Oxidative Removal of Cu from Carbon-saturated Iron *via* Ag Phase into B₂O₃ Flux

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The oxidative removal of Cu from carbon-saturated iron *via* the Ag phase into B₂O₃ flux was attempted at 1523 K. The Cu content was reduced from 4 to below 0.2 mass%, and Cu in the molten iron could be removed into the B₂O₃ flux by the method proposed in this study. Furthermore, the Cu distribution ratio between the B₂O₃ flux and Ag, $L_{\text{Cu(flux-Ag)}} (= [\text{mass\% Cu}]_{(\text{in flux})} / [\text{mass\% Cu}]_{(\text{in Ag})}$) and the activity coefficients of Cu₂O in the B₂O₃ flux, $\gamma_{\text{Cu}_2\text{O}(\text{in flux})}$, owing to the oxygen partial pressure were measured. The greatest value of $L_{\text{Cu(flux-Ag)}}$ was found to be 17 at 0.6 atm of oxygen partial pressure. Using this value, the distribution ratio of Cu between the B₂O₃ flux and carbon-saturated iron is calculated to be 120 at 1523 K. To predict the behavior of solute elements in the Ag phase, a numerical calculation of mass transfer based on Fick's second law is performed and the optimum execution method of oxidative removal of Cu is discussed.

KEY WORDS: tramp element; copper; silver; boron oxide; iron scrap; oxidation; recycle.

1. Introduction

In Japan, approximately 30 million tons of waste steel scrap is purchased each year and it is estimated that approximately 3 million tons thereof is exported.¹⁾ Almost all of the iron ore and coal used in Japan is imported and so, waste scrap is a valuable iron source and should be recycled as far as possible. Furthermore, recycling the thermochemically-reduced steel scrap reduces carbon dioxide emissions. However, waste steel scrap contains large amounts of Cu and Sn, which are deleterious elements in steel-making and cannot be removed by oxidizing-refining in a conventional steel-making process. Therefore, these elements accumulate in the molten iron and become a major problem in recycling steel scrap with Cu being the most troublesome element. The amount of available waste steel scrap with low Cu content is declining and such scrap is difficult to recycle without diluting the Cu content with pig iron. Therefore, the establishment of an industrial method for removing Cu from iron is on urgent necessity.

Cu attached to steel can be removed by advanced magnetic separation after shredding or Cu dissolution into a solvent such as molten Al²⁻⁴⁾ or aqueous NH₃ solution.⁵⁾ However, complete separation of the Cu from the steel is difficult in reality and the dissolution of some of the Cu into the molten iron is unavoidable.

The liquid phase of the Fe–Cu binary system is miscible over the whole composition range. It has been reported that the liquid separates into Fe- and Cu-rich phases by adding C^{6,7)} and B.⁸⁾ However, the Cu content of the Fe-rich phase is approximately 5 mass% and it is difficult to use this Fe-rich phase as an iron source. On the other hand, using the

immiscibility of Ag and Pb in Fe, the distribution of Cu between the Fe and Ag (Pb) phases and reduction of the Cu content of the Fe phase has been achieved.⁷⁾ However, because the distribution ratio of Cu between Ag (Pb) and Fe is insufficient, the quantity of Ag (Pb) necessary for this removal treatment is large and this method is not economically viable. We have attempted the oxidative removal of Cu⁹⁾ and Sn¹⁰⁾ from Fe–C(satd.) *via* Ag, and the Cu and Sn contents of the Fe–C(satd.) have been decreased to 0.4 mass% and below 0.001 mass%, respectively. The lower limit of Cu in the Fe–C(satd.) can be decreased by dissolving Cu oxide into the oxide flux and decreasing the Cu oxide activity. Therefore, designing the oxide flux with a strong affinity for the Cu oxide is important. In this work, the activity coefficient of Cu₂O in the B₂O₃ flux is measured. In addition, the oxidative removal of Cu from the Fe–C(satd.) *via* the Ag phase into the B₂O₃ flux is performed at 1523 K.

