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A MODEL ON SLAG–METAL REACTION KINETICS

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Synopsis: An electrochemical model on the kinetics of metal–slag reaction, directly deduced from the principle of electrochemistry, may be available quantitatively to describe the metal–slag reaction rate versus time. The established model combines kinetics with the calculation of thermodynamic equilibrium of multi–component and multi–phase reaction system. In furtherfore studying it was found that surface renewal theory is a special example of this model in the case when the diffusion of reactant is the control step of the reaction. This model was applied successfully to describe desulfurization of liquid iron by flux.

Key words: model, kinetics, electrochemistry, desulfurization

1. Introduction

In traditional concept, the rate of a reaction between molten slag and metal is expressed as

$$-\frac{dC_i^b}{dt} = k_i\left(C_i^b - C_i^*\right) \tag{1}$$

where C_i^b is content of reactant i in the bulk of metal or slag at time t, C_i^* is its equilibrium content, and k_i is a rate constant of the reaction and only depends on the temperature and stirring condition for certain reaction system. However, many investigations showed the parameter k_i is also concerned with the contents of reactant i and other reactants in the reaction system [1,2]. For example, Jiang [3] treated the experimental data on desulfurization of liquid steel by flux done by Den [4], with equation (1), and his result shows that k_i is decreasing with sulfur decreasing in steel. If we want to keep k_i as a constant corresponding to traditional concept, assuming a apparent reaction order is necessary. But it is more complex to describe the kinetics of the reaction system. Besides, for the system with more than one chemical reaction, one reaction rate must relate to the other reactions. How to establish their relationship has been few studied yet. In this paper, a parameter of driving force [3] is induced to model the slag–metal reaction kinetics by means of electrochemical theory. This model could make every reaction rate of the slag–metal system related each other.

2. Theoretical consideration

A electrode reaction in the slag–metal system can be generally written as

$$O_i + n_i e \underset{k_{b,i}}{\overset{k_{f,i}}{\rightleftharpoons}} R_i \tag{2}$$

The rate of the electrode reaction can be expressed as

$$r_i = k_{f,i} C^s_{O_i} - k_{b,i} C^s_{R_i} \tag{3}$$

where O_i and R_i mean the oxidized element i and reduced element i respectively, n_i is number of electron exchange, r_i is reaction rate, $C^s_{O_i}$ and $C^s_{R_i}$ are the contents of O_i and R_i respectively at slag–metal interface. $k_{f,i}$ and $k_{b,i}$ are named here for driving force parameters of the forward reaction and backward reaction respectively. $k_{f,i}$ and $k_{b,i}$ relate to the potential E of the slag–metal reaction system

$$k_{f,i} = k^{o}_{f,i} exp\left(\frac{\alpha_i n_i FE}{RT}\right) \tag{4}$$

$$k_{b,i} = k^{o}_{b,i} exp\left(-\frac{(1-\alpha_i) n_i FE}{RT}\right) \tag{5}$$

where α_i is a parameter whose value lies between zero and unity, F is Faraday constant, $k^{o}_{f,i}$ and $k^{o}_{b,i}$ are the rate constant of forward and backward reaction respectively. $k^{o}_{f,i}$ is relate to $k^{o}_{b,i}$ as following

$$E^{o}_{i} = \frac{RT}{n_i F} ln \frac{k^{o}_{f,i}}{k^{o}_{b,i}} = \frac{RT}{n_i F} ln \frac{C^{*}_{R_i}}{C^{*}_{O_i}} \tag{6}$$

where E^{o}_{i} is standard potential of the reaction (3), $C^{*}_{R_i}$ and $C^{*}_{O_i}$ are contents of R_i and O_i respectively in equilibrium condition, strictly speaking, they should be activities.

