Phase Equilibrium between Calcium Ferrite Slag and Copper Matte at 1523 K under High Partial Pressures of SO₂

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As a fundamental study for the oxygen-blowing copper smelting, the phase equilibrium between ferrite slag and copper matte was investigated at 1523 K under the partial pressures of SO₂ controlled at 10.1, 50.7 and 101.3 kPa, using a sulfur reservoir for controlling the partial pressure of S₂. An oxygen-sulfur potential diagram was constructed in relation to matte grade, and it was clarified that the ratio of ($p_{\text{O}_2}/p_{\text{S}_2}$) was constant against p_{SO_2} when the matte grade was specified. The solubilities of copper and sulfur in the slag and calcium in the matte as well as ($\% \text{Fe}^{3+} / \% \text{Fe}^{2+}$) in the slag were also determined in relation to matte grade. The solubilities of copper and sulfur were found to be independent of p_{SO_2} when the matte grade was specified and it was considered that this behavior was ascribable to the constancy of ($p_{\text{O}_2}/p_{\text{S}_2}$) against p_{SO_2} . The solubility of sulfur decreased gradually with increasing matte grade. On the other hand, the solubility of copper represented the minimum at matte grade with about 72.5 mass%Cu, which was analyzed thermodynamically based on a concept of oxidic and sulfidic dissolutions of copper component in the slag.

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I. Introduction

Oxidation of sulfur and iron contained in the copper concentrates can supply part or all of the fuel required for copper smelting, and the use of oxygen or oxygen-enriched air as the blowing gas has the special advantage of fully utilizing the fuel value of the concentrates and producing a smaller amount of the combustion gas with higher strength of p_{SO_2} . Hence, the combination of intensive smelting reactors with the use of oxygen or oxygen-enriched air has provided a number of improved copper smelting processes such as the INCO-Flash, Outokumpu-Flash and Mitsubishi-Continuous processes. Recently, Japanese flash smelters have increased the degree of oxygen-enrichment in the blowing gas at more than 40 mol%O₂ in order to increase the productivity of copper.

Phase equilibrium studies for the copper matte and slag under high partial pressures of SO₂ are of importance practically for thermodynamically discussing the above mentioned oxygen-smelting processes. Although a series of experimental studies were carried out by Yazawa and co-workers⁽¹⁾⁽²⁾, Jalkanen *et al.*⁽³⁾, Sehnalek and Imris⁽⁴⁾ and Kuxman and Bussman⁽⁵⁾ in a restricted condition of p_{SO_2} at about 10.1 kPa which corresponds to the smelting with air-blowing, there remain few data on the phase equilibrium under the high partial pressures of SO₂.

Tavera and Davenport⁽⁶⁾ studied the matte and fayalite slag phases under the partial pressures of SO₂ controlled at 10.1–101.3 kPa, but without controlling the partial pressures of sulfur and oxygen. As suggested by a potential diagram⁽⁷⁾ for the Cu–Fe–S–O system at 1523–1573

K, the partial pressure of S₂ equilibrated with the matte and fayalite slag (SiO₂-saturation) under the high SO₂ pressure is considerably high at 10–1000 Pa. This condition is likely to need the controlling of p_{S_2} as well as p_{SO_2} in the equilibrium experiments, otherwise, the equilibrium is hardly attained due to the continued flushing of sulfur from the system.

The objective of the present work has been to extend the slag/matte studies from the air-blowing condition at about 10.1 kPa of p_{SO_2} into the oxygen-smelting condition of p_{SO_2} more than 10.1 kPa. The partial pressure of S₂ gas was controlled by means of a liquid sulfur reservoir through which a stream of the controlled SO₂ gas passed before entering the matte/slag system. The phase equilibrium between the copper matte with 50–80 mass%Cu and the calcium ferrite slag with about 9–16 mass%Ca was investigated at 1523 K under the controlled partial pressures of SO₂ at 10.1, 50.7 and 101.3 kPa. Acuna *et al.*⁽²⁾ studied the same system under the controlled p_{SO_2} at 10.1 kPa while p_{S_2} was not controlled in their experiments.

