Copper Solubility in Matte Smelting Slag

Yoichi Takeda

Associate Professor, Department of Materials Science and
Technology, Faculty of Engineering, Iwate University,
Ueda 4-3-5, Morioka 020, Japan.
Tel. 81-196-21-6367, Fax. 81-196-21-6373

ABSTRACT

$FeO-SiO_2$ slag and copper matte kept under a flow of $10\%SO_2-S_2-Ar$ gas mixture at 1573K. The sample was melted in a magnesia crucible with varying of silica content in slag and copper content in matte. Oxygen measurement in matte phase by an oxygen sensor suggests that there is a sulfur transfer barrier on slag surface which prevents molten phase of slag and matte from equilibrating with gas phase. However sulfur potential in the melts is derived from measured oxygen potential and SO_2 partial pressure. An advanced estimation system of copper solubility in matte smelting slag is developed by applying activity coefficient of $CuS_{0.5}$ to the experimental data. The estimated copper solubility is consistent with experimental one. Sulfidic copper dissolution in the slag increases with decreasing silica content in slag and matte grade.

1. INTRODUCTION

Copper loss in matte smelting slag is concern in smelting practice. However it is difficult to estimate copper solubility in matte smelting slag based on experimental data without introducing any optional parameter because of presence of two anions, oxygen and sulfur, and many controlling factors. The concept of sulfidic and oxidic dissolution of copper is useful to analyze copper solubility in matte smelting slag[1, 2, 3]. Equilibrium experiments between iron silicate slag and copper mate under controlled SO_2 partial pressure were carried out in magnesia crucible at 1573K. Because the system has close relationship to practical slag, the experimental data provide us fundamental information on copper dissolution loss in matte smelting slag and moreover for developing estimation system for copper solubility in matte smelting slag.

The experiment is not easy from the reason of matte suspension in slag phase and of sulfur transfer barrier between gas and slag phase. The suspension of matte in slag phase was overcome by careful cleaning the matte phase with a cutting wheel. To investigate the equilibrium gas and molten phases of slag and matte, oxygen potential in the matte phase was measured with an oxygen sensor under controlling SO_2 and S_2 partial pressures. Oxygen and sulfur partial pressures and activity of copper are essential information to estimate copper solubility in matte smelting slag. Yazawa has estimated oxygen and sulfur partial pressures under slag-matte existence from activities of FeO and FeS[4]. Employing the activities of FeO and FeS to estimate the partial pressures is surely reasonable when there is no reliable experimental data. But getting the information on the actual FeO and FeS in such a complex system is more difficult than on the partial pressures.

Another important information to estimate copper solubility are activity coefficients of copper oxide and sulfide in slag. The activity coefficient of copper oxide under magnesia saturation[5] and the relationship between activity coefficient of copper sulfide and sulfur content in slag[6] has been presented. Applying the activity coefficients of copper oxide and sulfide to the experimental results, I estimate copper solubility in the iron silicate slag equilibrated with matte and compare the estimated solubility with the experimental one.

2. EXPERIMENTS

Master slag of $FeO-SiO_2$ system is melted in an iron crucible and quenched by spreading it on surface of stainless steel. Master matte is prepared by mixing Cu_2S and FeS, which are synthesized in ampoule and melted in inert atmosphere. The compositions, on mass per cent base for condensed phase, determined by chemical analysis are 78.5% Cu, 21.2% S and 0.3% O for Cu_2S, and 66.8% Fe, 31.5% S and 1.7% O for FeS. 8g of slag and 8g of matte are melted in a magnesia crucible, which has 18 mm of inner diameter, under controlled SO_2 and S_2 partial pressure at 1573K. The components in the system are 6 of Fe, Cu, S, O, SiO_2 and MgO, and the number of phases existing in the experiments are 4 of gas, slag, matte and crucible material, therefore the number of degrees of freedom is given by 6+2-4=4. There are five variables; temperature, partial pressures of SO_2 and S_2, per cent SiO_2 and matte grade, which are controllable in this experiment. The four variables have to be set up to establish equilibrium condition.

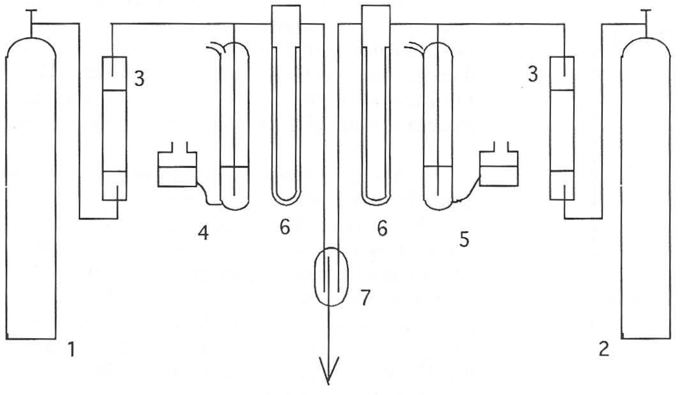
The apparatus is shown in Fig. 1. For addition of SO_2 partial pressure to gas phase a gas mixture of SO_2 and Ar prepared in the part of Fig. 1 (a) flowed through a sulfur saturator (b) which was controlled at a given temperature , then was introduced to the reaction tube as shown Fig. 1 (c). The gas system has been employed to control oxygen and sulfur partial pressures by Stofko[7] and Itagaki[8]. Weight of sulfur in the unite volume of the gas mixture from the sulfur saturator was calibrated as a temperature function of sulfur saturator prior to the experiment. When excess S_2 partial pressure was not added to gas phase, the gas mixture of SO_2 and Ar prepared in the part of (a) was introduced directly to the reaction tube, (c). A total flow rate was 200 ml/min. Oxygen partial pressure, P_{O2}/atm., in gas phase at experimental temperature is regulated by the equilibrium

$$1/2\ S_2(g) + O_2(g) = SO_2(g). \qquad (1)$$

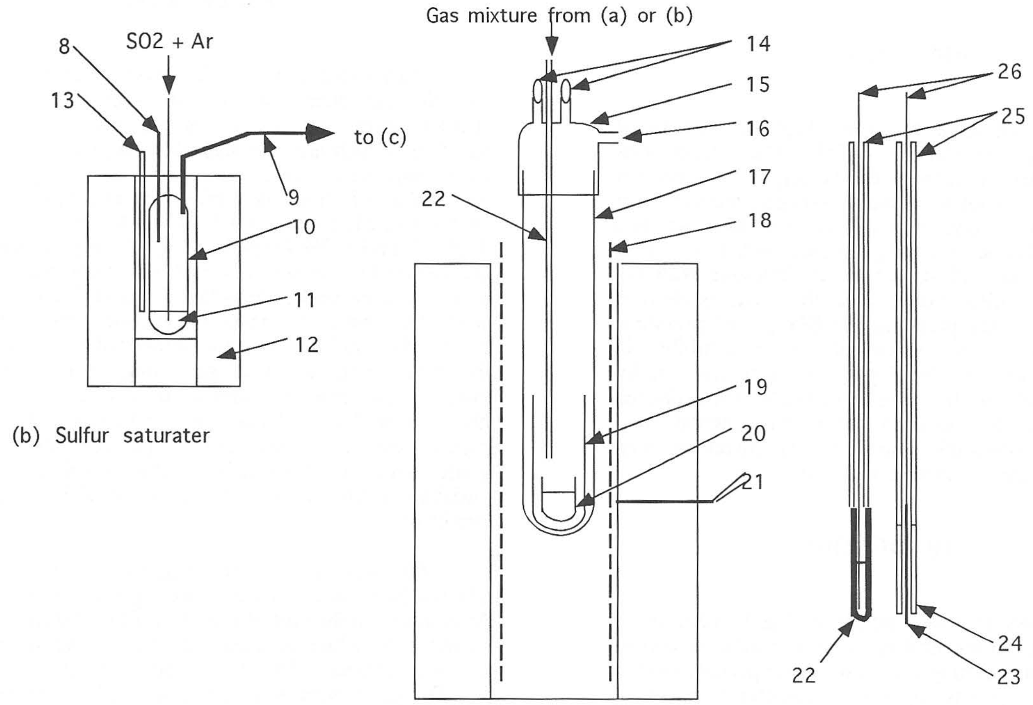
$$\Delta G°/J = -362000 + 73.136T^{9} \qquad (2)$$

