COPPER SOLUBILITY SiO$_2$-CaO-FeO$_x$ SLAG EQUILIBRATED WITH MATTE

Yoichi Takeda

Department of Materials Science of Technology, Iwate University
Ueda 4-2-5, 020-8551 Morioka, Japan

ABSTRACT

Copper solubility in slag is one of major factor in considering the optimal composition of copper smelting and converting slags. Objective is focused on the determination of copper solubility in SiO$_2$-CaO-FeO$_x$ slag equilibrated with copper matte under 10% SO$_2$ atmosphere at 1573K. Essential parameters are activity coefficients of copper oxide and sulfide, oxygen and sulfur potentials and activity of copper in the slag-matte system. Large number of experiments provides proper parameters to calculate copper solubility in slag. A classical thermodynamic model postulating CuO$_{0.5}$ and CuS$_{0.5}$ molecules assists in estimating copper solubility in slag. Additions of SiO$_2$ and CaO reduce copper solubility almost in any condition. Copper loss, that is function copper solubility and slag volume, in the silica saturated SiO$_2$-FeO$_x$ binary slag is minimal equilibrated with less than 66% copper matte while copper loss in the 45% FeO$_x$-SiO$_2$-CaO ternary slag saturated with 2CaO:SiO$_2$ is minimal equilibrated with over 66% copper matte. The composition around 50% FeO$_x$, 25% SiO$_2$ and 25% CaO in ternary system is a potential slag in practical operation under high oxygen potential such as continuous copper converting, direct copper production or high grade matte production. As extra information, iron content in matte as a controlling and operating factor in slag-matte system is more useful than copper content in matte.

INTRODUCTION

Smelting of copper concentrates and further converting of copper matte produces slags containing copper in the dissolved form as well as mechanically entrained inclusions. Solubility of copper in smelting and converting slags is of great importance in copper metallurgy due to significant impact on copper losses and effectiveness of slag cleaning processes. Additionally, in the range of high copper solubility dissolved copper affects slag properties having influence on phase separation and refractory corrosion.

Intensive smelting processes with oxygen enrichment producing high grade matte or even directly blister copper generate highly oxidized slags with growing participation of dissolved copper. Intensive and continuous matte converting processes take advantage of calcium ferrite type of slag utilizing lime or lime and silica fluxes. Therefore, the copper solubility in the wide range of slag composition of CaO-SiO$_2$-FeO$_x$ system is a major point of interest.

Copper solubility in the slag equilibrated with copper matte phase is difficult for evaluation due to system complexity and limited number of available experimental data. Objectives of this work have been focused on the determination of copper solubility in the slag of CaO-SiO$_2$-FeO$_x$ system in the wide range of chemical composition of the slag and copper matte, and related oxygen and sulfur potential fluctuation.
Basic considerations of CaO-SiO$_2$-FeO$_x$ system equilibrated with copper matte

Presence of two anions of oxygen and sulfur in the system needs additional assumption. The concept of sulfidic and oxidic copper [1-3] is very useful:

\[
(\%Cu)_t = (\%Cu)_o + (\%Cu)_s. \tag{1}
\]

A property X in slag phase is shown by (X) in brackets while Y in matte phase is shown by \{X\} in braces. Equilibrium constant of cuprous oxide formation at 1573K [4] is shown by equation (3)

\[
\text{Cu(l)} + \frac{1}{4}\text{O}_2(g) = \text{CuO}_{0.5}(l) \tag{2}
\]

\[
K = \frac{a_{\text{CuO}_{0.5}}}{a_{\text{Cu}} P_{\text{O}_2}^{1/4}} = 7.83. \tag{3}
\]

Oxidic dissolution of copper can be determined from equation:

\[
(\%Cu)_o = \frac{7.83 M_{\text{Cu}} (n_T) a_{\text{Cu}} P_{\text{O}_2}^{1/4}}{(Y_{\text{CuO}_{0.5}})} \tag{4}
\]