II. Experimentals

1. Gas controlling system

A MgO crucible was used in the experiments. The solubility of MgO in the CaO–FeO_x slag was found to be considerably small at about 2 mass%. At a given temperature, the number of freedom is three for the phase equilibrium between slag, matte, gas and solid MgO (crucible) in the Cu–Fe–S–O–Ca–Mg hexagonary system. We controlled the partial pressures of SO₂ and S₂ in the gas phase and fixed mass%Ca in the feed as the remaining variables. The mixture of Ar–SO₂–S₂ gas was used to

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Fig. 1 Relation between sulfur partial pressure and temperature of the sulfur bath.

control p_{SO_2} and p_{S_2} . Accordingly, p_{O_2} was also fixed at a given value, based on an equilibrium relationship for the reaction of $\frac{1}{2}S_2(g) + O_2(g) = SO_2(g)$. Although the mixture of $CO_2-H_2-SO_2-Ar$ gas⁽¹⁾ was available for controlling p_{SO_2} , p_{S_2} and p_{O_2} , its use will be restricted to the system under considerably low p_{SO_2} and p_{S_2} .

The mixture of SO_2 and Ar gas with a flow rate of $2.2-3.0 \times 10^{-6} \text{ m}^3/\text{s}$ was passed through the reservoir with liquid sulfur which was kept at a given temperature. The gas after passing the reservoir was led to the slag/matte system at 1523 K through a glass tube which was heated at 320–340 K to prevent the condensation of sulfur. Judging from the result of a thermodynamic calculation for the dissolution equilibrium between the polyatomic gas species of sulfur, it was considered that the evaporated sulfur could be completely dissociated into the diatomic gas after entering into the reaction system at 1523 K.

The relation between the partial pressure of S_2 at 1523 K and the temperature of the reservoir was determined previously by measuring the weight of sulfur in a duplicated glass condenser immersed in an ice bath, which was condensed from a given amount of argon gas passing through the reservoir with a flow rate of $2.2-3.0 \times 10^{-6} \text{ m}^3/\text{s}$. The relationship is shown in Fig. 1. The partial pressure of S_2 could be adjusted at 1–8000 Pa by controlling the bath temperature at 400–550 K.

2. Experimental procedure

FeS and Cu_2S for the matte components were made pyrometallurgically from the metals and sulfur with 99.9 mass% purity. Two kinds of mother slags with 23 mass% CaO–77% FeO and 10% CaO–90% FeO were synthesized in iron crucibles. 8 g of the slag and an equal amount of the matte composed of FeS and Cu_2S were put in the MgO crucible with an inner diameter of 22 mm and a height of 60 mm. To make the equilibrium between the slag and matte phases in a limited time, the copper content (matte grade) in the starting matte was adjusted to be higher than that in the equilibrium state because p_{S_2} in the inlet gas was considerably high at 10–1000 Pa and the

amount of sulfur required to sulfidize the iron oxide in the slag phase could be provided easily to the reaction system. If the copper content in the starting matte were lower than that in the equilibrated one, oxidation of FeS in the matte by oxygen in the inlet gas would take a very long time because p_{O_2} in the inlet gas was very low, namely $p_{O_2} = 10^{-4}-10^{-2} \text{ Pa}$. It was found in the preliminary experiment that the equilibration was made in 144 ks when the copper content in the starting matte was about 3% higher than that in the equilibrated one. Hence, the sample was heated at 1523 K for 162 ks in the present experiments. After that, it was cooled rapidly by flushing a large amount of argon gas onto a surface of the slag layer with a flow rate of more than $5 \times 10^{-3} \text{ m}^3/\text{s}$ to prevent the segregation of the slag components during the solidification.

Optical microscopic observation, EPMA analysis and chemical analyses were made for the solidified matte and slag specimens. The copper content in the matte was determined by titration with EDTA. Sulfur was analyzed gravimetrically after precipitation as barium sulfate. Iron was titrated with potassium dichromate. Ca and Mg in the matte and slag phases as well as Cu in the slag phase were determined by ICP.

III. Experimental Results

1. Phase separation into slag and matte

It was reported by Acuna *et al.*⁽²⁾ that a slag/matte phase separation was not observed when the matte sample with less than 50% Cu and a slag with 23% CaO were jointly melted at 1523 K under the controlled partial pressure of SO_2 at 10.1 kPa. The noted mutual dissolution was also found in the present experiments and the phase separation initiated when the matte grades were higher than 50, 60 and 70 mass% Cu at $p_{SO_2} = 10.1$, 50.7 and 101.3 kPa, respectively. It should be noted that the grade of matte after equilibration, at which the phase separation initiated, increased with increasing p_{SO_2} .

