NUCLEATION AND GROWTH BEHAVIORS OF PRIMARY PHASE IN AL-CU HYPEREUTECTIC ALLOY IN HIGH MAGNETIC FIELDS

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Abstract—The nucleation and growth of primary Al$_2$Cu phase in the Al-34.3wt%Cu hypereutectic alloy without and with magnetic fields have been investigated by differential thermal analysis (DTA). The DTA curves indicated that the nucleation temperature of primary phase was significantly reduced in a magnetic field. The X-ray diffraction (XRD) patterns confirmed that the c-axes of primary Al$_2$Cu crystals oriented along the direction parallel to a magnetic field. The microstructures showed that primary crystals aligned along a magnetic field and that their number distinctly increased with increasing a magnetic field as well. The suppression of nucleation in a magnetic field could be caused by the increase of the interfacial energy between the liquid and nucleus and the reduction of atom diffusion rates while the orientation of primary crystals were mainly attributed to both of the magnetic torque and the thermoelectric magnetohydrodynamic (TEMHD) flows.

1. INTRODUCTION

In recent decades, numerous new phenomena successively have been found in the materials processing by applying a high magnetic field. Among these phenomena, magnetic orientation has attracted many scientists. It is well-known that crystals with magnetic anisotropy can orient in a magnetic field, and therefore a high magnetic field has been widely used to prepare materials with oriented structures. As early as 1930s, Goetz [1] found that a magnetic field could induce
orientation in producing Bi single crystals. By the 1980s, Mikelson and Karklin [2] observed that the oriented structures were obtained in a series of alloys like Al-Cu alloys in a magnetic field. Savitisky et al. [3] found that ferromagnetic MnBi phase could orient along magnetic force lines in solidification experiments. Then, Rango et al. [4] succeeded in preparing bulk texture samples of YBa$_2$Cu$_3$O$_7$. Recently, many studies have concentrated on the effect of magnetic fields on oriented structures of superconducting materials [5], magnetic materials [6], nano materials [7], and even biological materials [8]. More recently, Tournier and Beaugnon [9] reviewed texturing by cooling a metallic melt in a magnetic field and pointed that texturing from a melt was successful when the overheating temperature was just a few degrees above $T_m$ and failed when the processing time above $T_m$ was too long or when the overheating temperature was too high. Based on the experimental results, they thought that intrinsic solid nuclei existed in the melt and proposed a model that predicts the existence of unmelted crystals above the melting temperature $T_m$ [10].

Nevertheless, to authors’ knowledge, there are few studies on the effect of a magnetic field on the nucleation and growth behaviors of oriented phase, both of which, without a doubt, play an important role on the formation of texturing in a magnetic field. In addition, no research pays attention to the process that oriented structures evolve accompanying crystal growth though it is well known that the crystal with susceptibility anisotropy in the weak constraint medium can rotate and orient on the action of a magnetic field. Thus, the work aims to investigate nucleation and growth of primary Al$_2$Cu phases in the Al-Cu hypereutectic alloy in a magnetic field by differential thermal analysis (DTA) in order to deeply understand the formation of oriented structures. A new explanation on formation mechanism of aligned crystals in a magnetic field has been proposed.

2. EXPERIMENTAL DETAILS

The DTA apparatus was used to detect the solidification behaviors of the alloy, which was described in detail in previous work [11]. The whole equipments mainly consisted of superconducting magnet (Oxford Instruments), DTA apparatus, programming controller and model 2700 (Keithley Instruments, Inc.). The magnet can produce a magnetic field with a maximum intensity up to 14 T. In experiments, the samples in the DTA apparatus were placed in the center of magnet, namely, the position of the maximum intensity of a magnetic field.

The alloy ingot was prepared with pure Al (99.99%) and Cu (99.99%) by induction melting in argon atmosphere. The chemical
analysis showed the alloy with a composition of Al-34.3wt%Cu. The cylindrical samples with a diameter of 4 mm and a height of 4 mm for DTA were obtained by wire cutting. The DTA tests were carried out in a temperature range from a room temperature up to 700°C. The samples were heated to 700°C at the rate of 10°C/min, hold for 20 min and then cooled at the rate of −5°C/min. The heating chamber was fluxed with high pure argon in runs.