In the same manner sulfidic copper, that is derived from the equilibrium constant of cuprous sulfide formation [5] can be determined:

\[
\text{Cu(l)} + \frac{1}{4}\text{S}_2(g) = \text{CuS}_{0.5}(l) \tag{5}
\]

\[
K = \frac{a_{\text{CuS}_{0.5}}}{a_{\text{Cu}} P_{\text{S}_2}^{1/4}} = 22.4 \tag{6}
\]

\[
(\%Cu)_s = \frac{22.4 M_{\text{Cu}} (n_T) a_{\text{Cu}} P_{\text{S}_2}^{1/4}}{(Y_{\text{CuS}_{0.5}})} \tag{7}
\]

Presented simple thermodynamic model assumes molecular component and lack of interaction parameters.

Determination of dissolved total copper, which has been assumed as a sum of dissolved copper in the form of cuprous oxide and sulfide requires the measurement of following parameters:
1) Activity coefficient of CuO$_{0.5}$ in slag
2) Activity coefficient of CuS$_{0.5}$ in slag
3) Oxygen potential
4) Sulfur potential
5) Copper activity.
Activity coefficient of copper oxide in slag can be measured and the activity of copper sulfide can be estimated from sulfur content in the slag. Oxygen potential can be estimated from gas
phase composition under the assumption that gas phase reaches equilibrium with condensed phases or measured directly using oxygen probe. Sulfur potential is usually calculated from a composition of a gas phase. Copper activity in equilibrated condensed phases is estimated from copper matte composition, particularly oxygen content in the matte. Finally, presented simple model allows for determination of copper solubility in the slag being in contact with copper matte from experimental data.

**EXPERIMENTAL**

**Materials**

For synthetic master slag a mixture of pure chemicals: CaO, SiO$_2$, Fe$_2$O$_3$ and Fe powder was melted in an iron crucible under inert atmosphere. After melting slag was quenched by pouring into a stainless steel plate. Copper sulfide or iron sulfide was synthesized separately from a mixture of copper metal and sulfur or of iron powder and sulfur in a quartz ampoule by heating. Next, Cu$_2$S or FeS has been melted in an alumina crucible under inert gas protection atmosphere.

**Experimental procedure**

Cu$_2$S and FeS mixed in various proportions (total mass 8 g) corresponding to the wide range of matte grade (0 - 80% Cu) and synthetic slag (8 g) placed in a magnesia crucible have been positioned in an alumina protection tube inside closed a quartz reaction tube. The reaction quartz tube with a crucible was heated up in a vertical electric furnace under controlled gas mixture (SO$_2$ - S$_2$ - Ar) atmosphere. S$_2$ partial pressure was controlled by temperature of a sulfur bath in which SO$_2$-Ar gas mixture was injected and bubbling. After melting of slag and copper matte and keeping to preliminary equilibrium (from 3 to 50 hours) an oxygen concentration cell has been immersed to the bottom of a crucible and EMF signal has been recorded frequently. System was kept at stable condition of temperature and gas composition during the period of time needed to reach equilibrium. Preliminary investigation showed that the time required to reach the equilibrium depends on the iron content in the slag and matte. Large number of experiments have been carried out at constant temperature of 1573 K. A series of tests has been performed using a silica crucible in order to ensure silica saturation conditions free from MgO and CaO, compared with major series of measurements performed in a magnesia crucible. After required time the quartz reaction tube was removed from the furnace and cooled down. Next, the crucible was cut vertically. One part was prepared for microscopic examination and the separated slag and matte samples from the second part directed to chemical analysis. Matte sample was analyzed for Cu, Fe, S, SiO$_2$ and Ca contents using classical method, and oxygen and sulfur contents by reduction with hydrogen. Slag sample was analyzed for Cu, Fe, S, CaO, MgO and SiO$_2$ contents. Detailed description of experimental procedure is presented in the paper [6].

