Impurity Removal from Carbon Saturated Liquid Iron using Lead Solvent

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A new technique for removal of tramp-elements from steel scrap is required for saving energy and protecting the environment. An extraction method using phase separation in a liquid Fe-Pb-C system was investigated at 1453 K to obtain fundamental information on removal of copper, tin and zinc from molten iron. A mixture of iron, lead and carbon melted in a carbon crucible separates into two phases of lead and iron containing carbon. The compositions on the miscibility gap in the Fe-Pb-C system are 95.4 mass% Fe-4.5 mass% C-0.1 mass% Pb and 99.9 mass% Pb-0.1 mass% Fe. Distribution ratios of copper, tin and zinc between the lead and the iron phases, $L_X = [\text{mass}\% X \text{ in molten Pb}] / (\text{mass}\% X \text{ in molten Fe})$, are 2.2, 2.2 and 1.4, respectively. By adding a same amount of lead to an iron scrap, 70% of copper and tin from the iron scrap can be eliminated. Gold, silver and palladium are enriched in the lead rich phase. However, platinum and rhodium are more distributed to the iron rich phase than to the lead phase.

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1. Introduction

A problem causing wide concern in the recycling of steel scrap is the accumulation of tramp-elements such as copper, tin and antimony in the scrap. Copper and tin dissolved in steel tend to bring hot shortness in the hot-rolling operation of the steel-making process. Tramp elements are dissolved into molten iron, so it is difficult to remove them from steel scrap economically. A number of suggestions have been proposed and studied for removal of copper and tin from steel scrap: vacuum distillation, evaporation using ammonia, urea or chlorine, sulfide fluxes and extraction by metal solvent.¹⁻¹⁴⁾ However, no economical process has been established because of their low efficiency, requirements for high cost, or high-energy consumption.

Present work is intended to establish the thermodynamic data in relation to removal of copper and tin by molten lead as a metal solvent. This method is based on the fact that affinity of copper or tin for lead is stronger than that for iron; in addition, there is a miscibility gap between molten lead and iron melt. Some investigations have addressed the removal of copper from iron using liquid lead or aluminum as metal solvents. However, they were focused on the removal of copper from solid iron.^{13,14)}

In the present study, an extraction method using phase separation in a liquid Fe-Pb-C system has been investigated at 1453 K to obtain fundamental information on the removal of copper, tin and zinc from molten iron. A mixture of iron, lead and carbon was melted in a carbon crucible. We confirmed initially that clear separation of the iron and lead phases occurred as a molten state: a separate top layer of iron phase and a bottom layer of lead phase settled in the crucible according to their respective densities. The distribution ratios of copper, tin and zinc between molten lead and Fe-C melt were measured at 1453 K. Moreover, distribution ratios of gold, silver, palladium, platinum, and rhodium were also determined as basic data of recovery of those precious metals from steel scrap.

2. Experimental Procedure

The starting Fe-C alloy synthesized in a carbon crucible was 95.7 mass% Fe-4.3 mass% C. Along with about 0.06-0.6 g of tin, 0.12-0.24 g of zinc or 0.12 g of silver, gold, palladium, platinum and rhodium, about 6 g of lead or Pb-Cu alloy (1-80 mass% Cu) and an equal amount of the Fe-C alloy were put in a carbon crucible with an inner diameter of 22 mm and height of 100 mm. The sample was heated at 1453 K at which both iron and lead concentrated phases were melted. After heating for 3.6 ks, the sample was taken out of the furnace and quenched in an argon atmosphere. The appearance of the phase separation was observed, then samples of iron and lead phases were cut out for chemical analysis. Carbon content in the iron and lead phases was analyzed by the infrared light absorption method. The contents of Cu, Fe, Pb, Sn, Zn and Ag in the alloy were determined by the atomic absorption spectroscopy. Au, Pd, Pt and Rh in each phase were also analyzed by the ICP atomic emission spectrometry.

3. Results and Discussion

3.1 Phase separation of the Fe-Pb-C system

Figure 1 shows a cross section of the two phases separation in the carbon saturated Fe-Pb-C system at 1453 K. The two phases, iron rich phase of top layer and lead rich phase of bottom layer, are clearly separated in crucible. Composition of iron rich and lead rich phases are 95.4 mass% Fe-4.5 mass% C-0.1 mass% Pb and 99.9 mass% Pb-0.1 mass% Fe, respectively. The lead content of the iron rich phase for the Fe-Pb-C ternary system determined in this study is 0.1 mass%, which is lower than the Fe-Pb binary system.¹⁵⁾ Addition of carbon widens the miscibility gap slightly.

