Effect of Electromagnetic Forces on Separation of Two Immiscible Liquids in the Fe–Cu–C System

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The recovery of rare earth elements, especially Nd and Dy, from used products is important for maintaining stable supplies. Two immiscible liquids in the Fe-Cu-C system, one that is Fe-rich and the other Cu-rich, are proposed for recycling motors that use Nd magnets. In this recovery system, mechanical separation of the Fe-rich and Cu-rich phases is important. This study aims to investigate the effect of electromagnetic forces on the separation of two immiscible liquids in Fe–Cu–C systems. The degree of mechanical separation of the Fe-rich and Cu-rich phases increases with increasing strength of the electromagnetic separation force. It was found that low magnetic field and high direct current are advantageous for the separation when the strength of the electromagnetic separation force is equal. Moreover, it was found that the electromagnetic separation force can remove the primary crystalized Fe particles from the Cu-rich liquid immediately. [doi:10.2320/matertrans.M2015364]

(Received September 29, 2015; Accepted November 30, 2015; Published January 25, 2016)

Keywords: iron-copper-carbon, two immiscible liquids, mechanical electromagnetic separation force, magnetic field

1. Introduction

Strong rare earth magnets are indispensable to high efficiency motors. Consumption of rare earth magnets that use neodymium (Nd) and dysprosium (Dy) is increasing because of the need for high efficiency motors in air conditioners, electric vehicles, and hybrid electric vehicles. Many Nd magnets are being discarded now because of the life of air conditioners and automobiles is about twelve years. Moreover, the resources of rare earth elements have uneven distribution, and the Clarke number of Dy is small. Thus, recovery of rare earth elements from used products is important to maintain stable supplies.1) The use of two immiscible liquids in the Fe-Cu-C system is proposed for recycling motors that use Nd magnets.2) When C is added to molten Fe-Cu, the molten metal separates into two immiscible liquids, one of which is a Fe-C-rich liquid and the other a Cu-rich liquid.3) It has been reported that Nd and Dy concentrate in the Cu-rich phase.4) This recovery system is reasonable because the motors consist of the electromagnetic steel sheets and electric copper wires.

In this recovery system, mechanical separation of the Fe-rich and Cu-rich phases is important. Stirring and agitation should facilitate the migration of the rare earth elements from the Fe-rich liquid to the Cu-rich liquid. However, stirring and agitation can create a suspension of one liquid in the other. Moreover, when cooling, liquid droplets appear in the parent liquid because the solubilities of Fe in Cu liquid and Cu in Fe liquid decrease with decreasing temperature. These phenomena inhibit the clean separation of the Fe-rich and Cu-rich phases. The general method of mechanical separation exploits the difference in density of the two liquids. Taking into account the surface tension and variation of the solubility, it is difficult to separate the liquids completely by gravity because the densities of Fe and Cu are 7.9 g/cm³ and 8.9 g/cm³ at room temperature. Usually in the case of a small density difference, centrifugation is used. But in this case, centrifugation is difficult because the Fe-rich and Cu-rich liquids have to be retained at a temperature higher than the melting points, i.e., about 1473 K. Accordingly, electromagnetic forces are used for separation in this study. The electromagnetic forces are Lorentz forces generated by a current and magnetic field. When the magnetic field and current density are uniform, the electromagnetic force is a body force that acts on the whole volume like gravity or a centrifugal force. When both a low resistance volume and a high resistance volume exist, the electromagnetic force on the low resistance volume is greater than that on the high resistance volume due to the greater current flow that results from the lower resistance. The resistance of Fe-4.2 mass%C liquid is 148 μΩ·cm at 1473 K,5) and the resistance of Cu liquid is 22.8 μΩ·cm at 1473 K.5) Under the assumption that the Fe-C liquid and Cu liquid comprise a parallel electrical connection and that they have the same cross-sectional area, the electromagnetic force expressed in terms of equivalent densities in the Fe-4.2 mass%C liquid and that in the Cu liquid are 544 g/cm³ and 3534 g/cm³ at 10 Tesla, 2 × 10⁶ A/m², respectively. Separation using electromagnetic force is very effective in this system because the electromagnetic force difference is much larger than the density difference.

The effect of a magnetic field on solidification in Cu-Pb monotectic alloys has been studied,7) and the authors report that the size of the Cu-rich spherical drops decreases when a static magnetic field is applied. Also, the effect of a direct current on solidification in Al-Pb monotectic alloys was reported.8) The authors found that by varying the current density during solidification they obtained samples with either a finely dispersed microstructure or a shell/core structure. The use of only a magnetic field or only a direct current disperses the droplets in the parent liquid when cooling. This phenomenon inhibits the degree of mechanical separation of the Fe-rich and Cu-rich phases.
The purpose of this study is to investigate the effect of electromagnetic forces on the separation of two immiscible liquids in the Fe–Cu–C system.