2. Principle

2.1. Oxidative Removal of Cu from Molten Iron *via* Ag

Oxidative refining does not apply to the removal of Cu because the Gibbs free energy of forming Cu oxide is higher than that of Fe. In this work, Ag is used as a solvent for Cu because Ag and Fe are immiscible and Cu is more easily oxidized than Ag. A schematic diagram of the oxidative removal of Cu from iron is shown in Fig. 1. The distribution of Cu between Fe–C (satd.) and Ag is expressed as shown in Eq. (1):

$$\frac{\text{Cu}_{(\text{in Fe-C})}}{\text{Cu}_{(\text{in Ag})}} = \dots\dots\dots (1)$$

The oxidation reaction of Cu in the Ag is expressed as

Fig. 1. Oxidative removal of Cu into oxide flux via Ag phase.

shown in Eq. (2):

By combining Eqs. (1) and (2), Eq. (3) is obtained and the oxidative removal of Cu from molten iron is possible without oxidation of the Fe–C(satd.). The Cu content of the Fe–C(satd.) is calculated from the equilibrium relation of Eq. (3) and is shown in Eq. (4)

$$N_{\text{Cu}(\text{in Fe-C})} = \frac{a_{\text{Cu}_2\text{O}}^{1/2}}{\gamma_{\text{Cu}(\text{in Fe-C})}^\circ K_{(3)} p_{\text{O}_2}^{1/4}} \quad \text{..... (4)}$$

where $N_{i(\text{in } j)}$, $K_{(3)}$, $\gamma_{i(\text{in } j)}^\circ$, p_{O_2} and a_i are the mole fraction of i in j , the equilibrium constant of Eq. (3) ($= 102.3$),¹¹⁾ the activity coefficient of i in j at infinite dilution in the pure substance reference, the partial pressure of oxygen and the activity of i in the pure substance reference, respectively. By substituting for $\gamma_{\text{Cu}(\text{in Fe-C})}^\circ (= 50.2)$,⁹⁾ $p_{\text{O}_2} (= 1 \text{ atm})$ and $a_{\text{Cu}_2\text{O}} (= 1)$, $N_{\text{Cu}(\text{in Fe-C})}$ is calculated to be 1.96×10^{-3} (0.26 mass%) and this value is the lower limit of Cu. In Eq. (4), the Cu content of the Fe–C(satd.) can be decreased by decreasing $a_{\text{Cu}_2\text{O}}$. Besides, the oxide flux, which is melted at the operating temperature and has a strong affinity for Cu_2O , should be selected for decreasing $a_{\text{Cu}_2\text{O}}$ effectively.

Morinaga *et al.*¹²⁾ regarded the basicity of slag as the quantity which was proportional to the reciprocal of the coulomb force between cation and oxide ion and proposed the basicity parameter, B , as shown in Eq. (5)

$$B'_i = \left[\frac{z_i \times 2}{(r_i + 1.40)^2} \right]^{-1}$$

$$B_i = \frac{B'_i - B'_{\text{SiO}_2}}{B'_{\text{CaO}} - B'_{\text{SiO}_2}} \quad \text{..... (5)}$$

$$B = \sum_i n_i B_i$$

where z_i , r_i and n_i are electrical charge, ion radius (Å) and ratio of composition of cation i , respectively. Values of the basicity parameter, B , of representative oxides based on Eq. (5) are shown in Table 1. In Table 1, oxides with large basicity parameter B are strongly basic. Because Cu_2O is classified as a basic oxide as shown in Table 1, oxides such as B_2O_3 and SiO_2 which are classified as acidic oxides seem to have a large Cu capacity.

Table 1. Values of the basicity parameter, B , of representative oxides.

Oxide	B
K_2O	3.381
Na_2O	2.349
Cu_2O	2.326
Li_2O	1.719
BaO	1.561
PbO	1.307
SrO	1.269
CaO	1.000
SnO	0.931
FeO	0.723
ZnO	0.723
CuO	0.703
MgO	0.641
Bi_2O_3	0.512
Fe_2O_3	0.282
Ga_2O_3	0.269
Al_2O_3	0.198
ZrO_2	0.190
SnO_2	0.148
TiO_2	0.133
TeO_2	0.078
GeO_2	0.045
B_2O_3	0.026
SiO_2	0.000
P_2O_5	−0.103

Fig. 2. Activity curve of Cu_2O – B_2O_3 system calculated by FactSage 6.1 at 1 523 K.

The melting point of B_2O_3 is 753K and the B_2O_3 is liquid at the experimental temperatures of this work at 1 523 K. The activity curve of the B_2O_3 – Cu_2O system calculated using FactSage 6.1 at 1 523 K is shown in Fig. 2. The B_2O_3 – Cu_2O system has a negative bias and the B_2O_3 is expected to have a large Cu capacity.

In this work, the activity coefficient of Cu_2O in the B_2O_3 flux, $\gamma_{\text{Cu}_2\text{O}(\text{in flux})}$, is measured to determine the Cu capacity. Besides, the oxidative removal of Cu from the Fe–C(satd.) via Ag into the B_2O_3 flux is attempted. The necessary quantity of Ag is low in principle because Ag is used for the distribution of Cu between the Fe–C(satd.) and Ag and as a

solvent for the oxidative removal of Cu.

