Liquid Immiscibility of Fe-Ag-Cu-B System

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Abstract

The equilibration experiments of the Fe-Ag-Cu-B system were performed at 1873 K and 1523 K, and the distribution ratio of Cu between Fe-B and Ag phases was measured. As the B content of the Fe-B phase increases, the distribution ratio of Cu, \( L_{Cu} \), increases. \( L_{Cu} \) becomes constant in the region of \([\text{mass\%B}]_{\text{Fe}}=3.96\) at 1873 K. The value of \( L_{Cu} \) is determined to be approximately 6 at \([\text{mass\%B}]_{\text{Fe}}=3\) in the region of \([\text{mass\%Cu}]_{\text{Fe}}<0.73\) at 1523 K. The first order interaction parameter of Cu and B in the Fe phase at 1523 K, \( \varepsilon_{Cu B}^{1} \), is determined to be 4.6 (±0.7). The second order interaction parameter of Cu and B in the Fe phase at 1873 K, \( \varepsilon_{Cu B}^{2} \), is derived to be -33.3 (±3.1).

Key words

Thermodynamics, Iron, Copper, Iron Scrap, Boron, Recycle

1. Introduction

From the view point of preventing the resource depletion and preserving the environment, the recycling of iron and steel scrap is important. In particular, the recycling contributes to the reduction of carbon dioxide emissions from iron- and steel-making processes. However, it is difficult to recycle the scrap containing larger amounts of tramp elements, such as copper and tin, which cannot be removed by oxidizing refining in a conventional steelmaking process. For this reason, in order to investigate the possibility of removing copper, the thermodynamic data of the system involving Fe and Cu are important.

The liquid phase of the Fe-Cu binary system is miscible over the whole composition range. It has been reported that it separates into the Fe- and Cu-rich phases by adding C[1-3], Si[4], P[5] or B[6, 7]. The recovery of iron and copper from the Fe-Cu-B alloy has been discussed by adding C[1-3], Si[4], P[5] or B[6, 7]. The recovery of iron and copper from the Fe-Cu-B alloy has been discussed by adding C[1-3], Si[4], P[5] or B[6, 7]. The recovery of iron and copper from the Fe-Cu-B alloy has been discussed by adding C[1-3], Si[4], P[5] or B[6, 7]. The recovery of iron and copper from the Fe-Cu-B alloy has been discussed by adding C[1-3], Si[4], P[5] or B[6, 7]. The recovery of iron and copper from the Fe-Cu-B alloy has been discussed by adding C[1-3], Si[4], P[5] or B[6, 7]. The recovery of iron and copper from the Fe-Cu-B alloy has been discussed by adding C[1-3], Si[4], P[5] or B[6, 7]. The recovery of iron and copper from the Fe-Cu-B alloy has been discussed by adding C[1-3], Si[4], P[5] or B[6, 7].

On the other hand, the distribution of Cu between carbon saturated iron and Ag[9] or Pb[3], which was immiscible with iron, was performed. It is possible to decrease Cu content of the Fe-C phase because the solvent, such as Ag and Pb, lowers the Cu activity, and carbon in the Fe-C phase contributes to increasing the distribution ratio of Cu[9]. The distribution ratio of Cu in the Fe-Ag system is higher than that in the Fe-Pb[3]. Boron is also considered to be effective to increase the distribution ratio of Cu between the Fe-B and Ag phases. In this work, the equilibration experiments of the Fe-Ag-Cu-B system are performed at 1873 K and 1523 K, and the effect of boron in the Fe-B phase on the distribution ratio of Cu is investigated.

