode against the counter electrode was monitored until it kept a stable value. On this experimental condition, the stationary D.C. polarization curve was measured by supplying a D.C. overpotential against the mixed potential between the electrodes in the range from -1.0 to $+1.0$ V.

Next, the frequency response for total impedance was continuously measured every 5 min by impedance analyzer until approach to steady state after overlapping the sinusoidal A.C. overpotential with wide range of frequency on the constant D.C. overpotential between the same electrodes. A personal computer was used for changing the frequency, measuring the frequency response and storing the data, and the operation took about 2 min.

The impedance of experimental instruments in the total impedance measured was corrected by the results of the blank test checked on the same experimental condition, when the volume of two electrodes was a little larger than that on the impedance measurement condition and two electrodes contacted each other in the Al_2O_3 crucible.

The cell constant of the system was estimated at room temperature by using 0.1 N KCl standard solution.

4. Experimental Results and Discussion

4.1. Cu-S/CaO- Al_2O_3 System

4.1.1. Polarization Curve

Figure 5 shows the experimental result of polarization curve observed in the system of Cu-S/CaO- Al_2O_3 by means of a potentiostatic method. The value on the axis of abscissas shows the overpotential, which is corrected by reducing the IR drop due to solution resistance of slag, R_{sol} , from the mixed potential of the working electrode against the counter electrode. Since there is not a suitable standard electrode in the electrochemical study of fused salts at high temperatures, the kinds of electrode reactions which occurred cannot be defined at a constant D.C. overpotential. The corrected result shown in Fig. 5 is drawn in Fig. 6 by means of the relation of Tafel's

Fig. 5. Polarization curve in Cu-1mass%S/49mass%CaO-51mass% Al_2O_3 system at 1673 K.

Fig. 6. Tafel plot for the electrode reaction between Cu-1mass%S and 49mass%CaO-51mass%Al₂O₃ melts at 1673 K.

Fig. 7. Complex impedance plots for the cathodic and anodic reactions between Cu-1mass%S and 49mass%CaO-51mass%Al₂O₃ melts at 1673 K. Numbers near the data plots are measurement frequencies.

equation. It is expected that desulphurization would take place as above-mentioned in the cathodic field, where the slope was a constant as $(1-\alpha) \cdot n = 0.812$ under -100 mV of overpotential and the transfer coefficient results in $\alpha = 0.59$. It is guessed that oxidation of Cu would take place in the anodic field, where the slope was a constant as $\alpha \cdot n = 0.584$ over 100 mV of overpotential and the transfer coefficient results in $\alpha = 0.58$.

4.1.2. Impedance Loci

Figure 7 shows two examples of impedance loci observed in steady state at 243 mV of overpotential in the anodic field and -121 mV in the cathodic field. The open circles show the observed impedance and are comparable with the open squares, which are the corresponding estimated values by means of the in-

Fig. 8. Overvoltage dependence of factors A , k , double-layer capacitance and charge-transfer resistance in Cu-1mass%S/49mass%CaO-51mass%Al₂O₃ system at 1673 K.

dividual kinetic factors determined in parameter fitting, and they are consistent with each other. The factors obtained in the present work are shown in Fig. 7. R_{sol} evaluated in the cathodic field was somewhat smaller than that in the anodic field, because the sulphur dissolved in slag by cathodic reaction increased the electric conductivity of slag. It was confirmed in our previous papers^{1,2)} that the conductivity obtained by the present method was reliable. Incidentally, the conductivity of the present slag of $0.17 \Omega^{-1} \text{cm}^{-1}$ at the mixed potential showed good agreement with the result of Mori and Matsushita.⁷⁾

4.1.3. Individual Kinetic Parameters

The individual kinetic factors of R_{sol} , A , k , C_{dl} and R_C , which are concerned in the electrode reactions, were able to be determined by parameter fitting in each impedance locus as shown in Fig. 7. Figure 8 shows the overvoltage dependence of the individual factors in this system. A maximum appeared in factor A , and its dependency on overvoltage corresponded exactly with the residual current around -0.1 V caused by mass transfer resistance in cathodic field on the polarization curve in Fig. 5. The factor k indicating the rate constant of cathodic reaction was much the same as that of anodic reaction. The dependency of electrical double-layer capacitance on D.C. overpotential might show that there is a relaxation step in the cathodic field, and the magnitude of the capacitance was almost constant in the anodic field. Charge-transfer resistance showed a constant value for the anodic electrode reaction.

Figure 9 shows two examples of Faradaic impedance, Z_F , relating to the electrode reactions at the interface between slag and metal at -253 and 243 mV of overvoltage, which were estimated by the parameter fitting. This figure shows the angular frequency dependency of each component in Faradaic impedance, that is, charge-transfer resistance, R_C , and the components of resistance, R_R , and capacitance, $1/\omega C$, in the reaction or crystallization impedance with diffusion, which were calculated by Eqs. (4) and (5). It was clarified

Fig. 9. Dependence of the components of the Faradaic impedance Z_F on $1/\sqrt{\omega}$ ($\omega/2\pi$ =frequency) for the cathodic and anodic reactions between Cu-1mass%S and 49mass%CaO-51mass%Al₂O₃ melts at 1673 K.