The equilibrium constant of the reaction (1) is derived from the standard free energy change of the reaction. The oxygen partial pressure is calculated by

$$\log P_{O2}/\text{atm.} = \log P_{SO2} - 1/2 \log P_{S2} - 18908/T + 3.82, \qquad (3)$$



(a) Arrangement for mixing of SO2 and Ar



(b) Sulfur saturater

(c) Reaction furnace

(d) Assembly of oxygen sensor

Fig. 1. Apparatus. (a) Arrangement for mixing of SO_2 and Ar. 1; SO_2 tank, 2; Ar tank, 3; diphosphorus pentaoxide, 4; bleeder with sulfuric acid, 5; bleeder with silicon oil, 6; capillary flow meter, 7; gas mixer,

(b) Sulfur saturator. 8; charging of sulfur, 9; gas outlet winding electric heater and to reaction tube, 22, 10; quartz tube, 11; molten sulfur, 12; electric furnace, 13; thermometer,

(c) Reaction furnace. 14; opening for oxygen sensor, 15; Pyrex cap, 16; gas outlet, 17; quartz reaction tube, 18; silicone carbide heating element, 19; alumina protection tube, 20; magnesia crucible with sample, 21; thermocouple
to regulator, 22; alumina tube for reaction gas inlet,

(d) Oxygen sensor. 22; zirconia tube with Ni·NiO mixture, 23; Re wire, 24; magnesia protection sheath, 25; mullite supporting tube, 26; Pt lead wire.

where partial pressures of sulfur and sulfur dioxide are regulated by initial gas flow rates and the temperature of the sulfur saturator. When the gas mixture of SO_2 and Ar is introduced to the reaction tube not through sulfur saturator, SO_2 gas is decomposed backward the reaction (2). Two mole of O_2 and one mole of S_2 are produced from one mole of SO_2. Taking account of mole balance, $n_{O2}=2n_{S2}$, that means $P_{O2}=2P_{S2}$, the oxygen partial pressure in this gas mixture is calculated by

$$\log P_{O2}/\mathrm{atm.} = 2/3 \log P_{SO2} -12605/T + 2.647. \qquad (4)$$

The sulfur partial pressure, P_{S2}/atm., is half of the oxygen partial pressure.

For confirmation of being in equilibrium between gas phase and melts oxygen potential in matte phase was measured with an oxygen sensor shown in Fig. 1 (d). The electrochemical cell construction for the sensor is as follows:

$$\mathrm{Pt/Ni\cdot NiO/ZrO_2\cdot MgO/matte/Re/Pt.}$$

Oxygen partial pressure in matte phase is calculated from the standard free energy change of NiO formation[10] by equation (5)

$$\log P_{O2}/\mathrm{atm.}=20171\mathrm{x}E/T-24409/T+8.869 \qquad (5)$$

where E /V is the EMF. of the oxygen sensor.

After measurement of EMF the furnace moved downwards and the crucible containing sample was cooled in the atmosphere. Slag and matte samples were cleaned by a wheel cutter. Careful attention was required to separate suspension matte from slag sample. Oxygen and sulfur in matte was analyzed by hydrogen gas reduction around 1100 to 1300K. Long reduction time, 24 hr for 0.3 g matte, was required, and 0.3 to 1.0 g of matte depending on oxygen content was analyzed. Metal residue after the reduction was decomposed by wet method for separation between copper and iron. Copper was deposited by electrowinning and weighted. Iron in matte and slag was titrated with potassium dichromate standard solution. Silica in matte and slag was analyzed by gravimetric method. Sulfur in slag, as $BaSO_4$, was analyzed also by the same method. Atomic absorption was applied to copper and magnesium analyses in slag.

3. RESULTS

3.1 Equilibrium between gas and slag-matte phases

Silica saturated $FeO\text{-}SiO_2$ slag, Cu_2S and copper metal were melted at 1573K under 10% SO_2-90% Ar, on volume per cent base for gas phase, gas current varying in sulfur partial pressure. Measured oxygen partial pressure in matte is plotted against holding time as shown in Fig. 2. Oxygen partial pressures in gas phase were regulated by reaction (1), and shown by horizontal lines in Fig. 2. Oxygen partial pressure having the initial molten phase are lower than that in every gas mixture. Each of the oxygen partial pressures in matte reaches constant level which depends on gas mixture. Acceptable oxygen partial pressure equilibrated with the three molten phases of the slag-Cu_2S-copper metal and 10% SO_2 is around $10^{-6.35}$ atm. which has been examined by Eguchi[11]. The oxygen partial pressure in matte under the 10% SO_2-Ar gas mixture without excess sulfur by sulfur saturator, shown by a circle in Fig. 2, is close to the acceptable one. Every gas mixture introduced for the experiment shown in Fig. 2 does not permit of equilibrium with the three melts of the slag, Cu_2S and copper metal. It is noted that higher oxygen partial pressures in matte than those in both of gas phase and initial sample, shown by square and triangle marks, are observed in Fig. 2, but does not reach the acceptable level. Silica saturated $FeO\text{-}SiO_2$ slag and matte were melted under 10% SO_2-90% Ar gas and 10% SO_2-0.4% S_2-89.6% Ar gas currents at 1573K. The variations of oxygen partial pressure in matte are plotted against holding time as shown in Fig. 3. Initial matte grade varied on four different levels, which is described by w_i =% Cu/(% Cu+% Fe) in initial matte. 1.00, 0.925, 0.590 and 0 of w_i in Fig. 3 correspond to 80, 73, 44 and 0% Cu in matte, respectively. The w_f in final matte which is determined by chemical analysis is also presented in the figure. Gas mixture having more sulfur, which has lower oxygen partial pressure, through sulfur saturator leads to lower oxygen partial pressure in matte than that without excess sulfur does. Matte composition shifts within small range depending on sulfur and oxygen partial pressure in gas mixture. The difference in oxygen partial pressure in matte between the gas compositions in Fig. 3 tends to be small with decrease in copper content in matte. From Figs. 2 and 3 we can see the difficulty in equilibrating slag and matte melts with the gas flow of S-O-Ar system without agitating the melts. One of the reason for the difficulty will be existence of sulfur transfer barrier on slag surface owing to surface segregation of iron sulfide. A thin solid crust was formed on slag surface with holding time proceeding even though both oxygen partial pressures in melts and gas phase were lower than the oxygen partial pressure of magnetite separation. A main component of the crust will be magnetite. The crust broke easily pushing by a solid electrolyte.

