Copper Enrichment of Iron-Base Alloy Scraps by Phase Separation in Liquid Fe-Cu-P and Fe-Cu-P-C Systems

Katsunori Yamaguchi, Takuya Ohara*, Shigeru Ueda and Yoichi Takeda

Department of Materials Science and Engineering, Faculty of Engineering, Iwate University, Morioka 020-8551, Japan.

A clear phase separation into liquid iron-rich and copper-rich alloys was observed when a mixture of Fe, Cu and P was melted in an alumina or carbon crucible at 1373 K. Since this phase separation is considered to be useful for recovering valuable copper from iron-base alloy scraps, the phase equilibrium in the Fe-Cu-P and Fe-Cu-P-C systems was investigated in this study. The effect of carbon to the phase separation was determined in the concentration range of phosphorous between 7 and 11 mass% at 1373 K. It was found that the addition of carbon enlarged the miscibility gap of the Fe-Cu-P system. Distribution ratios of some minor elements of Au, Ag and Pd were enriched in the copper-rich phase, while Pt and Mn were distributed in both phases, and Rh, Cr and Ni preferentially in the iron-rich phase.

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1. Introduction

The amount of municipal solid waste generated annually in Japan is approximately 50 million tons. Most of them is incinerated and the produced residues such as bottom and fly ashes are buried in landfills. However, the treatment of the incinerated ash has become a problem due to lack in the landfill sites. As a solution of this problem, melting process technologies for the incinerated ash have been widely used. The melting process has advantages of the volume reduction of incinerated ash and effective use of the slag produced in the melting treatment. The residues of the melting process are slag, metal and some secondary fly ashes. The slag is recyclable and can be used as construction materials for road and also as a useful material in the land reclamation. The fly ash is buried in a final disposal site. On the other hand, most of the metal residue generated in the melting process is difficult to be utilized due to the complexity of the alloy components. Table 1 shows some examples of the chemical composition of the alloy residues produced in the melting process. Iron is the main component and copper, phosphorus and silicon are remainders. The copper content is 5 to 20% and this level is too low to be economically recovered in a conventional copper smelter. Hence, a new approach to upgrade the valuable copper in the alloy residues is required.

Although the binary melt of iron and copper at high temperatures is miscible over all composition, the addition of carbon or phosphorus to the binary melt leads to a phase separation into liquid iron-rich and copper-rich phases. This phase separation is considered to be useful for upgrading the valuable copper in the alloy residues. Furthermore, since the copper phase can generally absorb some precious metals, their recovery in the conventional copper smelter will be possible. To obtain fundamental information for the new process, the phase relations and distributions of some minor elements such as Au, Ag, Pd, Pt, Rh, Cr, Mn and Ni in the liquid Cu-Fe-P and Cu-Fe-P-C systems have been investigated at 1373 K in the present study.

*Graduate Student, Iwate University

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe (mass%)</th>
<th>Cu (mass%)</th>
<th>Si (mass%)</th>
<th>P (mass%)</th>
<th>Cr (mass%)</th>
<th>Ni (mass%)</th>
<th>S (mass%)</th>
<th>C (mass%)</th>
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<tr>
<td>A</td>
<td>66.5</td>
<td>18.1</td>
<td>0.3</td>
<td>8.0</td>
<td>8.0</td>
<td>0.6</td>
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<tr>
<td>B</td>
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<td>11.7</td>
<td>7.1</td>
<td>3.9</td>
<td>1.3</td>
<td>0.04</td>
<td>1.3</td>
<td></td>
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<tr>
<td>C</td>
<td>62.2</td>
<td>15.2</td>
<td>—</td>
<td>4.8</td>
<td>—</td>
<td>1.5</td>
<td>—</td>
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2. Experimental Procedure

A starting Fe-P alloy synthesized in an alumina crucible was 89.8 mass% Fe-10.2 mass% P. In a typical run, about 6 g of Fe-P alloy (5–15 mass% P), an equal amount of copper and about 0.1–0.5 g of chromium, manganese, nickel, silver, gold, palladium, platinum or rhodium were put in an alumina or carbon crucible with 150 mm L and 10 mm ID. After the sample was heated at 1373 K for 3.6 ks in an argon atmosphere, it was taken out of the furnace and quenched. It was confirmed in a preliminary experiment that the equilibration of the sample was made in 3.6 ks. The quenched sample clearly separated into an iron-rich and copper-rich phases, and they were cut out for chemical analyses. The carbon content in both phases was analyzed by the infrared light absorption method. The contents of Cu, Fe and Ag were determined by the atomic absorption spectroscopy. P, Au, Pd, Pt and Rh were analyzed by the ICP atomic emission spectrometry.

