Interaction Parameter between Oxygen and Iron in Molten Copper and Distribution Ratio of Iron between $\text{NaO}_{0.5}\text{-CO}_2\text{-FeO}_{1.5}$ Slag and Molten Copper[†]

H. Fukuyama, E. Wada^{††}, T. Fujisawa and Ch. Yamauchi

Department of Materials Science and Engineering, School of Engineering,
Nagoya University, Nagoya 464-01, Japan

For the application of Na_2CO_3 slag to the elimination of iron from molten copper, the thermodynamic properties of the Cu-O-Fe system and the distribution behavior of iron between the $\text{NaO}_{0.5}\text{-CO}_2\text{-FeO}_{1.5}$ slag and molten copper have been investigated at 1523 K. The first order interaction parameter in molten copper was determined as,

$$\epsilon_{\text{Fe}}^{\text{O}} = -141 \text{ (1523 K)}$$

by the equilibrium distribution experiments between the NaFeO_2 -saturated slag and molten copper. By a combination of the value obtained above with the activity of $\text{FeO}_{1.5}$ determined as a function of the slag composition reported in the previous paper, the distribution ratios of iron between the slag and molten copper can be estimated over the composition range of $0.5 < N < 1$ ($N = n_{\text{Na}} / (n_{\text{Na}} + n_{\text{Fe}})$, n : the number of moles) under the partial pressure of CO_2 of 0.01 ~ 0.08 MPa.

The lower CO_2 partial pressure and the higher oxygen partial pressure are more preferable for the removal of iron from molten copper. However, due to the strong affinity between oxygen and iron in molten copper, the iron distribution ratio has a maximum value when oxygen partial pressure is 0.5 Pa. The ratio decreases with decreasing $\text{FeO}_{1.5}$ content in the NaFeO_2 -saturated slag. From the dependence of the ratio on the oxygen partial pressure in the homogeneous liquid slag, it was considered that iron exists as a trivalent form in the slag.

(Received September 27, 1994)

Keywords: thermodynamics, interaction parameter, copper-oxygen-iron system, sodium carbonate slag, $\text{NaO}_{0.5}\text{-CO}_2\text{-FeO}_{1.5}$ slag, iron, copper, distribution ratio

I. Introduction

In view of the application of sodium carbonate slag not only to the fire refining of crude copper but also to the production of high purity copper, the present authors have been conducting a series of fundamental studies to estimate the distribution ratios of various impurity elements between sodium carbonate-based slag and molten copper⁽¹⁾⁻⁽⁸⁾. In the present study, iron was picked up as an impurity element. There have been no reports on the distribution behavior of iron between the sodium carbonate-based slag and molten copper. The final purpose of this study is to determine the equilibrium distribution ratio of iron between the $\text{NaO}_{0.5}\text{-CO}_2\text{-FeO}_{1.5}$ slag and molten copper $\{ = (\text{mass \% of Fe in the slag}) / [\text{mass \% of Fe in Cu}] \}$ as a function of the slag composition and partial pressures of CO_2 and oxygen. In order to achieve it, the thermodynamic properties of the slag and the Cu-O-Fe system are required.

In the previous publications⁽⁷⁾⁽⁸⁾, the phase relationship and the activities in the $\text{NaO}_{0.5}\text{-CO}_2\text{-FeO}_{1.5}$ slag were determined for the slag composition of $0.5 < N < 1$ ($N =$

$n_{\text{Na}} / (n_{\text{Na}} + n_{\text{Fe}})$, n : the number of moles} at 1523 K. It should be noted that there exists a wide (solid $\text{NaFeO}_2 + \text{Na}_2\text{CO}_3$ -rich liquid) coexisting region in the slag.

Among the thermodynamic properties of the Cu-O-Fe system, the interaction parameter between iron and oxygen in molten copper has shown the big discrepancy among the investigators⁽⁹⁾⁻⁽¹⁶⁾ (see Fig. 2). This interaction parameter was determined in this paper^{†††}. Then, the distribution ratio of iron was determined based on the thermodynamics of both the slag and metal.

