Copper Distribution in Fe–Cu and Fe–C–Cu Alloys under Imposition of an Intense Magnetic Field

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Solidification experiments of Fe–0.44%S and Fe–3.95%C–0.40%C alloys were conducted to investigate the effects of an intense magnetic field on copper distribution in their solidified structures. Experiments with melting and solidifying the samples were carried out in a superconducting magnet. Around the center of the vertical cross-section of the solidified sample, multiple line analysis of copper concentration was conducted with the help of FE-SEM/EDS. The following results have been found. The copper distribution in Fe–0.44%C alloy is independent of the imposition of the magnetic field during the solidification. On the other hand, the solidifying process under a 10 T magnetic field tends to make a uniform micro distribution of copper in Fe–3.95%C–0.40%C alloy in comparison with the sample solidified without the magnetic field.

KEY WORDS: tramp elements; copper distribution; iron scrap; a magnetic field; solidification; segregation; electromagnetic processing of materials.

1. Introduction

It is well known that recycling scrap for steelmaking could economize consumption of energy and reduce the generation of CO₂ in comparison with the process for steelmaking from iron ore. The amount of scrap will be increasing sharply in coming years.1) However, some elements1–5) in the scrap are harmful and are difficult to eliminate from molten steel from the viewpoint of thermodynamics. These elements such as Cu, Sn, P, As, Cr, Mo and Pb are called tramp elements. For example, residual copper in the scrap is a significant problem for steel making because the solid solubility of copper in iron is so low that it concentrates at grain boundary, and thus causes detrimental effects like hot brittleness.4,5) Therefore, it is desired to minimize the negative effects of Cu on steel making process. Hitherto, a plenty of methods for eliminating of copper have been proposed such as shredder treatment,1) low-temperature crushing, automatic discriminative separation5) by analyzing the three elements of light, hue, chroma and lightness,5) iron-melting dilution method, utilization of solubility difference between Cu and Fe in molten aluminum,6) chloridizing of copper to evaporate by using gaseous mixture of chlorine and oxygen,7) evaporation of copper by ammonia gas blowing under reduced pressure,8) transforming Cu into Cu₂S by a liquid iron sulphide9) and so on. In these methods, however, we still face some problems to be solved such as high cost, difficulty in liquid copper separation from solid iron due to their high wettability, corrosion of equipment, increasing of undesired elements in steel and so on. Therefore, further efforts might be spent in dealing with tramp elements problems.

Under the development of superconducting technologies, many scientifically interesting phenomena have been found since an intense magnetic field has been introduced to a material processing such as phase transformation,10,11) crystalline alignment,12–15) micro and macro segregations,16,17) etc. One of these interesting demonstrations on tin segregation in a Fe–0.8at%Sn alloy during annealing was done by Tsurekawa and Watanabe etc.16) They clarified that tin concentration of the Fe–0.8at%Sn alloy at random boundaries in the magnetically (H/\textit{H}_{\text{Curie}} \geq 3T) annealed sample at 0.95 Curie temperature was almost the same as that in a grain, whereas the concentration at random boundaries in the sample annealed without the magnetic field was approximately 2.5 times that in the grain. This phenomenon is explained from the viewpoint of the magnetization energy. This result tells that a magnetic field is a useful tool to suppress boundary segregation of an added element in a ferromagnetic material. If segregation control using the magnetic field in non-magnetic materials such as aluminum, titanium and, δ and γ phases of steel can be achieved, its application will widely extend.

In this study, Fe–0.44mass%C and Fe–3.95mass%C–0.40mass%C alloy were solidified with and without an intense magnetic field and the effect of the magnetic field on the micro distribution of copper in the both alloys were investigated.

2. Experimental Procedures

Two kinds of alloys were used in this investigation; one is
Fe–Cu alloy, the other is Fe–C–Cu alloy. The mass content of copper in the both alloys is about 0.4%. Table 1 shows the chemical compositions of these samples. These samples were solidified with and without the magnetic field as shown in Table 2. Experiments with melting and solidifying the samples were carried out in a superconducting magnet as shown in Fig. 1. Each 10 g cylindrical sample was put into an alumina crucible, which was to be set in the center of the superconducting magnet bore, where a vertical magnetic field with a 10 T peak value exists without gradient. In experiment I and II, samples were melted and solidified in Ar/H$_2$$_{1.0}$ atmosphere, while N$_2$ atmosphere was adopted for experiment III and IV because it was enough to prevent Fe–C–Cu sample from being oxidized. The liquidus temperature of sample I and II is below 1536°C and their solidus temperature is estimated at 1530°C according to the Fe–Cu phase diagram as shown in Fig. 2. Consequently, the temperature history of experiment I and II was designed as shown in Fig. 3, in which the samples were kept in liquid phase for 15 min. On the other hand, the temperature history for sample III and IV was designed as shown in Fig. 4. We used Fe–C phase diagram to design the temperature history under the assumption that the effect of 0.4% copper addition in the alloy on the phase diagram is small enough to be neglected in comparison with 4% carbon addition in the alloy. The liquidus and solidus temperatures of sample III and sample IV were estimated at 1250°C and 1145°C, respectively. Therefore, sample III and IV were kept in liquid state for 10 min. For all the samples, we confirmed that the samples were liquid phase at the plateau region in the temperature histories by inserting an alumina stick into the samples. The samples was pulled out of the bore of the superconducting magnet and quenched in water. The magnetic field was applied to sample II and sample IV. It was turned on after the sample temperature exceeded the Curie temperature during the heating process and its intensity was increasing with time and finally it reached 10 T before the sample melt down.