3. Results and Discussion

3.1 Phase separation of the Cu-Fe-P and Cu-Fe-P-C systems

A cross section of the solidified sample obtained in the experiment for the Cu-Fe-P system at 1373 K is shown in Fig. 1. The two phases are observed in the upper and bottom portions, which correspond to the iron-rich and copper-rich alloys, respectively. The compositions of the iron-rich and copper-rich phases are 81.8 mass% Fe-6.9 mass% Cu-11.3 mass% P and 96.3 mass% Cu-3.3 mass% Fe-0.4 mass% P,
respectively. Figure 2 shows a cross section of the solidified sample obtained in the experiment for the carbon saturated Cu-Fe-P-C system at 1373 K. The two phases corresponding to the iron-rich and copper-rich alloys are also clearly separated in the carbon crucible. The compositions of the iron-rich and copper-rich alloys are 82.9 mass% Fe-4.7 mass% Cu-10.4 mass% P-2.0 mass% C and 96.9 mass% Cu-2.5 mass% Fe-0.6 mass% P, respectively. Although the Fe-Cu binary melt is miscible over all composition, a considerably large miscibility gap appeared by the addition of phosphorus or carbon to the binary melt. The phase separation is considered to be ascribed to the chemical
affinity of phosphorous or carbon to iron which is stronger than that to copper.

3.2 Copper solubility in iron-rich phase and iron solubility in copper-rich phase

The solubility of copper in the iron-rich phase and that of iron in the iron-rich phase in the Cu-Fe-P and carbon saturated Cu-Fe-P-C systems were determined in relation to the phosphorus content in the iron-rich phase. Table 2 shows analytical data for the Fe-Cu-P ternary and Fe-Cu-P-C quaternary systems. The solubility of copper in the iron-rich phase and that of iron in the iron-rich phase are shown in Figs. 3 and 4, respectively. The closed circles in the figures show the respective solubility of copper and iron for the Fe-Cu-C ternary system at 1453 K. As shown in Fig. 3, the copper solubility in the iron-rich phase of the Cu-Fe-P and carbon saturated Cu-Fe-P-C systems increases drastically with increasing phosphorus content in the iron-rich phase. The addition of carbon slightly reduces the copper solubility in the iron-rich phase. It is shown in Fig. 4 that the iron solubility in the copper-rich phase for both systems decreases slightly with increasing phosphorus content in the iron-rich phase. The solubility of iron in the Cu-Fe-P-C system is about 2 mass% lower than that of the Cu-Fe-P system saturated with carbon at 1453 K. As shown in Fig. 4, the copper solubility in the iron-rich phase of the Cu-Fe-P and carbon saturated Cu-Fe-P-C systems increases drastically with increasing phosphorus content in the iron-rich phase. The addition of carbon slightly reduces the copper solubility in the iron-rich phase. It is shown in Fig. 3 that the iron solubility in the copper-rich phase for both systems decreases slightly with increasing phosphorus content in the copper-rich phase. The solubility of iron in the Cu-Fe-P-C system is about 2 mass% lower than that of the Cu-Fe-P ternary system. Figure 5 represents the miscibility gap in the Cu-Fe-P ternary system and the carbon saturated Cu-Fe-P-C pseudo ternary system determined from the experimental results at 1373 K. It is found that the addition of carbon widens the miscibility gap. From the practical point of views, the solubility of copper in the iron-rich phase will affect the copper recovery from the alloy residues, while the solubility of iron in the copper-rich phase will influence the grade of matte in copper smelting.

3.3 Effect of carbon on copper solubility in carbon saturated Cu-Fe-P-C system

The authors have reported that the carbon solubility in the iron-rich phase is closely related to the copper solubility in the phase. The copper solubility in the iron-rich phase in the Cu-Fe-C-P system at 1373 K along with that in the Cu-Fe-C-X (X:Al, Cr, Mn, S, Si) system at 1573 K is shown in Fig. 6 in relation to the carbon content in the iron-rich phase. It is found that the copper solubility in the Cu-Fe-C-P system decreases with increasing carbon solubility. It is approximately expressed by

\[
\%Cu = -1.53 \%C + 7.45
\]