II. Interaction Parameter between Iron and Oxygen in Molten Copper

The activity of $\text{FeO}_{1.5}$ in the (solid $\text{NaFeO}_2 + \text{Na}_2\text{CO}_3$ -rich liquid) coexisting region was previously determined from the Gibbs standard free energy change of

and the $\text{NaO}_{0.5}$ activity measured by EMF method⁽⁷⁾⁽⁸⁾. Using this (solid + liquid) coexisting slag, the interaction parameter between iron and oxygen in molten copper was determined by conducting the slag/metal equilibrium experiments.

[†] This paper was originally published in Japanese in J. Japan Inst. Metals, **58** (1994), 176.

^{††} Graduate Student, Nagoya University. Present address: NKK Corporation, Fukuyama 721, Japan.

^{†††} The interaction parameter determined in the present paper was used to determine the activity of $\text{FeO}_{1.5}$ in the homogeneous liquid slag by the slag/metal equilibrium method in previous papers⁽⁷⁾⁽⁸⁾.

1. Experimental principle

When iron exists as tri-valent oxide in the slag, the distribution reaction of iron between the slag and molten copper can be represented as,

The Gibbs standard free energy change of this reaction is given as eq. (3) from the thermodynamic data in Table 1.

$$\Delta G^\circ / \text{J} = -747000 + 339.0T \quad (3)$$

The equilibrium constant of reaction (2), $K_{(2)}$, can be given by

$$\log K_{(2)} = \log a_{\text{FeO}_{1.5}} - (\log [\% \text{Fe}] + e_{\text{Fe}}^{\text{Fe}} [\% \text{Fe}] + e_{\text{Fe}}^{\text{O}} [\% \text{O}]) - (3/2)(\log [\% \text{O}] + e_{\text{O}}^{\text{O}} [\% \text{O}] + e_{\text{O}}^{\text{Fe}} [\% \text{Fe}]) \quad (4)$$

where $a_{\text{FeO}_{1.5}}$ is the activity of FeO_{1.5} and e_i^j the first order interaction parameter on mass% scale. Using the self-interaction parameters listed in Table 1 and the reciprocal relationship between e_{Fe}^{O} and e_{O}^{Fe} ,

$$e_{\text{O}}^{\text{Fe}} = e_{\text{Fe}}^{\text{O}} \cdot \frac{M_{\text{O}}}{M_{\text{Fe}}} + \frac{(M_{\text{Fe}} - M_{\text{O}})}{230M_{\text{Fe}}} \quad (5)$$

where M_i denotes the atomic weight of an element i , the following relation is derived at 1523 K:

$$\log [\% \text{Fe}] + (3/2) \log [\% \text{O}] - 0.0948 [\% \text{Fe}] - 0.1955 [\% \text{O}] = e_{\text{Fe}}^{\text{O}} (-[\% \text{O}] - 0.429 [\% \text{Fe}]) + \log a_{\text{FeO}_{1.5}} - \log K_{(2)} \quad (6)$$

In the (solid + liquid) coexisting region, $(\log a_{\text{FeO}_{1.5}} - \log K_{(2)})$ has a constant value for fixed temperature and CO₂ partial pressure. When the left side of eq. (6) is plotted against $(-[\% \text{O}] - 0.429 [\% \text{Fe}])$, a linear relationship with a slope of e_{Fe}^{O} and an intercept of $(\log a_{\text{FeO}_{1.5}} - \log K_{(2)})$ is expected.

2. Experimental procedure

The experimental apparatus and procedure were essentially same as that described in the previous paper⁽¹⁾. To

assure the equilibrium, iron was distributed from metal to the slag or vice versa as follows.

(1) An alumina crucible charged with copper (>99.99 mass%) and Cu₂O was placed in a furnace and heated to 1523 K under an argon atmosphere. After the addition of metallic iron (99.9 mass%) as much as enough to saturate Na₂CO₃ slag with NaFeO₂(s), premelted Na₂CO₃ slag was put into the melt.

(2) The saturated slag with NaFeO₂(s) was placed in an alumina crucible with copper and Cu₂O and heated to 1523 K.