The post-treated samples were cut along the directions parallel and perpendicular to a magnetic field. The microstructures of samples on different sections were examined by using an optical microscopy after mechanically polishing and etching. The crystallographic orientation was studied by X-ray diffraction (XRD) with Cu-Ka.

3. RESULTS

In order to detect the effect of a magnetic field on nucleation of primary phase in the Al-34.3wt%Cu alloy, the DTA tests have been carried out with and without magnetic fields at the cooling rate of −5°C/min. As showed in Figure 1, two exothermic peaks are readily observed on each DTA curve. Minor peaks originate from the precipitation of primary Al$_2$Cu crystals and the major ones are from the growth of Al-Al$_2$Cu eutectics. The nucleation temperatures $T_n$ of primary Al$_2$Cu crystals in magnetic fields are obviously lower than that without a magnetic field. The nucleation temperature in 12 T magnetic field even is about

![Figure 1](image)

**Figure 1.** DTA curves of the Al-34.3wt%Cu alloy at cooling rate of −5°C/min. The nucleation temperature $T_n$ is defined as the temperature at which DTA curve initially departs from the baseline on the high temperature side of the exotherm.
8 °C below that without a field. It demonstrates that a magnetic field suppresses the nucleation of primary phase in the melt. Moreover, the nucleation temperature is reduced as a magnetic field increases. It means that it is more difficult for primary Al$_2$Cu crystals to nucleate in the melt in higher magnetic field.

The XRD patterns of the samples obtained with and without a 12 T magnetic field are displayed in Figure 2. All the (h k l) peaks with zero l values of Al$_2$Cu crystals on the longitudinal section of samples appear in the presence of a magnetic field in comparison with those without a magnetic field, as showed in Figure 2(a). XRD patterns on the transversal sections show (00l) peaks of Al$_2$Cu crystals either appear, e.g., (002), or are enhanced, e.g., (004) in a 12 T magnetic field. Thus, the XRD patterns clearly confirmed that the c-axes of Al$_2$Cu crystals oriented along the direction parallel to a magnetic field.

Figure 3 shows microstructures solidified of the Al-34.3wt%Cu alloy on different sections with and without magnetic fields. In the absence of a magnetic field, primary Al$_2$Cu phase (white) display preferential growth along the radial direction, as showed in Figures 3(a) and (b). When applying a 2 T magnetic field, a few primary crystals orient along a magnetic field (Figure 3(c)). In higher magnetic fields, it is easily observed that the majority of primary crystals orient along a magnetic field (Figures 3(e) and (g)). Therefore, structural evolution on the longitudinal sections indicates that the degree of orientation of primary phase become higher with increasing a magnetic field. Microstructures on the transversal sections indicate that primary crystals become smaller and their number distinctly increases as a
Figure 3. Microstructures of the Al-34.3wt%Cu alloy at cooling rate of −5°C/min with and without magnetic fields. (a) Longitudinal, 0 T, (b) transversal, 0 T, (c) longitudinal, 2 T, (d) transversal, 2 T, (e) longitudinal, 6 T, (f) transversal, 6 T, (g) longitudinal, 12 T, (h) transversal, 12 T.
magnetic field increases (Figures 3(d), (f) and (h)) in comparison with those without a field (Figure 3(b)). It signifies that the number of critical nuclei of primary phase from the melt increases in a magnetic field. The results are in good agreement with the reduction of nucleation temperature $T_n$ of primary phase in the DTA tests.

In order to distinctly show the orientation of primary phase in samples, we constructed three dimensional diagrams of microstructures of Al-34.3wt%Cu alloy, as showed in Figure 4. From the pictures, one readily obtains the spatial distribution of oriented primary phase. Obviously, most primary crystals orient along a magnetic field and grow to elongated shapes in magnetic fields of 6 T and 12 T (Figures 4(b) and (c)).

