Effect of a High Static Magnetic Field on the Origin of Stray Grains during Directional Solidification

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The formation of stray grains in directionally solidified Al-4.5 mass% Cu alloy under an axial high static magnetic field up to 6 T has been investigated. Electron backscattering diffraction (EBSD) was performed to analyze the orientation of the stray grains. The experimental results suggest that the formation of the stray grains are significantly affected by the external magnetic field. The modification of dendrite morphology demonstrates the existence of thermoelectric magnetic effect on dendritic scale. It is implied that the thermoelectric magnetic force (TEMF) gives rise to the pinch-off of the sidebranches. When the fragments form, they will become the source of the stray grains. Moreover, free dendritic fragment will rotate in melt and tend to align the (310) crystallographic axis along the direction of the magnetic field. This is because of the magnetic torque induced by the anisotropic susceptibility of α-Al crystal. [doi:10.2320/matertrans.MG201601]

1. Introduction

To exploit the anisotropic properties of crystals, directional solidification (DS) technology is widely utilized for manufacturing components with columnar or single crystal structure that align a particular crystallographic axis to the growth direction.¹ However, due to the disturbance in liquid and/or solid phases, defects often emerge during the DS process.² Among these crystalline faults, stray grain (also called misaligned grain or spurious grain) is a misorientation imperfection that not only breaks the integrity of matrix, but also forms high angle grain boundaries which is sensitive for crack initiation.³ On the other hand, the randomly orientated stray grains would overgrow the well aligned crystals, leading to undesired orientation after solidification.⁴,⁵ Consequently, the origin of the stray grains has drawn great research attention in order to eliminate this defect in practical production.⁶-⁹

Recently, the application of a high static magnetic field in the area of casting brings about a promising method to tailor microstructures. A crystal with magnetic anisotropy will align the easy magnetization axis, e.g., the axis of maximum magnetic susceptibility, to the direction of the magnetic field.¹⁰ Therefore, a combination of the high static magnetic field and DS would produce columnar or single crystal components with desired orientation.¹¹-¹³ However, it is hither to in lack of experimental study for stray grain formation during DS process under the high static magnetic field.

The purpose of this paper is to investigate the effects of the high static magnetic field on stray grain formation during DS of metallic alloy. The Al-4.5 mass% Cu alloy samples grown form (100) single-crystal seeds were directionally solidified at various experimental conditions. This single phase alloy is selected by the following reasons: i) The liquid in the mushy zone is enriched in rejected Cu solute and denser than bulk liquid. In positive temperature gradient, the solute gradient will stabilize the interdendritic melt. Therefore, the effect of magnetic field can be better evaluated; ii) the α-Al crystal is paramagnetic so that influence of magnetization would be mitigated; iii) the electrical transport properties of Al-Cu Alloys are well-known.

2. Experimental Procedure

Al-4.5 mass% Cu alloy was prepared by melting pure aluminum (99.99%) and copper (99.999%) in an induction furnace under the protection of high purity argon. The melted metal was casted into a cylindrical graphite mold. Alloy rods with dimensions of 3 mm in diameter and 150 mm in length were obtained by cutting the ingot. Then the rods were placed into high purity corundum tubes for DS experiment.

The details of the Bridgman apparatus in the high magnetic field are shown in Fig. 1. The superconducting magnet can produce an axial static magnetic field with an adjustable intensity up to 6T. The heating element is a cylindrical silicon carbide tube. Temperature gradient is controlled by adjusting the temperature of the hot zone. DS was conducted by pulling the crucible assemblies downward. All alloy rods were directionally solidified without magnetic field at first. The axial orientation near the end of solidified rod was examined. If the dendrite array was the (001) crystallographic direction, the rod was selected as a seed. Then, the seed was placed into the corundum and carefully positioned in the furnace to ensure that only part of it melted in order to preserve the axial (001) orientation. The crucible assemblies were solidified again under various temperature gradients and magnetic fields at a fixed pulling rate (v = 50 µm s⁻¹). After desired length solidified, quenching was carried out by quickly withdrawing the specimen into a water-cooled cylinder containing Ga-In-Sn liquid metal.

The transverse sections of the solidified samples were mechanically ground and electrolytic polished. Microstructures were revealed by Leica DM6000 optical microscope (OM) after etching in a dilute HF solution (0.5% HF). Electron back-scattering diffraction (EBSD) measurements were carried out using an Apollo 300 SEM microscope equipped with an Oxford Nordlys detector. The recording and
indexing of the pseudo-Kikuchi lines was performed by the software Channel5 from HKL Technology.