Carbon plays an important role in lowering the melting point of iron and raising the distribution ratio of Cu between the Fe and Ag.

3. Experimental

The experimental apparatus consisted of a mullite tube (70 mm outer diameter, 60 mm inner diameter, 1 000 mm length) and vertical MoSi₂ electric resistance furnace connected to a proportional integral derivative action controller with a Pt–6%Rh/Pt–30%Rh thermocouple.

3.1. Measurement of the Activity Coefficient of Cu₂O in the B₂O₃ Flux

The experimental conditions are shown in **Table 2**. Ten grams of reagent grade Ag (purity: 99.9%), 0.20–0.22 g of reagent grade Cu (purity: 99%) and reagent grade B₂O₃ (purity: 99.9%) were charged in an alumina crucible (38 mm outer diameter, 45 mm height, 30 cm³ capacity). The crucible was inserted into an alumina holder (52 mm outer diameter, 42 mm inner diameter, 100 mm height) and the samples were melted in a furnace under argon atmosphere at 1 523 K. After the sample had melted, the mixed oxygen and argon gas (total flow: 150 cm³/min (STP), p_{O_2} : 0.1–1 atm) was blown onto the Ag–Cu alloy from 20 mm above the sample for over 1–12 h to attain equilibrium. The alumina holder was withdrawn from the furnace, and the sample was quenched rapidly under argon gas flow. The Cu content of the Ag and the Ag, Cu, Al and B contents of the flux were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

3.2. Oxidative Removal of Cu from Carbon-saturated Iron via Ag Phase into B₂O₃ Flux

The alumina crucibles and tubes shown in **Figs. 3(a)** (Run 9), **3(b)** (Runs 10–17) were used in the experiment with experimental conditions shown in **Table 3**. Runs 9–11 were performed without B₂O₃. The B₂O₃ and B₂O₃–Al₂O₃–Ag₂O fluxes used for the experiments were made in advance in the following manner and the compositions of these fluxes were analyzed by ICP-AES:

(1) B₂O₃ flux: the reagent B₂O₃ contained in an alumina crucible (38 mm outer diameter, 45 mm height, 30 cm³ capacity) was inserted into the furnace at 1 523 K under an

argon atmosphere for 3 h. The Al₂O₃ content of the flux was 0.4 mass% and this value is lower than the solubility from the phase diagram of the B₂O₃–Al₂O₃ system (approximately 4 mass%).¹³⁾

(2) B₂O₃–Al₂O₃–Ag₂O flux: the reagent B₂O₃ and sufficient mass of Ag reagent were contained in the alumina crucible (38 mm outer diameter, 45 mm height, 30 cm³ capacity) and inserted into the furnace at 1 523 K under an argon atmosphere and the B₂O₃ and Ag were pre-melted. An alumina tube (3 mm outer diameter, 2 mm inner diameter) was inserted in the melt and oxygen gas (150 cm³/min (STP)) was blown into the melts for 1.5 h. The B₂O₃–6–7 mass%Al₂O₃–15 mass%Ag₂O was obtained.

A small path was made at the lowest point of the alumina tube (21 mm outer diameter, 16 mm inner diameter, 50 mm length), and the tube was set in the alumina crucible as shown in **Figs. 3(a)** and **3(b)**. The reagents Ag and Cu were weighed and placed in and outside the alumina tube. A graphite tube was inserted into the alumina tube, and the prepared Fe–4 mass% Cu–C(satd.) alloy was placed in the graphite tube. A graphite lid was placed on the graphite tube and the alumina tube was sealed with an alumina lid and cement. The alumina crucible was placed in an alumina holder (52 mm outer diameter, 42 mm inner diameter, 100 mm height) and inserted into the furnace under an argon atmosphere (100 cm³/min (STP)) at room temperature. The furnace was heated to 1 523 K for 2.5 h. For Run 11 shown in **Fig. 3(b)**, oxygen gas (15 cm³/min (STP)) was blown into the Ag from the alumina tube (3 mm outer diameter, 2 mm inner diameter) for 0.5 h. For Runs 12–17, oxygen gas (150 cm³/min (STP)) was blown onto the Ag from the alumina tube which was set approximately 40 mm above the metal surface, as shown in **Fig. 3(b)**. For Runs 9–13, the samples were pre-melted at 1 373 K under an argon atmo-

Fig. 3. Schematic cross section of the crucible.

