Enrichment of Iron and Copper by the Use of Two Liquid Phases Separation

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Abstract
The equilibrium relation of the phase separation in the Fe-Cu-B system is investigated more in detail at the lower boron content at 1873K. By combining the Taylor series equation proposed by Wagner and that of the quadratic formalism proposed by Darken, the thermodynamic interaction parameters of copper and boron in molten iron are derived. As a result, it is confirmed that two liquid phases separation occurs even at the lower boron content in iron, [mass%B]_{in Fe}=0.006. The interaction parameters of copper and boron in molten iron at 1873K are derived.

Key words
Recycling, Steel Scrap, Tramp Element, Copper, Boron, Quadratic Formalism, Immiscibility

1. Introduction
The recycling of iron and steel scrap is industrially very important from the viewpoints of the depletion of resources and the protection of the environment. It contributes to the reduction of carbon dioxide emission from iron- and steelmaking processes, in particular. However, it is difficult to recycle the scrap because of the higher amounts of tramp elements, such as copper and tin, which cannot be removed by the oxidizing refining in a conventional steelmaking process. For this reason, it is anticipated that a large amounts of iron and steel scrap have accumulated without being recycled.

The liquid phase of the Fe-Cu binary system is miscible over the whole composition. It has been reported that it separates into the Fe-rich and Cu-rich phases by adding C[1-3], Si[4] or P[5]. We previously reported on two liquid phases separation in the Fe-Cu-B system[6] and also reported on the recovery of iron and copper from the Fe-Cu alloy by using the separation into two liquid phases[7]. However, the effect of boron on the liquid immiscibility of the Fe-Cu system has not been fundamentally clarified enough because of the lack of experimental results at lower boron content. In this study, the equilibrium relation of the phase separation in the Fe-Cu-B system is investigated more in detail at the lower boron content at 1873K. Using this additional data, the interaction parameters of B for Cu are re-evaluated. In the re-evaluation, the method of combining the Taylor series equation proposed by Wagner[8] and that of the quadratic formalism proposed by Darken[9,10], which is recently performed by Miki et al.[11,12], is applied. Miki et al., determined a lot of thermodynamic parameters in the multi-component system by using the Redlich-Kister type polynomial. In this work, the equations proposed by Darken and Wagner are combined to reduce unknown interaction parameters in the Fe-Cu-B system. Moreover, the enrichment of iron and copper is considered by using the separation into two liquid phases, the Fe-rich and Cu-rich phases.

2. Experimental
The experimental apparatus is shown in Fig.1. The high purity electrolytic iron and the reagent grade of boron (purity: 99.8%) put in an alumina crucible were inductively heated up to 1873K in an Ar-H2 atmosphere, and the Fe-1mass%B alloy was preliminary prepared. The experimental apparatus consisted of a mullite furnace tube (60-mm o.d., 52-mm i.d., 1000-mm long) and a vertical MoSi2 electric resistance furnace, which was connected to a proportional integral and derivative action (PID) controller with a Pt-6%Rh/Pt-30%Rh thermocouple. The resultant Fe-1mass%B alloy, the electrolytic iron totally weighing 10 g and the reagent grade of copper (purity: 99.0%) weighing 10 g were put in an alumina crucible (15-mm o.d., 12-mm i.d., 100-mm height). The alumina crucible was inserted in a graphite holder (42-mm o.d., 34-mm i.d., 150-mm height) and was set in the furnace. The sample was held over 5 h in an argon atmosphere at 1873 K, and the equilibrium of the Fe-rich and Cu-rich phases was attained. Then, the graphite holder was withdrawn from the furnace, and the sample was rapidly quenched in iced-cooled water. The boron and copper contents of the Fe-rich phase and the boron and iron contents of the Cu-rich phase were analyzed by an inductively coupled plasma (ICP) emission spectrometry. In this work, a small amount of aluminum may be dissolved in the iron from the alumina crucible. However, the effect of the aluminum in the iron is not taken into account as it is considered negligible from the results of several similar experiments[6,13].

