Electrochemistry of oxygen ion transport in slag①

LU Xiong-gang(鲁雄刚)[1], DING Wei-zhong(丁伟中)[1], LI Fu-shen(李福燊)[2],
LI Li-fen(李丽芬)[2], CHOU Guo-zhi(周国治)[2]
(1. State Enhance Laboratory of Ferrometallurgy, Shanghai University, Shanghai 200072, China;
2. Laboratory on Solid Electrolytes and Metallurgical Testing Techniques,
University of Science and Technology Beijing, Beijing 100083, China)

[Abstract] A systematic experiment relating to the electrochemistry of oxygen ion transport in slag has been studied in lab. An equivalent circuit has been used to describe ion transfer between metal and slag in this paper and a kinetic model with electrochemical characteristic representing oxygen ion immigration has been worked out. The different experimental phenomena can be explained generally by this model. It can be seen that the theoretical results are in good agreement with experiments. The comparison of experimental data with model calculation proved that the electrochemical model is right.
[Key words] metal-slag reaction; oxygen ion; electrochemical model
[CLC number] TF 704; TF 703. 6　　　　　　　　　[Document code] A

1 INTRODUCTION

The reaction between a metal droplet and slag is a very interesting subject in metallurgical research, since it is directly related to iron and slag reaction existing in many metallurgical processes. The result of this research will be very helpful for understanding and controlling metallurgical processes. Many scientists have studied this problem and found many interesting phenomena[1~ 3]. For example, when an iron droplet containing 4% carbon was reacted with an oxidation slag, the decarburization rate would be very fast at the beginning, however, when the carbon content reached to around 2%, the reaction stopped. It is completely against the thermodynamic calculation, since the system was still far from equilibrium. The interesting thing was that, if a molybdenum foil was placed inside the crucible to support the iron droplet, the decarburization reaction would continue until reaching equilibrium. This phenomenon could not be explained by means of the traditional mechanism. Speelman and co-workers[4] showed that oxygen transfer might be enhanced by improving the electronic conduction in slag. Recently, Pal[5] et al found that as external EMF was applied between slag and metal, the reaction rate was accelerated. We have studied this topic checking the old experiments and designing a series of new experiments[6~ 10], based on which we successfully used an electrochemical kinetic theory in it.

2 THEORETICAL

The oxidation-reduction reaction may be visualized as consisting of reactions at slag/ gas and slag/ metal interfaces and the transport of ionic such as O^{2-}, Fe^{3+}, Fe^{2+}, and electrons e^- through the slag layer as illustrated in Fig. 1.

Equivalent circuit has been used to represent the ions immigration process in some solid electrolyte studies[11]. Analyzing the immigration process existed in gas/ slag and slag/ metal melt as depicted in Fig. 1, the reaction mechanism can be simplified to equivalent circuit as shown in Fig. 2. In which, R_i represents the resistance of constitute i, E_n is the Nernst voltage, E_{ex} is the external applied voltage and R_{ex} is the external resistance.

Applying the Ohm law to the equivalent circuit of Fig. 2, the following equations can be obtained:

$$I_{O^{2-}} + I_{Fe^{2+}} = I_{Fe^{3+}} + I_e + I_{ex} \tag{1}$$

$$E_n + I_{O^{2-}} R_{O^{2-}} - I_{Fe^{2+}} R_{Fe^{2+}} = 0 \tag{2}$$

$$E_n + I_{O^{2-}} R_{O^{2-}} + I_{Fe^{3+}} R_{Fe^{3+}} = 0 \tag{3}$$

$$E_n - I_{O^{2-}} R_{O^{2-}} - I_e R_e = 0 \tag{4}$$

$$E_n + I_{O^{2-}} R_{O^{2-}} - E_{ex} + I_{ex} R_{ex} = 0 \tag{5}$$

where I_i represents electrical current produced by constituent i.

Combining the above five equations and using the relation existed between resistance R and conductance σ, obtaining:

$$I_{O^{2-}} = - E_n \cdot \left| \frac{\sigma_{O^{2-}} \cdot \sum\limits_{i \neq O^{2-}} \sigma_i}{\sum \sigma_i} \right| - E_{ex} \cdot \left| \frac{\sigma_{O^{2-}} \cdot \sigma_{ex}}{\sum \sigma_i} \right| \tag{6}$$