After the quenching, each sample was cut into two pieces with longitudinal cross-section and then mechanically polished and buff-finished until a mirror surface with 0.05 μm Al$_2$O$_3$ particles. Then two parallel lines with a length of 940 μm were drawn around the center of the cross-section of the samples. The distance between the two lines was within a few micrometers. Each line was divided into four sections. The copper distribution was analyzed along the line in section in order to increase the reliability of the experimental data with the help of FE-SEM/EDS (S-800/HTAACHI, EDS2000/IXRF SYSTEM).

In the line analysis, the diameter of the EDS spot was approximately 0.1 μm, point (we call the spot analyzed in samples as point in the following) interval was approximately 0.92 μm, the length of each line was 235 μm, and the illumination time for each point was 5 s. The accelerating voltage of emission of X-ray was 20 kV. The copper concentration analyzed here was not absolute value but the relative one because of the lack of the copper concentration standard sample for the SEM/EDS. Furthermore, the microstructure was observed for the every sample. For Fe–0.44%Cu alloy, etching solution composed of alcohol (95%) and nitric acid (65%) in the ratio of 100:1–10:1.
was adopted for microstructure observation. In the case of Fe–3.95%C–0.40%Cu alloy, the microstructure could be observed without chemical etching. Therefore, the position of the scanning lines for the copper distribution measurement was specified in the case of Fe–3.95%C–0.40%Cu alloy while it was not specified in the case of the Fe–0.44%Cu alloy.

3. Experimental Results

3.1. The Results of Fe–0.44%Cu Alloy

Figure 5 shows the microstructures and the illustrations of grain boundaries for the easy observation of grain sizes. The grain sizes in the samples with and without the magnetic field are smaller than the total scanning line length of 940 μm so that the line analysis must have some intersections with grain boundaries. The deviation of copper concentration, which is defined as the difference between the concentration at each point and the average of the measured values at overall points on the each scanning line, was evaluated and one of the results is shown in Fig. 6. According to this figure, the copper distribution solidified with the magnetic field is similar to that solidified without the magnetic field. The value of deviation is within 2% in the both cases. Furthermore, the standard deviation of the copper distribution in each line were calculated and shown in Table 3 with their average values. The average of the standard deviation solidified without the magnetic field is the same value of 0.73 with that solidified with the magnetic field. Furthermore, the standard deviation scatters between 0.41 and 0.88 in the case solidified without the magnetic field and that in the case solidified with the magnetic field does between 0.48 and 0.87. That is, the scatter ranges of the standard deviations in the both cases are almost the same. Therefore, the effects of the magnetic field on the copper distribution are not found in the alloy adopted here.

3.2. The Results of Fe–3.95%C–0.40%Cu Alloy

Figure 7 shows the microstructures and the grain boundary illustration of the samples with and without the magnetic field. Their enlarged views of the microstructures and the scanning line for the copper distribution measurement are shown in these figures. They have some intersections with the phase boundaries. The deviation of copper concentration at each point in the lines shown in Fig. 7 is plotted in Fig. 8. The copper concentration in the sample solidified without the magnetic field has some sharp peaks at the po-

![Fig. 5. Microstructures and illustrations of grain boundary in Fe–0.44%Cu alloy. (a) SEM picture, B=0 T, (b) SEM picture, B=10 T, (c) illustration, B=0 T, (d) illustration, B=10 T.](image)

![Fig. 6. Deviation of Cu concentration from the average value in Fe–0.44%Cu alloy solidified with and without magnetic field. (a) B=0 T; (b) B=10 T.](image)