3.4 Carbon solubility of iron-rich phase in carbon saturated Cu-Fe-P-C system

The carbon solubility in the iron-rich phase of the Cu-Fe-P-C system saturated with carbon is shown in Fig. 7 against the phosphorus content in the phase. The carbon solubility in the iron-rich phase leads to the decrease in the carbon solubility. The relationship between the carbon solubility and the phosphorus content can be given by

\[
\%C = \%C^0 + K_C \%P
\]

where \(\%P\) is the phosphorus content and \(\%C^0\) is the carbon solubility for the under cooling Fe-Cu-C ternary at 1373 K. \(K_C\) is the tangent of the line in Fig. 6, which is constant within the limited phosphorus content. \(K_C\) obtained in the present study for the carbon saturated Cu-Fe-P-C is \(-0.12\). This value is higher than that of \(-0.33\) for the Fe-C-P system at 1773 K presented by Ohtani.
3.5 Copper recovery

Based on the mass-balance reaction and the solubility of copper in the iron-rich alloy and that of iron in the copper-rich alloy obtained in this study, the recovery of copper from the incineration metal residue containing iron and copper was calculated. Assuming that all copper in the copper-rich phase is recovered, and the copper dissolved in the iron-rich phase is lost, the copper recovery is represented against the copper grade in the residue as shown in Fig. 8. When the copper recovery is attempted by applying the phase separation in the Cu-Fe-P system, the recoveries from the metal residues containing 10 and 30% copper are 35 and 80%, respectively. On the other hand, the recoveries applying the phase separation in the Cu-Fe-P-C system are 50 and 90% from the metal residues containing 10 and 30% copper, respectively.

3.6 Distribution ratio of minor elements between iron-rich and copper-rich phases

The ability to extract valuable metals (X) from the incineration metal residues can be evaluated by the distribution ratio, $L_{Fe/Cu}^X$, defined as follows:

$$L_{Fe/Cu}^X = \frac{\text{mass} \% \ X}{\text{mass} \% \ X}$$

(3)

where (mass% $X$) and [mass% $X$] are mass percentages of $X$ in the iron-rich and copper-rich phases, respectively. The distribution ratios of silver, gold, palladium, platinum, rhodium, chromium, manganese and nickel are listed in Table 3. It is shown that gold, silver and palladium are enriched in the copper-rich phase, while rhodium, chromium

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**Fig. 5** Miscibility Gap in the Cu-Fe-P Ternary and the carbon saturated Cu-(Fe-C)-P Pseudo Ternary Systems at 1373 K.

**Fig. 6** Effect of Carbon Content on Copper Content in Iron Phase under Carbon Saturation at 1373 K.

**Fig. 7** Effect of Phosphorus Content on Carbon Content in Iron Phase under Carbon Saturation at 1373 K.

**Fig. 8** Copper Recovery against Copper Grade in Incineration Metal Residue.
and nickel are more distributed to the iron-rich phase than to the copper-rich phase. Platinum and manganese are comparatively distributed to both phases.

### 4. Conclusion

The phase relations in the Fe-Cu-P system and the carbon saturated Fe-Cu-P-C system at 1373 K were investigated as a fundamental study for the enrichment of valuable copper in the iron-base alloy scraps. Two liquid phases of iron-rich and copper-rich alloys in both systems were clearly separated at 1373 K. The copper solubility in the iron-rich phase increased with increasing phosphorus content in the iron-rich phase. The addition of carbon to the Fe-Cu-P ternary system widened the miscibility gap. The solubility of carbon in the iron-rich phase decreased with increasing phosphorus content in the phase. It was clarified that gold, silver and palladium were enriched in the copper-rich phase, while platinum and manganese were distributed in both phases, and rhodium, chromium and nickel were more distributed to the iron-rich phase than to the copper-rich phase.

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### REFERENCES

2) T. B. Massalski: *Binary Alloy Phase Diagram* (Ohio, ASM, 1990) 982.

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<table>
<thead>
<tr>
<th>System</th>
<th>$L_A^{Fe/Cu}$ Ag</th>
<th>$L_A^{Fe/Cu}$ Au</th>
<th>$L_A^{Fe/Cu}$ Pd</th>
<th>$L_A^{Fe/Cu}$ Pt</th>
<th>$L_A^{Fe/Cu}$ Rh</th>
<th>$L_A^{Fe/Cu}$ Cr</th>
<th>$L_A^{Fe/Cu}$ Mn</th>
<th>$L_A^{Fe/Cu}$ Ni</th>
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<td>79</td>
<td>0.70</td>
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