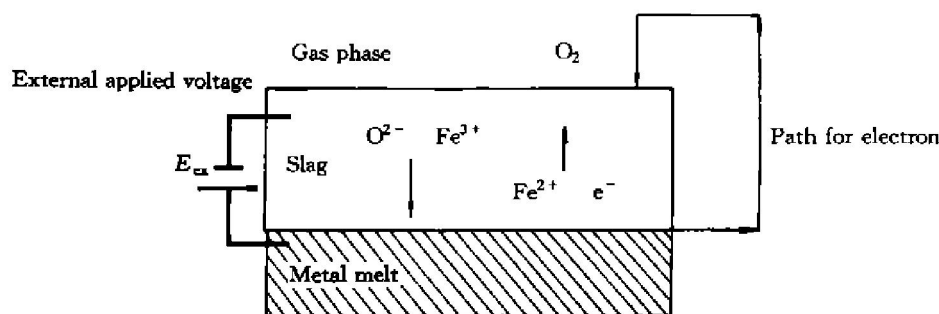where $\sum \sigma_i$ is the total ionic conductance of slag

Fig. 1   Schematic diagram of transport of ionics and electron
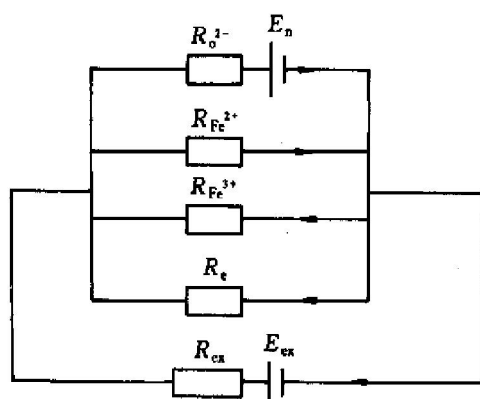

Fig. 2   Equivalent circuit of reaction process

and $\displaystyle\sum_{i\neq 0^{2-}}\sigma_i$ is the total ionic conductance except oxygen ionic conductance in slag.

According to the Nernst equation:

$$E_n = \frac{RT}{2F}\ln\frac{[O]_r}{[O]_i} \tag{7}$$

where $[O]_i$ is the oxygen concentration at interface of slag/ metal melt which is dependent on carbon concentration in metal melts, $[O]_r$ is oxygen concentration at reference state which is dependent on gas atmosphere. Combining Eqns. (6) and (7) and differentiating, the following equation gained:

$$\frac{d[O]_i}{dt} = \frac{d[O]_r}{dt}\cdot \exp(\beta) + [O]_r \cdot \frac{2F}{RT\displaystyle\sum_{i\neq 0^{2-}}\sigma_i}\cdot\frac{\sum\sigma_i}{\sigma_{0^{2-}}}\cdot\exp\frac{dI_{0^{2-}}}{dt} \tag{8}$$

where

$$\beta = \frac{2F}{RT\displaystyle\sum_{i\neq 0^{2-}}\sigma_i}\cdot\left[\frac{I_{0^{2-}}\cdot\sum\sigma_i}{\sigma_{0^{2-}}} + E_{ex}\cdot\sigma_{ex}\right] \tag{9}$$

Oxygen diffusion in the melt can be described using Fick's first law, the following equation holds:

$$J = D\cdot A\cdot\frac{([O]_i - [O]_b)}{\partial x}$$
$$= \alpha\cdot A\cdot([O]_i - [O]_b)$$

$$= -\frac{I_{0^{2-}}\cdot M_0\cdot 10^6}{2FW} \tag{10}$$

where J is the flux of oxygen ions in the slag, D is diffusion coefficient, $\alpha = D/\delta$ is oxygen transfer coefficient at slag/ metal layer, A is interface area of slag/ metal layer, $[O]_b$ is oxygen concentration in slag, M_0 is atomic mass of oxygen, F is Faraday constant, W is mass of slag.

Eqn. (10) can be differentiated to obtain

$$\frac{d[O]_i}{dt} = \frac{d[O]_b}{dt} - \frac{M_0\cdot 10^6}{2\alpha AFW}\cdot\frac{dI_{0^{2-}}}{dt} \tag{11}$$

Because Eqn. (8) is equal to Eqn. (11), then:

$$\frac{dI_{0^{2-}}}{dt} = \frac{-\dfrac{I_{0^{2-}}\cdot M_0\cdot 10^6}{2FW} + \dfrac{d[O]_r}{dt}\cdot\exp(\beta)}{\dfrac{M_0\cdot 10^6}{2\alpha AFW} + [O]_r\cdot\dfrac{2F}{RT\displaystyle\sum_{i\neq 0^{2-}}\sigma_i}\cdot\dfrac{\sum\sigma_i}{\sigma_{0^{2-}}}\cdot\exp(\beta)} \tag{12}$$

Thus, the electrochemical full process kinetic model has been established, all phenomena in experiment can be explained using Eqn. (6) and Eqn. (12).