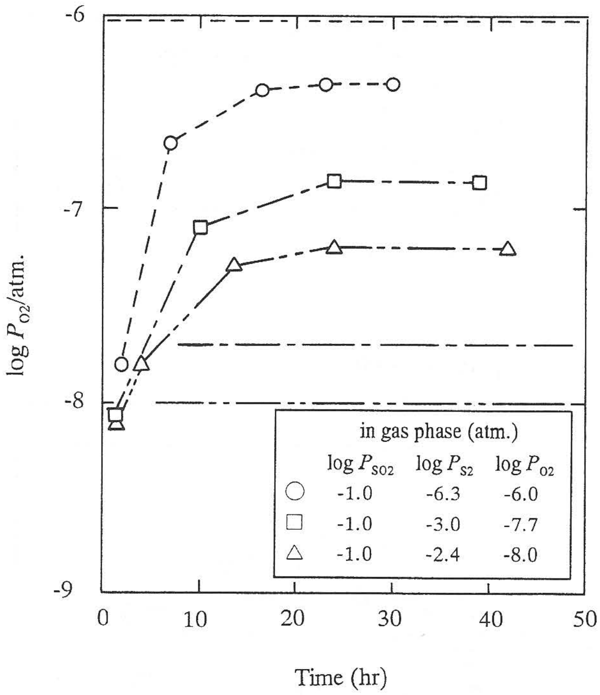


Fig. 2. Oxygen partial pressure vs. time for three molten phases equilibrium of slag, matte and copper metal under a flow of different gas composition at 1573K.

Silica saturated $FeO-SiO_2$ slag and matte were melted at 1573K under flow of three different gas mixture. The holding time at 1573K was over 24 hr to ensure steady state in sample. The measured oxygen partial pressure in matte is plotted against copper content in matte, {% Cu}, as shown in Fig. 4. A larger difference in the oxygen partial pressure in matte than in gas mixture is not observed at given copper content. Sulfur partial pressure in gas mixture affects measured oxygen partial pressure in matte, however the oxygen partial pressure in matte is not always equilibrated with gas mixture. Accepted equilibrium oxygen partial pressure in the slag-matte melts at P_{SO2}=0.1 atm. is shown by a closed mark. It is suggested that gas mixture of which sulfur partial pressure is around one third of equilibrium one flows over the melts to get equilibrium state. Difference in slag and matte composition according to difference of sulfur partial pressure in gas mixture is not so big as detected by chemical analysis.

3.2 Oxygen and sulfur partial pressures in the system

Oxygen and sulfur partial pressures in Silica saturated $FeO-SiO_2$ slag and matte system at P_{SO2}=0.1 atm. is shown in Fig. 5 against logarithmic iron content in matte, {% Fe}. The sulfur partial pressure is calculated from the measured oxygen partial pressure in matte by equation (3). Experimental points is presented in a separate paper in the proceedings. Iron in matte affects the oxygen and sulfur partial pressure more directly than copper in matte does. Decrease in silica content in slag, i.e. increase in iron

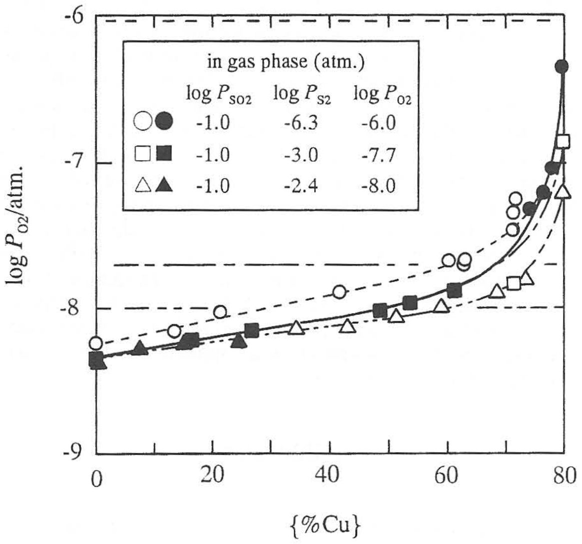


Fig. 4. Measured oxygen partial pressure in matte coexisted silica saturated FeO_x-SiO_2 slag vs. copper content in matte. Closed marks shows the accepted oxygen partial pressure.

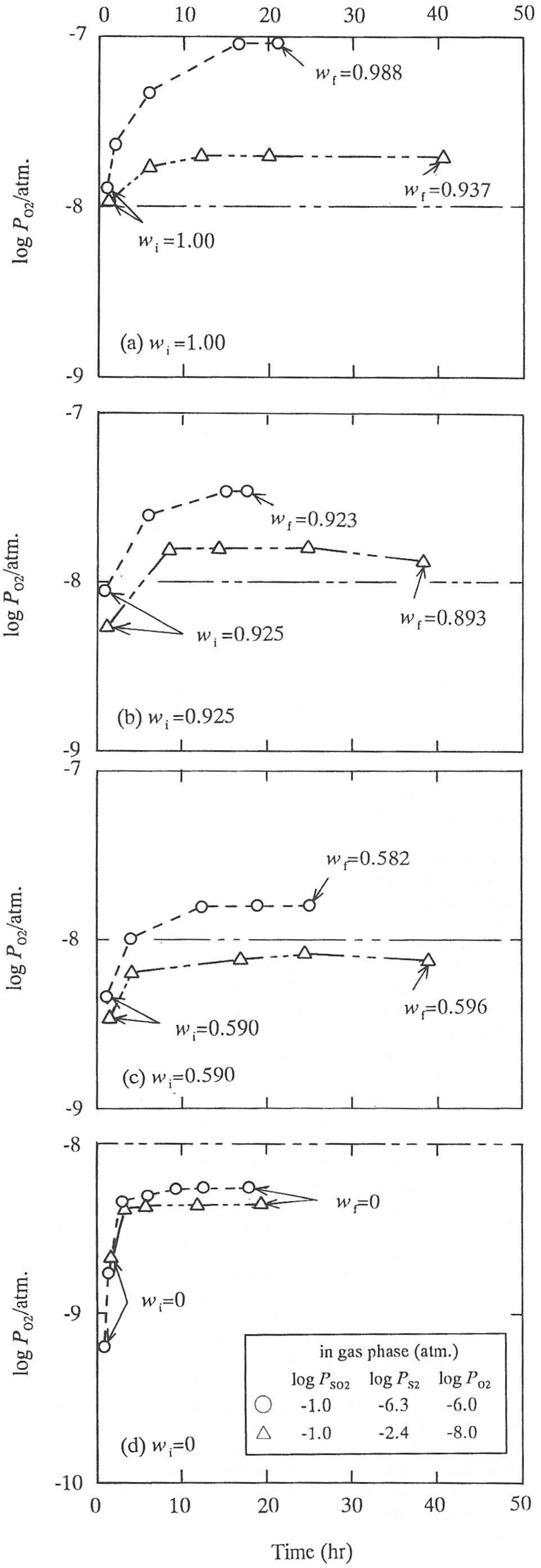


Fig. 3. Oxygen partial pressure vs. time for two molten phases equilibrium of slag, matte at 1573K. Initial matte grade, that is designated by w_i = % Cu/(% Cu + % Fe), varies corresponding to figures (a), (b), (c) and (d).