![Fig. 1 Experimental apparatus](image-url)
3. Results
The experimental results are tabulated in Table 1. Table 1 shows that the boron content in the Cu-rich phase is much lower than that in the Fe-rich phase, and liquid immiscibility is confirmed even at the low boron content in iron, [mass%B]_{Fe} = 0.006. The effect of the boron content on the copper content in the Fe-rich phase and on the iron content in the Cu-rich phase are shown in Figs.2(a) and (b), respectively. In Fig.2, the results at the higher boron content are from our previous study [6]. These results are also plotted on the isothermal section of the Fe-Cu-B ternary system at 1873K in Fig.3. It is shown from these figures that the miscibility gap between the two liquid phases smoothly widens, as increasing the boron content in the Fe-rich phase.

Table 1 Experimental results for two liquid phases separation in Fe-Cu-B system at 1873K

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Fe-rich (upper site) [mass%B]</th>
<th>Cu-rich (lower site) [mass%B]</th>
<th>[mass%Fe]</th>
<th>[mass%B]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40.9</td>
<td>0.006</td>
<td>34.8</td>
<td>0.001</td>
</tr>
<tr>
<td>2</td>
<td>46.5</td>
<td>0.012</td>
<td>39.6</td>
<td>0.007</td>
</tr>
<tr>
<td>3</td>
<td>42.2</td>
<td>0.016</td>
<td>39.4</td>
<td>0.007</td>
</tr>
<tr>
<td>4</td>
<td>44.7</td>
<td>0.019</td>
<td>28.1</td>
<td>0.004</td>
</tr>
<tr>
<td>5</td>
<td>45.4</td>
<td>0.027</td>
<td>31.7</td>
<td>0.007</td>
</tr>
<tr>
<td>6</td>
<td>39.8</td>
<td>0.033</td>
<td>30.5</td>
<td>0.006</td>
</tr>
<tr>
<td>7</td>
<td>42.1</td>
<td>0.091</td>
<td>41.1</td>
<td>0.058</td>
</tr>
<tr>
<td>8</td>
<td>36.5</td>
<td>0.183</td>
<td>23.0</td>
<td>0.038</td>
</tr>
<tr>
<td>9</td>
<td>32.0</td>
<td>0.250</td>
<td>25.0</td>
<td>0.029</td>
</tr>
<tr>
<td>10</td>
<td>29.5</td>
<td>0.433</td>
<td>17.5</td>
<td>0.019</td>
</tr>
<tr>
<td>11</td>
<td>23.9</td>
<td>0.568</td>
<td>14.4</td>
<td>0.016</td>
</tr>
<tr>
<td>12</td>
<td>19.6</td>
<td>0.840</td>
<td>12.5</td>
<td>0.023</td>
</tr>
</tbody>
</table>

Fig. 2 Boron content in Fe-rich phase on the copper content in Fe-rich phase (a) and on the iron content in Cu-rich phase (b)

4. Discussion
4.1 Determination of interaction parameters between copper and boron in molten iron
By applying the Taylor series equation proposed by Wagner [8], the activity coefficient of Cu in the Fe-rich phase is expressed as follows:

\[
\ln \left( \frac{Y_{\text{Cu}(\text{Fe})}}{Y_{\text{Cu}(\text{Fe})}} \right) = \varepsilon_{\text{Cu}}^{B} N_{\text{Cu}(\text{Fe})} + \varepsilon_{\text{Cu}}^{\alpha} N_{\text{Fe}(\text{Fe})} + \varepsilon_{\text{Cu}}^{\alpha \alpha} N_{\text{Cu}(\text{Fe})} N_{\text{Fe}(\text{Fe})} + \varepsilon_{\text{Cu}}^{\alpha B} N_{\text{Cu}(\text{Fe})} N_{\text{B}(\text{Fe})} + \varepsilon_{\text{Cu}}^{B B} N_{\text{Cu}(\text{Fe})} N_{\text{B}(\text{Fe})} N_{\text{B}(\text{Fe})}
\]  