Table 2. Experimental conditions for the measurement of the activity coefficient of Cu₂O.

No.	Initial mass of reagent (g)			Time (h)	p_{O_2} (atm)
	Ag	Cu	B ₂ O ₃		
1	10	0.20	0.45	6	0.1
2	10	0.20	0.50	6	0.4
3	10	0.20	0.50	6	0.6
4	10	0.21	0.46	6	0.6
5	10	0.21	0.51	1	1
6	10	0.20	0.46	6	1
7	10	0.22	0.50	12	1
8	10	0.22	0.97	12	1

Table 3. Experimental conditions of oxidative removal of Cu into B₂O₃ flux via Ag.

No.	Flux	Ag (g)	Cu (g)	Fe alloy (g)	[mass% Cu] (in Fe)	Flux (g)	p_{O_2} (atm)	Time (h)	Flow rate (cm ³ /min)
9		30	0.61	9.9	3.0			7	15
10	–	65	2.0	7.4	3.0	–	1	0.25	100
11		65	2.0	7.7	3.9			0.5	15
12	B ₂ O ₃ –Al ₂ O ₃	60	0.55	8.0	3.9	3.5	1	3	150
13		60	0.17	8.0	3.9	3.6		3	
14		59	0.55	7.9	3.9	6.0		1	
15	B ₂ O ₃ –Al ₂ O ₃ –Ag ₂ O	60	1.0	7.9	3.9	3.5	1	3	150
16		59	0.56	7.9	3.9	6.0		1	
17		60	1.0	7.8	3.9	3.7		3.5	

Table 4. Experimental results from the measurement of the activity coefficient of Cu_2O .

No.	In Ag (mass%)	In oxide flux (mass%)					Flux composition (mole fraction)				$\gamma_{\text{Cu}_2\text{O}}$
	Cu	Cu	Ag	Al	B	$L_{\text{Cu (flux-Ag)}}$	$N_{\text{Cu}_2\text{O}}$	$N_{\text{Ag}_2\text{O}}$	$N_{\text{Al}_2\text{O}_3}$	$N_{\text{B}_2\text{O}_3}$	
1	0.779	7.1	26.6	8.5	7.22	9.1	0.084	0.184	0.234	0.498	0.676
2	0.543	7.3	35.4	9.9	7.66	13.4	0.076	0.216	0.242	0.467	0.729
3	0.475	8.0	38.1	10.1	7.45	16.8	0.082	0.229	0.242	0.447	0.634
4	0.492	7.6	39.3	9.9	7.53	15.4	0.077	0.236	0.236	0.451	0.719
5	0.499	7.5	39.0	9.3	7.19	15.1	0.079	0.242	0.232	0.447	0.927
6	0.537	8.0	40.5	10.5	4.08	14.8	0.099	0.297	0.306	0.298	0.861
7	0.638	8.3	38.6	10.8	3.63	13.0	0.106	0.292	0.327	0.275	1.128
8	0.352	5.1	41.7	10.8	4.79	14.6	0.062	0.295	0.306	0.338	0.595

Fig. 4. Determination of equilibration time.

sphere (100 cm³/min (STP)) for 0.5 h to melt the Ag–Cu alloy and the furnace was heated to 1523 K and held for 0.5 h to distribute Cu between the Fe–C(satd.) and Ag. Thereafter, oxygen gas was blown onto the flux.

The alumina holder was withdrawn from the furnace, and the sample was quenched rapidly under argon. The Cu content of the Ag, the Cu and Ag contents of the Fe–C(satd.) and the Cu, Ag, Al and B contents of the flux were analyzed by ICP-AES. The powder X-ray diffraction spectrum of the oxides which were formed at the path in Run 9 was performed. Analysis of the Ag both inside and outside the alumina tube was performed separately. In this work, the C content of the Fe–C(satd.) was approximately 4.5 mass%.⁹⁾

4. Results

4.1. Measurement of the Activity Coefficient of Cu_2O in the B_2O_3 Flux

The experimental results are shown in **Table 4**. The mole fraction of each oxide is calculated assuming the component oxides are B_2O_3 , Cu_2O , Al_2O_3 and Ag_2O . The distribution ratio of Cu between the i and j phases is defined by $L_{\text{Cu}(i-j)} (= [\text{mass}\% \text{Cu}]_{(\text{in } i)} / [\text{mass}\% \text{Cu}]_{(\text{in } j)})$. In previous work, the Cu content of the Ag was measured to be approximately 1.5 mass%, measured without oxide flux in an oxygen atmosphere (1 atm) at 1523 K.⁹⁾ In contrast with previous work, the Cu content of the Ag of this work (Runs 1–8) is measured to be below 1.5 mass% which shows that the B_2O_3 flux has an absorption capacity for Cu_2O . The relationship between the holding time and Cu content of the Ag is shown in **Fig. 4** for the experiments performed in oxygen atmosphere (1 atm) and for the same initial mass ratio between

Fig. 5. Relationship between oxygen partial pressure and Cu content of Ag and flux.