3. Results

3.1 Observation of stray grains in DS samples

Figure 2 shows transverse microstructures and orientations of the samples directionally solidified under various magnetic fields at the temperature gradient of $27 \text{ K cm}^{-1}$. Under the magnetic fields of 0 and 2 T, the axial orientations of the dendrite arrays locate around $(001)$ direction and no stray grains emerge (Fig. 2(a) and (b)). In the magnetic field of 4 T, two stray grains occur (marked 2 and 3 in Fig. 2(c)). When the magnetic field increases to 6 T, four misaligned grains (marked 2, 3, 6 and 7 in Fig. 2(d)) are observed. The orientations of grains marked 2, 6 and 7 lie closely to $(310)$ direction. These results indicate that stray grains are inclined to form in higher magnetic fields ($>2$ T). Figure 3 exhibits the grain morphology on the longitudinal sections correspond to Fig. 2(a) and (d). Without magnetic field, the $(001)$ dendrite trunks are well aligned to the temperature gradient. In the presence of 6 T magnetic field, stray grains appear at the edge of the mould wall. The favored growth direction of the stray grains is not parallel to the heat flow. On the other hand, the sidebranches in the region between the two primary trunks become quit irregular than that of no magnetic field. Figure 4 presents the transverse sections of the samples directionally solidified at higher temperature gradients under 6 T magnetic field. When the temperature gradient increases to $65 \text{ K cm}^{-1}$ and $101 \text{ K cm}^{-1}$, the formation of stray grains is suppressed and the dendrite arrays exhibit axial $(001)$ orientation inherited from seed. The results suggest that the formation of misaligned grains is not favored at higher temperature gradient if the intensity of magnetic field is fixed.

3.2 Evolution of stray grains during DS

To examine the evolution of the stray grains, OM observation and EBSD analysis at different distances along the growth direction of a sample were performed. The results are shown in Fig. 5. In section I, it could be observed that the orientation of the seed crystal is $(001)$ crystallographic direction. The small size grains with random orientation at the edge of the seed crystal are due to the freezing of melt fell into the gap between the seed and crucible wall. At initial pulling stage, four stray grains appear in section II. These
grains are randomly oriented and have no orientation relationship with the seed. As growth proceeds, these stray grains are overgrown by [001] dendrites from the seed and only one stray grain survives in section III. However, at the distance of 30 mm from initial solid-liquid interface (section IV), a new stray grain colored yellow emerges near the center of the cross-section. Finally, in section V, several stray grains are observed at the perimeter of the sample. These experimental results show that the stray grains in the later growth stage of the sample is not linked to the anomaly grains formed at the beginning of solidification.

3.3 Orientation relationship between the stray grains and dendrite array

It is noted that the orientation of the new formed stray grains in the upper section of the sample are not totally random, but tend to align their (310) crystallographic axis to the magnetic field (Fig. 2(c) and (d)). With the aim of exploring the origin of these grains, grains 4 and 6 in Fig. 2(d) are selected to identify the orientation relationship. Figure 6(a) shows the position of the two grains in the cross section of the sample. As can be seen, the dot of [001] dendrite trunk direction of grain 4 is in the center of the (001) pole figure; the points that represent the [100] and [010] secondary arms are located at the circumference. The overlapping of pole points of grain 4 and 6 in the blue circle indicates that grain 6 stems from the secondary arm of grain 4 (see Fig. 6(b)). Meanwhile, the points in (013) pole figure shows the orientation change of the stray grain as marked by the blue arrows. One of the pole points of the grain 6 lies on the center of (013) pole figure (see Fig. 6(c)). This means that (310) direction of grain 6 aligns to the direction of magnetic field.