The solidified samples were investigated by a microscope and an electron probe microanalyzer. Figure 2 shows the micro structure of a nonseparating sample obtained when the matte sample with 47.5% Cu and the slag sample with 23% CaO were jointly melted at 1523 K under the partial pressure of SO_2 at 10.1 kPa. The following crystallites were recognized in the phase as main constituents. (i) large dark dendrite of a CaO–FeO– Fe_2O_3 compound (Ca 13.0, Fe 53.1 mass%) surrounded by a FeS matrix, (ii) greenish matrix of the FeS containing a small amount of Cu_2S , (iii) white dendrite of the copper metal which could be formed by desulfidization of Cu_2S , (iv) dark gray particle of the sulfide-oxide mixture composed of the Fe, Cu, Ca, S and O elements, (v) fine dark dendrite of the bornite which is spread out on the FeS matrix.

An investigation of the micro structures of separating matte with 52.5% Cu and slag with 10% Ca clarified that both phases contained these five kinds of crystallites

Fig. 2 Micro structure of nonseparating sample with 47.5% Cu obtained at 1523 K under p_{SO_2} of 10.1 kPa. (i) $\text{CaO-FeO-Fe}_2\text{O}_3$ crystallite, (ii) matrix of FeS with a little amount of Cu_2S , (iii) white dendrite of copper, (iv) fine dendrite of bornite, (v) sulfide-oxide mixture composed of Fe, Cu, S, Ca and O elements.

as main constituents but with considerably different proportions. The $\text{CaO-FeO-Fe}_2\text{O}_3$ crystallite (i) was predominant in the slag phase while the matrix of FeS (ii) and the matrix consisting of bornite and FeS (iv) were predominant in the matte phase. The sulfide-oxide mixture composed of the Fe, Cu, Ca, S and O elements (v) was also found in both separating phases but its proportion was considerably smaller than that in the non-separating phase.

The five kinds of the crystallites of (i)–(v) were also recognized as main constituents in the micro structures of two non-separating phases obtained with the starting matte sample with 58 and 68 mass%Cu under the partial pressure of SO_2 at 50.7 and 101.3 kPa, respectively.

2. Relation between matte grade and p_{S_2} or p_{O_2}

The phase equilibrium was investigated for the systems composed of the separating matte and slag. The relation between the matte grade and p_{S_2} as well as p_{O_2} which was calculated by using an equilibrium constant⁽⁷⁾ of the reaction, $\frac{1}{2}\text{S}_2(\text{g}) + \text{O}_2(\text{g}) = \text{SO}_2(\text{g})$, are shown in Fig. 3 for given p_{SO_2} of 10.1, 50.7 and 101.3 kPa. It is noted that p_{S_2} decreases with increasing matte grade while p_{O_2} increases and the decrement of p_{S_2} and the increment of p_{O_2} are remarkable when the matte grade is over 75%Cu. At a given matte grade, p_{O_2} and p_{S_2} increase with increasing p_{SO_2} .

Yazawa⁽⁸⁾ reported the relationship between the matte grade and p_{S_2} as well as p_{O_2} for the two-phase equilibria between the copper matte and iron-silicate slag (SiO_2 -saturation) at 1523 K under the partial pressure of SO_2 at 10.1 kPa. It agrees fairly well with the present result obtained under the same conditions. This agreement may be ascribed to a similarity in the constituents of the matte phase between the system with the iron-silicate slag and

Fig. 3 Relation between oxygen or sulfur partial pressure and copper content in the matte under p_{SO_2} of 10.1, 50.7, 101.3 kPa at 1523 K.

Fig. 4 Solubility of copper in the slag against copper content in the matte under p_{SO_2} of 10.1, 50.7 and 101.3 kPa at 1523 K (—: Acuna *et al.*⁽²⁾ under p_{SO_2} of 10.1 kPa, at 1523 K).

that with the calcium ferrite slag. Both mattes are considered to be fundamentally composed of Cu_2S , FeS and FeO ⁽⁸⁾.

3. Solubility of component in slag and matte

Solubilities of copper and sulfur in the slag and calcium in the matte were determined in relation to the matte grade. As shown in Fig. 4, the copper content in the slag decreases with increasing matte grade up to about 72.5%Cu and increases abruptly in the region of higher matte grade. The solubility of copper is likely to be independent of the partial pressure of SO_2 within the scatter of experimental points. On the other hand, as shown

Fig. 5 Solubility of sulfur in the slag against copper content in the matte under p_{SO_2} of 10.1, 50.7 and 101.3 kPa at 1523 K (— · —: Acuna *et al.*⁽²⁾ under p_{SO_2} of 10.1 kPa at 1523 K).