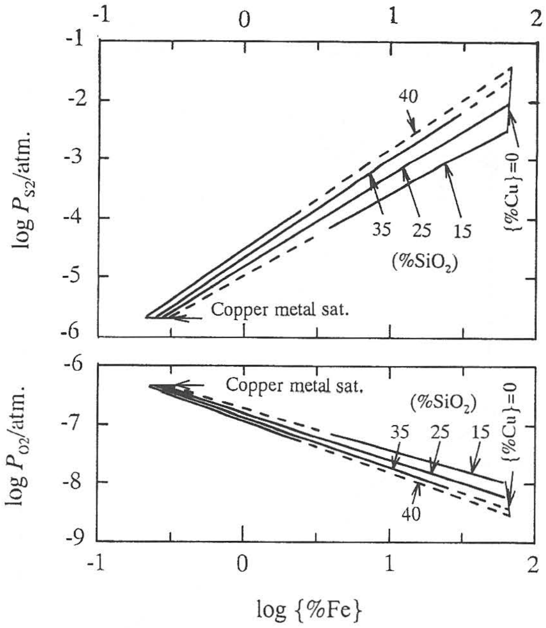


Fig. 5. Oxygen (bottom) and sulfur (top) partial pressures in the system of silica saturated FeO_x-SiO_2 slag, matte and 0.1 atm. SO_2 vs. iron content in matte at 1573K.

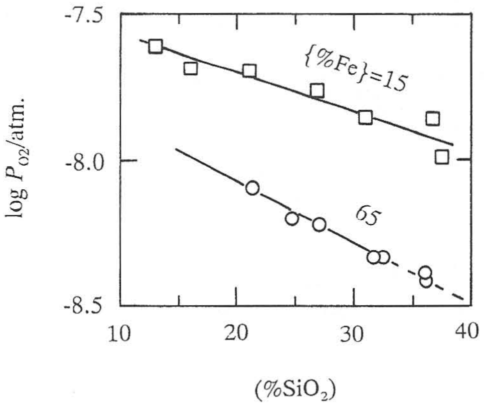


Fig. 6. Oxygen partial pressure in the system of FeO_x-SiO_2 slag, matte and 0.1 atm. SO_2 vs. silica content in slag as a parameter of iron content in matte at 1573K.

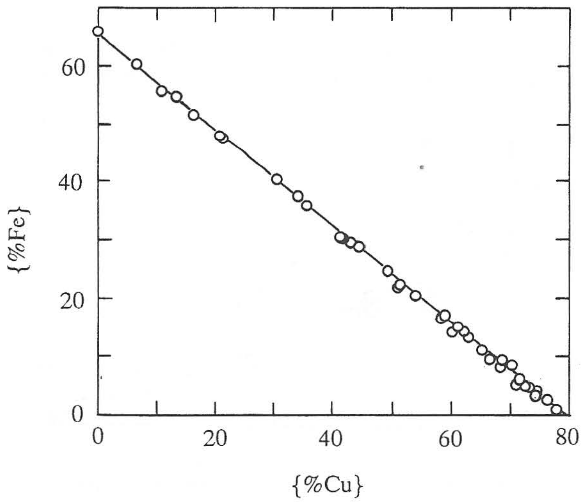


Fig. 7. Relation between iron and copper contents in matte equilibrated with FeO_x-SiO_2 slag and 0.1 atm. SO_2.

content, results in increasing the oxygen partial pressure under keeping constant matte grade as shown in Fig. 6. Copper content in matte, which is called as matte grade, has almost linear relation to iron content in matte. The relation under 10% SO_2 gas mixture at 1573K is shown in Fig. 7 and presented by

$$\{\%\ Cu\} = 79.5 - 1.214\{\%\ Fe\}. \qquad (6)$$

3.3 Slag and matte compositions under silica saturation

Copper content in slag saturated with silica and magnesia, (% Cu), and sulfur content in the slag, (% S), are plotted against copper content in matte as shown in Fig. 8. Both of copper and sulfur contents are smaller than those melted in a silica crucible at 1573K, shown with dotted line in the figures, which have been presented by Watanabe[12] and Yazawa[3]. When the sample is melted in a magnesia crucible, slag dissolves 5 to 9% MgO as shown in the top figure of Fig. 9. Magnesia dissolved from a crucible raises silica solubility, in the middle figure, and consequently iron content in slag is reduced considerably, in the bottom figure. Primary factor to affect sulfur solubility in slag, most of sulfur combines with iron, is silica content in slag. Sulfur content in slag has influence on sulfidic dissolution of copper in slag. Copper solubility in slag melted in a magnesia crucible is lower than that melted in a silica crucible especially in low grade matte range owing to reducing sulfur content in slag. Oxygen and sulfur contents in the matte are plotted against copper content in matte as Fig. 10. Oxygen in matte affects activity of $CuS_{0.5}$ as described later.

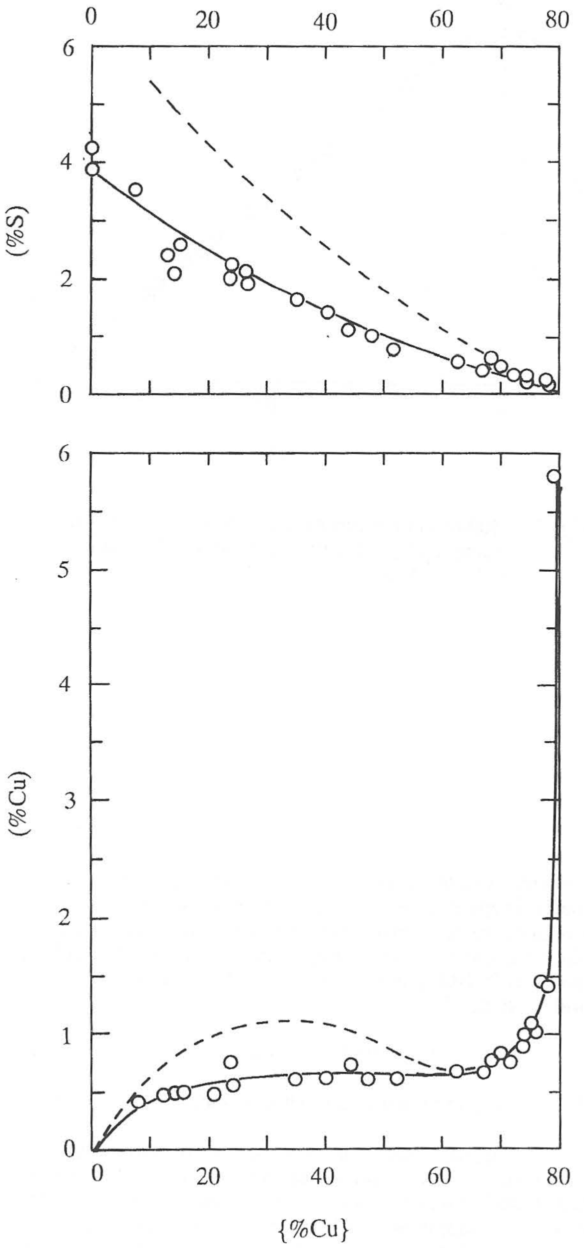


Fig. 8. Copper (bottom) and sulfur (top) contents in silica saturated FeO_x-SiO_2 slag vs. copper content in matte. Slag and matte is melted in a magnesia crucible under 0.1 atm. SO_2 at 1573K. Dotted line shows those silica saturated FeO_x-SiO_2 melted in a silica crucible presented by Yazawa[3].