Slag varied in composition as shown in Fig. 1. In order to show the ratio of basic to acidic oxides, $Qm$ is introduced:

$$Qm = \frac{\%CaO + \%MgO}{\%CaO + \%MgO + \%SiO_2},$$

(8)
In this article percentage is on a basis of mass. The experiments were carried out varying iron contents of slag and matte at constant $Qm$. The silica saturated $\text{SiO}_2$-$\text{FeO}_x$ slag free from CaO and matte were melted in a silica crucible in the experiment of $Qm$=0. For the experiment of $Qm$=0.17, $\text{SiO}_2$-$\text{FeO}_x$ slag free from CaO and matte were melted in a magnesia crucible.

Apart from the objective of this work liquidus temperature of slag is important and shown in Fig. 1 under the iron saturation [7] and air atmosphere [8] but has not been investigated systematically under the oxygen potential of copper smelting and converting.

**RESULTS**

Contents of $\text{SiO}_2$, CaO and MgO in slag after experiment are shown in Figs. 2 to 4 against iron content in slag. These contents in slag are somewhat affected by composition of matte. Magnesia in slag is dissolved from crucible. The $\text{SiO}_2$-$\text{FeO}_x$ is shown by $Qm$=0. The $\text{SiO}_2$-$\text{FeO}_x$ slag melted in a magnesia crucible is shown by $Qm$=0.17.

The relation between iron and copper contents in matte is shown in Fig. 5 and by following equations:

\[
\log{\%\text{Fe}} = 65.7 - 0.835{\%\text{Cu}} \quad \text{for} \quad 10 \leq {\%\text{Cu}} \leq 73 \\
\log{\%\text{Fe}} = 58.5 - 0.737{\%\text{Cu}} \quad \text{for} \quad 73 \leq {\%\text{Cu}} \\
\log{\%\text{Fe}} = 52.8 - 0.669{\%\text{Cu}} \quad \text{for} \quad 45 \leq {\%\text{Cu}} \quad \text{and} \quad Qm = 1
\]

Over 73% of copper content in matte the relation deviates from Equation (9) and shown by Equation (10). Because mutual dissolution between the CaO-$\text{FeO}_x$ slag and matte is accelerated due to lack of silica, the relation is shown by Equation (11).

Whenever multi component solution is evaluated thermodynamically, essential factor is activity coefficient that is derived from experimental work. The activity coefficient of CuO$_{0.5}$ in the SiO$_2$-CaO-$\text{FeO}_x$ slag at 1573K is shown in Fig. 6 that is derived from the slag-copper equilibrium experiment in a magnesia crucible [9]. Logarithmic relation of activity coefficient of CuS$_{0.5}$ and sulfur content is shown in Fig. 7. The relation is derived from the result combining the slag-copper with slag-matte-copper equilibrium data under iron saturation [10] and presented by Equation (12) in slag phase.

\[
\log(\gamma_{\text{CuS}_{0.5}}) = 2.369 - 1.33\log(\%\text{S})
\]

While activity coefficient of CuS$_{0.5}$ in CuS$_{0.5}$-FeS pseudo-binary system is close to unity, activity coefficient of CuS$_{0.5}$ in CuS$_{0.5}$-FeS$_x$-$\text{FeO}_y$ matte system is affected by oxygen content in matte and shown in Fig. 8 and Equation (13) [6].

\[
\{\gamma_{\text{CuS}_{0.5}}\} = 1.08 - 0.0119(\%\text{O}) + 0.0188(\%\text{O})^2.
\]
$Q_m=0.17$ slag as an example are demonstrated in Figs. 9 to 11, respectively, where the SiO$_2$-FeO slag and matte are melted in a magnesia crucible under 10% SO$_2$ gas stream at 1573K. The oxygen and sulfur partial pressures and activity of copper for the slags of $Q_m=0.40$, 0.55, 1 are also determined separately from experimental data. For the $Q_m=0$ slag that is SiO$_2$-FeO slag free from CaO and MgO, these factors are estimated from the data for silica saturated SiO$_2$-FeO slag and the $Q_m=0.17$ slag that is SiO$_2$-FeO slag melted in a magnesia crucible. Iron (or silica) content in slag and iron (or copper) content in matte are variable in the experimental condition. Linear relation between logarithmic oxygen partial pressure and iron content in matte, not copper, is observed in Fig. 9. Next characteristic of Fig. 9 is that oxygen partial pressure at specified iron content in matte increases with decreasing silica content in slag, increasing iron content. Sulfur partial pressure is converted from the oxygen partial pressure by Equation (14) that is derived from the standard free energy of SO$_2$ formation [11].

