Effect of Alternating Magnetic Field on the Microstructure and Solute Distribution of Cu–14Fe Composites

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The influence of a low frequency alternating magnetic field (LFAMF) during solidification was investigated for Cu–14Fe composites. The microstructure was investigated by optical microscope; the solute distribution in different phases was analyzed by scanning electron microscopy and energy-dispersive X-ray spectrometry; the oxygen content was tested by oxygen & nitrogen analyzer; the conductivity was measured by eddy current conductivity meter; and the micro-hardness was measured by Vickers hardness tester. AMF treatment reduced rod shape and large size Fe dendrites, changed some Fe dendrites into club shape and equiaxed grains, and promoted the homogenization of Fe phase distribution. In addition, AMF treatment increased the Cu content in Fe phase and decreased the Fe content in Cu matrix. The effect of AMF during solidification was discussed from the view of thermodynamics and kinetics. This was attributed to the refinement of primary Fe dendrites and the precipitation of Fe atoms from Cu matrix.

Keywords: copper–iron in situ composites, alternating magnetic field, Fe dendrite, solute distribution

1. Introduction

Since deformation-processed Cu-Nb in situ composites were first discovered by Bevk in 1978,13 Cu-X in situ composites have been the subjects of considerable studies, where X are body centered cubic (b.c.c) transition metals such as Cr, Zr, V, Fe or face-centered cubic (f.c.c) metals Nb and Ag.2-12

The Cu–Fe composite has attracted the attention of researchers because of the relatively low cost of Fe, compared to the other possible alloying elements. However, Fe in solid solution in Cu matrix seriously reduces the conductivity of Cu, and the precipitation rate of Fe atoms from supersaturated Cu solid solution is slow.13-17

Recent research has explored two main approaches to improve the comprehensive properties of Cu–Fe in situ composite. They are to refine or spheroidize primary Fe dendrites, and to promote the precipitation of Fe from Cu matrix, respectively.11,15,16

Previous studies of the research group revealed that, the Fe content in the Cu matrix of the Cu–Fe composites prepared by casting obviously exceeded its equilibrium concentration. Therefore, an intermediate heat treatment is necessary to improve the conductivity of the composite. However, the diffusion rate of Fe in Cu matrix is slow at low temperature. Fe could hardly precipitate from Cu matrix after heat treatment at 400°C for 2 hours. The conductivity of composites could be improved by long time diffusion annealing, but the strength would decrease rapidly because of the coarsening of Fe fibers during heat treatment process.18,19 Addition of extra alloy elements could improve the strength to some extent, but the conductivity and cold workability would be deteriorated. Ag could comprehensively improve the strength and conductivity of Cu-Fe composites, because the conductivity of Ag is excellent, and Ag has an electronic structure and crystal structure similar to Cu. However, composites containing a certain amount of Ag would be expensive because of the high cost of Ag.15,20

At the present time, the application of magnetic fields can be considered as an effective tool to organize well-defined flow structures in liquid metals. The alternating magnetic field or magetostatic field can refine the grain size effectively, and change the distribution of alloying elements on grains and grain boundaries during solidification. Steinbach et al. investigated the effect of rotating magnetic field (RMF) on Al–Si–Mg alloys, and found that the microstructure was obviously changed.21 Zhang et al. reported that magnetic field decreased the precipitation of alloying elements on grain boundaries, and the decrement increased with decreasing magnetic field frequency.22 Ban et al. researched Al–Cu alloy solidified under AC magnetic field; and found that the liquidus temperature and solidus temperature increased, the solidification interval decreased, and these changes intensified with increasing magnetic field intensity.23 Results show that magnetic field has obvious effect on the microstructure and phase transition of materials during solidification. However, the physical mechanism of interaction between solidification and flow field is insufficiently understood until now, and the knowledge about that is of high technological importance.

The aims of this work were to understand the effect of magnetic field on the microstructure and solute distribution of Cu–14Fe composites, to explore the influence mechanism on the microstructure and solute distribution.