Fig. 6 Solubility of calcium in the matte against copper content in the matte under p_{SO_2} of 10.1, 50.7 and 101.3 kPa at 1523 K.

in Fig. 5, the sulfur content in the slag decreases gradually with increasing matte grade. The solubility of sulfur also seems to be independent of p_{SO_2} . The solubilities of copper and sulfur in the slag which were determined by Acuna *et al.*⁽²⁾ for the slag/matte equilibria under the partial pressure of SO_2 at 10.1 kPa are shown with dash-dot lines in Figs. 4 and 5, respectively. Their tendencies against the matte grade agree well with the present ones. As shown in Fig. 6, the solubility of calcium in the matte is considerably small at about 2.4% when the matte grade is 52.5%Cu. It decreases with increasing matte grade and becomes zero at the matte grade of 80%Cu. The partial pressure of SO_2 seems to have no effect on the solubility. Owing to the low solubility of calcium in the matte and because the amount of the slag does not change from that of the starting slag, the calcium content in the slag remained at about 10% against the matte grade.

4. $\% \text{Fe}^{3+} / \% \text{Fe}^{2+}$ in the slag

$\% \text{Fe}^{2+}$ and $\% \text{Fe}^{3+}$ in the slag for the slag/matte under

Fig. 7 $\% \text{Fe}^{3+}$ and $\% \text{Fe}^{2+}$ in the slag against copper content in the matte under p_{SO_2} of 10.1 kPa at 1523 K.

Fig. 8 $\% \text{Fe}^{3+} / \% \text{Fe}^{2+}$ in the slag against copper content in the matte under p_{SO_2} of 10.1, 50.7 and 101.3 kPa at 1523 K.

the partial pressure of SO_2 at 10.1 kPa are shown in Fig. 7. $\% \text{Fe}^{2+}$ is prevailing and almost constant in a region of the matte grade up to 62.5%Cu, and then decreases remarkably with increasing matte grade. On the other hand, $\% \text{Fe}^{3+}$ is almost constant in the region of low matte grade. The ratio of $\% \text{Fe}^{3+}$ to $\% \text{Fe}^{2+}$ in the slag is shown in Fig. 8 against the matte grade, which was obtained at $p_{\text{SO}_2} = 10.1, 50.7$ and 101.3 kPa. At a given matte grade, it seems that the ratio increases slightly with increasing p_{SO_2} .

5. Effect of CaO content in slag

The results described in III.1–4 were obtained for the slag/matte equilibria in which the calcium content in the starting slag was almost constant at about 16.5%. To know the effect of the calcium content on the solubility of copper and sulfur in the slag, further experiments were conducted in which the matte with about 70%Cu was equilibrated with the slag with varying calcium content under the partial pressures of SO_2 at 10.1 and 50.7 kPa at 1523 K. The copper and sulfur contents in the slag

Fig. 9 Copper and sulfur against calcium content in the slag equilibrating with the matte with about 70%Cu under p_{SO_2} of 10.1 (○), and 50.7 (●) kPa at 1523 K.

are shown in Fig. 9, in relation to %Ca in the slag. It is noted that they are almost constant against %Ca in the slag in the region between 10 and 18%Ca. Thus, no serious effect by calcium content was found.

IV. Discussion

The relation between p_{S_2} and p_{O_2} in the slag/matte equilibria is given by the following equations.

$$\log p_{\text{O}_2} = \log p_{\text{S}_2} + 2 \log K_1 + 2 \log (a_{\text{FeO}} / a_{\text{FeS}}) \quad (2)$$

where K_1 is the equilibrium constant for the reaction (1), and a_{FeO} and a_{FeS} are activities of FeO and FeS, respectively. In a case that, at a given matte grade, the activity ratio ($a_{\text{FeO}} / a_{\text{FeS}}$) is constant against p_{SO_2} , the $\log p_{\text{O}_2} - \log p_{\text{S}_2}$ plots for the given matte will present a straight line with a slope of unity, that is, $\log (p_{\text{O}_2} / p_{\text{S}_2})$ will be constant.