2. Experimental

The Fe-5.0mass%B alloy was prepared as follows: high purity electrolytic iron and reagent grade boron (purity: 99.8%) were charged in an alumina crucible and were melted at 1873 K in an Ar-10vol%H\(_2\) atmosphere using an induction furnace. The experimental apparatus consisted of a mullite tube (60 mm outer diameter, 52 mm inner diameter, 1000 mm length) and a vertical MoSi\(_2\) electric resistance furnace, which was connected to a proportional integral derivative (PID) action controller with a Pt-6%Rh/Pt-30%Rh thermocouple. Totally 10 g of the electrolytic iron and the resultant Fe-5.0 mass%B alloy, 10 g of reagent grade silver (purity: 99.9%) and 0.1-1 g of reagent grade copper (purity: 99%) were charged in an alumina crucible (15 mm outer diameter, 12 mm inner diameter, 100 mm height). The alumina crucible was inserted into a graphite holder (42 mm outer diameter, 34 mm inner diameter, 150 mm height) and placed in the furnace under an argon atmosphere for over 5 h at 1873 K or 1523 K to attain the equilibrium of the Fe-B and Ag phases. The graphite holder was then withdrawn from the furnace, and the sample was rapidly quenched in an argon gas flow. The B, Cu and Ag contents of the Fe-B phase and the B, Fe and Cu contents of the Ag phase were analyzed by an inductively coupled plasma atomic emission spectrometry (ICP-AES). For the liquid-liquid equilibration of the Fe-B and Ag phases at 1523 K, over 3 mass% of the B was added in the Fe-B phase. In this work, a small amount of aluminum from the alumina crucible may dissolve in the iron. However, the effect of the aluminum in the iron is not taken into account as it is considered negligible as indicated by the results of several similar experiments[6, 10].

3. Results

The experimental results are shown in Table 1. Fig. 1 shows vertical sections of the samples for Runs 9 and 10 performed at 1523 K. In this system, liquid immiscibility of the Fe-B and Ag phases occurs clearly. In all samples, the B content of the Ag phase is less than 0.001 mass%. The Ag content of the Fe-B phase is relatively lower at 1523 K than that at 1873 K.
As the B content of the Fe-B phase increases at 1873 K, the Cu content of the Fe-B phase decreases but it does not decrease in the region of \([\text{mass}\%\text{B}]_{\text{in Fe}} > 3.96\).

Fig. 2 shows the relationship between B content of the Fe-B phase and the distribution ratio of Cu between the Fe-B and Ag phases, \(L_{\text{Cu}}\), when the initial Cu content of the system is fixed to be 3.2 mass% at 1873 K and 1523 K, where \(L_{\text{Cu}}\) is defined as follows:

\[
L_{\text{Cu}} = \frac{[\text{mass}\%\text{Cu} \text{Cu}]_{\text{in Ag}}}{[\text{mass}\%\text{Cu}]_{\text{in Fe}}} \quad (1)
\]

The \(L_{\text{Cu}}\) values at 1523 K are larger than those at 1873 K and both increase as the B content of the Fe-B phase increases. Fig. 3 shows the Cu content of the Fe-B and Ag phases at \([\text{mass}\%\text{B}]_{\text{in Fe}} \approx 3\) due to the initial mass of Cu at 1523 K. From the slope, the value of \(L_{\text{Cu}}\) is determined to be approximately 6 in the range of \([\text{mass}\%\text{Cu}]_{\text{in Fe}} < 0.73\). In the Fe-Cu-B system, the Cu content of the Fe-B phase was 4.6 mass% when the B content of the Fe-B phase was 2.9 mass%[6]. The Cu content of the Fe-B phase can reduce because the Cu activity lowers due to the distribution of Cu between the Fe-B and Ag phases.

### Table 1 Experimental results on Cu distribution between Fe and Ag phases at 1873 and 1523 K

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temperature (K)</th>
<th>Concentration (mass%)</th>
<th>Fe phase</th>
<th>Ag phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>B Cu Ag</td>
<td>B Cu Ag</td>
</tr>
<tr>
<td>1</td>
<td>1873</td>
<td>0.98 1.48 0.42</td>
<td>3.91 0.44</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1873</td>
<td>1.91 1.34 0.32</td>
<td>&lt;0.001 4.14 0.31</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1873</td>
<td>2.86 1.14 0.20</td>
<td>&lt;0.001 4.19 0.19</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1873</td>
<td>3.96 1.00 0.18</td>
<td>&lt;0.001 4.31 0.31</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1873</td>
<td>4.72 0.99 0.15</td>
<td>&lt;0.001 4.30 0.58</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1873</td>
<td>4.82 0.97 0.19</td>
<td>&lt;0.001 4.19 0.51</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1873</td>
<td>2.97 0.73 0.07</td>
<td>&lt;0.001 4.38 0.09</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1873</td>
<td>3.16 0.73 0.05</td>
<td>&lt;0.001 4.51 0.14</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1873</td>
<td>3.88 0.67 0.05</td>
<td>&lt;0.001 4.61 0.06</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1873</td>
<td>4.51 0.62 0.04</td>
<td>&lt;0.001 4.58 0.11</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1873</td>
<td>5.14 0.59 0.07</td>
<td>&lt;0.001 4.52 0.11</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1873</td>
<td>3.17 0.80 0.06</td>
<td>&lt;0.001 4.01 0.07</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1873</td>
<td>3.17 0.24 0.05</td>
<td>&lt;0.001 1.33 0.09</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1873</td>
<td>3.21 0.41 0.05</td>
<td>&lt;0.001 2.25 0.10</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1873</td>
<td>3.30 0.54 0.05</td>
<td>&lt;0.001 3.20 0.10</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>1873</td>
<td>3.16 0.87 0.07</td>
<td>&lt;0.001 4.38 0.09</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1 View of liquid immiscibility of the Fe-Cu-B-Ag system at 1523 K