For a multi–phase and multi–component reaction system, the $C^{*}_{R_i}$ and $C^{*}_{O_i}$ in equation (6) is changeable due to the change of composition of the system. For example, if the initial activity of oxygen in steel is $1.0 \cdot 10^{-5}$, and sulfur capacity of slag is 0.5, the initial equilibrium partition of sulfur between slag and metal ($C^{*}_{S^{2-}} / C^{*}_{S}$) would be 500 . The activity of oxygen in steel would increase during the reaction process. If at time t, the activity of oxygen became $1.5 \cdot 10^{-5}$, the equilibrium partition of sulfur would be 333, i.e., E^{o}_{i} is varing with the composition changing of the system in reaction process. Only when the contents of other components have no change, or its changes can be neglected, $C^{*}_{R_i} / C^{*}_{O_i}$ could be considered to be a constant. It is obviously to simultaneously consider the content change of every component in slag–metal reaction system is very difficult in order to describe the kinetics of the reaction in a complex slag–metal system.

To calculate potential E of the system with multi–reaction is very difficult. But with the developing of equilibrium calculation of multi–phase and multi–component system by means of computer, to quantitatively describe the reaction kinetics in a complex slag–metal system is becaming possible.

The potential E of slag–metal reaction system has every one reaction related with the others. Suppose there are two cathodic reactions $A^{+n_A} + n_A e = A$ and $B^{+n_B} + n_B e = B$, and $E^{o}_{A} > E^{o}_{B}$. When $E > E^{o}_{A}$, then $I = I_A + I_B > 0$, i.e., A and B are reduced. When $E < E^{o}_{B}$, then $I = I_A + I_B < 0$, i.e., A and B are oxidized. When $E^{o}_{B} < E < E^{o}_{A}$, then A is oxidized and B is reduced. When $E = 0$, the reaction system is in equilibrium.

3. Potential of slag–metal reaction system

For the system just with single cathodic reaction or anodic reaction, the potential can be calculated by using equation (7)

$$E = E^{o}_{i} - \frac{RT}{n_i F} ln \frac{a_{R_i}}{a_{O_i}} \tag{7}$$

where a_{R_i} is activity of the reduced reactant i , a_{O_i} is activity of the oxidized reactant i .

While the system with more than one reaction, at any time t , the potential can be calculated by using equation (8) [6]

$$E = \frac{-\triangle G}{\sum n_i F} \tag{8}$$

where $\sum n_i$ is the overall mole number of exchanging electrons from time t to the system getting equilibrium. $\triangle G$ is rest Gibbs free energy of the system.

$$\triangle G = G_{system,eq} - (G_{slag,t} + G_{metal,t}) \tag{9}$$

where $G_{slag,t}$ and $G_{metal,t}$ are Gibbs free energy of slag and metal respectively at time t , and $G_{system,eq}$ is

Gibbs free energy of the system in equilibrium. $G_{slag,i}$,$G_{metal,i}$ and $G_{system,eq}$ can be calculated according to the principle of " minimum Gibbs free energy of a closed equilibrium system at the conditions of constant pressure and temperature ". The calculation should be complex. Here, we just introduce the principle of calculation method as following [7]

$$\text{Minimize} \qquad G = \sum_{j=1}^{c} x_j U_j \tag{10}$$

$$\text{Subject to} \qquad A \cdot \vec{x} = \vec{b} \tag{11}$$

where $\vec{x}$ is vector of component contents in the system, $\vec{b}$ is vector of atom contents in the system, A is atom matrix, c is number of components in system, x_j is amount of component j (i.e., component j in the system) in the vector $\vec{x}$, U_j is chemical potential energy of component j, G is Gibbs free energy of the system.

4. Mathematical model

To the steady slag–metal reaction system, the electrical current of a electrode reaction is

$$I_i = D_{O_i} n_i F\left(\frac{\partial C_{O_i}(x,t)}{\partial x}\right)_{x=0} = n_i F\left(k_{f,i} C_{O_i}(0,t) - k_{b,i} C_{R_i}(0,t)\right) \tag{12}$$

where t is time, $x = 0$ means the interface of slag–metal, x is distance from the interface, D_{O_i} is the diffusion coefficient of reactant O_i . Besides, the transfer of reactant O_i could be expressed as

$$\frac{\partial C_{O_i}(x,t)}{\partial t} = D_{O_i}\left(\frac{\partial^2 C_{O_i}(x,t)}{\partial x^2}\right) \tag{13}$$