2. Experimental Procedures

Electrolytic Cu (99.96 mass%), and Fe (99.99 mass%) were used to prepare Cu–Fe composites containing up to 86 mass% Cu. The composites were melted in a magnesia crucible in a medium frequency induction furnace and were solidified in a graphite crucible in a magnetic field generating system. The graphite crucible was preheated to 800°C, then the melt was poured into the crucible and solidified in alternating magnetic fields. The magnetic field frequency was...
26 Hz. The exciter currents were 30, 40, 50 and 60 A for the magnetic flux density of 20, 25, 33 and 40 mT, respectively. Figure 1 presents the magnetic field generating system. The magnetic field generator is composed of three parts of induction coil, iron core and water jacket. The coil is fixed on the iron core and powered by a three phase current. An alternating magnetic field produces as low frequency current through the coil.

The microstructures of Cu-14Fe composites were investigated using a Leica DMI3000M optical microscope. The solution distribution in different phases was observed using a Quanta 200 SEM and was analyzed using an OXFORD EDXS. Each value was calculated from an average of at least ten measurements. The oxygen concentration was tested using LECO TC-600 oxygen & nitrogen analyzer. The conductivity was measured using an eddy current conductivity meter. The micro-hardness was measured using a HXS-1000 Vickers hardness tester.

3. Results

3.1 Microstructures

Figure 2(a) presents the microstructure of as-cast Cu–14Fe without magnetic field. The second-phase Fe dendrites were evenly distributed in the Cu matrix and randomly oriented with respect to the ingot axis, the length of needle and dendritic grains more than 100 µm. Figures 2(b)–(e) presents the effect of different magnetic flux densities on the microstructure of as-cast Cu–14Fe. Figure 2 shows that rod shape and large size Fe dendrites were decreased, some Fe needle and dendritic grains were changed into club shape and equiaxed grains, and the Fe phase distribution was evener after AMF treatment; the secondary dendrite arm was shortened, the dendrites became smaller (70–80 µm) and were progressively changed into spherical grains with increasing magnetic flux density.

3.2 Solute distribution

As shown in Cu–Fe binary phase diagram, the maximum equilibrium solubility of Fe in Cu is 4.6% at 1096°C, the solid solubility decreases with decreasing temperature, and the Fe atoms dissolved in Cu matrix precipitate during solidification. The content of Fe in Cu matrix is composed of
Fe atoms dissolved in Cu matrix and Fe particles precipitated from Cu matrix. The change of Fe concentration in Cu matrix can be evaluated by elemental analysis.

As shown in Fig. 3, three areas were chosen to conduct EDS analysis (spectrum1-Fe dendrite, spectrum2-Cu matrix near Fe phase, spectrum3-Cu matrix away Fe phase). Figure 4(a) presents the Cu contents in the Fe dendrites of Cu-14Fe composites at different magnetic flux densities of 0, 20, 25, 33 and 40 mT. With AMF treatment, the solubility of Cu in Fe dendrites increased, while the solubility had little change with magnetic flux density. Figure 4(b) presents the Fe contents in the Cu matrices of Cu-14Fe composites at different magnetic flux densities of 0, 20, 25, 33 and 40 mT. The Fe contents in the Cu matrices near Fe dendrites were higher than those away Fe dendrites. With AMF treatment, the Fe contents in the matrices near and away Fe phases decreased, and the Fe content in the matrix away Fe phase decreased with increasing magnetic flux density.

3.3 Removal efficiency of oxygen
To investigate the effect of AMF on removal oxygen, same weight Cu-14Fe composites were produced using the magnetic field generating system at different magnetic flux densities. The sampling locations were in the ingot center. Figure 5 presents the oxygen content of Cu-14Fe composites at different magnetic flux densities of 0, 20, 25, 33 and 40 mT. With AMF treatment, the oxygen concentration decreased and reached a valley value at 20 mT, and then increased at higher magnetic flux density, the removal efficiency of oxygen reached to 73% at the magnetic flux density of 20 mT. The stirring intensity improved with increasing magnetic flux density, which increased the amount of inhaled gas due to the melt without protection of covering agent during solidification.

3.4 Conductivity and micro-hardness
Figure 6 presents the conductivity and micro-hardness of Cu-14Fe composites without AMF treatment, and with AMF treatment at different magnetic flux densities of 20, 25, 33 and 40 mT, respectively. With AMF treatment, the conductivity of Cu-14Fe composite increased obviously, the matrix hardness value decreased, and the decrement increased with increasing magnetic flux density.