For both runs, a CO₂-CO-Ar gas mixture was blown into the melt through an alumina tube to control the partial pressures of CO₂ and oxygen. The experiments were conducted under $P_{\text{CO}_2} = 0.08$ MPa and $P_{\text{O}_2} = 0.00025 \sim 0.5$ Pa at 1523 K. After the experiments, black precipitate was observed on the surface of the gas blowing tube and the crucible, which was identified as NaFeO₂ by the X-ray diffraction analysis. It was, therefore, confirmed that the slag was saturated with NaFeO₂. After the equilibration, the oxygen content in the copper specimen was analyzed by the inert gas fusion-infrared absorptiometry (Horiba EMGA-650) and the iron content was analyzed by AAS and ICP spectrometry. To correct the effect of coexisting Cu in the sample solution on the analysis of iron, the 6N-Cu (Rare Metallic Co., LTD, 99.9999 mass%, Fe < 0.2 mass ppm) was added to the iron standard solution.

3. Experimental results and discussion

The left side of eq. (6) and $\{-[\% \text{O}] - 0.429 [\% \text{Fe}]\}$ term were calculated and are plotted in Fig. 1, using the contents of oxygen and iron obtained in the equilibrium experiments. The black filled point corresponds to the value of $(\log a_{\text{FeO}_{1.5}} - \log K_{(2)})$, where $\log a_{\text{FeO}_{1.5}} = -0.786$ for $P_{\text{CO}_2} = 0.08$ MPa at 1523 K determined in the previous papers⁽⁷⁾⁽⁸⁾. A least square regression analysis fixing the value of the black point was used to determine the value of e_{Fe}^{O} as,

$$e_{\text{Fe}}^{\text{O}} = -2.46(0 \leq [\% \text{O}] + 0.429 [\% \text{Fe}] < 0.2, 1523 \text{ K}) \quad (7)$$

Table 1 Thermodynamic data used in the present work.

Standard free energy change for the formation of FeO _{1.5} (s)		Ref.
Fe(s) + (3/4)O ₂ (g) = FeO _{1.5} (s)	$\Delta G^\circ / \text{J} = -403550 + 123.3T$ (1000–1700 K)	(17)
Standard free energy changes for the dissolution reaction into molten copper		
(1/2)O ₂ (g) = O(mass%, Henry)	$\Delta G^\circ / \text{J} = -76580 + 12.01T$	(18)(19)
Fe(s) = Fe(mass%, Henry)	$\Delta G^\circ / \text{J} = 84830 - 64.22T$	(15)
Raoultian activity coefficients at infinite dilution		
$\log \gamma_{\text{O}}^\circ = 2.028 - (3999/T)^*$ (1373–1673 K)		(18)(19)
$\log \gamma_{\text{Fe}(s)}^\circ = -1.41 + (4430/T)$ (1373–1473 K)		(15)
Self-interaction parameters on mass% in molten copper		
$e_{\text{Fe}}^{\text{Fe}} = 0.3314 - (656.1/T)$		(14)
$e_{\text{O}}^{\text{O}} = 14.159 - (31929/T)$		(18)(19)

* The activity coefficient of oxygen dissolved in molten copper is defined by, $(P_{\text{O}_2}/P^\circ)^{1/2} = \gamma_{\text{O}} \cdot X_{\text{O}}$, where P_{O_2} is an oxygen partial pressure in Pa unit, $P^\circ = 101325$ Pa and X_{O} the molar fraction of oxygen in molten copper.

and from the reciprocal relationship of eq. (5)

$$e_{\text{O}}^{\text{Fe}} = -0.701 \quad (1523 \text{ K}) \quad (8)$$

is obtained. The interaction parameter on molar fraction, $\varepsilon_{\text{Fe}}^{\text{O}}$, was also calculated to be

Fig. 1 Determination of the interaction parameter $\varepsilon_{\text{Fe}}^{\text{O}}$ in molten copper at 1523 K.

Fig. 2 Comparison among the interaction parameters $\varepsilon_{\text{Fe}}^{\text{O}}$ in molten copper reported by various authors.

$$\varepsilon_{\text{Fe}}^{\text{O}} = 230 e_{\text{Fe}}^{\text{O}} \cdot \frac{M_{\text{O}}}{M_{\text{Cu}}} + \frac{M_{\text{Cu}} - M_{\text{O}}}{M_{\text{Cu}}} = -141 \quad (9)$$

The obtained value of $\varepsilon_{\text{Fe}}^{\text{O}}$ is compared with the ones reported by various investigators in Fig. 2. The present result is in good agreement with the data reported by Kuxmann and Meyer-Grünow⁽¹⁴⁾.