Solving equation (13) and after Laplace variation [5], we could get

$$C_{O_i}(x,t) = C^b_{O_i} + \frac{k_{f,i} C^b_{O_i} - k_{b,i} C^b_{R_i}}{\beta_i \sqrt{D_{O_i}}} \cdot \left\{ \exp\left(\frac{\beta_i x}{\sqrt{D_{O_i}}} + \beta_i^2 t\right) \mathrm{erfc}\left(\frac{x}{2\sqrt{D_{O_i} t}} + \beta_i \sqrt{t}\right) - \mathrm{erfc}\left(\frac{x}{2\sqrt{D_{O_i} t}}\right) \right\} \tag{14}$$

where the parameter β_i is

$$\beta_i = \frac{k_{f,i}}{\sqrt{D_{O_i}}} + \frac{k_{b,i}}{\sqrt{D_{R_i}}} \tag{15}$$

where $C^b_{O_i}$ and $C^b_{R_i}$ are the contents of O_i and R_i respectively in the bulk, D_{O_i} and D_{R_i} are diffusion coefficients of O_i and R_i respectively in slag or metal.

Combine the equation (12) with equation (14), and let $x = 0$, then the equation (12) is rewritten as

$$I_i = n_i F\left(k_{f,i} C^b_{O_i} - k_{b,i} C^b_{R_i}\right) \exp\left(\beta_i^2 t\right) \mathrm{erfc}\left(\beta_i \sqrt{t}\right) \tag{16}$$

For the system including N electrode reactions, the overall electrical current is zero according to the law of mass balance, i.e.,

$$\sum I_i = 0 \tag{17}$$

The interface state is usually un–steady particularly under the condition of stirring. In the case as shown in Fig. 1, contents of the reactants inner slag or metal could be taken as uniform. While on the interface of slag–metal, the content of reduced reactant in a small unit could be described with equation (14). Suppose the average velocity of small metal unit is $\bar{v}_M$ relative to the layer of slag, the time τ_e of a rising metal unit from reaching the interface to leaving from the interface is

$$\tau_e = \frac{L}{\bar{v}_M} \tag{18}$$

where L is length of the metal unit contacting with slag.

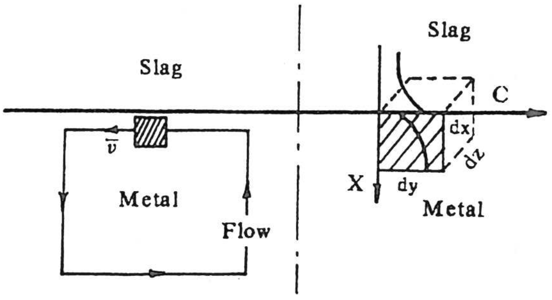


Fig.1 Schematic diagram of a metal unit reaction with slag

During the time τ_e, for the reaction (2), the overall mole amount of electrons through cathodic electrode is

$$Q_i = \int_0^{\tau_e} I_i dt = n_i F\left(k_{j,i} C_{O_i}^b - k_{b,i} C_{R_i}^b\right)\beta_i^{-2}\left\{exp\left(\beta_i^2 \tau_e\right)erfc(\beta_i\sqrt{\tau_e}) + 2\beta_i\sqrt{\frac{\tau_e}{\pi}} - 1\right\} \tag{19}$$

Because τ_e is a little amount, the change of reactant i in the bulk of metal or slag could be neglected in the short time τ_e. During the time t of slag–metal reaction, the overall mole amount of the reacted reactant i is

$$\triangle C_i = \sum_{m=1}^{[t/\tau_e]} \left(k_{j,i}^m C_{O_i}^{b,m} - k_{b,i}^m C_{R_i}^{b,m}\right)\beta_i^{m\ -2}\left\{exp\left(\beta_i^{m\ 2}\tau_e\right)erfc\left(\beta_i^m\sqrt{\tau_e}\right) + 2\beta_i^m\sqrt{\frac{\tau_e}{\pi}} - 1\right\} \tag{20}$$

where superscript m means $No.m$ time τ_e interval, $C_{O_i}^{b,m}$ and $C_{R_i}^{b,m}$ are contents of O_i and R_i in the bulk of metal or slag respectively in $No.m$ time τ_e interval.