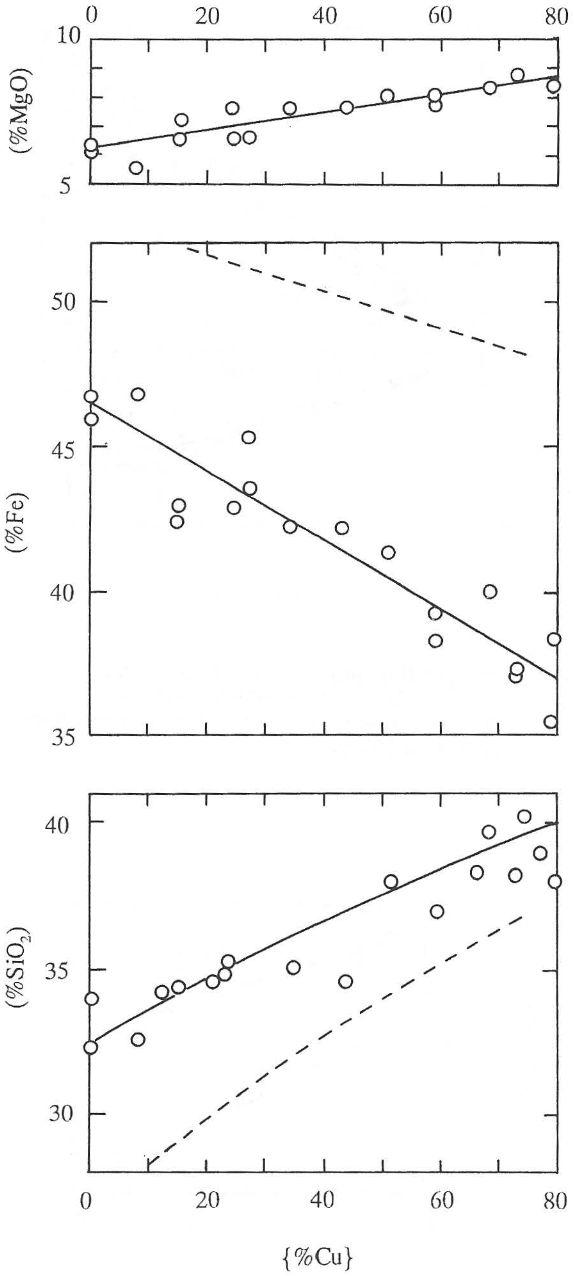


Fig. 9. Silica (bottom), iron (middle) and magnesia (top) contents in slag vs. copper content in matte at 1573K. Dotted line shows those silica saturated FeO_x-SiO_2 melted in a silica crucible presented by Watanabe[12].

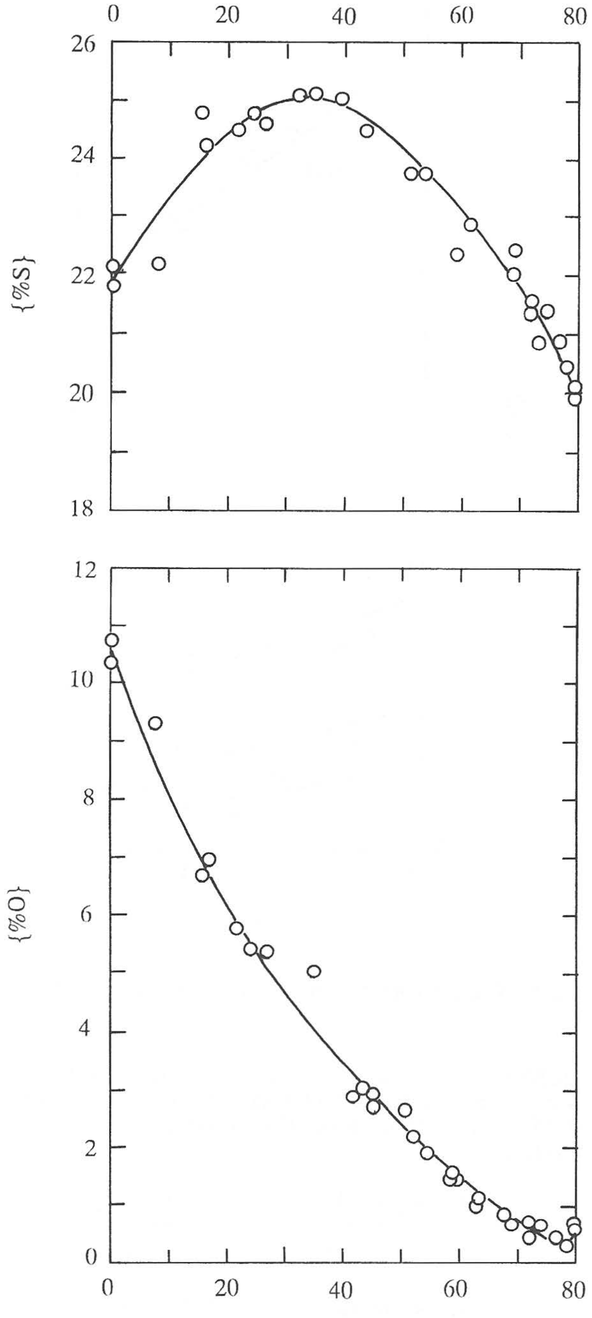


Fig. 10. Oxygen (bottom) and sulfur (top) contents in matte equilibrated with silica saturated FeO_x-SiO_2 slag and 0.1 atm. SO_2 vs. copper content in matte at 1573K.

3.4 Effect of silica content on copper and sulfur solubility in slag

Several reports on copper solubility in slag equilibrated with copper matte have presented. Many of them are for silica saturated slag or commercial slag. In order to investigate effect of silica in slag on copper and sulfur solubility in slag, the FeO-SiO_2 slag with various silica contents and matte melted in a magnesia crucible under 10% SO_2-Ar gas flow at 1573K. Fig. 11 shows the copper and sulfur contents in slag with keeping copper content in matte constant. Both of copper and sulfur contents increase with decreasing silica content in slag. Slag and matte with low copper content does not separate less than 10% SiO_2 in slag. The relation between copper solubility and silica content in Fig. 11 is significant for practical copper smelting. Fig. 12 shows iron and magnesia contents in the slag. Magnesia solubility increases from 2 to 8% with increasing silica content in slag. Oxygen content in the matte is shown in Fig. 13

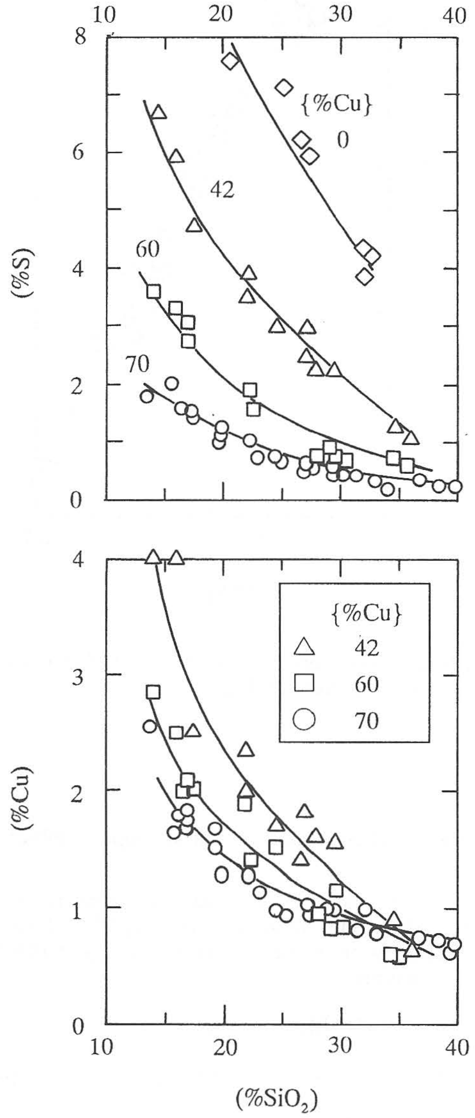


Fig. 11. Influence of silica content in slag on copper (bottom) and sulfur (top) contents in slag equilibrated with matte and 0.1 atm. SO_2 at 1573K.