2. Experimental Apparatus

The experimental apparatus uses a superconducting magnet that is able to produce a magnetic field of up to 10 Tesla at the center of a bore of 150-mm diameter (Fig. 1). The sample, which is cylindrical, is placed between two carbon electrodes in an alumina tube and set in the experimental apparatus (Fig. 2), which firmly holds the alumina tube with stainless steel cylinders. The electrodes that supply the current are firmly fixed in the ends of the tube to prevent leakage of molten liquid when forces are applied. Temperature is measured by a K-type thermocouple in the tube. An electric carbon furnace to heat and melt the sample is set around the tube.

3. Experimental Procedure

Fe–Cu–C rod samples with a diameter of 6 mm were prepared by casting Fe-4.3 mass% C melts into copper tubes under an argon atmosphere. Electrolytic iron with a purity of 99.99 mass%, carbon powder with a purity of 99.9 mass%, and phosphorus-deoxidized copper tubes with an outer diameter of 6 mm and a thickness of 0.8 mm were used.

The Fe–Cu–C rod sample with a length of 20 mm was placed between two carbon electrodes in an alumina tube with an inner diameter of 6 mm and an outer diameter of 15 mm. Argon was passed through the inside of the stainless-steel cylinders, but the atmosphere in the cylinders cannot be controlled completely. Consequently, rare earth elements were not used because they oxidize very easily. The sample was heated to 1523 K in about 2.5 hours. The molten sample was kept at this temperature for 2 minutes and then cooled in the heating furnace. Electromagnetic vibrations are generated in a molten metal when alternating current is passed through it perpendicular to the static magnetic field, and it has been reported that electromagnetic vibrations refine the grain size by the induced motion of the solid and liquid phases.9) Under the assumption that the rare earth elements, if they were present, would migrate from the Fe-rich liquid to the Cu-rich liquid, electromagnetic vibrations (60 A, 500 Hz) were applied for 10 seconds just before the end of temperature holding time. When the electromagnetic forces were applied to the sample, the magnetic field of the superconducting magnet was increased to the desired value during the sample heating. After the electromagnetic vibrations, the electromagnetic force was applied by passing the direct current through the sample to 1223 K.

The degree of mechanical separation of the Fe-rich and Cu-rich phases was examined by optical microscopy without etching. The samples were cut in half so that the observation surfaces were parallel to the electromagnetic force. Optical micrographs of the samples were analyzed in three steps as follows:

(1) Binarization processing was performed. The Cu, Fe, and graphite phases were separated. The pixel size was 2.3 µm × 2.3 µm.
(2) Because boundary areas can complicate the analysis, the boundary lines of regions having an area of more than 1 mm² were shifted 300 µm inward.
(3) The area ratio of Cu grains in the Fe-phase and that of Fe grains in the Cu-phase were calculated. Flaky graphite grains in the Fe-phase were regarded as part of the Fe-phase because this phase consists of gray cast iron and white cast iron.

The Cu content of the Fe-phase and Fe content of the Cu-phase were examined by x-ray energy dispersive spectroscopy (EDS) in a scanning electron microscope. The average composition was calculated using EDS results from three or four areas, each with a size of 1.4 mm × 1.4 mm.

4. Results and Discussion

4.1 The effect of pre-electromagnetic vibrations

Figure 3 shows the effect of the pre-electromagnetic vibrations (PreEMV) on (a) the area ratio and (b) Cu or Fe content. The area ratio graphs show both the ratio of Cu grains in the Fe phase and Fe grains in the Cu phase. The Cu and Fe content graphs show the Cu content of the Fe phase and the Fe content of the Cu phase. Both samples were prepared at 10 T and without the use of direct current for the
electromagnetic separation force. The area ratio of Fe grains in the Cu phase was slightly increased by the PreEMV, but the area ratio of Cu grains in the Fe phase was increased much more than that of Fe grains in Cu. It has been reported that the surface tension of Fe liquid is higher than that of Cu liquid. Thus, the Fe more easily forms droplets that precipitate out from the Cu liquid. This phenomenon is assumed to cause the difference in the effect of the PreEMV. The Cu content of the Fe phase and Fe content of the Cu phase in the sample not subjected to PreEMV were the same to within the accuracy of the measurements.

4.2 The effects of the strength of the electromagnetic separation force

Figure 4 shows the effect of the strength of the electromagnetic separation force on the cross-sectional optical micrographs. All samples were prepared with the PreEMV. The direct current for the electromagnetic separation was fixed at 60 A, and the strength of the electromagnetic separation force was varied with the magnetic field. Gray areas are the Cu-rich phase, and white areas are the Fe-rich phase and flaky graphite grains. The Cu-rich phase migrates in the direction of the electromagnetic separation force. Moreover, when the electromagnetic separation force is stronger or the magnetic field is high, the Cu-rich phase migrates toward one electrode. When the Fe-rich and Cu-rich phases separate, as in the sample shown in Fig. 4(c), the two phases are electrically connected in series. This separation condition is stable under the electromagnetic force because the forces in Fe-rich and Cu-rich phases become the same.