4. Discussions

During DS, the existence of inoculants in melt often leads to heterogeneous nucleation of stray grains. Since the samples are obtained by melting high purity alloy, the precipitation of these particles is not favored. Besides, the heterogeneous nucleation would happen on mould wall, especially at the beginning of DS process. Stanford et al. pointed out that this grain defects occurred only over a distance of 2 mm in the growth direction; after this distance no further nucleation is observed. This is agreement with our observation that the number of misaligned grains is decreased as the solidification front advanced from section II to III (see Fig. 5). From Fig. 5, we can also find that the stray grains in section IV have no orientation relationship with the defect grains in section II. It can be concluded that the stray grains formed under high static magnetic field is not due to the heterogeneous nucleation. On the other hand, the detachment of dendrite arms is accepted for stray grain formation. As mentioned above, the EBSD analysis suggests that the stray grains initiate from the secondary arms. Secondly, the size of some stray grain (grain 3 in Fig. 2(c)) is comparable with the diameter of the secondary arm. At last, in the presence of the high magnetic field, the sidebranches in the interdendritic region are seriously distorted (Fig. 3(b)). Therefore, it is suggested that the high magnetic field exerts great impact on the sidebranches and promotes the detachment.
The pile-up of rejected solute has been proved to trigger sidebranch fragmentation.\(^\text{18}\) Since distribution of solute element is affected by convective mass transport, the detachment behavior of sidebranch would be affected by the fluid flow. When a conductive crystal grows in DS assemblies, the difference of Seebeck coefficients between the solid and liquid phases will induce thermoelectric currents (TEC). When a static magnetic field is imposed, the Lorentz force is created by the interaction of the TEC and the field. This is the thermoelectric magnetic effect. The Lorentz force will drive melt motion, i.e., the thermoelectric magnetic convection (TEMC).\(^\text{19}\) If the columnar dendrite well aligns to the magnetic field, the TEMC is a vortex and flows in the plane perpendicular to the primary trunk.

Figure 7 shows the dendrite morphologies in the traverse sections without and with a 6 T magnetic field at the temperature gradient of 27 K cm\(^{-1}\). The TEMC causes high-order sidebranch in upstream direction to grow faster than the downstream side, which lead to a pinwheel-like pattern.\(^\text{20}\) This morphology change proves the existence of the TEMC around the columnar dendrite and the TEMC is not damped up to 6 T magnetic field. The stirring effect by the TEMC could reduce the solute build-up. To confirm this, Energy Dispersive Spectrometer (EDS) was applied to measure the solute microsegregation in interdendritic region. The measurements were carried out along secondary dendrite arms in the transverse sections. As shown in Fig. 8, the interdendritic solute accumulation is reduced in magnetic field. Therefore, the likelihood of fragment formation due to solute enrichment is reduced by the TEMC.

The mechanical loading also plays a substantial role in dendrite fragmentation.\(^\text{21}\) As mentioned above, due to thermoelectric magnetic effect, Lorentz force exists in solid. We term the Lorentz force acted on solid "thermoelectric magnetic force (TEMF)". The amplitude of the TEMF is written as:\(^\text{22}\)

\[
\mathbf{f}_{\text{TEMF}} = \frac{\sigma_\text{L} \sigma_\text{S} f_\text{L}}{\sigma_\text{L} f_\text{L} + \sigma_\text{S} f_\text{S}} (S_{\text{s}} - S_{\text{l}}) GB
\]  

where \(\sigma_\text{s}, \sigma_\text{l}\) are the electric conductivities of the solid and liquid phases; \(f_\text{s}, f_\text{l}\) the solid and liquid fractions; \(S_{\text{s}} \text{ and } S_{\text{l}}\) are the Seebeck coefficients of the solid and liquid phases, respectively, \(B\) is the magnetic field and \(G\) is the temperature gradient. When the columnar dendrite well aligns to the direction of \(G\), the thermoelectric current in the primary trunk is nearly parallel to \(B\) and no Lorentz force is generated. On the other hand, the thermoelectric current around the primary trunk is not parallel to the magnetic field. This is proved by the existence of the TEMC. The secondary dendrite arms in mushy zone will suffer the TEMF. The integrity of these forces could impose a torque on the columnar dendrite. Since the TEMF is a body force, the magnitude of the torque is proportional to the volume of the sidebranches. The volume of a fully developed secondary arm is:

\[
V_1 = \left(\frac{d}{2}\right)^2 L_1
\]  

where \(d\) and \(L_1\) are the diameter and the length of the secondary dendrite arm, respectively. \(L_1\) is equal to half of primary dendrite spacing. For a fixed pulling speed, \(L_1\) is written as:

\[
L_2 = k_1 G^{-1/2}
\]  

where \(k_1\) is a constant number for a fixed pulling rate. The number of the secondary arms \(n\) could be expressed as \(n = 4 L_0 L_2^{-1}\). The \(L_0\) is the length of mushy zone:

\[
L_0 = \Delta TG^{-1}
\]  

where the \(\Delta T\) is the temperature interval between the solidus and the liquidus. The secondary arm spacing \(L_2\) is:\(^\text{23}\)

![Fig. 7 Evolution of the tertiary sidebranch in the plane perpendicular to the primary trunk: (a) without and (b) with a 6 T magnetic field. The samples were directional solidified at \(G = 27\) K cm\(^{-1}\).](image1)