3.2 Solubility of copper and carbon in iron rich phase

Solubility changes of copper and carbon in the iron rich phase were determined in relation to the copper content in the lead rich phase. In Figs. 2 and 3 (mass% X) and [mass% X] are mass percentage of X in the iron and lead rich phases, respectively. As shown in Fig. 2, the copper solubility in the

Fig. 1 View of the two phases in Fe-Pb-C system at 1453 K. (Fe-rich phase: 95.4 mass% Fe-4.5 mass% C-0.1 mass% Pb, Pb-rich phase: 99.9 mass% Pb-0.1 mass% Fe).

Fig. 2 Solubility of copper in Fe-rich phase against copper content in Pb-rich phase at 1453 K.

iron rich phase increases drastically in the region of copper content in the lead rich phase up to about 10 mass% Cu and gradually above this content with increasing copper content. It is shown in Fig. 3 that the carbon solubility in the iron rich phase decreases remarkably with increasing copper content in the lead rich phase, approaching the minimum at about 35 mass% Cu and then increases in the region of higher copper content.

3.3 Distribution ratios of copper, tin and zinc

The ability of a lead solvent to extract copper, tin and zinc from iron can be evaluated by the distribution ratio, $L_X^{\text{Pb/Fe}}$, defined as follows:

Fig. 3 Solubility of carbon in Fe-rich phase against copper content in Pb-rich phase at 1453 K.

$$L_X^{\text{Pb/Fe}} = [\text{mass\% X}] / (\text{mass\% X}). \quad (1)$$

Here [mass% X] and (mass% X) are mass percentages of X in lead-phase and carbon-saturated iron rich phase, respectively.

The distribution ratio of $L_{\text{Cu}}^{\text{Pb/Fe}}$ at 1453 K is shown in Fig. 4 in relation to mass% Cu of the lead rich phase. The value of the $L_{\text{Cu}}^{\text{Pb/Fe}}$ of less than about 2 mass% Cu in the lead rich phase is 2.16. This value is higher than that of the Fe-Pb binary system at 1873 K reported by Langenberg.¹⁶⁾ Addition of carbon to the Fe-Pb system tends to slightly increase the distribution ratio of copper. Above 2 mass% Cu of the lead rich phase, $L_{\text{Cu}}^{\text{Pb/Fe}}$ increases with increasing copper content of the lead rich phase. For scrap iron initially containing about 1 mass% Cu, it is confirmed that the copper

Fig. 4 Distribution ratio of copper between Pb-rich phase and Fe-rich phase at 1453 K.

Fig. 5 Distribution ratios of tin and zinc between Pb-rich phase and Fe-rich phase at 1453 K.

content in the molten iron can be reduced to about one-third with the extraction method using phase separation in the liquid Fe-Pb-C system.

The distribution ratios of tin and zinc between the lead rich and the carbon saturated iron rich phases were determined at 1453 K. The relations between $L_X^{Pb/Fe}$ and contents of tin and zinc in the lead rich phase are shown in Fig. 5. The effects of tin or zinc content on $L_X^{Pb/Fe}$ are very small. Therefore, $L_X^{Pb/Fe}$ displays constant values in the experimental composition ranges. Distribution ratios of tin and zinc are 2.24 and 1.42, respectively. Tin content in the molten iron can be reduced to about one-third by this solvent extraction.

3.4 Removals of copper, tin and zinc

Copper and tin distribution ratios between lead rich and the carbon saturated iron rich phases obtained in this study may seem insufficient to remove them from iron in a single operation. Techniques of a repetition or a counter flow may be effective for improving the efficiency of copper and tin removals. Extraction of copper and tin from molten iron by a lead solvent is conducted through several stages.