Figure 5 shows the effect of the strength of the electromagnetic separation force on (a) the area ratio and (b) Cu or Fe content in the samples shown in Fig. 4. The points labeled (10 T, 0 A) at the left edge of the plots are data from samples not subject to the electromagnetic separation force shown for reference. The area ratio of the Cu grains in the Fe phase and that of Fe grains in the Cu phase decrease with increasing strength of the separation force. In particular, the Fe-rich and Cu-rich phases were separated almost completely in the samples that were processed at more than 5 T. With error bars taken into account, Fig. 5(b) shows that the Cu content of the Fe phase was essentially unchanged compared with that of the (10 T, 0 A) sample regardless of strength of the separation force. However, the Fe content of the Cu phase decreased from 3 mass% to 2 mass% when the sample was subjected to the separation force.

Figure 6 shows the pseudo-binary phase diagram of (Fe-4.3 mass% C)-Cu system calculated with Thermo-Calc software. The solidification of the Cu phase is found to be peritectic. At point (A), the Cu-rich liquid consists of 96.4 mass% Cu, 3.4 mass% Fe, and 0.2 mass% C at 1433 K. This composition corresponds with that of the sample for which no separation force was applied. At point (B), the Cu-rich solid consists of 97.3 mass% Cu, 2.6 mass% Fe and 0.1 mass% C at 1369 K. This composition corresponds with that
of the samples on which the separation force was applied. When the Fe-rich phase and the Cu-rich phase are liquid, the compositions are the same as the calculated phase diagram because diffusion rates in the liquids are high and the samples are small. Therefore at the temperature corresponding to point (A), the composition of the Cu-rich phase becomes the composition of point (A). However, below this temperature, fine Fe particles crystalize in the Cu-rich phase. Because these particles cannot move freely in the Cu-rich phase, it is thought that, in the samples not subjected to the separation force, the composition of the Cu-rich phase maintains the composition of point (A) at temperatures lower than that of point (A). On the other hand, in the samples for which the separation force was applied, it is thought that the force removes the crystalized Fe particles from the Cu-rich liquid phase to the Fe-rich solid phase above the temperature at which the Cu-rich phase solidifies. Therefore, the composition of the Cu-rich phase becomes the composition of point (B). Thus, it is thought that the electromagnetic separation force can remove the primary crystalized Fe particles from the Cu-rich liquid immediately.

4.3 The effects of magnetic-field strength

Figure 7 shows the effect of the strength of the magnetic field on the cross sectional optical micrographs. All samples were prepared with the PreEMV and an electromagnetic separation force that has the same strength. The magnetic field and the direct current for the samples are (a) 1.5 T, 100 A, (b) 2.5 T, 60 A and (c) 10 T, 15 A, respectively.

Fig. 6 Pseudo-binary phase diagrams of (Fe-4.3 mass% C)-Cu system calculated with Thermo-Calc software.

Fig. 5 The effect of the strength of the electromagnetic separation force on (a) the area ratio and (b) Cu or Fe content. The points labeled (10 T, 0 A) at the left edge of the plots are data from the sample which was not subjected to the separation force shown for reference.

Fig. 7 The effect of the strength of the magnetic field on the cross sectional optical micrographs. All samples were prepared with the PreEMV and an electromagnetic separation force that has the same strength. The magnetic field and the direct current for the samples are (a) 1.5 T, 100 A, (b) 2.5 T, 60 A and (c) 10 T, 15 A, respectively.
system. The contact angle between the liquid metal and crucible wall was reported to have increased due to magnetic-field-induced surface tension.\(^{11}\) In Fe–Cu–C system, magnetic-field-induced surface tension seems to cause migration to one area when the magnetic field is high.

Figure 8 shows the effect of the strength of the magnetic field on (a) the area ratio and (b) Cu or Fe content in the samples shown in Fig. 7. The points labeled (10 T, 0 A) at the left edge of the plots are data from the sample which was not subjected to the separation force shown for reference.

**5. Conclusions**

The effect of electromagnetic forces on the separation of two immiscible liquids in the Fe–Cu–C system has been investigated, and the following conclusions have been drawn.

1. The degree of mechanical separation of the Fe-rich and Cu-rich phases increases with increasing strength of the electromagnetic separation force. Moreover, it was found that low magnetic field and high direct current are advantageous to the separation when the strength of the electromagnetic separation force is equal.

2. It was found that the electromagnetic separation force can remove the primary crystalized Fe particles from the Cu-rich liquid immediately. As a result, the Fe content of the Cu phase decreases from 3 mass% to 2 mass% as a consequence of the separation force.

3. When the magnetic field is high, it was found that interfacial tension increases, so that the Cu-rich phase migrates to one area. Magnetic-field-induced surface tension appears to cause this phenomenon.

**Acknowledgments**

The author thanks Mrs. T. Yamaguchi for technical assistance.

**REFERENCES**