3   DISCUSSION AND VERIFICATION

Based on Eqn. (12), it can be presumed that reaction can be enhanced when transfer coefficient α of oxygen ion at slag/ metal layer and interface area A were increased. From Eqn. (6), It can be deduced that as the composition of slag is unchanged, which means the conductance of ions and electrons (holes) is constants, current of oxygen ion in slag is dependent on Nernst voltage or external applied voltage. Because the Nernst voltage is controlled by oxygen pressure differential between gas phase and slag/ metal interface, so, the current of oxygen ion will increase and the reaction can be processed with the increase of oxygen partial pressure in atmosphere. The positive and negative polarity of external applied voltage can either enhance or hinder the reaction. Under the condition of no external applied voltage, the Eqn. (6)

can be simplified to

$$I_{O^{2-}} = - E_n \cdot \left| \frac{\sigma_{O^{2-}} \cdot \sum\limits_{i \neq O^{2-}} \sigma_i}{\sum \sigma_i} \right| \quad (13)$$

at the initial period of metal-slag reaction, different ions concentration is very big and electrical conductivity due to oxygen ion O^{2-} is small, so $\sigma_{O^{2-}} \ll \sigma_i$, then current of oxygen ion $I_{O^{2-}}$ will be controlled by conductance of oxygen ion:

$$I_{O^{2-}} = - E_n \cdot \sigma_{O^{2-}} \quad (14)$$

as time going on, the concentration of ferric ion decreased, the reaction will appeared as complex controlling reaction mechanism, the current of oxygen ion is controlled by the mechanism determined by Eqn. (13). At the later period of reaction, the react ion such as Fe^{2+} and Fe^{3+} is decreased to very small, so the condition that $\sigma_{O^{2-}} \gg \sigma_i$ appeared, the Eqn. (13) changes to

$$I_{O^{2-}} = - E_n \cdot \sum\limits_{i \neq O^{2-}} \sigma_i \quad (15)$$

under this condition, oxygen ionic current is controlled by conductance of electron and/ or hole. This theory is supported by the fact[3] that when the slag and the droplet (or metal melt) were brought in contact with an inert metallic conductor (Mo foil or Pt lead) which is much less electronically resistive than the slag, the decarburization reaction proceeded to thermodynamic equilibrium.

The past studies[12] had shown that electrical conductivity and electronic conductivity is in the range of 2~ 0.4 S·cm^{-1} and 10^{-4}~ 10^{-2} S·cm^{-1} respectively. The conductance due to oxygen ion is small which can be estimated by Nernst-Einstein equation and the parameters using for model calculation with Eqn. (12) are listed in Table 1.

Table 1   Experimental conditions and parameters using for calculation ($T = 1\,773$ K)

Exp. No.	Mass of metal/ g	Mass of slag/ g	Area/ cm^2
1	100	80	21.9
2	100	80	22.1
3	100	80	20.8
4	100	80	21.9

Transfer coefficient / (cm·s^{-1})	Oxygen concentration[13] / 10^{-6}	Oxygen ionic conductance[14] / (S·cm^{-1})
1×10^{-4}	1 000	0.020
1×10^{-5}	800	0.017
1×10^{-3}	1 200	0.024
1×10^{-4}	1 000	0.020

Experimental results and calculation values under different experimental conditions are shown in Fig. 3 and Fig. 4. It can be seen that the theoretical results are in good agreement with experiments. This also proved that the mechanism of reaction is very right.
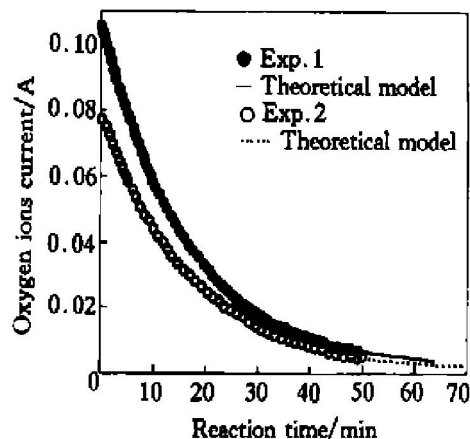

Fig. 3   Comparison between experimens and theoretical model under different oxygen partial pressure
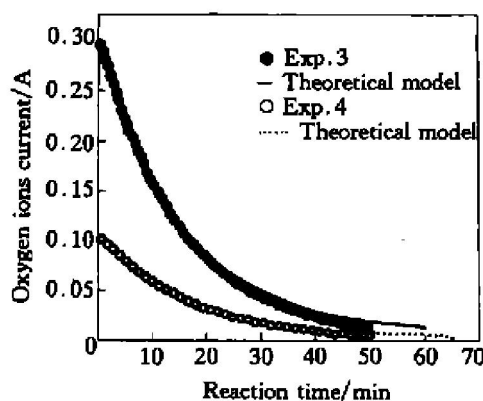(Exp. 1 without Ar, Exp. 2 with Ar flow rate of 80 mL/ min)