Fig. 6. Change of distribution ratio owing to oxygen partial pressure.

Fig. 7. Oxidation of Ag into the B_2O_3 flux.

B_2O_3 and Cu (approximately 2). As shown in **Fig. 4**, the Cu content of the Ag reaches a constant value after approximately 1 h. Therefore, the equilibration time is determined to be less than 1 h and the other experiments were performed for longer than 6 h to give sufficient time for equil-

Table 5. Experimental results of the oxidative removal of Cu into B₂O₃ flux via Ag.

No.	Before oxidation (calc.) (mass%)		Experimental result (mass%)									$L_{\text{Cu(Ag-Fe)}}$	
	In Ag	In Fe	In Ag		In Fe		In B ₂ O ₃						
	Cu		Cu (outer)	Cu (innner)	Cu	Ag	Cu	Ag	B	Fe	Al	(outer)	(inner)
9	2.92	0.41	2.75	1.61	0.38	0.08						4.2	7.2
10	3.27	0.46	—	—	—	—			—			—	—
11	3.53	0.49	3.22	3.12	0.47	0.06						6.6	6.9
12	1.40	0.20	1.47	1.37	0.18	0.06	0.068	0.193	30.6	0.51	1.46	8.3	7.0
13	0.79	0.11	0.81	0.78	0.11	0.07	0.044	0.151	32.1	0.49	1.46	7.3	7.1
14	1.48	0.21	1.25	1.36	0.19	0.06	1.73	17.9	20.0	0.19	9.46	6.5	6.6
15	2.13	0.30	1.72	—	0.29	0.09	6.89	25.2	14.4	1.71	10.7	6.0	—
16	1.49	0.21	1.37	—	0.20	0.07	0.98	9.81	21.1	4.61	9.71	7.0	—
17	2.11	0.30	1.71	—	0.41	0.12	2.08	3.77	10.3	27.4	11.6	4.1	—

Fig. 8. Powder X-ray diffraction spectrum of the oxides formed in Run 9.

ibration. For Runs 1–7, the relationship between p_{O_2} and the Cu content of the Ag and flux phases is shown in **Fig. 5**. The relationship between p_{O_2} and $L_{\text{Cu(flux-Ag)}}$ is shown in **Fig. 6**. p_{O_2} affects the Cu content of the Ag and the greatest value of $L_{\text{Cu(flux-Ag)}}$ is 17 at a partial oxygen pressure of 0.6 atm under the experimental conditions used in this work. The relationship between p_{O_2} and the Ag content of the flux is shown in **Fig. 7**. The Ag content of the flux rises with increase in p_{O_2} .

4.2. Oxidative Removal of Cu from Carbon-saturated Iron via Ag into B₂O₃ Flux

The experimental results are shown in **Table 5**. The Cu content of the Ag and Fe–C(satd.) before oxidation is calculated from the initial mass of Fe, Ag and Cu and $L_{\text{Cu(Ag-Fe)}}$ (=7.15).⁹⁾ In Runs 9 and 11, the Cu content of the Fe–C(satd.) and Ag are slightly lower than those before oxidation. In Run 10, the molten iron moves outside of the alumina tube and iron oxide is formed. In the experiments performed with B₂O₃–(Al₂O₃–Ag₂O) flux (Runs 12–17), the experimental results are classified into three types: (1) Both the Cu and Ag contents of the flux are low and the Cu content of the Fe–C(satd.) and Ag phases do not decrease (Runs 12 and 13), (2) The Cu is dissolved into the B₂O₃ flux and the Fe is not dissolved (Runs 14 and 15), (3) Both the Cu and Fe are dissolved into the B₂O₃ flux (Runs 16 and 17). For Runs 15–17, the Cu content of the Ag inside the alumina tube cannot be measured because there is an inadequate amount of the Ag phase present. From the result of Run 14, it has been clarified that the Cu content of the Fe–C(satd.)

can be decreased to below 0.2 mass% with the B₂O₃–Al₂O₃–Ag₂O flux.