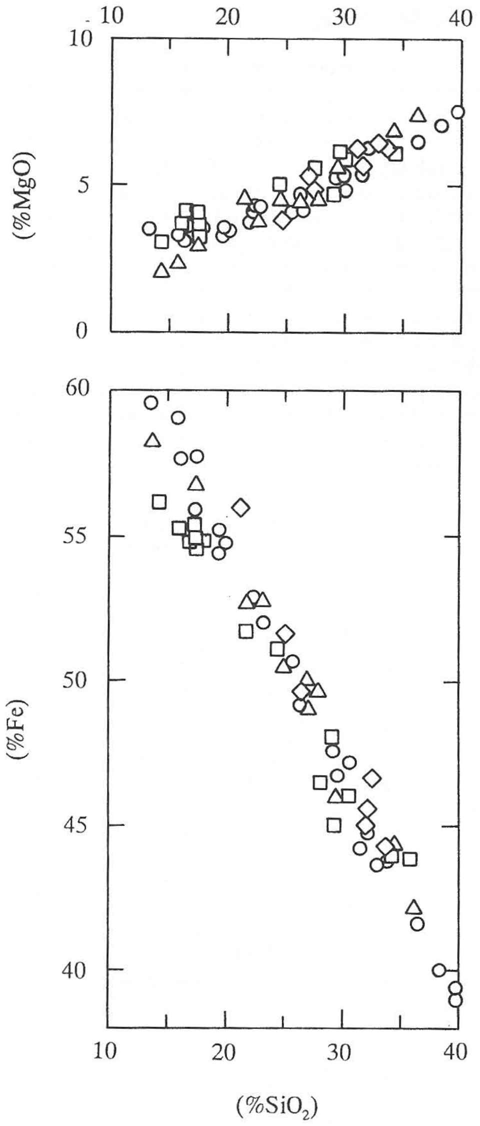


Fig. 12. Iron (bottom) and magnesia (top) contents in slag vs. silica content in slag.

3.5 Developed estimation system of copper solubility

Postulating that the total dissolved copper is the sum of oxidic and sulfidic dissolution of copper[1, 2], I analyze copper solubility in matte smelting slag by employing following reactions

$$Cu(l) + 1/4\ O_2(g) = CuO_{0.5}(l) \qquad (7)$$

$$\Delta G°/J = -60670 + 21.46T\ ^{13}, \qquad (8)$$

$$Cu(l) + 1/4\ S_2(g) = CuS_{0.5}(l) \qquad (9)$$

$$\Delta G°/J = -71648 + 19.70T\ ^{14}. \qquad (10)$$

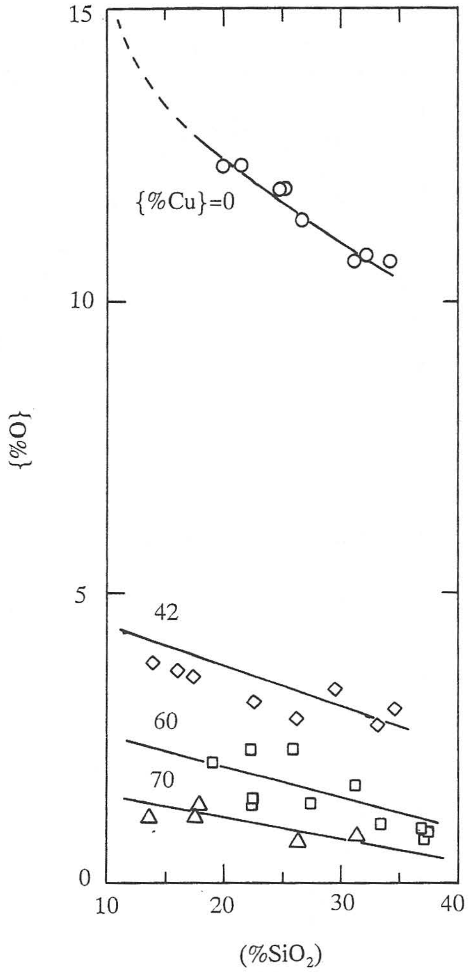


Fig. 13. Oxygen content in matte vs. silica content in slag.

Equilibrium constants for reactions (7) and (9) at 1573K are $K_{(7)}$=7.83 and $K_{(9)}$=22.39. Oxidic dissolution of copper, (% Cu)o, and sulfidic dissolution of copper, (% Cu)s, are calculated by

$$(\%\ Cu)o = \frac{K_{(7)}\, a_{Cu}\, (n_T)\, M_{cu}\, p_{O2}^{\ 1/4}}{(\gamma_{CuO0.5})} = \frac{746\, a_{Cu}\, p_{O2}^{\ 1/4}}{(\gamma_{CuO0.5})}, \quad (11)$$

$$(\%\ Cu)s = \frac{K_{(9)}\, a_{Cu}\, (n_T)\, M_{cu}\, p_{S2}^{\ 1/4}}{(\gamma_{CuS0.5})} = \frac{2134\, a_{Cu}\, p_{S2}^{\ 1/4}}{(\gamma_{CuS0.5})}, \quad (12)$$

where a_{Cu}, (n_T) and M_{cu} are activity of copper, total mole of constituents in 100 g of slag and atomic weight of copper, respectively. Because (n_T), which is a function of slag composition, has not large variation from the reason of close molecular weight of the main slag constituents, (n_T) is 1.5 for the sake of simplifying calculation. Activity coefficients of $CuO_{0.5}$, $(\gamma_{CuO0.5})$, and $CuS_{0.5}$, $(\gamma_{CuS0.5})$, are essential for copper solubility estimation in matte smelting slag, and have to be measured by experiment. Activity coefficients of $CuO_{0.5}$ is rather easily determined by slag-metal equilibrium experiment. The activity coefficient of $CuO_{0.5}$ for the slag of FeO_x-SiO_2-MgO system has been

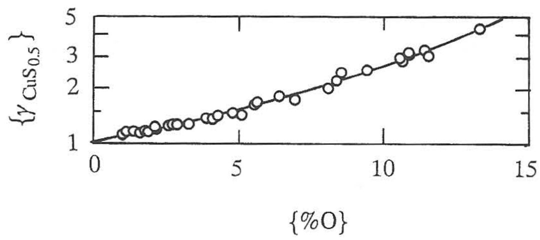


Fig. 14. Relation between activity coefficient of $CuS_{0.5}$ in matte and oxygen content in matte under existence of slag, matte and copper metal saturated with solid iron at 1573K[6].