Fig. 4   Comparison between experimens and theoretical model with and without electronic conductor
(Exp. 3 with electronic conductor, Exp. 4 without electronic conductor)

4 CONCLUSIONS

An electrochemical model for oxygen ion current transport in slag has been carried out in this paper. Oxygen ion current through slag which represent the rate of decarburization reaction can been drawn as:

$$\frac{dI_{O^{2-}}}{dt} = \frac{- \dfrac{I_{O^{2-}} \cdot M_O \cdot 10^6}{2FW} + \dfrac{d[O]_r}{dt} \cdot \exp(\beta)}{\dfrac{M_O \cdot 10^6}{2\alpha A FW} + [O]_r \cdot \dfrac{2F}{RT \sum\limits_{i \neq O^{2-}} \sigma_i} \cdot \dfrac{\sum \sigma_i}{\sigma_{O^{2-}}} \cdot \exp(\beta)}$$

where

$$\beta = \frac{2F}{RT \displaystyle\sum_{i \neq 0^{2-}} \sigma_i} \cdot \left[\frac{I_{0^{2-}} \cdot \displaystyle\sum \sigma_i}{\sigma_{0^{2-}}} + E_{ex} \cdot \sigma_{ex} \right]$$

this model can explain different experimental results fully. The model has been proved accurately through experimental results and phenomena.

[REFERENCES]

[1]　Gare T, Hazeldean G S. Basic oxygen steelmaking: decarburization of binary Fe-C droplets and ternary Fe-C-X droplet in ferruginous slags [J] . Ironmaking and Steelmaking, 1981, 8(4): 169– 181.

[2]　Krishna Murthy G G, Sawada Y, Elliott J F. Reduction of FeO dissolved in CaO-SiO$_2$-Al$_2$O$_3$ slags by Fe-C droplets [J] . Ironmaking and Steelmaking, 1993, 20 (3): 179– 190.

[3]　Krishna Murthy G G, Hasham A, Pal U B. Reduction rates of FeO in CaO-SiO$_2$-Al$_2$O$_3$-X slags by Fe-C droplets [J] . Ironmaking and Steelmaking, 1993, 20(3): 191– 200.

[4]　Speelman J L, Caley W F, Leewis K G. Electrochemical transport through a lime-silica-alumina slag [J] . Metall Trans, 1989, 20B(1): 31– 37.

[5]　Woolley D E, Pal U B. Experimental evidence for electrochemical natural of the reaction between iron oxide in calcia-silica-alumina slag and carbon in liquid iron [J] . Metall Trans, 1999, 30(5): 877– 889.

[6]　LU Xiong-gang, LI Fu-shen, LI Li-fen, et al. Influence of conductivity of slag on decarburization reaction [J] . Journal of University of Science and Technology Beijing, 1998, 5(1): 20– 22.

[7]　LU Xiong-gang, LI Fu-shen, LI Li-fen, et al. Electrochemical characteristic of decarburization reaction [J] . Journal of University of Science and Technology Beijing, 1999, 6(1): 27– 30.

[8]　LU Xiong-gang, LI Fu-shen, LI Li-fen, et al. Effect of applied voltage and electrode on reaction between melt and slags [J] . Engineering Chemistry & Metallurgy, (in Chinese), 1999, 20(4): 402– 404.

[9]　LU Xiong-gang, LI Fu-shen, LI Li-fen, et al. Decarburization reaction of Fe-C droplets with slag [J] . Journal of Iron and Steel Research, (in Chinese), 1999, 11(3): 5– 8.

[10]　LU Xiong-gang, LI Fu-shen, LI Li-fen, et al. Electronic conductivity of CaO-SiO$_2$-Al$_2$O$_3$-FeO$_x$ slag system [J] . Journal of Iron and Steel Research International, 2000, 7(1): 9– 13.

[11]　Hasham Z, Pal U, Chou Kou-chih. Deoxidation of molten steel using a short-circuited solid oxide electrochemical cell [J] . J Electrochem Soc, 1995, 142(2): 469– 475.

[12]　LU Xiong-gang, DING Wei-zhong, LI Fu-shen, et al. To study electronic conductivity of slags with Wagner polarization technique [J] . Acta Metallurgical Sinica, (in Chinese), 2001, 37(2): 184– 188.

[13]　Sasabe M, Goto K S. Permeability, diffusivity, and solubility of oxygen gas in liquid slag [J] . Metall Trans, 1974, 5B(5): 2225– 2233.

[14]　Goto K S, Sasabe M, Kawakami M. Relation between tracer diffusivity and electrical conductivity on multi-component oxide slags at 900 ℃ to 1 600 ℃ [J] . Trans Iron Steel Inst Jpn, 1977, 17(1): 212– 214.

(Edited by ZHU Zhoong-guo)