### 4. DISCUSSION

From the above results, a magnetic field significantly influences the nucleation, e.g., reduction of nucleation temperature, and growth of primary phase, e.g., orientation.

Firstly, let us consider the nucleation in a magnetic field. In the classical nucleation theory, the difference of bulk Gibbs free energy between the liquid and crystal phases and the interfacial energy together determine activation energy of nucleation. The activation energy $\Delta G^*$ can be written as [12]

$$\Delta G^* = \frac{16\pi \gamma_{sl}^3}{3\Delta G_V^2} f(\theta)$$

In the Equation (1), $\Delta G_V$ is the difference in bulk Gibbs free energy, $\gamma_{sl}$ is the solid-liquid interfacial energy and $f(\theta)$ is catalytic factor.

It is not expected that the magnetic field with the order of 10 T exerts an appreciable effect on Gibbs free energy because the magnetic
Gibbs free energy induced by a magnetic field is extremely subtle for non-magnetic materials according to Magomedov’s report [13], which can be ignored compared with bulk Gibbs free energy. Additionally, although only minor undercoolings were obtained in the course of solidification in the present experiments, there was no reason to believe that a magnetic field changed catalytic factor in the same experimental conditions, such as crucible walls, inclusions, except a magnetic field. However, as we know, the interfacial energy is closely related to undercooling and even their relation was used to calculate the solid-liquid interfacial energy in the case of maximum undercooling [14]. Thus, it is inferred that a magnetic field changes the interfacial energy between the liquid and nucleus and further alters the activation energy for nucleation according to the change in nucleation temperature. There were some reports showing that a magnetic field could change the interfacial energies of some substances, e.g., water [15], pure aluminum [16]. For the Al-Cu alloy, moving Al and Cu atoms in the melt will be subjected to the Lorentz force in a magnetic field, which causes unstable atoms on the interface to migrate to a more stable position [16]. It may be said that it is more difficult for atoms to attach themselves to a nucleus. According to definition of interfacial energy that the work $dW$ required to create a new area $dA$ of interface is 
$$dW = \gamma dA$$
[17], more energy, $dW$, is needed to form a new interface by increasing the number of atoms on the interface, namely, the interfacial energy should be increased in a magnetic field. In addition, another factor should be considered, i.e., atom diffusion. For solidification of alloys, as Turnbull pointed out [18], long-range diffusion was to be expected in phase transformations that involve more than one component. The activation energy for diffusion was determined by the most slowly moving component. There are a number of reports showing that a magnetic field could effectively suppress the atom diffusion in the conducting liquids [19, 20] and alloys [21]. On the one hand, a magnetic field suppresses the convection of the melt and the mass transfer is mainly dominated by atom diffusion rather than convection. On the other, a magnetic field reduces the diffusivity of solute atoms in the melt. This means that activation energy for diffusion increases in a magnetic field. The change of the diffusivity and attachment kinetics in a magnetic field leads to increase the nucleation barrier and delay the formation of critical nuclei. Hence, the undercooling correspondingly increases in a magnetic field, which is characterized as the reduction of nucleation temperature $T_n$.

Once critical nuclei form, they will begin to grow. As is known, crystals with magnetic anisotropy in the melt will rotate due to the magnetic torque and finally orient along a certain direction which
depends on the magnetic properties of a crystal in order to keep the lowest magnetic energy. The magnetic energy of the grain in a magnetic field can be expressed as following [22]

\[ E_m(\theta, H) = -\frac{V H^2}{2} (\chi_{ab} + \Delta \chi \cos^2 \theta) \]  

(2)

In the Equation (2), \( \Delta \chi = \chi_c - \chi_{ab} \), where \( \chi_c \) is magnetic susceptibility along c-axis. \( \chi_{ab} \) is the susceptibility in the a or b-axis direction. \( V \) is the volume of the grain, \( H \) is a magnetic field, \( \theta \) is the angle between a magnetic field and c-axis. For the Al\(_2\)Cu crystal, it has a tetragonal structure. From XRD diffraction patterns, it can be concluded that the Al\(_2\)Cu crystal possesses magnetic anisotropy and its magnetic susceptibility \( \chi_{ab} \) is lower than \( \chi_c \). Therefore, the c-axis of the Al\(_2\)Cu crystal orients along a magnetic field due to \( E_m(0, H) < E_m(\pi/2, H) \).