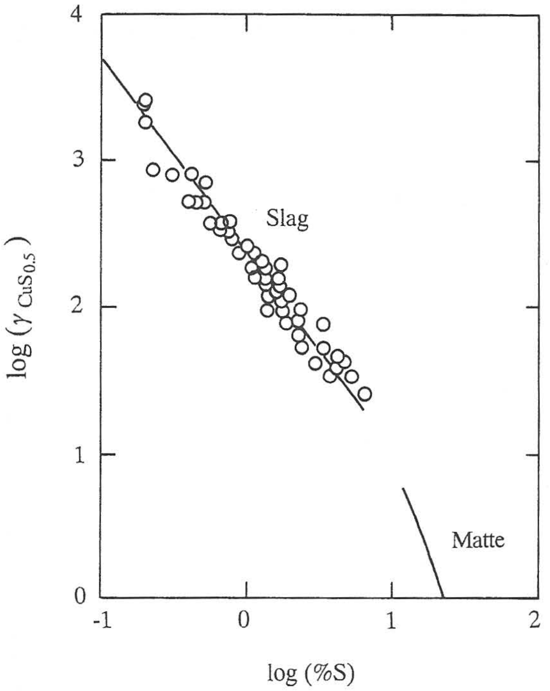


Fig. 15. Relation between activity coefficient of $CuS_{0.5}$ in slag and sulfur content in slag under existence of slag, matte and copper metal saturated with solid iron at 1573K[6].

presented[5], and fluctuates from 3.3 to 4.6. $(\gamma_{CuO_{0.5}})=4.0$ is employed for the analysis. Oxygen and sulfur partial pressures to measure or estimate above-mentioned. Activity of copper is impossible to measure in the system. Then activity of copper and the activity coefficient of $CuS_{0.5}$ in slag phase arises as interest.

When slag, matte and copper metal are equilibrated, activity of copper is controlled, oxygen partial pressure is measurable with an oxygen sensor and sulfur partial pressure is possible to estimate from metal composition of Cu-S-Fe system. The experiment equilibrating the three molten phases of $FeO\text{-}SiO_2\text{-}CaO$ slag, matte and copper metal has been carried out under iron saturation and the data has presented by author[6]. Fig. 14 shows activity coefficient of $CuS_{0.5}$, $\{\gamma_{CuS_{0.5}}\}$, in the matte of $CuS_{0.5}\text{-}FeS_x\text{-}FeO_y$ system as a function of oxygen content in matte. Activity coefficient of $CuS_{0.5}$ increases with increasing oxygen content in matte. Thermodynamic studies on the Cu-Fe-S matte have shown that activity coefficient of $CuS_{0.5}$ in pseudo-binary system of $CuS_{0.5}\text{-}FeS_x$ is not far from unity in any composition even under higher sulfur partial pressure than metal saturation[15]. The matte of left terminal point in Fig. 14 is the pseudo-binary system of $CuS_{0.5}\text{-}FeS_x$. Fig. 15 is activity coefficient of $CuS_{0.5}$ in slag, $(\gamma_{CuS_{0.5}})$, in the $FeO\text{-}SiO_2\text{-}CaO$ slag as a function of sulfur content in slag. The relation between the activity coefficient and sulfur content on logarithmic scales shows a line not depending on CaO content and is expressed by

$$(\gamma_{CuS_{0.5}}) = 234\,(\%\ S)^{-1.33}. \qquad (13)$$

Slag contains around 30% of oxygen, and matte does around 20% sulfur. Extrapolating activity coefficient of $CuS_{0.5}$ at 30% oxygen from the extending line in Fig. 14, around 20 in the activity coefficient is estimated, which is the lowest one in slag phase in Fig. 15. When we extend the line in Fig. 15 as far as around 20% sulfur of which composition is matte phase, the line is connected with that shown in Fig. 14. There is not any qualitative discrepancy between both results of Figs. 14 and 15.

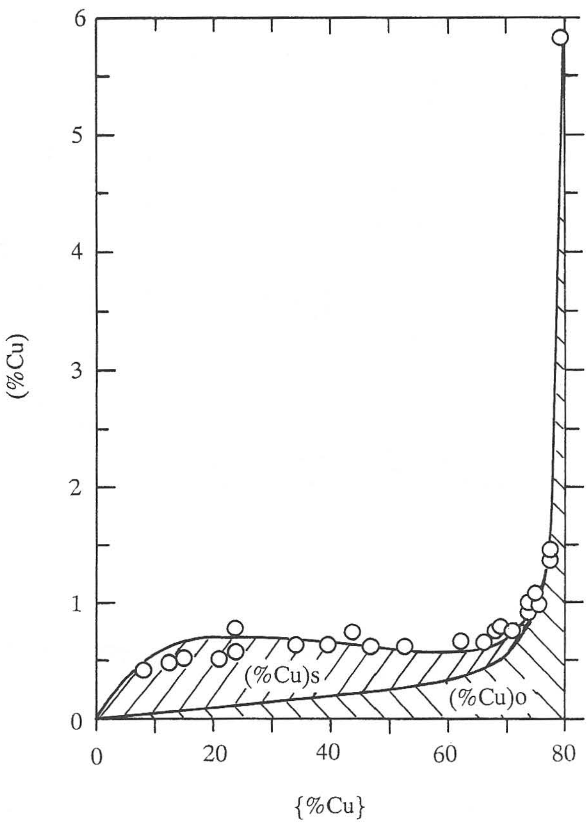


Fig. 16. Estimated sulfidic and oxidic copper contents in iron silicate slag saturated with silica and magnesia with experimental data shown by circles.

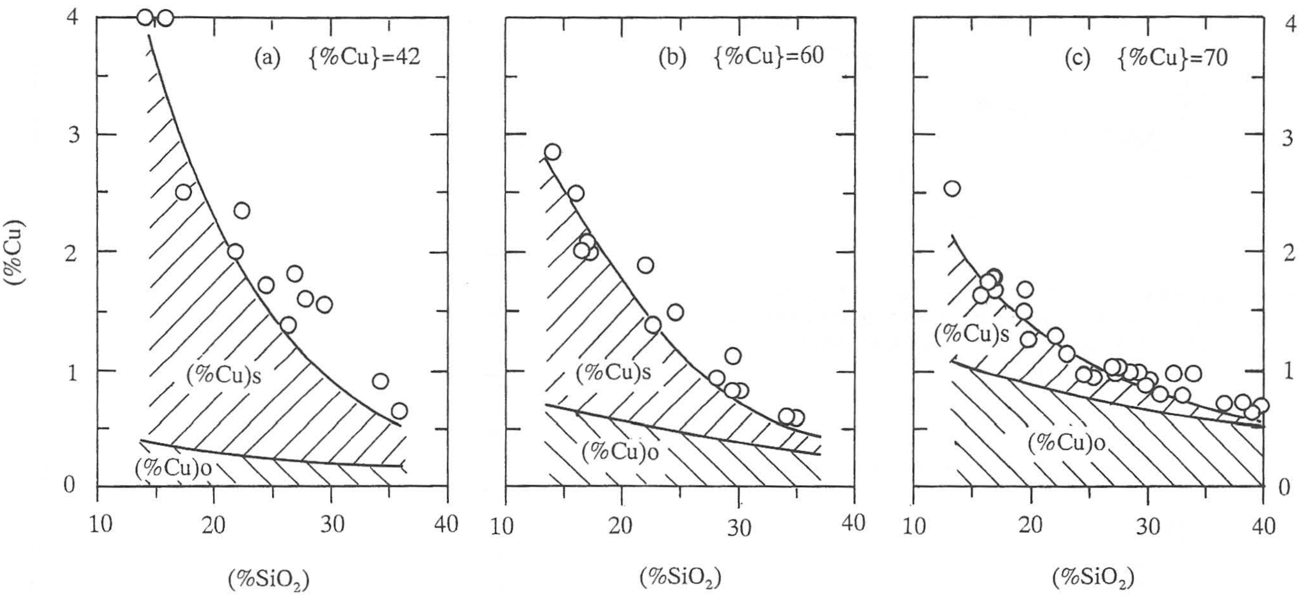


Fig. 17. Estimated sulfidic and oxidic copper contents in slag vs. silica content in slag with experimental data shown by circles.