The results shown in Fig. 1 include the values for the quite low oxygen partial pressure, $P_{\text{O}_2} = 0.00025 \text{ Pa}$. Even for such a low P_{O_2} , iron is considered to exist as a trivalent form in the slag, based on the dependence of the iron distribution ratio on P_{O_2} as discussed later.

III. Equilibrium Distribution Ratio of Iron

The equilibrium distribution ratio of iron was estimated for both the wide (solid + liquid) coexisting region and the limited homogeneous liquid region of the slag, based on the obtained interaction parameter and the thermodynamic properties of the slag determined in the previous papers⁽⁷⁾⁽⁸⁾.

1. Iron content in molten copper equilibrated with the (solid + liquid) coexisting slag

Substituting e_{Fe}^{O} and $a_{\text{FeO}_{1.5}}$ into eq. (6), the relation between [%Fe] and [%O] in molten copper equilibrated with the (solid + liquid) coexisting slag was calculated at 1523 K and is shown in Fig. 3, where $\log a_{\text{FeO}_{1.5}} = -0.965$

Fig. 3 Relation between the concentrations of iron and oxygen in molten copper equilibrated with Na_2CO_3 -based slag saturated with $\text{NaFeO}_2(\text{s})$ at 1523 K.

Fig. 4 Relation between the concentration of iron and partial pressure of oxygen in molten copper equilibrated with Na_2CO_3 -based slag saturated with $\text{NaFeO}_2(s)$ at 1523 K.

and -1.181 for $P_{\text{CO}_2}=0.03$ MPa and 0.01 MPa, respectively⁽⁷⁾⁽⁸⁾. The experimentally obtained points are also plotted in Fig. 3.

Equilibrium P_{O_2} can be calculated from the contents of iron and oxygen in molten copper, using the present result, $e_{\text{Fe}}^{\text{Fe}}$, and the thermodynamic data in Table 1. Figure 4 shows the relation between $[\% \text{Fe}]$ and P_{O_2} equilibrated with the (solid+liquid) coexisting slag. At $P_{\text{CO}_2}=0.01$ MPa and $P_{\text{O}_2}=0.5$ Pa, for example, the iron content was calculated as 2.68 mass ppm.

2. Distribution ratio of iron between homogeneous liquid slag and molten copper

(1) Distribution ratio of iron

From the following distribution reaction of iron between the slag and molten copper,

the distribution ratio of iron, L_{Fe} , can be given by

$$L_{\text{Fe}} = \frac{(\% \text{Fe})}{[\% \text{Fe}]} = \frac{K_{(10)} \cdot (n_{\text{T}}) \cdot \gamma_{\text{Fe}}}{[n_{\text{T}}] \cdot \gamma_{\text{FeO}_{1.5}}} \cdot p_{\text{O}_2}^{3/4} \quad (11)$$

where $K_{(10)}$ is the equilibrium constant of eq. (10), $[n_{\text{T}}]$ and (n_{T}) the molar amounts of 100 g copper and slag, respectively, γ_{Fe} and $\gamma_{\text{FeO}_{1.5}}$ the Raoultian activity coefficients of iron in molten copper and $\text{FeO}_{1.5}$ in the

Fig. 5 Estimated distribution ratio of iron between $\text{NaO}_{0.5}\text{-CO}_2\text{-FeO}_{1.5}$ slag in the homogeneous liquid region and molten copper at 1523 K.

slag, respectively. p_{O_2} is the standardized oxygen partial pressure[†].

It was previously reported that $\gamma_{\text{FeO}_{1.5}}$ has a constant value over the homogeneous liquid slag region at constant P_{CO_2} , $[n_{\text{T}}]$ and (n_{T}) are also constant due to the limited region of the homogeneous liquid slag. In addition, the value of γ_{Fe} can be approximated as constant because of the very low concentration of iron in molten copper equilibrated with the homogeneous liquid slag at a constant partial pressure of oxygen. Thus, the distribution ratio for the homogeneous liquid slag can be equated to the ones for the liquidus slag compositions.