![Fig. 7. Macrostructures with scanning line and illustration of grains in Fe–3.95%C–0.40%Cu alloy. (a) SEM picture, B=0 T, (b) SEM picture, B=10 T, (c) illustration, B=0 T, (d) illustration, B=10 T.](image)

| Table 3. Standard deviation of Cu concentration in Fe–0.44%Cu alloy solidified with and without magnetic field. |
|---|---|---|---|---|---|---|---|---|
| No. of scanning lines | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Intensity of magnetic field | 0 T | 10 T | 0 T | 10 T | 0 T | 10 T | 0 T | 10 T |
| average value | 0.410 | 0.580 | 0.670 | 0.780 | 0.820 | 0.830 | 0.840 | 0.870 |
| standard deviation | 0.250 | 0.320 | 0.350 | 0.380 | 0.400 | 0.410 | 0.420 | 0.430 |
sitions P1, P2, …, and P6 which are also shown in Fig. 7. Almost all these peaks are located in the vicinity of the boundary between the primary phase and the eutectic phase. On the other hand, the distribution of the copper concentration in the sample solidified with the magnetic field has no sharp peaks though the scanning line has some intersections with the boundaries. Actually, the copper concentration deviates roughly between $\pm 2\%$ and $11\%$ for the sample solidified without the magnetic field while that for the sample solidified with the magnetic field is between $-2\%$ and $2\%$. The standard deviations of the every scanning line are shown in Table 4. The standard deviation for the sample solidified with the magnetic field is between 0.68 and 0.87. This distribution range is clearly narrow in comparison with that solidified without the magnetic field that is between 0.77 and 1.44. In addition, the averages of the standard deviations in the samples solidified with and without the magnetic field are 0.79 and 1.02, respectively. From these results, we can say that the imposition of the 10 T magnetic field during solidification has a function of uniforming the copper distribution in the Fe–3.95%C–0.44%Cu alloy.

### 4. Discussion

The Common Tangent Method is helpful to determine the concentration of copper in the $\gamma$ and liquid phases during the solidification of the Fe–C–Cu alloy at a certain temperature under the assumption of quasi-equilibrium condition.

As shown in Fig. 9 the curve $\gamma$ and curve L represent Gibbs free energy of the $\gamma$ phase and the liquid phase, respectively, and $C_{\gamma}$ and $C_L$ are the copper concentration in the $\gamma$ phase and the liquid phase, respectively. Under the imposition of a magnetic field, the Gibbs free energy of the liquid phase ($G'_L$) and the $\gamma$-Fe phase ($G'_\gamma$) are written as follows:

$$G'_L = G_L^0 - \frac{m_c}{\rho_f} \mu_0 \chi \gamma H^2 \quad \text{......(1)}$$

where $H$ is the strength of a magnetic field, $m$ the molar mass, $\rho$ is density, $\chi$ the a magnetic susceptibility and $\mu_0$ the permeability in vacuum. The superscript '0' and '1' indicate the conditions without and with a magnetic field respectively. According to Eqs. (1) and (2), the free energy of these phases is decreased under a magnetic field because the $\gamma$-Fe and liquid phases are paramagnetic with magnetic susceptibilities of $2.528 \times 10^{-3}$ (at about 1225°C)\(^1\) and $2.145 \times 10^{-3}$ (at about 1550°C),\(^1\) respectively. And the decreased amount of the free energy in the $\gamma$ phase is 1.47 J/mol while that in liquid phase is 1.37 J/mol. Therefore, concentration change of copper in the $\gamma$ phase from $C_{\gamma}$ to $C_{\gamma}'$ by imposing a magnetic field and that in the liquid phase $C_L$ to $C_L'$ might be small. This means that interpretation of the experimental result is difficult from the viewpoint of Gibbs free energy change with and without the magnetic field. For future work, solute distribution coefficient, Cu segregation and the flow of molten alloy under magnetic field will be introduced to make the experimental results analysis clearer and more accurate.

### 5. Conclusion

Fe–Cu and Fe–C–Cu alloys were solidified under an intense magnetic field to investigate the effect of the magnetic field on copper distribution. The following results have been obtained:

1. The copper distribution in the Fe–0.44%Cu alloy is more uniform than that in the Fe–3.95%–0.40%Cu alloy under the non-magnetic field condition.

2. The process using the 10 T magnetic field tends to make a uniform micro distribution of copper in the Fe–3.95%–0.40%Cu alloy while this effect can not be observed in the Fe–0.44%Cu alloy.

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**Table 4.** Standard deviation of Cu concentration in Fe–3.95%C–0.44%Cu% alloy solidified with and without magnetic field.

| No. of scanning lines | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | average value |
|-----------------------|----|----|----|----|----|----|----|----|---------------|
| 0T                    | 0.770 | 0.820 | 0.871 | 1.061 | 1.151 | 1.231 | 1.441 | 1.020         |
| 10T                   | 0.680 | 0.690 | 0.770 | 0.800 | 0.840 | 0.840 | 0.860 | 0.871         |

**Fig. 8.** Deviation of Cu concentration of Fe–3.95%–0.44%Cu with and without magnetic field (a) $B=0$T; (b) $B=10$ T.

**Fig. 9.** Gibbs free energy with and without magnetic field.

$$G'_L = G_L^0 - \frac{m_c}{\rho_f} \mu_0 \chi \gamma H^2 \quad \text{......(2)}$$
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