![Fig. 8 Microsegregation profiles of the Al-4.5 mass%Cu alloys under various magnetic fields. The samples were directional solidified at \(G = 27\) K cm\(^{-1}\).](image2)
Where $k_2$ is the constant number for a fixed pulling rate. The force acted on the secondary arms is:

$$F = f_{\text{TEMF}} V = n f_{\text{TEMF}} V_1$$

The torque $M_t$ on the primary trunk is:

$$M_t = \frac{F D}{2}$$

where $D$ is the diameter of the primary trunk. The maximum shear stress $\tau_{\text{max}}$ is:

$$\tau_{\text{max}} = \frac{16 M_t}{\pi D^3}$$

As a result, the primary trunk would be twisted by this shear stress.

In dendrite network, further twisting of the columnar dendrite will be impeded by the neighboring dendrites or crucible wall. Then, the TEMF imposed on the whole columnar dendrite will concentrate and induce bending moment $M_2$ in secondary dendrite arms. This bending moment is expressed as:

$$M_2 = FL_1$$

For a fixed pulling rate, this bending moment is proportional to $BG^{-5/3}$ as deducing from above by using the relationship $D = d = 0.31L_2$.\(^{23}\) Finally, the secondary arm can be pinched-off to form stray grain. This is the reason why strays are preferred to form as the intensity of magnetic field enhanced (Fig. 2), while not be favored for high temperature gradient (Fig. 4). This mechanism is schematically illustrated in Fig. 9.

When the fragments are formed, they will not settle to the bottom of the interdendritic region due to an upward flow.\(^{24}\) This flow is a counter flow of the TEMC. As the fragments floated in melt, they will undergo a magnetic torque $\Gamma$ caused by the magnetic anisotropy of the aluminum crystal:\(^{25}\)

$$\Gamma = \frac{\Delta \chi}{2\mu_0} B^2 V \sin 2\theta$$

Table 1 The magnetic anisotropy of pure aluminum crystal.\(^{26}\)

<table>
<thead>
<tr>
<th>Crystallographic Directions</th>
<th>Magnetic susceptibility ($10^{-6} \text{ cm}^3 \text{g}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>0.541</td>
</tr>
<tr>
<td>(100)</td>
<td>0.561</td>
</tr>
<tr>
<td>(110)</td>
<td>0.614</td>
</tr>
<tr>
<td>(210)</td>
<td>0.625</td>
</tr>
<tr>
<td>(121)</td>
<td>0.612</td>
</tr>
<tr>
<td>(310)</td>
<td>0.745</td>
</tr>
<tr>
<td>(311)</td>
<td>0.730</td>
</tr>
</tbody>
</table>

where $\Delta \chi$ the difference of the susceptibilities of two crystallographic directions, $\mu_0$ the permeability in a vacuum, $B$ magnetic field, $V$ the volume of the crystal, $\theta$ the angle between the magnetic field $B$ and the crystallographic direction of the greatest susceptibility. If the crystal can rotate freely, its crystallographic axis of largest susceptibility will align to the direction of the magnetic field. Zhu\(^ {26}\) measured the magnetic susceptibility of various crystallographic axes of aluminum crystal (shown in Table 1) and found that the (310) direction exhibited the maximum magnetic susceptibility. This result illustrates why the stray grains usually align the (310) direction along the magnetic field.

5. Conclusions

The formation behaviors of stray grains in directionally solidified Al-4.5 mass% Cu alloys under an axial high magnetic field are studied. The following conclusions could be made.

(1) The emergence of stray grains during DS is associated with the detachment of secondary dendrite arms. The number of stray grains is significantly affected by the intensity of magnetic field and temperature gradient. Low temperature gradient and high magnetic field is favored for stray grain formation.

(2) The application of high magnetic field could alter the
fluid flow pattern in interdendritic region and reduce microsegregation. The fragmentation due to solute enrichment is reduced.

(3) As a high magnetic field imposed, primary dendrite trunks are twisted by the TEMF acted upon secondary arms. The impediment of the further distortion of primary dendrite trunks by neighboring dendrites or crucible wall arises bending moment on secondary arms and leads to fragmentation.

(4) After the fragments are formed, they will align their (310) direction to magnetic field due to the maximum value of magnetic susceptibility in this crystalline direction of \(\alpha\)-Al crystal.

Acknowledgments

This work is supported by the National 973 Project (No. 2011CB610404), the Shanghai Committee of Science and Technology (No. 13DZ1101102, 13521101102 and 14521102900), and the Natural Science Foundation of China (No. 51404148 and 51401116).

REFERENCES