**4. Discussion**

#### 4.1 Comparison of \(L_{\text{Cu}}\) in Fe-Ag-Cu-M system

The relationship between \(L_{\text{Cu}}\) and \([\text{mass}\%\text{M}]_{\text{in Fe}}\) in the Fe-Ag-Cu-M (M= B, C[9, 11], Si[9]) system is shown in Fig. 4. In Fig. 4, both of B and C are effective for the increase of \(L_{\text{Cu}}\), whereas the Si is not effective. It is difficult to conclude from Fig. 4 which B or C is more effective element for the removal of Cu in the Fe because the Cu content of the system is different each other in the experiments and because not only the M content but also the Cu content of the Fe-M phase has an effect on \(L_{\text{Cu}}\).

#### 4.2 Determination of interaction parameter between B and Cu in iron at 1523 K

The distribution of Cu between the Fe and Ag phases is represented as Eq.(2). \(M_{\text{in } i}\) shows the dissolution of element M in solvent i. The equilibrium relation is expressed by Eqs. (3) or (4) when the Raoultian standard state is taken for the M in the solvent i.
Fig. 4 Dependence of the distribution ratio of Cu, \( L_{\text{Cu}} \), on the M(=B, C, Si) content of the Fe phase

\[
\frac{[\text{Cu}]}{[\text{Fe}]} = \frac{\text{Cu}_{\text{in Fe}}}{\text{Cu}_{\text{in Ag}}}
\]

\( a_{\text{Cu}(\text{in Fe})} = a_{\text{Cu(\text{in Ag})}} \)

\[
\gamma_{\text{Cu(Fe)}} \gamma_{\text{Cu(Fe)}} = \gamma_{\text{Cu(Fe)}} \gamma_{\text{Cu(Fe)}}
\]

where \( \gamma_{\text{Cu(Fe)}} \) and \( \gamma_{\text{Cu(Fe)}} \) are the activity coefficient of Cu in the Fe phase at infinite dilution and the mole fraction of Cu in the Fe phase, respectively. Here, the Cu in the Ag phase is considered to be infinite dilution in this experimental condition because the distribution ratio of Cu between Ag and Fe-3 mass%B alloy is constant at [mass%Cu]_{\text{in Ag}} < 5 from Fig. 3. Accordingly, the activity coefficient of Cu in the Ag phase is set at infinite dilution. \( \gamma_{\text{Cu(Fe)}} \) in Eq.(4). On the other hand, the \( \gamma_{\text{Cu(Fe)}} \) is expressed as follows:

\[
\ln(\gamma_{\text{Cu(Fe)}}/\gamma_{\text{Cu(Fe)}}) = \varepsilon_{\text{Cu}} N_{\text{Cu(Fe)}} + \varepsilon_{\text{Cu}} N_{\text{B(Fe)}}
\]

where \( \varepsilon_{\text{Cu}} \) is the first order mole fraction interaction parameter of Cu for Ag in Eq.(5), the term related to Ag is ignored because the Ag content of the Fe-B phase is negligibly small. The distribution ratio of Cu expressed as molar fraction can be represented as Eq.(6) by substituting Eq.(4) into Eq.(5).

\[
\ln(\frac{N_{\text{Cu(Fe)}}/N_{\text{Cu(Fe)}}}{N_{\text{Cu(Fe)}}/N_{\text{Cu(Fe)}}}) = \frac{\varepsilon_{\text{Cu}} N_{\text{Cu(Fe)}} + \varepsilon_{\text{Cu}} N_{\text{B(Fe)}}}{\varepsilon_{\text{Cu}} N_{\text{Cu(Fe)}}} + \ln(\gamma_{\text{Cu(Fe)}}/\gamma_{\text{Cu(Fe)}})
\]

When the B content of the Fe-B phase is constant, Eqs.(7) and (8) are derived from Eq.(6).