Using above equations, we could describe the reaction kinetics of a slag–metal system as shown in Fig. 1. The key work is to determine $k_{j,i}$ and $k_{b,i}$ at any time t. But in some case, the calculation could be simplified as discussed latter in this paper.

5. Application

The experiments of desulfurization of liquid iron by flux were carried out in 100 kg induction furnace. The flux was continuously charged from the top of furnace by N_2 transport. The experimental conditions are showed in table 1.

Table 1. The experimental conditions of desulfurization of liquid iron by flux in induction furnace

Run No.	Metal Weight	Temperature	Rate of Charging Flux	Time of Charging Flux	Induction Power	$[S]_0$	Type of Flux	Frequency of Electromagnetic Field : 1000 Hz
1	80 kg	1570 ± 20℃	0.40kg / min	20 min	~35 KW	0.149%	A	
2	80 kg	1600 ± 20℃	0.86kg / min	8 min	~55 KW	0.494%	B	Radius of Bath : 300 mm
3	80 kg	1600 ± 20℃	0.85kg / min	13 min	~55 KW	0.173%	C	
Composition of Flux	A: 60.8% CaO 13.3% MgO 7.5% SiO_2 1.9% Al_2O_3 15.7% CaF_2 B: 29.0% CaO 6.3% MgO 15.8% SiO_2 16.3% Al_2O_3 14.8% CaF_2 16.7% CaC_2 C: 38.0% CaO 8.3% MgO 18.3% SiO_2 20.2% Al_2O_3 14.1% CaF_2							

For the cathodic reaction

$$[S] + 2e = S^{2-} \tag{2.a}$$

the standard potential is written as

$$E_S^o = \frac{RT}{2F} lnL_S \tag{6.a}$$

where L_S is equilibrium partition of sulfur between slag and metal. Generally, to the secondary refining desulfurization slag–metal reaction system, L_S is large, i.e., $k_{j,S} \gg k_{b,S}$. Because the change of other components can be neglected in every above given system shown in table 1, the L_S can be maintained as a constant during the desulfurization process. In the condition of gas injection stirring, the average velocity $\bar{v}_M$ (m / s) of metal on the slag–metal interface is estimated using following equation [4]

$$\bar{v}_M = 4.54 \cdot 10^{-2} V_g^{1/3} \tag{21}$$

where V_g is gas flow rate (NM^3 / min).

Suppose in the condition of induction stirring, equation (21) could also be used to estimate the velocity $\bar{v}_M$. But in this case, V_g in equation (21) should be a equivalent amount of gas flow rate calculated according to special stirring energy. The special stirring energy were [8,9]

for injection stirring

$$\dot{\varepsilon} = \frac{6.18 V_g T_M}{W_M} \left\{ \left(1 - \frac{T_g}{T_M} \right) + ln \left(1 + \frac{Z_M}{1.48} \right) \right\} \tag{22}$$

for induction stirring

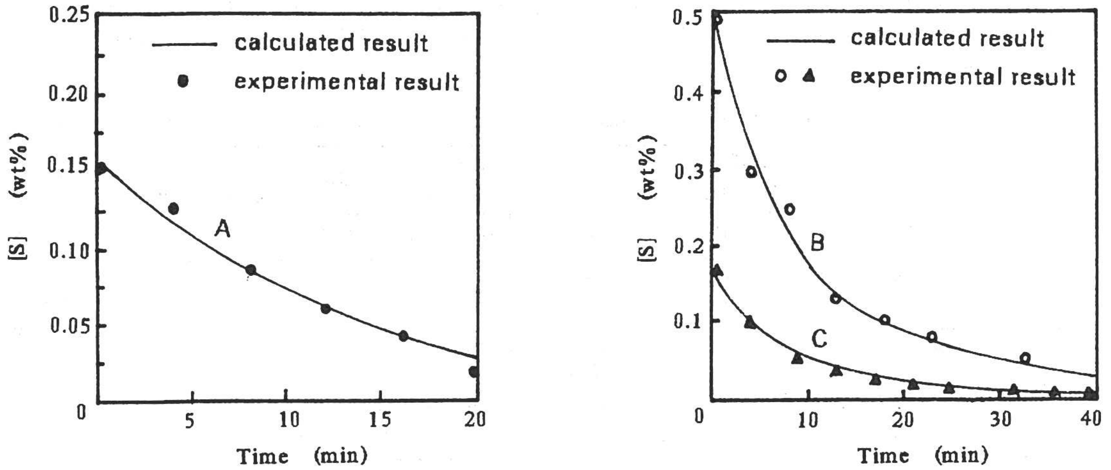
$$\dot{\varepsilon} = \frac{1.2 \times 10^{-3} d_M^2 \rho_M \sqrt[3]{h^2}}{W_M} \tag{23}$$