Based on the experimental results shown in Fig. 3, a $\log p_{\text{O}_2} - \log p_{\text{S}_2}$ potential diagram was illustrated in Fig. 10 for the matte grades of 70, 72.5 and 75%Cu, in relation to p_{SO_2} . For each matte, the $\log p_{\text{O}_2} - \log p_{\text{S}_2}$ plots are located on a straight line with a slope of unity, indicating

Fig. 10 Sulfur-oxygen potential diagram for the matte grades of 70, 72.5 and 75%Cu, in relation to p_{SO_2} at 1523 K.

that ($a_{\text{FeO}} / a_{\text{FeS}}$) and ($p_{\text{O}_2} / p_{\text{S}_2}$) are constant against p_{SO_2} at each matte grade. This result has important meaning in the following discussion on the dissolutions of copper and sulfur in the slag.

The solubility of copper in the slag, (%Cu), is given by the sum of an oxidic part, (%Cu)_o, and a sulfidic part, (%Cu)_s, as follows⁽⁹⁾⁻⁽¹¹⁾.

$$(\% \text{Cu}) = (\% \text{Cu})_{\text{s}} + (\% \text{Cu})_{\text{o}} \quad (3)$$

from the following reaction,

the oxidic part is given by

$$(\% \text{Cu})_{\text{o}} = a_{\text{CuS}_{0.5}} (A / \gamma_{\text{CuO}_{0.5}}) (p_{\text{O}_2} / p_{\text{S}_2})^{1/4}. \quad (5)$$

Where $a_{\text{CuS}_{0.5}}$ is activity of the $\text{CuS}_{0.5}$ component in the matte, $\gamma_{\text{CuO}_{0.5}}$ is the activity coefficient of the $\text{CuO}_{0.5}$ component in the slag and A is constant to which equilibrium constant of the reaction (4) pertains. On the other hand, the sulfidic part is expressed as

$$(\% \text{Cu})_{\text{s}} = a_{\text{CuS}_{0.5}} (B / \gamma_{\text{CuS}_{0.5}}). \quad (6)$$

Where $\gamma_{\text{CuS}_{0.5}}$ is the activity coefficient of the $\text{CuS}_{0.5}$ component in the slag and B is a constant which contains the total number of moles of the components in the slag. By combining eqs. (5) and (6), eq. (3) can be rewritten as

$$(\% \text{Cu}) = a_{\text{CuS}_{0.5}} [(A / \gamma_{\text{CuO}_{0.5}}) (p_{\text{O}_2} / p_{\text{S}_2})^{1/4} + (B / \gamma_{\text{CuS}_{0.5}})]. \quad (7)$$

Based on eq. (7), it can be considered how (%Cu) will change with p_{SO_2} when the matte grade is specified. Information on $\gamma_{\text{CuO}_{0.5}}$ and $\gamma_{\text{CuS}_{0.5}}$ in eq. (7) is very limited and it is not known how $\gamma_{\text{CuO}_{0.5}}$ changes with p_{SO_2} . In the event that both $\gamma_{\text{CuO}_{0.5}}$ and $\gamma_{\text{CuS}_{0.5}}$ in the slag equilibrating with a given matte are constant against p_{SO_2} , (%Cu) will be constant because the $(p_{\text{O}_2} / p_{\text{S}_2})^{1/4}$ term in eq. (7) does not change with p_{SO_2} as clarified in the present experiments. Hence, (%Cu) will be dependent only on $a_{\text{CuS}_{0.5}}$, in other words, the grade of matte. This prediction is in accordance with the present results shown in Fig. 4 in that

(%Cu) is independent of p_{SO_2} when the matte grade is specified. Conversely, it is predicted from the present results that $\gamma_{\text{CuO}_{0.5}}$ and $\gamma_{\text{CuS}_{0.5}}$ in the slag equilibrating with a given matte are constant against p_{SO_2} .

By using the data on $a_{\text{CuS}_{0.5}}$ in the matte reported by Koh and Yazawa⁽¹²⁾ and $\gamma_{\text{CuO}_{0.5}}$ in the CaO-FeO_x slag reported by Yazawa and Takeda⁽¹³⁾, the oxidic dissolution was calculated from eq. (5), and by subtracting the calculated value from the experimental value of (%Cu), the sulfidic dissolution was deduced as shown in Fig. 11. It is noted that (%Cu)_s is considerably higher in the region of low matte grade while (%Cu)_o prevails in the region of high matte grade.