In Run 9, the Cu content of the Ag inside and outside the alumina tube differs, and the distribution ratio of the Cu between the Ag inside the alumina tube and the Fe phases, $L_{\text{Cu(Ag(inside)-Fe)}}$, corresponds to the equilibrium value. The powder X-ray diffraction spectrum of the oxides formed at the path in Run 9 is shown in **Fig. 8**. FeAl₂O₄ is identified and it separates from the Ag phase at the path.

5. Discussion

5.1. Activity Coefficients of Cu₂O and Ag₂O in the B₂O₃ Flux

The activity coefficient of the Cu₂O in the flux, $\gamma_{\text{Cu}_2\text{O(in flux)}}$, is shown in Eq. (7) based on the equilibrium of Eq. (6).

$$\gamma_{\text{Cu}_2\text{O(in flux)}} = \frac{\gamma_{\text{Cu(in Ag)}}^2 N_{\text{Cu(in Ag)}}^2 p_{\text{O}_2}^{1/2} K_{(6)}}{N_{\text{Cu}_2\text{O(in flux)}}} \quad \text{..... (7)}$$

The value of the $\gamma_{\text{Cu}_2\text{O(in flux)}}$ is calculated by substituting $K_{(6)}$ (=102.3),¹¹⁾ $\gamma_{\text{Cu(in Ag)}}^{\circ}$ (=3.14)¹⁴⁾ and the experimental conditions and results into Eq. (7). The relationship between $N_{\text{B}_2\text{O}_3\text{(in flux)}}$ and $\gamma_{\text{Cu}_2\text{O(in flux)}}$ is shown in **Fig. 9**. $\gamma_{\text{Cu}_2\text{O(in flux)}}$ decreases owing to the increase in $N_{\text{B}_2\text{O}_3\text{(in flux)}}$. From the results, the B₂O₃ flux has an affinity for Cu₂O and it is possible to remove the Cu into the B₂O₃ flux.

The distribution ratio of Cu between the flux and molten iron, $L_{\text{Cu(flux-Fe)}}$, is expressed as a product of $L_{\text{Cu(flux-Ag)}}$ and $L_{\text{Cu(Ag-Fe)}}$. The value of $L_{\text{Cu(Ag-Fe)}}$ measured in previous work is 7.15⁹⁾ in the region of the dilute solution. From this work, the largest value of $L_{\text{Cu(flux-Ag)}}$ is 17 at a partial oxygen pressure of 0.6 atm under these experimental conditions and $L_{\text{Cu(flux-Fe)}}$ is estimated to be up to approximately 120.

On the other hand, the oxidation of Ag is expressed as follows.¹¹⁾

$$\Delta G_{(8)}^{\circ} = -53\,100 + 84.1T \text{ (J/mol)} \quad \text{..... (9)}$$

Because pure Ag₂O is decomposed entirely at 1 523 K, the standard of activity is selected as solid Ag₂O as was used

Fig. 9. Relationship between $N_{B_2O_3}(\text{in flux})$ and $\gamma_{Cu_2O}(\text{in flux})$ at 1523 K.

Fig. 10. Relationship between $N_{B_2O_3}(\text{in flux})$ and $\gamma_{Ag_2O}(\text{in flux})$ at 1523 K.

by Wakasugi *et al.*¹⁵⁾ a_{Ag_2O} is determined by the p_{O_2} because a_{Ag} is assumed to be nearly unity. Fig. 10 shows $\gamma_{Ag_2O}(\text{in flux})$ as a function of $N_{B_2O_3}(\text{in flux})$. The value of $\gamma_{Ag_2O}(\text{in flux})$ decreases owing to the increase in $N_{B_2O_3}(\text{in flux})$ and is smaller than that of $\gamma_{Cu_2O}(\text{in flux})$. The value of $\gamma_{Cu_2O}(\text{in flux})$ increases owing to the increase in p_{O_2} because the B_2O_3 content of the flux decreases as a result of the increase in $Ag(Ag_2O)$ content at high p_{O_2} , as shown in Fig. 7. As a result, there is an optimal p_{O_2} (0.6 atm) which maximizes the value of $L_{Cu(\text{flux-Ag})}$ as shown in Fig. 6.