where $\dot{\varepsilon}$ is special stirring energy (KW / Ton), T_g and T_M are gas temperature before input and metal temperature respectively (K), W_M is weight of metal (ton), Z_M is height of bath (m), d_M is diameter of bath (cm), ρ_M is density of metal (g / cm^3), h is theoretical height of liquid metal rising (cm)

$$h = 316 \sqrt{\frac{\mu}{\varphi j} \frac{P}{S} \frac{1}{\rho_M}} \tag{24}$$

where μ is coefficient of magnetic conductivity of hot metal, φ is coefficient of electric resistance of hot metal, P is electric power supply (KW), S is area of the bath (cm^2), j is frequency of electric induction.

Using above equations (21)~ (24), the average velocity of metal unit on interface of slag–metal could be calculated. In the conditions shown in table 1, the average velocities are around 50 cm / s and 70 cm / s corresponding to 35 KW and 55 KW of power supply respectively. Fig. 2 shows the experimental results and calculated results by using the model. The parameters used for calculation were taken from references [3,10].



(a) Power P = 35 KW (b) Power P = 55KW

Fig.2 Comparison between the experimental results and calculated results.

6. Discussion

In equation (16), if $\beta_i^2 t \gg 5$, then

$$exp\left(\beta_i^2 t\right)erfc(\beta_i\sqrt{t}) \approx \frac{1}{\beta_i\sqrt{\pi t}} \tag{25}$$

Equation (16) could be rewritten as

$$I_i = n_i F C^b_{O_i}\sqrt{\frac{D_{O_i}}{\pi t}}\left(1-\frac{k_{b,i}C^b_{R_i}}{k_{f,i}C^b_{O_i}}\right)\Big/\left(1+\frac{k_{b,i}}{k_{f,i}}\sqrt{\frac{D_{O_i}}{D_{R_i}}}\right) \tag{26}$$

If $k_{f,i} \gg k_{b,i}$, we could get the maximum current

$$I_{i,max} = n_i F\sqrt{\frac{D_{O_i}}{\pi t}}\left(C^b_{O_i} - C^i_{O_i}\right) \tag{27}$$

where $C^i_{O_i}$ is content of O_i on interface.

This equation (27) means mass transfer in the phase containing O_i is the limit step. In the time τ_e of a metal unit contacting with slag, the average electrode current

$$\bar{I}_i = \frac{\int_0^{\tau_e} I_{i,max}\,dt}{\tau_e} = 2n_i F\sqrt{\frac{D_{O_i}}{\pi\tau_e}}\left(C^b_{O_i} - C^i_{O_i}\right) \tag{28}$$

Equation(28)is the formula of the surface renewal theory. Similarly, if $k_{f,i} \ll k_{b,i}$, we could get the kinetic equation when mass transfer in the phase containing R_i is limit step.

7. Concluding Remarks

In the present work, a model has been presented which is a attempt modeling kinetics of slag–metal reaction by combining electrochemical kinetics with mass transport. The work described in this paper will be useful in understanding the effect of one reaction on another reaction in a multi–reaction slag–metal system. The model of surface renewal theory is only a special case of the present model.

This model has been applied to simulate the data from small scale experiments of desulfurization of molten iron by CaO–based flux in induction furnace, and it shows good agreement with experiments. The model would be hopeful to describe kinetics of slag–metal reaction system with more than one reaction. So further refined work is yet needed.

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