The distribution ratios were calculated from the iron contents in molten copper equilibrated with the saturated slag (see Fig. 4) and the iron contents in the slag of the liquidus composition determined in the previous papers⁽⁷⁾⁽⁸⁾. Figure 5 shows the calculated distribution ratios for various partial pressures of CO_2 together with the experimentally obtained ones. The black filled points are the results for the saturated slags and the open white points for the homogeneous liquid slags. The black filled points are not the values evaluated directly from the saturated slag composition analyzed chemically but the ones from the corresponding liquidus composition. It is because the theoretical eq. (11) is valid only for the homogeneous liquid

[†] $p_{\text{O}_2} = (P_{\text{O}_2}/\text{Pa}) / (P^\circ/\text{Pa})$, where P_{O_2}/Pa is a partial pressure of oxygen at the slag/metal interface and $P^\circ/\text{Pa} = 101325$.

Fig. 6 Relation between $\log L'_{Fe}$ and $\log P_{O_2}$ at 1523 K.

slags. In the distribution experiments for the saturated slags, the iron content in the slag determined by the chemical analysis corresponds to the sum of the iron dissolved and the $NaFeO_2$ precipitated in the slag, and the distribution ratios evaluated directly have apparently larger values and can not be compared with the calculated one from eq. (11).

The calculated results agree well with those determined experimentally. The distribution ratio increases as P_{CO_2} decreases. At high P_{O_2} , the relationship between the distribution ratio and P_{O_2} deviates from the straight line. It is because that γ_{Fe} can not be constant against the P_{O_2} at such high P_{O_2} , due to the strong interaction between iron and oxygen in molten copper.

(2) Valence of iron

Based on the distribution reaction of iron between the slag and molten copper:

the following distribution ratio, L'_{Fe} , is introduced using Henrian activity of iron on mass% scale, h_{Fe} , in molten copper, which includes the effect of the interaction between oxygen and iron in molten copper.

$$L'_{Fe} = \frac{(\%Fe)}{h_{Fe}} = \frac{K_{(12)} \cdot M_{Fe} \cdot (n_T)}{\gamma_{FeO_{1.5}}} \cdot P_{O_2}^{3/4} \quad (13)$$

For a given P_{CO_2} and temperature in the homogeneous

Fig. 7 Estimated distribution ratio of iron between $NaO_{0.5}$ - CO_2 - $FeO_{1.5}$ slag and molten copper for $P_{CO_2}=0.08$ MPa at 1523 K.

Fig. 8 Estimated distribution ratio of iron between $NaO_{0.5}$ - CO_2 - $FeO_{1.5}$ slag and molten copper for $P_{CO_2}=0.03$ MPa at 1523 K.

liquid slag region,

$$\frac{K_{(12)} \cdot M_{Fe} \cdot (n_T)}{\gamma_{FeO_{1.5}}} = \text{const.} \quad (14)$$

Therefore, one can discuss the valence of the iron dissolved in the slag from the slope of the linear relationship between $\log L'_{Fe}$ and $\log P_{O_2}$. Figure 6 shows that the experimentally obtained values are in good agreement with the calculated lines with a slope of 3/4 over the whole region of oxygen partial pressure, suggesting that the iron presents as a tri-valent state in the slag.

Fig. 9 Estimated distribution ratio of iron between $\text{NaO}_{0.5}\text{-CO}_2\text{-FeO}_{1.5}$ slag and molten copper for $P_{\text{CO}_2}=0.01$ MPa at 1523 K.

3. Distribution ratio of iron between $\text{NaFeO}_2(s)$ -saturated slag and molten copper

The iron contents in molten copper equilibrated with the saturated slag have been already shown in Fig. 4. It is possible to calculate the value of (%Fe) as a function of the slag composition N based on the results of the solubility measurements of NaFeO_2 determined in the previous papers⁽⁷⁾⁽⁸⁾. Then the equilibrium distribution ratio of iron between the saturated slag and molten copper can be estimated.

Figures 7, 8 and 9 show the estimated results for $P_{\text{CO}_2}=0.08, 0.03$ and 0.01 MPa at 1523 K, together with the experimentally obtained results for the homogeneous liquid slags. With decreasing N and P_{CO_2} , the distribution ratios decrease. As P_{O_2} increases, the distribution ratio increases and has a maximum value at $P_{\text{O}_2}=0.5$ Pa (corresponding to the minimum point shown in Fig. 4).