$$\log P_{S_2}/\text{atm} = 2\log P_{SO_2} - 2\log P_{O_2} - 37816/T + 7.64 \quad (14)$$

The oxygen and sulfur potentials in slag-matte system under high SO$_2$ atmosphere can be measured or calculated from equilibrating gas composition in spite of experimental difficulty, but activity of copper, shown in Fig. 11, under the condition of metal free system remains as most difficult factor to estimate. Equation (7) is applied to matte phase. Activity coefficient of CuS$_{0.5}$ is evaluated from oxygen content in matte, shown in Fig. 13, and the relation of Fig. 11, then the activity coefficient and sulfur partial pressure of Fig. 10 are put in the terms of Equation (7). Copper content in matte is analyzed experimentally.

Essential factors, oxygen and sulfur partial pressure and activity of copper have been presented. The activity coefficient of CuO$_{0.5}$ in slag has been measured as shown in Fig. 6. The activity coefficient of CuS$_2$ in slag phase is calculated from sulfur content in slag, Fig. 12, and Equation (12). Then the dissolved sulfide and oxide copper contents are calculated by Equations (4) and (7). The dissolved copper in the $Q_m=0.17$ slag, that is sum of sulfide and oxide coppers, is illustrated in Fig. 14. Above procedure to calculate copper solubility in the slags of $Q_m=0$, 0.40, 0.55 and 1 has been performed. The results, copper solubility in the CaO-SiO$_2$-FeO$_x$-MgO slag under 10% SO$_2$ atmosphere at 1573K, are illustrated in Figs. 15 to 19.

**A choice of operation factor, matte grade**

Before discussing copper solubility in slag, a suggestion about matte grade as a practical operation factor might be proposed. In matte smelting, matte grade, that is copper content in matte, is worldwide accepted as controlling or operating factor in both of theoretical and practical aspects. Iron content in matte, {$%\text{Fe}$}, in spite of matte grade has advantage theoretical and practical points of view and is proposed as controlling and operating factor in matte smelting. Theoretically oxygen and sulfur potentials in matte-slag system are controlled by iron content in matte, not copper content as shown in Figs. 9 and 10 because the affinity of iron with oxygen is bigger than that of copper. It is well recognized that multi-component system is controlled by content of an element that has the biggest affinity with its essential element. Oxygen and sulfur potentials in the system affects also distribution behavior of detrimental elements. High copper content matte is recently produced in matte smelting furnace for plant efficiency in production rate. In the condition of high copper content matte production, error in chemical analysis of copper in matte more seriously affects results such as Figs. 9, 10 and 14 than that of iron does. The effect of relative error in copper analysis in
matte is ten times bigger than that in iron analysis at 70 % copper matte. Moreover the iron content is related to the energy, flux and time consumption etc. in next step while the copper content is done to those in past step. Future is more important for everyone than past. The copper content changes from 0 to 80 % theoretically, that corresponds to 67 to 0 % of the iron content. Figuratively speaking, a Marathon runner who has run 35 km already will make his tactic How I run remainder 7 km to win. Modern matte smelting is in similar position to him. Old matte smelting operation several decades ago would be in the position as a Marathon runner who was returning at half way, hence his past achievement would be meaningful.

Copper solubility

Analysis of the optimal composition of smelting and converting slags should consider as one of the major factor copper solubility. Presented simple model allows for prediction of total copper solubility as well as its oxidic and sulphidic forms. The model needs activity coefficients of cuprous oxide and cuprous sulfide, copper activity at defined gas phase composition. Presented example results as a part of large population of measurements at temperature 1573 K introduced large portion of necessary information.