5.2. Behavior of Solute Elements in the Oxidative Removal of Cu with B_2O_3 Flux

In Run 9, the Ag phase is separated at and around the path because the Fe and O in the Ag phase and the alumina react to form $FeAl_2O_4$. In Run 10, the experiment, of which the apparatus is shown in Fig. 3(b), is performed on condition that the path is widened sufficiently. As a result, molten iron is pushed from the inside to the exterior of the alumina tube. This is because the dissolved oxygen reaches the Fe–Ag interface, and the inner pressure of the alumina tube rises because of the CO gas generation. In Run 9, the molten iron is not pushed out of the tube because the transfer of oxygen inside the alumina tube is prevented. In a similar way, the distribution ratio of Cu between Fe–C(satd.) and Ag inside the alumina tube is equal to the equilibrium value (≈ 7.15)⁹⁾ because transfer of the Cu is also prevented. Therefore, control of the oxygen supply is important.

On the other hand, the B_2O_3 flux is expected to control the amount of oxygen transported in Runs 12 and 13. However, oxidation of the Cu in the Ag phase does not occur because the velocity of the oxygen solution into the flux is low. On the other hand, the Cu is dissolved into the flux in the experiment using the B_2O_3 – Al_2O_3 – Ag_2O flux whose

oxygen potential is high (Runs 14–17).

The cross sectional area at the path of Runs 16 and 17 is larger than that of Runs 14 and 15. As a result, the Cu and Ag are dissolved into the flux in Runs 14 and 15, and the Cu, Fe and Ag are dissolved into the flux in Runs 16 and 17. From the results, most of the Cu dissolved in the flux seems to be derived from the Cu in the Ag which exists in the initial stage before oxidation. In Runs 16 and 17, the Fe is oxidized *via* Ag into the flux because of the sufficient cross sectional area at the path. The behavior of the Fe, Cu and O in the Ag is discussed as described by numerical calculation in Section 5.3.

5.3. Behavior of Solute Elements as Described by Numerical Calculation

The diffusion coefficients of Cu, Fe and O in the Ag at 1523 K are 4.49×10^{-9} (m^2/s), 4.93×10^{-9} (m^2/s) and 1.76×10^{-8} (m^2/s), respectively.¹⁶⁾ The solubility of the oxygen in the Ag is 0.24 mass% at a partial oxygen pressure of 1 atm.¹⁷⁾

The one dimensional Ag phase whose length is 20 mm is defined for the calculation. The Fe–Ag interface and the Ag–flux interface are located at 0 and 20 mm, respectively. Initially, the behavior of the diffusion of Cu, Fe and O is calculated based on Fick's second law without consideration of the oxidative reaction. The calculation conditions are as follows:

- (1) At 0 mm, the mole fractions of Cu and Fe in the Ag are fixed at 0.05 and 0.0012 (3.0 mass% and 0.06 mass%), respectively.
- (2) At 0 mm, the mole fraction of O is fixed to be zero because the oxygen that reaches the Fe–Ag interface and carbon contained in the Fe–C(satd.) react and CO gas is generated.
- (3) At 20 mm, the mole fraction of Cu is fixed to be 0.0252 (1.5 mass%). This value is determined from previous work performed without oxide flux at a partial oxygen pressure of 1 atm.⁹⁾ The mole fraction of the Fe is fixed to be zero because the transported Fe is fully oxidized.
- (4) At 20 mm, the mole fraction of O is fixed to be 0.016 (0.24 mass%), which is the solubility of the oxygen in the Ag at a partial oxygen pressure of 1 atm.

The mole fractions of Cu, Fe and O are calculated based on these conditions and their steady states are shown in Fig. 11. Contents are expressed as mole fraction, N_i ($i = \text{Cu, Fe, O}$). The absolute quantity of Cu is larger than that of Fe. Therefore, the calculation is performed in consideration of the oxidative reaction of Cu and out of consideration of that of Fe. The calculation conditions are as follows:

- (1) Under the initial condition, the mole fraction of Cu over the whole position is 0.05.
- (2) The mole fraction of Cu at 0 mm is fixed at 0.05.
- (3) Under the initial conditions, the mole fractions of O at 20 mm and the other position are 0.016 and 0, respectively.
- (4) The Cu and O react immediately and the Cu_2O formed is removed from the system.
- (5) The lowering limit of Cu is 0.0252, which is the equilibrium value at a partial oxygen pressure of 1 atm.

Calculation result of the Cu and O mole fractions is shown in Fig. 12. The Cu content of the Ag decreases with time and reaches steady state in approximately 11 ks. The

Fig. 11. Diffusion of Cu, O and Fe disregarding the oxidative reaction.