Nevertheless, the magnetic torque, on one hand, compels the c-axis with the maximum susceptibility of primary tiny crystals to rotate to the direction parallel to a magnetic field. On the other hand, the thermal energy disturbs the rotation of tiny crystals in the melt. As primary phases grow, the magnetic energy will exceed thermal energy. The condition can be read as [23],

\[ |\Delta E| > kT \]  

(3)

where \( \Delta E \) is magnetic energy difference between mutually perpendicular axes. \( k \) is the Boltzmann constant. If we insert the expressions \( E_m(0, H) \) and \( E_m(\pi/2, H) \) into Equation (3), then

\[ \frac{1}{2} \Delta \chi V H^2 > kT \]  

(4)

From Equation (4), the magnetic energy difference increases as the grain grows and finally exceed the thermal energy. In the case, the crystal succeeds to rotate and orient. Moreover, the time for rotation is extremely short, such as, the time is about 1ms in a magnetic field of 10 T [24]. It is assumed that the grain is spherical and its radius is \( r_c \) when the magnetic energy difference is equal to the thermal energy. From the preceding analysis, when the radius of tiny crystals \( r \) is less than \( r_c \), the magnetic field cannot overcome thermal energy and thus the grain does not orient or vice versa.

Mikelson and Karklin [2] found that the oriented structures were readily obtained if the magnetic field was switched on in the partial-melting zone between solidus and liquidus line. The results meant that the rotation due to the magnetic torque could happen for only sufficiently large crystals (the size of crystals is larger than that of a critical nucleus) in the partial-melting zone rather than nuclei or
Figure 5. Schematic diagram of formation of an elongated primary phase in a magnetic field.

embryos. The magnetic torque $M$ for a crystal in a homogeneous magnetic field can be expressed as following:

$$M = \frac{\Delta \chi B^2 V}{2\mu_0} \sin 2\alpha$$  \hspace{1cm} \text{(5)}$$

where $\alpha$ is the angle between a magnetic field $B$ and the axis with maximum susceptibility. From the Equation (5), the higher a magnetic field, the larger the magnetic torque. Therefore, the degree of orientation should be higher as a magnetic field increases. This has been testified from longitudinal microstructures in magnetic fields, as showed in Figure 3. However, it can be imagined that tiny crystals in shape from the melt initially do not exhibit elongated Al$_2$Cu crystals along a magnetic field although the shape anisotropy is also an important factor for the orientation of crystals because the formation of resulting elongated primary crystals depends on growth kinetics. It may be inferred that the change of growth rates in different directions in a magnetic field leads to the formation of the elongated primary phases. Consequently, the elongated primary crystals can be achieved through three steps below and the forming progress of oriented crystals can be illustrated as displayed in Figure 5.

Step 1: Critical nuclei with radius $r^*$ form in the melt as the temperature falls.

Step 2: Tiny crystals with radius $r_c > r^*$, which nuclei grow to, succeed to rotate and orient in the condition that the magnetic energy is larger than the thermal energy.

Step 3: Oriented crystals continue to grow. Crystals grow more quickly along the $c$-axis parallel to a magnetic field while they grow more slowly along $a$- and $b$-axes due to the difference of growth conditions in different directions in a magnetic field. The primary
phase finally grow to the elongated crystals.

The first two steps have been discussed in preceding section. How does a magnetic field affect the growth rates in the different directions? We discuss how the grains grow to the elongated crystals in a magnetic field as following.