Figure 14 shows copper solubility in SiO$_2$-FeO$_x$ slag against iron content in matte melted in a magnesia crucible under 10% SO$_2$ at 1573K. The silica in slag depresses copper solubility in slag particularly equilibrated with high iron content matte. Although it is recognized that silica is effective flux to separate iron oxide and sulfide, mutual dissolution between slag and matte accelerates with decreasing silica content, accordingly copper solubility in slag increases particularly equilibrated with high iron content matte. Most of copper in slag with high iron content in matte is estimated as sulfide copper that is calculated as a function of sulfur solubility in slag. Activity coefficient of oxide copper in slag as shown in Fig. 6 is not significantly affected by silica content in slag, thus copper solubility in slag equilibrated with low iron content in matte, is not so depend on silica content in slag as that with high iron content in matte.

Copper solubility in SiO$_2$-CaO-FeO$_x$ slag equilibrated with 23.9, 15.6, 7.3, 3.1 and 0.3% iron contents in matte under 10%SO$_2$ at 1573K is shown in Figs. 15 to18. The solubility data is useful for selection of slag composition. The isobars in copper solubility shown in Figs.15 to 18 are explicable from the concept of oxidic and sulfidic dissolution of copper. When high iron content matte, low copper content, is equilibrated, the minimum solubility of copper is observed in the slag that has high silica and low iron as shown in Fig. 15. In the case predominant copper is sulfide, hence the solubility is mainly affected by sulfur solubility in slag which is depend on silica and iron contents in slag. With decreasing iron content in matte, or increasing copper content, the minimum solubility as shown in Fig. 19 shifts to CaO rich composition, that has the maximum activity coefficient of CuO$_{0.5}$ as shown in Fig. 6. Most of copper in slag under the condition of slag-white metal-copper equilibration shown in Fig. 19 is oxide because of little sulfur solubility in slag.

Dissolved copper loss in slag

Dissolved copper loss is the function of copper solubility and slag volume. Major impurity in row material of copper smelting is usually iron that is removed into slag. Copper content, kg, in slag to unite iron content, ton, in slag is an index of copper loss in the case in which SiO$_2$, CaO as flux is supposed to add for iron removal. The copper loss, kg, to unite iron
removal, ton, are shown in Figs. 20 to 24. When predominant copper dissolution is sulfide under equilibration of high iron content matte, low grade matte, the minimum dissolution copper loss is observed the silica saturated pseudo SiO$_2$-FeO$_x$ binary slag as shown in Figs. 20 and 21. Addition of CaO as a flux has not significant effect on copper loss equilibrating with 11% iron, 66% copper matte, but equilibrating less than 11% iron content matte addition of CaO which is almost proportional to reducing amount of SiO$_2$ flux is effective to copper loss reduction. The minimum copper loss equilibrating low iron content matte, high grade matte is observed in the slag composition close to the pseudo SiO$_2$-CaO-FeO$_x$ saturated with 2CaOSiO$_2$ as shown in Figs. 22, 23 and 24. With decreasing iron content in matte and increasing copper content, sulfur content in slag reduces and oxygen potential increases, predominant copper in slag shifts to oxide. Oxide copper solubility under specified oxygen potential and activity of copper is related to activity coefficient of CuO$_{0.5}$ as shown in Fig. 6. Although the maximum in the activity coefficient for $Qm=0.55$ is 13 in 20% iron content in slag, the minimum copper loss is observed in the slag composition containing 40 to 50% FeO$_x$ (30 to 40% Fe) in Figs. 22 to 24 because of compensating the activity coefficient and slag volume.

The composition around 50% FeO$_x$-25% CaO-25% SiO$_2$ is a potential slag in continuous copper converting, direct copper production or high grade matte production in which condition predominant copper in slag is oxide. The slag composition is mild against refractory materials.

**CONCLUSIONS**

1. Minimum dissolution loss of copper in the SiO$_2$-CaO-FeO$_x$ slag, that loss is function of copper solubility and slag volume, equilibrating with over 11% iron content matte (less than 66% copper) is observed in the silica saturated pseudo SiO$_2$-FeO$_x$ slag. Minimum dissolution loss of copper in slag with less than 11% iron content matte is in the SiO$_2$-CaO-FeO$_x$ slag that contains 40 to 50% iron oxide and is saturated with 2CaOSiO$_2$.
2. The composition around 50% FeO$_x$-25% CaO-25% SiO$_2$ is a potential slag in continuous copper converting, direct copper production or high grade matte production in which condition predominant copper in slag is oxide.
3. Iron content in matte in stead of matte grade is proposed to use as controlling and operating factor in slag-matte system.