\[
\ln(\frac{N_{\text{Cu(Fe)}}/N_{\text{Cu(Fe)}}}{N_{\text{Cu(Fe)}}/N_{\text{Cu(Fe)}}}) = \frac{\varepsilon_{\text{Cu}} N_{\text{Cu(Fe)}} + \varepsilon_{\text{Cu}} N_{\text{B(Fe)}}}{\varepsilon_{\text{Cu}} N_{\text{Cu(Fe)}}} + \ln(\gamma_{\text{Cu(Fe)}}/\gamma_{\text{Cu(Fe)}})
\]

\[
C_{\text{Cu}} = \frac{\varepsilon_{\text{Cu}} N_{\text{Cu(Fe)}} + \ln(\gamma_{\text{Cu(Fe)}}/\gamma_{\text{Cu(Fe)}})}{\varepsilon_{\text{Cu}} N_{\text{Cu(Fe)}}}
\]

Fig. 5 shows the relationship between \( N_{\text{Cu(Fe)}} \) and \( \ln(\frac{N_{\text{Cu(Fe)}}/N_{\text{Cu(Fe)}}}{N_{\text{Cu(Fe)}}/N_{\text{Cu(Fe)}}}) \) at 1523 K when \( N_{\text{B(Fe)}} \) is 0.14 (±0.01). As shown in Fig. 5, the first order self-interaction parameter of Cu, \( \varepsilon_{\text{Cu}} \), is determined to be 18.3(±16.1) from the slope of the regression line at 1523 K. The value of \( \varepsilon_{\text{Cu}} \) has a large margin of error.

When the change of the B content of the Fe-B phase is taken into account, Eqs.(9) and (10) are derived from Eq.(6).

\[
\ln(\frac{N_{\text{Cu(Fe)}}/N_{\text{Cu(Fe)}}}{N_{\text{Cu(Fe)}}/N_{\text{Cu(Fe)}}}) = \frac{\varepsilon_{\text{Cu}} N_{\text{Cu(Fe)}} + \varepsilon_{\text{Cu}} N_{\text{B(Fe)}}}{\varepsilon_{\text{Cu}} N_{\text{Cu(Fe)}}} + C_{\text{Cu}}
\]

\[
C_{\text{d}} = \ln(\gamma_{\text{Cu(Fe)}}/\gamma_{\text{Cu(Fe)}}) = \text{const.}
\]

The relationship between the left hand side of Eq.(9) and \( N_{\text{Cu(Fe)}} \) is shown in Fig. 6. Though the value of \( \varepsilon_{\text{Cu}} \) has a large margin of error, the effect of the error on the calculation of the left hand side of Eq.(9) is small because the Cu content of the Fe-B phase is low enough. The value of \( \varepsilon_{\text{Cu}} \) is determined to be 4.6(±0.7) from the slope of the regression line in the region of 0.14<\( N_{\text{B(Fe)}} <0.22 \). This value is smaller than that determined at 1873 K in our previous work[7], \( \varepsilon_{\text{Cu}} = 12.1 \). This is probably because the value of \( \varepsilon_{\text{Cu}} \) at 1523 K is determined by using only the data at higher B content to hold the liquid phase whereas that at 1873 K was determined at the wide B content range including the data at low B content.
4.3 Derivation of the second order interaction parameter of B for Cu at 1873 K

In the previous work[7], the interaction parameters of B for Cu, \( \rho_{B,Cu}^b = \rho_{B,Cu}^b = 12.1(\pm0.6) \) and \( \rho_{B,Cu}^b = -18.9(\pm11.0) \), were derived at 1873 K by combining the Taylor series equation proposed by Wagner[13] and that of the quadratic formalism proposed by Darken[14, 15], where \( \rho_i^j \) is the second order interaction parameter of \( i \) for \( j \), \( \rho_i^j \) is the second order interaction parameter of \( i \) and \( j \) for \( i \), respectively. However, the activity coefficient of Cu in the Fe-Cu-B system seems to have some error at high B content because of the large margin of error on \( \rho_{B,Cu}^b \). In this section, the value of \( \rho_{B,Cu}^b \) is revaluated by the experimental results in this work on the assumption that the values of \( \varepsilon_{Cu}^b \) and \( \rho_{Cu}^b \) are valid.