(1)

where \( \varepsilon_{\text{Cu}}^{i} \) and \( \rho_{\text{Cu}}^{i} \) are the first and the second order interaction parameters of j for i, \( \rho_{\text{Cu}}^{i} \) is the second order interaction parameter of i and for i, \( y_{\text{Cu}} \) is the activity coefficient of component i at infinite dilution and \( N_{\text{Cu}(\text{Fe})} \) is the mole fraction of component i in the Fe-rich phase. On the other hand, from the equation of quadratic formalism proposed by Darken [9,10], the activity coefficient of the Cu in the Fe-rich phase of the Fe-Cu-B system is also expressed as follows:

\[
\ln \left( \frac{Y_{\text{Cu}(\text{Fe})}}{Y_{\text{Cu}(\text{Fe})}} \right) = -2\alpha_{\text{Fe-Cu}} N_{\text{Cu}(\text{Fe})} + \left( \alpha_{\text{Fe-B}} - \alpha_{\text{Fe-Cu}} \right) N_{\text{B}(\text{Fe})} + \alpha_{\text{Fe-Cu}} N_{\text{Cu}(\text{Fe})} N_{\text{B}(\text{Fe})} + \alpha_{\text{Fe-Cu}} + \alpha_{\text{Fe-B}} N_{\text{B}(\text{Fe})} N_{\text{B}(\text{Fe})}
\]  

(2)

where \( \alpha_{\text{Cu}} \) is a constant which characterizes the thermodynamic property of i-j binary system at constant temperature and pressure. By comparing the coefficients for each term in Eqs.(1) and (2), the unknown parameters, \( \varepsilon_{\text{Cu}}^{B} \) and \( \rho_{\text{Cu}}^{B} \), are related as follows:

\[
\varepsilon_{\text{Cu}}^{B} = \alpha_{\text{Fe-Cu}} - \alpha_{\text{Fe-B}} - \rho_{\text{Cu}}^{B}
\]  

(3)

Taking Eq.(3) into consideration, Eq.(2) can be rewritten as Eq.(4):

\[
\ln \left( \frac{Y_{\text{Cu}(\text{Fe})}}{Y_{\text{Cu}(\text{Fe})}} \right) = \varepsilon_{\text{Cu}}^{B} N_{\text{Cu}(\text{Fe})} - \varepsilon_{\text{Cu}}^{\alpha} N_{\text{Fe}(\text{Fe})} - \varepsilon_{\text{Cu}}^{\alpha \alpha} N_{\text{Cu}(\text{Fe})} N_{\text{Fe}(\text{Fe})} = \{1 - N_{\text{Cu}(\text{Fe})} N_{\text{Fe}(\text{Fe})} \} \varepsilon_{\text{Cu}}^{B} + \rho_{\text{Cu}}^{B}
\]

(4)

In Eq.(4), the known values are available for \( y_{\text{Cu}(\text{Fe})} = 8.58 \) [14], \( y_{\text{Cu}}^{\text{Fe}} = -6.74 \) [15] and \( \rho_{\text{Cu}}^{B} = 9.9 \) [15]. The activity of copper is known from the activity data for the Fe-Cu binary alloy [16] because the boron content in the Cu-rich phase is negligibly small. Accordingly, the activity coefficient of Cu in iron, \( y_{\text{Cu}} \), is determined by taking the equilibrium of copper between the Fe-rich and
Cu-rich phases into account. The left hand side of Eq.(4) is plotted against the $(1-N_{Cu(in\ Fe)})/N_{B(in\ Fe)}$ term in the region of $N_{B(in\ Fe)} > 0.014$ in Fig.4. The values for $\varepsilon^b_{Cu}$ and $\rho^b_{Cu}$ are respectively derived from the slope and the intercept on the ordinate of the regression line described in Fig.4. The derived values are as follows:

$$
\varepsilon^b_{Cu} = -\rho^b_{Cu} = 12.1(\pm 0.6), \rho^b_{Cu} = -18.9(\pm 11.0) \quad (N_{B(in\ Fe)} < 0.34)
$$