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**REFERENCES**

Fig. 1 Experimental slag composition and liquidus lines at 1573K

Fig. 2 SiO₂ content in slag

Fig. 3 CaO content in slag
Fig. 4  MgO content in slag

Fig. 5  Copper content in matte against iron content in matte

Fig. 6  Activity coefficient of CuO_{0.5} in SiO_{2}-CaO-MgO-FeO_{x} slag at 1573K in the log P_{O2}/atm range of –6 to –8

Fig. 7  Activity coefficient of CuS_{0.5} in slag against sulfur content in slag at 1573K under the iron saturation condition
Fig. 8  Activity coefficient of CuS_{0.5} in matte against oxygen content in matte at 1573K under the iron saturation condition

Fig. 9  Oxygen partial pressure as a function of iron content in matte at 1573K and 0.1 atm. SO_{2} partial pressure for Q_m=0.17 slag free from CaO

Fig. 10  Sulfur partial pressure as a function of iron content in matte at 1573K and 0.1 atm. SO_{2} partial pressure for Q_m=0.17 slag free from CaO
Fig. 11  Activity of copper in the SiO$_2$-FeO$_x$ slag-matte system melted in a magnesia crucible at 1573K and 0.1 atm. SO$_2$ partial pressure

Fig. 12  Sulfur content in SiO$_2$-FeO$_x$ slag equilibrated with matte melted in a magnesia crucible under 0.1 atm. SO$_2$ partial pressure at 1573K

Fig. 13  Oxygen content in matte equilibrated with SiO$_2$-FeO$_x$ slag melted in a magnesia crucible under 0.1 atm. SO$_2$ partial pressure at 1573K
Fig. 14  Copper solubility in SiO$_2$-FeO$_x$ slag melted in a magnesia crucible under 0.1 atm. SO$_2$ partial pressure at 1573K

Fig. 15  Copper solubility in slag equilibrated with 23.9% Fe (50% Cu) matte under 0.1 atm. SO$_2$ partial pressure at 1573K
Fig. 16  Copper solubility in slag equilibrated with 15.6% Fe (60% Cu) matte under 0.1 atm. SO$_2$ partial pressure at 1573K

Fig. 17  Copper solubility in slag equilibrated with 7.3% Fe (70% Cu) matte under 0.1 atm. SO$_2$ partial pressure at 1573K
Fig. 18   Copper solubility in slag equilibrated with 3.1% Fe (75% Cu) matte under 0.1 atm. SO$_2$ partial pressure at 1573K

Fig. 19   Copper solubility in slag equilibrated with 0.3% Fe (79% Cu) matte and copper metal under 0.1 atm. SO$_2$ partial pressure at 1573K
Fig. 20  Dissolved copper loss (kg) in slag per unite iron removal (ton) equilibrated with 23.9% Fe (50% Cu) matte under 0.1 atm. SO₂ partial pressure at 1573K

Fig. 21  Dissolved copper loss (kg) in slag per unite iron removal (ton) equilibrated with 15.6% Fe (60% Cu) matte under 0.1 atm. SO₂ partial pressure at 1573K
Fig. 22  Dissolved copper loss (kg) in slag per unite iron removal (ton) equilibrated with 7.3% Fe (70% Cu) matte under 0.1 atm. SO$_2$ partial pressure at 1573K

Fig. 23  Dissolved copper loss (kg) in slag per unite iron removal (ton) equilibrated with 3.1% Fe (75% Cu) matte under 0.1 atm. SO$_2$ partial pressure at 1573K
Fig. 24  Dissolved copper loss (kg) in slag per unite iron removal (ton) equilibrated with 0.3% Fe (79% Cu) matte and copper metal under 0.1 atm. SO₂ partial pressure at 1573K.