The activity coefficient of Cu in the Fe phase is expressed as follows:

\[
\ln(\gamma_{Cu(Fe)}/\gamma_{Cu(Fe)}) = \varepsilon_{Cu}^{N(Fe)} + \varepsilon_{Cu}^{B(Fe)} + \rho_{Cu}^{N(Fe)} + \rho_{Cu}^{N(Fe)}N_{B(Fe)}^{N(Fe)} N_{B(Fe)}^{N(Fe)} (11)
\]

The literature values are given as follows: \( \gamma_{Cu}^C = 8.58 \)[12], \( \varepsilon_{Cu}^b = -6.74 \)[16], \( \rho_{Cu}^b = 9.9 \)[16] and \( \rho_{Cu}^{b} = -12.1 \)[7]. The Cu activity is determined from the activity data on the Ag-Cu binary system[17] because the Fe and B contents of the Ag phase are negligibly small. Eq.(12) is obtained by transposing the terms of right hand side in Eq.(11) other than \( \rho_{Cu}^bN_{B(Fe)}^{N(Fe)} \) to left:

\[
\ln(\gamma_{Cu(Fe)}/\gamma_{Cu(Fe)}) - \varepsilon_{Cu}^{N(Fe)} - \varepsilon_{Cu}^{N(Fe)} - \varepsilon_{Cu}^{N(Fe)} - \varepsilon_{Cu}^{N(Fe)} - \varepsilon_{Cu}^{N(Fe)} - \varepsilon_{Cu}^{N(Fe)} = \rho_{Cu}^{b}N_{B(Fe)}^{N(Fe)} (12)
\]

Fig. 7 shows the relationship between the left hand side of Eq. (12) and the \( N_{B(Fe)}^{N(Fe)} \) at 1873 K. The value for \( \rho_{Cu}^{b} \) is derived to be \(-33.3(\pm3.1)\)\(N_{B(Fe)}^{N(Fe)}<0.34\) from the slope of the regression line in Fig. 7. In the previous work, Eq.(13) was used for determining the values of \( \varepsilon_{Cu}^{b} \) and \( \rho_{Cu}^{b} \).[7]

\[
\{\ln(\gamma_{Cu(Fe)}/\gamma_{Cu(Fe)}) - \varepsilon_{Cu}^{N(Fe)} - \varepsilon_{Cu}^{N(Fe)} - \varepsilon_{Cu}^{N(Fe)} - \varepsilon_{Cu}^{N(Fe)} - \varepsilon_{Cu}^{N(Fe)} - \varepsilon_{Cu}^{N(Fe)} \} = (1 - N_{Cu(Fe)}^{N(Fe)})/N_{B(Fe)}^{N(Fe)} \rho_{Cu}^b + \rho_{Cu}^b \]

Fig. 8 shows the relationship between the left hand side of Eq. (13) and the \((1 - N_{Cu(Fe)}^{N(Fe)})/N_{B(Fe)}^{N(Fe)} \), and the previous data[6, 7] are plotted in this figure. The \( \varepsilon_{Cu}^b = 12.1 \) and \( \rho_{Cu}^b = -33.3 \) are the slope and the intercept of the straight line in Fig. 8. The previous data can be reasonably explained by the re-derived \( \rho_{Cu}^b \).

5. Conclusions

Distribution ratio of Cu in the Fe-B and Ag phases in the Fe-Ag-Cu-B system was investigated at 1873 K and 1523 K; yielding the following conclusions:

(1) The distribution ratio of Cu, \( L_{Cu} \) increases as the B content of the Fe-B phase increases at 1873 K and 1523 K, however it becomes constant in the region of [mass%B] = 3.96 at 1873 K.

(2) The value of \( L_{Cu} \) is determined to be approximately 6 at [mass%B] = 3 in the region of [mass%Cu] = <0.73 at 1523 K.

(3) The first order mole fraction interaction parameter of B for Cu in the Fe-B phase at 1523 K is derived as follows:

\[ \varepsilon_{Cu}^b = 4.6(\pm0.7) \] \(0.14 < N_{B(Fe)}^{N(Fe)} < 0.22)\), at 1523 K

(4) The second order mole fraction interaction parameter of B for Cu in the Fe-B phase, \( \rho_{Cu}^b \), is re-derived at 1873 K. The revaluated values for \( \varepsilon_{Cu}^b \) and \( \rho_{Cu}^b \) are as follows:

\[ \varepsilon_{Cu}^b = -\rho_{Cu}^b = 12.1 \] \( \rho_{Cu}^b = -33.3(\pm3.1) \), at 1873 K

References