$\gamma_{\text{CuS}_{0.5}}$ in the slag was calculated by combining the derived (%Cu)_s with eq. (6) and is shown in Fig. 12 in relation to %S in the slag. ($\gamma_{\text{CuS}_{0.5}}$) decreases remarkably with increasing %S in slag owing to the changes in the %S in slag and the activity of CuS_{0.5} against %Cu in matte. The observed linear relationship is given by the following equation.

$$(\gamma_{\text{CuS}_{0.5}}) = 340(\%S)^{-1.5}. \quad (8)$$

From the standpoint of the molecular theory of the

Fig. 11 Sulfidic and oxidic dissolutions of copper in the slag along with total copper content in the slag against matte grade at 1523 K.

Fig. 12 Activity coefficient of CuS_{0.5} in the slag against sulfur content in the slag under p_{SO_2} of 10.1, 50.7 and 101.3 kPa at 1523 K.

slag, sulfur exists in the slag phase as FeS(FeS_{1.5}), CuS_{0.5}, CaS and MgS. When the ionic model is taken into consideration, sulfur may dissolve in the slag according to the exchange reaction first suggested by Richardson and Withers⁽¹⁴⁾.

Within the limit of dilute solution of sulfur, reaction (9) leads to the following relation.

$$(\%S) = C(p_{\text{O}_2}/p_{\text{S}_2})^{1/2} \quad (10)$$

Where C is a constant which contains the activity of O^{2-} . In the event that $a_{\text{O}^{2-}}$ in the slag equilibrating with a given matte is constant against p_{SO_2} , the solubility of sulfur does not change with p_{SO_2} because the sulfur-oxygen pressure ratio is constant, as was clarified in the present study. As shown in Fig. 5, the present experimental results for the behavior of sulfur solubility against p_{SO_2} are accordant with this prediction.

Finally, the influence of p_{SO_2} on $\% \text{Fe}^{3+} / \% \text{Fe}^{2+}$ in the slag is briefly discussed. As shown in Fig. 7, Fe^{2+} is predominant over Fe^{3+} in the range of low matte grade. The dissolution of sulfur in the slag as the FeS component may be partly described to the abundance of Fe^{2+} in this region. On the other hand, the proportion of Fe^{3+} increases abruptly in the range of high matte grade, and it is considered that $(\% \text{Fe}^{3+} / \% \text{Fe}^{2+})$ is mainly governed by the following equation because the dissolution of sulfur in the slag is not considerable in this region.

Reaction (11) leads to a prediction that $(\% \text{Fe}^{3+} / \% \text{Fe}^{2+})$ increases with p_{O_2} , in other word, p_{SO_2} at a given matte grade, provided that this ratio is approximately proportional to the activity ratio, $(a_{\text{FeO}_{1.5}}/a_{\text{FeO}})$. In the present results shown in Fig. 7, $(\% \text{Fe}^{3+} / \% \text{Fe}^{2+})$ has a tendency to increase with p_{SO_2} in the region of high matte grade.

V. Conclusion

Phase equilibria between the copper matte and calcium ferrite slag were investigated at 1523 K under high partial pressures of SO_2 as a fundamental study for thermodynamically discussing some oxygen-smelting processes to produce copper. The partial pressures of S_2 and O_2 over the slag/matte and mutual dissolutions of Cu, S and Ca components as well as $\% \text{Fe}^{3+} / \% \text{Fe}^{2+}$ in the slag were determined at 1523 K at $p_{\text{SO}_2} = 10.1, 50.7$ and 101.3 kPa, in relation to the matte grade. The copper and sulfur solubilities in the slag were found to be independent of p_{SO_2} when the matte grade was specified, and it was clarified thermodynamically that this behavior was ascribed to the constancy of $(p_{\text{O}_2}/p_{\text{S}_2})$ against p_{SO_2} at a given matte. It was found that the solubility of sulfur in the slag decreased with increasing matte grade, while the solubility of copper represented the minimum at about 72.5% Cu

grade. The behavior of copper solubility against the matte grade was analyzed thermodynamically using a concept of the oxidic and sulfidic dissolutions. Owing to a remarkable mutual dissolution between the calcium ferrite slag and copper matte phases, the slag/matte separation did not occur in the range of low matte grade and it was found that the matte grade initiating the phase separation shifts towards the higher value with increasing p_{SO_2} . Although this phenomenon seems interesting both in terms of matte and slag and practical operations, a thoughtful discussion will be required to explain it reasonably.

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