Fig. 10. Tafel plot for the electrode reaction between Fe-3.7mass%C-0.1mass%S and 49mass%CaO-51mass%Al₂O₃ melts at 1673 K.

from the results shown in Fig. 9 that R_C was the largest magnitude among each component, *i.e.*, the rate determining step was charge-transfer process at high frequencies, and the kinetic factor of Z_R , specially, the components of resistance, R_R , was 4 to 5 times as large as R_C , *i.e.*, the rate determining step was the reaction or crystallization impedance with diffusion at low frequencies, in both of anodic and cathodic reactions.

4.2. Fe-C-S/CaO-Al₂O₃ System

4.2.1. Polarization Curve

Figure 10 shows the experimental result of polarization curve observed in the system of Fe-C-S/CaO-Al₂O₃. The result shown in Fig. 10 was drawn by means of the relation of Tafel's equation. In our previous observation,^{3,4)} gas evolved at higher overvoltage than that for oxidation of metal in anodic reaction, accompanied by the observation of fluctuation of current value in polarization curve. Therefore, it is expected in this system that desulphurization would take place in the cathodic field, where the slope was a constant under -80 mV of overpotential and the transfer coefficient results in $\alpha=0.29$. It is guessed that oxidation of Fe would take place in the anodic field, where the slope was a constant

Fig. 11. Complex impedance plots for the cathodic and anodic reactions between Fe-3.7mass%C-0.1mass%S and 49mass%CaO-51mass%Al₂O₃ melts at 1673 K. Numbers near the data plots are measurement frequencies.

over 30 mV of overpotential and the transfer coefficient results in $\alpha=0.35$.

4.2.2. Impedance Loci

Figure 11 shows two examples of impedance loci observed in steady state at 103 mV of overpotential in the anodic field and -75 mV in the cathodic field. The open circles show the observed impedance and are comparable with the open squares, which are the corresponding estimated values by means of the individual kinetic factors determined in parameter fitting, and they are consistent with each other. The factors obtained in the present work are shown in Fig. 11. The reason was the same as that in Cu-S system why R_{sol} evaluated in the cathodic field was somewhat smaller than that in the anodic field. But the value in this system was larger than that in Cu-S system, because the sulphur content in slag was lower than in Cu-S system.

4.2.3. Individual Kinetic Parameters

The individual kinetic factors, which are concerned in the electrode reactions, were able to be separately determined by parameter fitting in each impedance locus as shown in Fig. 11. Figure 12 shows the overvoltage dependence of the individual factors in this system. Factor A decreased monotonously with increasing overvoltage in cathodic field, and *vice versa* in anodic field. The factor k indicating the rate constants of cathodic and anodic reactions in this system were about 4 and 8 times as large as those in Cu-S system, respectively. Therefore, it was clarified that the rate of desulphurization from iron to slag was faster than that from copper to slag, and the rate of oxidation of iron was faster than that of copper. The magnitude of

Fig. 12. Overvoltage dependence of factors A , k , double-layer capacitance and charge-transfer resistance in Fe-3.7mass% C-0.1mass% S/49mass% CaO-51mass% Al_2O_3 system at 1673 K.

Fig. 13. Dependence of the components of the Faradaic impedance Z_F on $1/\sqrt{\omega}$ ($\omega/2\pi$ =frequency) for the cathodic and anodic reactions between Fe-3.7mass% C-0.1mass% S and 49mass% CaO-51mass% Al_2O_3 melts at 1673 K.

electrical double-layer capacitance between slag and Fe-C-S was smaller than that between the slag and Cu-S in the cathodic and anodic fields, so that the thickness of electrical double-layer in Fe-C-S/slag system was thicker than that in Cu-S/slag system. Charge-transfer resistance increased somewhat with increasing overvoltage in the cathodic and anodic electrode reactions, the magnitude in this system was almost same as that in Cu-S system.

Figure 13 shows two examples of the angular frequency dependency of each component in Faradaic impedance, Z_F , relating to the electrode reactions at the interface between slag and metal at -152 and 188 mV of overvoltage, which were estimated by the parameter fitting. Compared with Faradaic impedance in Cu-S system, the impedance in this system was about 1/2 to 1/3 for the cathodic reaction and 1/2 for the anodic reaction. It was also clarified from the results shown in

Fig. 13 that R_C was the largest magnitude among each component, i.e., the rate determining step was charge-transfer process at high frequencies, and the kinetic factor of Z_R , specially, the components of resistance, R_R , was about 2 times as large as R_C , i.e., the rate determining step was the reaction or crystallization impedance with diffusion at low frequencies, for both of anodic and cathodic reactions in this system.

5. Conclusions

The application of an A.C. impedance method was tried to clarify the individual kinetic parameters concerning the slag-metal reactions in iron- and steel-making process, the followings were concluded.

(1) The individual kinetic factors of electrolyte resistance, R_{sol} , capacitance of electric double-layer, C_{dl} , overvoltage of charge transfer, R_C , kinetic factor related to preceding or following chemical reaction with diffusion, A , and the rate constant of reaction, k , which are concerned with the electrode reactions in Cu-S/CaO- Al_2O_3 and Fe-C-S/CaO- Al_2O_3 systems, were able to be separately determined by comparing the frequency response observed with that of electrically equivalent circuit of the electrode.

(2) In each component of Faradaic impedance, Z_F , relating to the electrode reactions at the interface between slag and metal, which were estimated by the parameter fitting, the magnitude of charge-transfer resistance, R_C , was about 1/2 to 1/5 of that of resistant component in reaction or crystallization impedance with diffusion, R_R , for the anodic and cathodic reactions in both systems.

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