Although the experiment to get the results of Figs. 14 and 15 was carried out under iron and copper saturation, the results are applied to analysis of the date under 10% SO_2-Ar. Activity of copper is calculated by

$$a_{Cu} = \frac{\{\%\ \mathrm{Cu}\}\{\gamma_{CuS0.5}\}}{K_{(9)}\ \{n_T\}\ M_{cu}\ p_{S2}^{\ 1/4}}, \qquad (14)$$

$\{\%\ \mathrm{Cu}\}$ is copper content in matte, and $\{n_T\}$ is total mole of constituents in 100 g matte of the $CuS_{0.5}$-FeS_x-FeO_y system. Oxidic and sulfidic copper contents in slag are easily calculated by equations (11) and (12). The results are shown in Fig. 16 against copper content in matte and in Fig. 17 against silica content in slag with experimental total copper contents. The sum of calculated oxidic and sulfidic copper contents is consistent with experimental copper content as shown in the figures. Oxidic copper content in slag increases with increasing matte grade owing to increasing oxygen partial pressure in Fig. 16. Sulfidic copper content in slag has the maximum equilibrated around 20% copper content in matte because sulfur content in slag increases with decreasing copper content in matte and contrarily activity of $CuS_{0.5}$ decreases. Both of oxidic and sulfidic copper contents increase with decreasing silica content in slag in Fig. 17. Because oxygen partial pressure and activity of copper increase with decreasing silica content, oxidic copper content increases. Sulfidic copper content is affected primarily by sulfur content in slag which is related to silica content in slag and iron content in matte. Silica plays more important role for dissolution loss of copper in slag under existence of lower matte grade. Calculated total copper content in slag saturated magnesia is shown against copper content in slag as a parameter of silica content in slag. It is predicted that iron silicate slag without magnesia dissolves more large amount copper than that shown in Fig. 18.

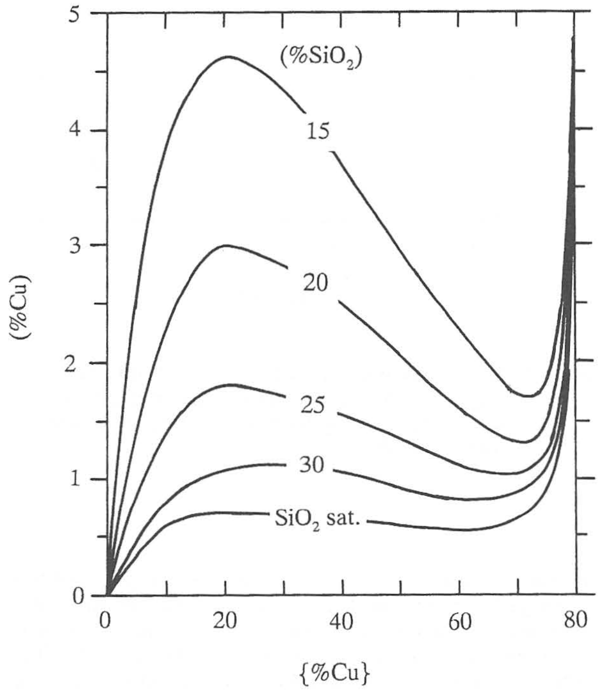


Fig. 18. Estimated total copper content in iron silicate slag saturated magnesia vs. copper content in matte at 1573K.

4. CONCLUSION

(1) It is difficult to equilibrate slag and matte with S-O-Ar gas system owing to sulfur transfer barrier on slag surface. However oxygen potential is measured by an oxygen sensor, and sulfur potential in the system is estimated under 0.1 atm. partial pressure.

(2) Copper solubility in the FeO_x-SiO_2 slag saturated with magnesia at 1573K is measured as functions of matte grade and silica content in slag.

(3) Advanced estimation system of copper solubility in matte smelting slag is developed by applying activity coefficients of $CuS_{0.5}$ in slag and matte phases to the experimental data.

REFERENCES

1. F. Sehnalek and I. Imris, "Slags from continuous copper production", Advance in Extractive Metallurgy and Refining, Inst. Mining Metal., 1972, pp. 39-77.

2. M. Nagamori, "Metal Loss to Slag: Part I. Sulfidic and Oxidic Dissolution of Copper in Fayalite Slag from Low Grade Matte", Met. Trans., Vol. 5, March, 1974, pp. 531-538.

3. A. Yazawa, M. Oida and Y. Nishikawa, "Dissolution Equilibria for Ni, Co, As, Sb and Cu between Matte and Slag", J. Min. Metall. Inst. Japan, Vol. 98, No. 1135, 1982, pp. 963-968.

4. A. Yazawa, "Thermodynamic Considerations of Copper Smelting", Can. Met. Quart., Vol. 13, No. 3, 1974, pp. 443-453.

5. Y. Takeda, "The effects on Basicity on Oxidic Dissolution of Copper in Slag", Metallurgical Processes for the Early Twenty-First Century, Vol. I Basic Principles, TMS, 1994, pp.453-466.

6. Y. Takeda, "Oxidic and Sulfidic Dissolution of Copper In Matte Smelting Slag", Proceedings of 4th International Conference on Molten Slags and Fluxes, ISIJ, 1992, pp. 584-589.

7. M. Stofko, J. Schmiedl and T. Rosenqvist, " Thermodynamics of Iron-Sulphur-Oxygen Melts at 1200°C", Scand. J. Metall., Vol. 3, 1974, pp. 113-118.

8. K.Itagaki, Privet Communication, to be presented in the conference.

9. J.P. Coughlin, "Contributions to the Data on Theoretical Metallurgy", Bureau of Mines, Bulletin 542.

10. G.G. Charette and S.N. Flengas, "Thermodynamic Properties of the Oxides of Fe, Ni, Pb, Cu and Mn, by EMF Measurements", J. Electrochem. Soc., Vol. 115, No. 8, 1968, pp.796-804.

11. M. Eguchi, H. Sawaguchi and A. Yazawa, "Dissolution of Copper into Silica-saturated Slag Coexisting with Liquid Copper and White Metal", J. Min. Metall. Inst. Japan, Vol. 93, No. 1067, 1977, pp. 963-968.

12. K. Watanabe, G. Kaiwra and A. Yazawa, "The Behaviour of Lead in Copper Smelting Systems", J. Min. Metall. Inst. Japan, Vol. 97, No. 1123, 1981, pp. 957-962.

13. Y. Kayahara, "Thermodynamic Study of the Liquid Cu-O system", Trans. JIM, Vol. 22, No. 7, 1981, pp.493-500.

14. J. Niemelä and P. Taskinen, "Activities and Phase Equilibria in Cu-S Melts by EMF Techniques", Scand. J. Metall., Vol. 13, 1984, pp.382-390.

15. J. Koh and A. Yazawa, "Thermodynamic Properties of the Cu-S, Fe-S and Cu-Fe-S Systems", Bulletin of the Research Institute of Mineral Dressing and Metallurgy, Tohoku University, Vol. 38, No. 2, 1982, pp. 107-118.