4. Discussion
4.1 Microstructures
The growing process of dendrite was controlled by thermal diffusion and solution diffusion. In the process of solidification, the heat and solute discharged into liquid phase from dendrite at the same time, both are the significant factors for the dendrite growth. Therefore the change of dendrite morphology has direct relationship with these two factors. AMF caused electromagnetic stirring in the metal liquid.

Figure 7 presents the force diagram of melt. The unit produced induced current $j$ in the magnetic field. The direction of induced current field was consistent with the
direction of the induced electric field \( E \). On the other hand, the conductor move with speed \( v \) in the magnetic field \( B \) would produce motional electromotive force \( E' = v \times B \), thus the induced current can produce Lorentz force \( f = \sigma E \times B \) (where \( \sigma \)) is conductivity of material).\(^{24}\) Lorentz force can be decomposed to radial component \( f_r \) and tangential component \( f_\theta \), as shown in Fig. 7. In the experiment, the melt flow mainly was caused by the tangential component of Lorentz force.

Melt flow caused temperature fluctuation in melt. When the wave amplitude was large enough to exceed liquidus on the solid-liquid interface, the dendrite arm would be remelted and dissociated into liquid, and the grains in the melt were increased and distributed more uniformly.\(^{25,26}\) On the other hand, because of the intense erosion of liquid flow, the crystal nuclei formed with chilling effect on the crucible wall were very easy to fuse or fall off into the liquid. Due to the liquid flow promoted the melt temperature uniformly, these free crystal nucleuses would grow up to spherulitic grains before remelting.\(^{27}\) Moreover, forced convection could also delay the temperature fall near the crucible wall and prevent the formation of surface solidification shell, so that more free grains could be generated.

Dendrites would discharge solute into liquid in the process of growth, which formed a narrow constitutional supercooling zone in front of the interface. A normal convection is difficult to affect the boundary layer so that the solute atoms only transfer through diffusion.\(^{29}\) The existence of supercooling zone is one of conditions to promote dendrite growth. However the forced convection caused by AMF can act on the boundary layer, and promote the solute to be distributed uniformly, which inhibits the dendrite growing.

The melt solidification was influenced by AMF treatment in these two aspects, which changed the morphology of solidification structure. The melt convection strengthened with increasing magnetic flux density, which intensified the spheroidization of Fe dendrites.

### 4.2 Solute distribution

According to the mass conservation law of solute and Scheil equation, it is assumed that there is convection in liquid phase and no diffusion in solid phase, the solute distribution in dendrite can be evaluated by:

\[
C_s = k_0 C_0 (1 - f_s)^{k_0 - 1/q} \tag{1}
\]

where \( C_s \) is the solute concentration in dendrite, \( k_0 \) is the ratio of solute content in solid phase and liquid phase, \( C_0 \) is the original composition of melt, \( f_s \) is the solid volume percentage. \( q \) is the function about alloy solidification shrinkage rate \( \beta \), solidification rate \( u \) and liquid flow rate \( v \):

\[
q = (1 - \beta)(1 - v/u) \tag{2}
\]

AMF caused melt convection, and improved flow velocity with increasing magnetic flux density, which promoted the temperature to tend to be uniform in melt. The solidification rate decreased due to the fact that the temperature gradient decreased on the solid-liquid interface. In the process of solidification, if \( C_0 \) and \( \beta \) are constant, the value of \( q \) is dependent on \( u \) and \( v \). For Cu–14Fe composites, \( k_0 < 1 \), the increase of liquid flow rate \( v \) and the decrease of solidification rate \( u \) would raise solute concentration in dendrites. Accordingly, the Cu content in Fe dendrites increased with AMF treatment.

The liquidus temperature of Cu–14Fe is about 1360°C. The solid would discharge solute into melt as Fe phase beginning solidification, and form a narrow iron-rich layer in front of the interface. Therefore the solute concentration near dendrites is higher than that away dendrites. The forced convection caused by AMF could promote the balanced distribution of solute concentration due to the increase of the flow rate on the solid-liquid interface, which reduced the solute enrichment on interface. The greater the magnetic flux density is, the more quick the flow rate is, and the lower the solute concentration is.