Fig. 12. Diffusion of Cu and O including the oxidative reaction owing to diffusion time at 1523 K.

oxidative reaction occurs at a fixed position (4 mm), on condition that a stable supply of Cu and oxygen gas is provided and the length of the Ag phase is 20 mm. In a similar way, the O content increases with time, and the reaction achieves steady state for 11 ks. These results show that fixing the position of the oxidative reaction outside the alumina tube makes it possible to promote the oxidative reaction of Cu without reaching the oxygen at the Fe–Ag interface. The calculation results at steady state are shown in Fig. 13 where the initial mole fractions of Cu at the Fe–Ag interface are fixed to be 0.1, 0.05 and 0.04. The initial mole fraction of Cu in the Fe–Ag interface decreases, the position of the oxidative reaction gradually moves to the negative direction. When the Cu content of the Fe–C(satd.) becomes low, the Cu content of the Fe–Ag interface also becomes low and the oxygen gets close to the Fe–Ag interface. When the Cu content of the Fe–C(satd.) and Ag phases reaches equilibrium, transportation of the Cu appears to cease. As a result, oxygen dissolved in the Ag reaches the Fe–Ag interface and CO gas appears to be generated. In fact, oxygen reaches the Fe–Ag interface and CO gas is generated before the Cu content reaches equilibrium in Runs 15–17. Because of the generation of the CO gas, part of the Ag inside the alumina tube appears to be pushed out of the alumina tube in Run 15, and part of the Fe and most of the Ag inside the alumina tube are pushed out in Runs 16 and 17. Besides, once the oxygen reaches inside the alumina tube, the formed Fe and Cu oxides appear to reach the Fe–Ag interface and are reduced by carbon. Therefore, only the decarburization reaction

Fig. 13. Relationship between Cu and O contents in the Ag phase owing to initial Cu content.

Fig. 14. Oxidation of Cu where the lower limit of Cu is decreased by oxide flux at 1523 K.

appears to occur. Under the experimental conditions of this work, oxygen will easily reach the inside of the alumina tube because the Cu content of the Fe–C(satd.) before oxidative removal is close to the lower limit (0.26 mass%) and the amount of Cu which moves from the Fe–C(satd.) to the Ag phases is low. Based on this discussion, it is possible to increase the driving force of the distribution of Cu by decreasing the value of $a_{\text{Cu}_2\text{O}}$ with the oxide flux. The calculation result is shown in Fig. 14 when the lower limit of Cu in the Ag decreases to 0.01 (0.6 mass%) using the oxide flux. The value of $a_{\text{Cu}_2\text{O}}$ is calculated to be 0.10 under this condition. Other calculating conditions are the same as the calculation in Fig. 12(b). As a result, the time to achieve steady state is 17 ks and the reaction position is 5 mm. By comparison of Fig. 14 with Fig. 12(b), the reaction position moves towards the Ag-flux interface by 1 mm and the time to reach steady state becomes long because the amount of reactive Cu increases. From the comparison, using the oxide flux for Cu removal seems to be effective in inhibiting the movement of oxygen into the alumina tube.

Based on this discussion, the methods for promoting effective Cu removal appear to be as follows:

(1) To decrease the lower limit of Cu with the oxide flux to allow for the oxidative reaction to occur outside the alumina tube,

(2) To move the reaction position of Cu and O close to the Ag-flux interface by stirring the Ag phase between the Fe–Ag interface and the reaction position or by stopping the oxygen supply temporarily for the enhancement of the distribution of Cu.

6. Conclusion

Measurement of the activity coefficient of Cu_2O in the B_2O_3 flux and the oxidative removal of Cu from the Fe–C(satd.) *via* Ag into the B_2O_3 flux were performed at 1523K for the removal of Cu dissolved in molten iron. The conclusions are as follows:

(1) The B_2O_3 flux has a large capacity for Cu because it decreases $\gamma_{\text{Cu}_2\text{O}(\text{in flux})}$. Not only Cu but also Ag is dissolved in the flux as an oxide and this provides the most suitable partial oxygen pressure for the treatment. Under this experimental condition, the largest value of $L_{\text{Cu}(\text{flux-Ag})}$ is 17 at an oxygen partial pressure of 0.6 atm. The value of $L_{\text{Cu}(\text{flux-Fe})}$ is estimated to be approximately 120 from the value of $L_{\text{Cu}(\text{flux-Ag})}$ and $L_{\text{Cu}(\text{Fe-Ag})}$.

(2) From the oxidative removal of Cu from the Fe–C(satd.) *via* Ag into the B_2O_3 flux, the Cu in the metal is dissolved into the flux by using the B_2O_3 – Al_2O_3 – Ag_2O flux.

(3) From the numerical calculation, controlling the rate of oxygen supply, stirring the Ag phase inside the alumina tube and decreasing the lower limit of Cu with the oxide flux are required for the continuous oxidative removal of Cu.

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