Based on the mass-balance relations and distribution ratios determined in this study, contents of copper, tin and zinc in molten iron using plural repetition stages are given as

$$(\text{mass}\% \text{Cu})_n = (\text{mass}\% \text{Cu})_{n-1} \times \left[1 - \left(\frac{216R}{100 + 216R} \right) \right] \quad (2)$$

$$(\text{mass}\% \text{Sn})_n = (\text{mass}\% \text{Sn})_{n-1} \times \left[1 - \left(\frac{224R}{100 + 224R} \right) \right] \quad (3)$$

$$(\text{mass}\% \text{Zn})_n = (\text{mass}\% \text{Zn})_{n-1} \times \left[1 - \left(\frac{142R}{100 + 142R} \right) \right] \quad (4)$$

and

$$R = w_{\text{Pb}}/w_{\text{Fe}} \quad (5)$$

where $(\text{mass}\% X)_n$, $(\text{mass}\% X)_{n-1}$ represent mass per-

Fig. 6 Copper removal against weight ratio of lead to iron.

tages of the component X ($X = \text{Cu}, \text{Sn}, \text{Zn}$) in the molten iron at n th and $(n-1)$ th stages, respectively. The w_{Pb} and w_{Fe} are weights of lead and iron.

Figure 6 shows copper removal against the weight ratio of the lead to the iron, where n is the number of the extraction stage. When weights of the lead and iron are the same, copper removal is about 68% with a single treatment. On the other hand, the value of removal after two stages of copper extraction is about 90%; after three stages, it is estimated to be about 96%. Tin removal against the weight ratio of the lead to iron is shown in Fig. 7, where n is the number of the extraction stage. By adding a same amount of lead to an iron, 69% of tin can be eliminated from the iron. Tin removal is about 90% after two stages of extraction; it is about 97% after three stages.

When the impurity removal of iron scrap by applying phase separation between iron and lead in the Fe-Pb-C system is carried out, large amounts of the iron containing 0.1 mass% Pb and the lead dissolving impurities are produced. The copper and zinc in molten lead are separated from the lead above melting point of lead by cooling. The tin

Fig. 7 Tin removal against weight ratio of lead to iron.

Table 1 Distribution ratios of X (X : Cu, Sn, Zn, Ag, Au, Pd, Pt, Rh) between Pb-rich phase and Fe-rich phase at 1453 K.

Element	Cu	Sn	Zn	Ag	Au	Pd	Pt	Rh
$L_X^{\text{Pb/Fe}}$	2.16	2.24	1.42	230	16	23	0.054	0.069

in the liquid lead can also be removed from the lead by Harris process using NaOH or NaNO₃. However, removal of lead from the iron will be a next focus.

3.5 Distribution ratios of precious metals

Distribution ratios $L_X^{\text{Pb/Fe}}$ as defined by eq. (1), of precious metals between the lead and iron rich phases are determined as basic data for recovery of precious metal from scrap. Table 1 lists distribution ratios of silver, gold, palladium, platinum, and rhodium along with data for copper, tin and zinc. We can recognize that silver, gold and palladium are enriched in the lead rich phase, on the contrary, platinum and rhodium are enriched in the iron rich phase.

Recovery of precious metals from molten iron using lead solvent extraction was estimated based on the distribution ratios determined in this study. Figure 8 shows the recovery of precious metals, where n is the number of extraction stages. When a same amount of lead is added to an iron, recovery of silver, gold and palladium are about 100%, 95% and 96%, respectively. Silver, gold and palladium can recover efficiently into the lead phases. However, platinum and rhodium are hardly transferred to the lead rich phase.

Fig. 8 Recovery of precious metals against weight ratio of lead to iron.

4. Conclusion

Some fundamental experiments on solvent extraction were conducted using liquid lead as a solvent to remove copper, tin and zinc from carbon saturated molten iron. Iron rich 95.4 mass% Fe-4.5 mass% C-0.1 mass% Pb alloy forms a clearly separated top layer and lead rich 99.9 mass% Pb-0.1 mass% Fe alloy forms a bottom layer in a carbon crucible at 1453 K. Distribution ratios of copper, tin and zinc between the lead and the iron phases are 2.16, 2.24 and 1.42, respectively. Copper and tin are enriched in the lead rich phase. About 70% of copper and tin can be eliminated from scrap iron by adding a same amount of lead to an iron scrap. Gold, silver and palladium are enriched in the lead rich phase; in contrast, platinum and rhodium are more distributed to the iron rich phase than to the lead phase.

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