In addition, the magnetic field not only caused melt flow through force field, but also did work on the melt as energy field. As shown in Fig. 8, the formation of crystal nucleus depends on atoms jumping from liquid to solid, where \( \Delta G^* \) is the potential barrier from liquid to solid, \( \Delta G' \) is the changes of potential barrier when environment does work on melt. Accordingly, \( (\Delta G^* - \Delta G') \) is the potential barrier from liquid to solid when environment does work.

As analyzed above, tangential component of Lorentz force \( f_\theta \) caused melt rotation and radial component \( f_r \) caused melt flow along radial direction. Melt convection intensified with increasing magnetic flux density, which increased unordered atoms of liquid phase. The increase of unordered atoms caused the structural fluctuation and energy fluctuation of melt, and then affected nucleation free energy.\(^{29}\) The potential barrier from liquid to solid decreased with intensifying energy fluctuation due to the fact that the energy of crystal growth come from the energy fluctuation of melt, i.e., \( (\Delta G^* - \Delta G') < \Delta G^* \), and \( \Delta G' > 0 \). AMF did positive work on melt, which decreased the potential barrier from liquid to solid. The potential barrier of nucleation decreased with increasing magnetic flux density, which promoted the increase of Fe precipitates from Cu matrix. Therefore, the Fe content decreased in Cu matrix of Cu-14Fe composites with AFM treatment.

### 4.3 Properties

The total oxygen in ingots includes free oxygen and oxygen impurity. In the same materials, the content of free oxygen is relatively stable, so the total oxygen can be evaluated indirectly by the oxide content. The application of AMF decreased the oxygen content of ingots, which
suggested that AMF promoted the removal of oxygen impurity in ingots.

The conductivity is determined by the microstructure and composition of the constituent phases. The volume fraction of Fe phase was similar for Cu-14Fe composites with and without AMF treatment, and the resistivity of Fe phase is much higher than that of Cu matrix. Therefore, the resistivity of Cu-14Fe composites is mainly determined by the resistivity of Cu matrix, which can be evaluated using Matthiessen’s rule as follows:

$$\rho = \rho_{\text{imp}} + \rho_{\text{dis}} + \rho_{\text{int}} + \rho_{\text{pho}} \quad (3)$$

where $\rho_{\text{imp}}$ is the resistivity caused by impurity scattering, $\rho_{\text{dis}}$ dislocation scattering, $\rho_{\text{int}}$ interface scattering, $\rho_{\text{pho}}$ phonon scattering. The as-cast composites have very small value of $\rho_{\text{dis}}$ and $\rho_{\text{pho}}$ in room temperature. The interface between the Cu matrix and Fe phase was similar for the composites with impurity scattering Cu matrix and removal of impurity, which decreased the resistance of dislocation motion. AMF treatment promoted Fe precipitates from Cu matrix, which decreased the resistance of dislocation motion. AMF treatment increased the conductivity of Cu matrix, which was reported in many previous investigations.14,20,30,31

Fe solid solution in Cu matrix causes lattice distortion, which results in slip plane becoming “roughly” and increases the resistance of dislocation motion. AMF treatment promoted Fe precipitates from Cu matrix, which decreased the matrix hardness value due to the decrease of the lattice distortion of Cu matrix.

5. Conclusions

(1) AMF treatment produced Lorentz force in melt, and the tangential component of Lorentz force caused violent melt rotation, which promoted the melt temperature and solute uniform distribution.

(2) In Cu-14Fe composites, the Fe content in Cu matrix near dendrites is higher than that away dendrites.

(3) AMF treatment changed the Fe dendrites into the club shape and equiaxed grains. The secondary dendrite arm was shortened, the dendrites became smaller and were progressively changed into spherical grains with increasing magnetic flux density.

(4) AMF treatment increased the Cu content in Fe phase, decreased the Fe content in the Cu matrix near and away Fe phase, and the Fe content in the matrix away Fe phase decreased with increasing magnetic flux density.

(5) AMF treatment increased the conductivity of Cu-14Fe composites and decreased the hardness of Cu matrix, which was attributed to AMF promoted Fe precipitates from supersaturated Cu solid solution, and removal of oxygen. The effect of applied magnetic field on the microstructure and properties of Cu-14Fe composites was much greater than that of magnetic field intensity.

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