It is well known that the rates of crystal growth are mainly governed by heat and mass transfer. Primary phase can grow more quickly in the directions where the diffusivities of heat and atom are larger. In the absence of a magnetic field, the sample more quickly dissipated heat in the radial direction as the furnace temperature fell. Consequently, primary phase tended to grow along the radial direction (Figure 3(a)). Nevertheless, when applying a magnetic field, the rates of radial heat loss could be reduced since a magnetic field effectively suppressed thermal convection [25]. Radial growth became slow accordingly. Additionally, although convection of electrically conducting melt could be damped by a magnetic field in macroscopic scale [26], the thermoelectric magnetohydrodynamic (TEMHD) flows in micro scale exerted an appreciable effect on crystal growth [27]. Much research work fully demonstrated that the TEMHD flows induced by a magnetic field played an important role on solidification of metallic alloys. Moreau et al. [28] found that an external magnetic field could cause TEMHD flows around dendrites during solidification of the Bi-Sn alloy. Gorbunov [29] first investigated the effect of TEMHD on single crystal growth. Li et al. [30] observed that TEMHD flows had a marked effect on interface shape and cellular morphology during directional solidification and evaluated the magnitude of the flows at different scales.

![Figure 6.](image)

**Figure 6.** (a) Schematic illustration of TEMHD flows around the primary crystal and (b) growth of primary phase in a magnetic field.
In the growth of primary Al\(_2\)Cu crystals, the temperature gradient appears near the solid-liquid interfaces due to latent heat release. The thermoelectric currents \(j\) can be produced when the gradients of thermoelectric power \(S\) and temperature \(T\) are not parallel. It can be read as [31]

\[
j = -\sigma \Delta S \nabla T
\]

(6)

where \(\sigma\) is electrical conductivity of the material, \(\Delta S\) is the thermoelectric power of the metal pair, \(\nabla T\) is the temperature gradient. The interaction between an applied magnetic field and a thermoelectric current generates a thermoelectric force \(F\), which drives a TEMHD flow.

\[
F = -\sigma \Delta S \nabla T \times B
\]

(7)

Following Li et al’s evaluation [30], The TEMHD flows dominate the convection of the melt when the magnetic field is less than the critical magnetic field \(B_{\text{max}}\). It can be expressed as following

\[
B_{\text{max}} = \frac{1}{L} \left(\frac{\mu}{\sigma}\right)^{1/2}
\]

(8)

where \(L\) is characteristic length, \(\mu\) is the dynamic viscosity. In the current experiments, the typical values for Al-Cu alloys are listed below: \(L = 1\ \mu\text{m}\), \(\mu(700^\circ\text{C}) = 1.15 \times 10^{-3}\ \text{Pa} \cdot \text{s} [27]\), \(\sigma(700^\circ\text{C}) = 3.0 \times 10^6\ \Omega^{-1}\text{m}^{-1}\ [32]\), \(\nabla T = 10\ \text{K} \cdot \text{cm}^{-1}\). Substituting these parameters into the Equation (8), one easily deduces that the value of \(B_{\text{max}}\) is about 19 T. Obviously, the applied magnetic fields (12 T) are less than 19 T. Thus, the thermoelectric force can drive the flows of the melt beyond the magnetic damp on micrometer scale. According to the relation between directions of thermoelectric currents and a magnetic field, one readily obtain directions of thermoelectric force and TEMHD flows, as showed in Figure 6(a). From the picture, the TEMHD flows continually sweep the solid-liquid interface, which make it more difficult that solute atoms deposit to a crystal. The amplitude of TEMHD flows near lateral interfaces is relatively larger than that on others owing to a vertical magnetic field. Hence, the rates of crystal growth in \(x\)-direction are slower than those in \(z\)-direction, as displayed in Figure 6(b). The TEMHD flows, therefore, change the rates of atom deposition, i.e., growth rates, on different positions of the interface. The primary phase finally grow up to the elongated crystals along a magnetic field.

5. CONCLUSION

The high magnetic field DTA apparatus has successfully been used to monitor the nucleation of primary Al\(_2\)Cu phase in the Al-
34.3wt%Cu. The DTA curves showed that the nucleation of primary phase was markedly suppressed in magnetic fields, which was further demonstrated by the increase of the number of primary crystals on the transversal sections. The suppression of nucleation could be attributed to the increase of interfacial energy and the reduction of diffusion rates while the magnetic torque and the TEMHD flows were responsible for the formation of oriented crystals.

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