These values can be converted to the mass percent interaction parameters, $\varepsilon^b_Cu$ and $\rho^b_Cu$, as follows:

$$
\varepsilon^b_Cu = 0.254(\pm 0.014), \rho^b_Cu = -0.032(\pm 0.014) \quad ([mass\%_{B}]_{in\ Fe} < 8.9)
$$

The derived parameters are valid for the concentration range of $N_{B(in\ Fe)} < 0.34$. In our previous work[6], the first and the second order interaction parameters were determined separately to be $\varepsilon^b_{Cu} = 0.18 \quad ([mass\%_{B}]_{in\ Fe} < 3.3)$ and $\rho^b_{Cu} = -0.015 \quad ([mass\%_{B}]_{in\ Fe} < 8.9)$. In this work, a slightly larger value is derived for the first order interaction parameter of B for Cu by applying the method of combining the equations proposed by Darken and Wagner.

4.2 Enrichment of Fe and Cu by adding boron

The enrichment of iron and copper from the Fe-Cu alloy by addition of boron can be simulated. We consider the case that 3 mass% boron is added to the Fe-Cu alloy at 1873K. Almost all the boron is contained in the Fe-rich phase because Cu and B are immiscible, as shown in Fig.3. When 3 mass% B is added, both of the Cu content in the Fe-rich phase and the Fe content in the Cu-rich phase are about 6 mass% from Fig.2. The enrichment ratio of M(=Fe, Cu), $R_M$, defined by Eq.(7) can be calculated from these conditions.

$$
R_M(\%) = \frac{\text{Mass of M in M - rich phase}}{\text{Initial mass of M(g)}} \times 100
\quad (M=\text{Fe, Cu})
$$

The relationship between the composition of the initial Fe-Cu alloy and $R_M$ is shown in Fig.5. As shown in Fig.5, over 90% of iron can be enriched when Cu content in the Fe-Cu alloy is below 62 mass% ([mass% Cu]<62), and over 90% of copper can be enriched when Cu content in the Fe-Cu alloy is over 40 mass% ([mass% Cu]>40). The metal in automobile shredder residue (ASR) is mainly composed of iron and copper, and, as an example, we consider the enrichment of iron and copper from the ASR. When the composition of the metal recovered from the ASR is Fe-20 mass% Cu alloy, it is found that about 75% of Cu can be enriched in the Cu-rich phase from Fig.5.

![Fig. 5 Enrichment ratio of Fe and Cu from Fe-Cu alloy](image)

5. Conclusions

Two liquid phases separation of iron and copper has been investigated at 1873K in the Fe-Cu-B system. The conclusions are as follows:

(1) It is confirmed that two liquid phases separation occurs even at the lower boron content in iron, $[mass\%_{B}]_{in\ Fe}$=0.006.

(2) The first and the second order interaction parameters of copper and boron in molten iron are derived from the experimental results by combining Wagner’s equation with the quadratic formalism proposed by Darken at 1873K, as follows:

$$
\varepsilon^b_{Cu} = -\rho^b_{Cu} = 12.1(\pm 0.6), \rho^b_{Cu} = -18.9(\pm 11.0) \quad (N_{B(in\ Fe)} < 0.34)
$$

$$
\varepsilon^b_{Cu} = 0.254(\pm 0.014), \rho^b_{Cu} = -0.032(\pm 0.014) \quad ([mass\%_{B}]_{in\ Fe} < 8.9)
$$

(3) The enrichment of iron and copper from the Fe-Cu alloy is considered by using the separation into two liquid phases. When the initial composition of the metal is Fe-20mass% Cu alloy, about 75% of Cu can be enriched in the Cu-rich phase.

References