IV. Concluding Remarks

The thermodynamic properties of the Cu-O-Fe system and the distribution behavior of iron between the $\text{NaO}_{0.5}\text{-CO}_2\text{-FeO}_{1.5}$ slag and molten copper have been investigated at 1523 K and following results were obtained:

The first order interaction parameter between oxygen and iron in molten copper was determined as,

$$\varepsilon_{\text{Fe}}^{\text{O}} = -141 \text{ (1523 K)}$$

by the equilibrium distribution experiments between the NaFeO_2 -saturated slag and molten copper.

By a combination of the value obtained above with the activity of $\text{FeO}_{1.5}$ determined as a function of the slag composition reported in a previous paper, the distribution ratios of iron between the slag and molten copper were estimated over the composition range of $0.5 < N < 1$ ($N = n_{\text{Na}} / (n_{\text{Na}} + n_{\text{Fe}})$, n : the number of moles) under the partial pressure of CO_2 of $0.01 \sim 0.08$ MPa.

The lower CO_2 partial pressure and the higher oxygen partial pressure are more preferable for the removal of iron from molten copper. However, due to the strong affinity between oxygen and iron in molten copper, the ratios have a maximum value when oxygen partial pressure is 0.5 Pa. The ratios decrease with decreasing $\text{FeO}_{1.5}$ content in the NaFeO_2 -saturated slag. From the dependence of the ratio on the oxygen partial pressure in the homogeneous liquid slag, it was considered that iron exists as a tri-valent form in the slag.

Acknowledgments

This work was partly supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 03453061) which is acknowledged.

REFERENCES

- (1) Ch. Yamauchi, T. Fujisawa, Sh. Goto, H. Fukuyama and K. Matsuda: J. Japan Inst. Metals, **53** (1989), 407.
- (2) T. Fujisawa, T. Kuno, H. Fukuyama, Sh. Takai and Ch. Yamauchi: J. Japan Inst. Metals, **53** (1989), 558.
- (3) T. Fujisawa, H. Fukuyama, T. Kato, Y. Ikitsu and Ch. Yamauchi: Mater. Trans., JIM, **33** (1992), 683.
- (4) H. Fukuyama, T. Fujisawa and Ch. Yamauchi: J. Japan Inst. Metals, **57** (1993), 521.
- (5) H. Fukuyama, M. Tonsho, T. Fujisawa and Ch. Yamauchi: Metall. Review of MMIJ, Vol. 10, No. 2 (1994), 72.
- (6) T. Fujisawa, H. Fukuyama, J. Shimotori and Ch. Yamauchi: Mater. Trans., JIM, **35** (1994), 414.
- (7) H. Fukuyama, E. Wada, T. Fujisawa and Ch. Yamauchi: J. Japan Inst. Metals, **57** (1993), 905.
- (8) H. Fukuyama, E. Wada, T. Fujisawa and Ch. Yamauchi: Mater. Trans., JIM, **35**, (1994), 602.
- (9) E. S. Tankins: Can. Metall. Quart., **9** (1970), 353.
- (10) W. A. Fischer and D. Janke: Z. Metallk., **62** (1971), 747.
- (11) B. A. Pichugin, B. V. Linchevskiy and V. M. Chursin: Izv. Akad. Nauk SSSR Met., (1974), 87.
- (12) K. P. Abraham: Trans. Indian Inst. Metall., March, (1969), 5.
- (13) D. Janke and W. A. Fischer: Metall, **29** (1975), 1189.
- (14) U. Kuxmann and H. Meyer-Grünow: Erzmetall, **35** (1982), 363.
- (15) A. D. Kulkarni: Metall. Trans, **4** (1973), 1713.
- (16) T. Oishi, Y. Sawaragi and J. Moriyama: J. Japan Inst. Metals, **40** (1976), 426.
- (17) I. Barin: Thermochemical Data of Pure Substances, Part I, II, VCH Publishers, (1989).
- (18) T. Oishi and K. Ono: Bull. Japan Inst. Metals, **25** (1986), 291.
- (19) S. H. Sadat-Darbandi: Dissertation, T. U. Berlin, (1977).