Materials Research. 2018; 21(6): e20180381
DOI: http://dx.doi.org/10.1590/1980-5373-MR-2018-0381

Preparation and Growth Characterization of Al_2Cu Phase Crystal with the Single Orientation Under Directional Solidification

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Received: May 29, 2018; Revised: August 13, 2018; Accepted: August 17, 2018

Through decreasing the sample size, the regular faceted rectangular Al_2Cu phase crystal was prepared under directional solidification. Effects of sample size on the microstructure morphologies and orientations of intermetallic Al_2Cu phase crystal growth at 10 μm/s have been characterized and investigated. The transverse-section microstructure of primary Al_2Cu phase crystal transited from L-shaped pattern to regular faceted rectangular pattern with a single preferred orientation at [001] direction with sample size decreasing. By using the serial sectioning technique, the three-dimensional (3D) microstructure of Al_2Cu phase in 0.45 mm sample was observed as rectangular parallelepiped. Moreover, the faceted interfaces of Al_2Cu phase crystal were determined as {110} planes. Based on growth characteristics of the Al_2Cu phase crystal, a growth mode in different sizes samples under directional solidification was proposed. The experimental results show that a regular microstructure with preferred single orientation can be achieved in small-size sample during directional solidification.

Keywords: *Solidification, Intermetallic alloys and compounds, Regular faceted rectangular, Orientation, Crystal growth.*

1. Introduction

The intermetallic compounds crystal with crystalline anisotropy may grow along preferred growth direction under directional solidification, and could result in various microstructure morphologies[1-4]. However, in directional solidification, thermal gradient and solute segregation often cause the thermosolutal convection in liquid, resulting in these crystals growth without any apparent preferred orientations. To avoid the thermosolutal convection effect and control crystal to grow well, Trivedi *et al*.[5,6] had prepared the sample by reducing sample size and investigated the effect of sample size on microstructure during directional solidification. They found that with sample size decreasing, the Al_2Cu phase microstructure morphology could be well controlled because of the weakened thermosolutal convection. But they had not discussed and analysed whether or not the crystal orientation changes in their work. Until recently, few works have been done to investigate the effect of sample size on crystal orientation. However, microstructure morphology was decided by its orientation. And the intermetallic Al_2Cu phase has crystalline anisotropy, thus it could be displayed various growth patterns with specific growth direction during different directional solidification conditions[1]. Therefore, to well control the Al_2Cu crystal growth, it is urgently necessary to study its orientation by reducing the sample size.

However, heavy convection was still present even if the sample diameter of Al-Cu hypereutectic alloy had been decreased to 0.8 mm [7]. In order to control Al_2Cu crystal well growth with a single preferred orientation in Al-Cu hypereutectic alloy, it is essential to further reduce the sample diameter. Nevertheless, due to capillary effect, liquid could not fill in a thin container, which causes that the method introduced by Trivedi[6] was limited. Thus it needs to develop a new method to prepare the small (thin thickness) sample to control crystal growth well.

In this work, a method is firstly developed to realize the smaller size solidified samples, in which micro thermosolutal convention solidification can be achieved. On the basis, the aim of this work is to prepare regular faceted rectangular Al_2Cu phase with the single orientation, then investigate the effect of sample size on the microstructure morphology and orientation of Al_2Cu phase crystal under directional solidification. The experimental results show that the small directionally solidified samples can obtain regular microstructure with a single growth direction of Al_2Cu phase crystal.

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2. Experimental Methods

2.1 Materials

Al-40 wt.% Cu alloy was prepared using 99.99% purity aluminium (Aluminum Corporation of China Limited, China) and 99.5% purity copper (Copper Corporation of China Limited, China) in a vacuum induction melting furnace. Figure 1(a) presents the schematic drawing of the 4 mm sample with a single high-purity alumina crucible (Beijing Ding Sheng Technology, China) under directional solidification. Different with that in the single crucible, the device for the 0.45 mm sample preparing was designed based on the method introduced by Trivedi *et al.*[6] as shown in Figure 1(b). The sample was embedded in the middle of two high-purity alumina crucibles (inner crucible with a diameter of 3.1 mm and outer crucible of 4 mm). In this case, the average thickness of the sample is only 0.45 mm, which is greatly reduced compared with 0.8 mm introduced by Lee *et al.*[7]. Moreover, the thickness of sample can be further reduced by increasing the size of the inner crucible.

2.2 Sample preparation

Directional solidification experiments were carried out using a Bridgman vertical vacuum furnace described elsewhere[8]. The thermal gradient was measured using a Φ0.5 mm NiCr-NiSi thermocouple. In directional solidification process, the sample was heated by a graphite heater at 700 ºC and then kept isothermal for 20 minutes so as to homogenize the original ingot composition. Subsequently,

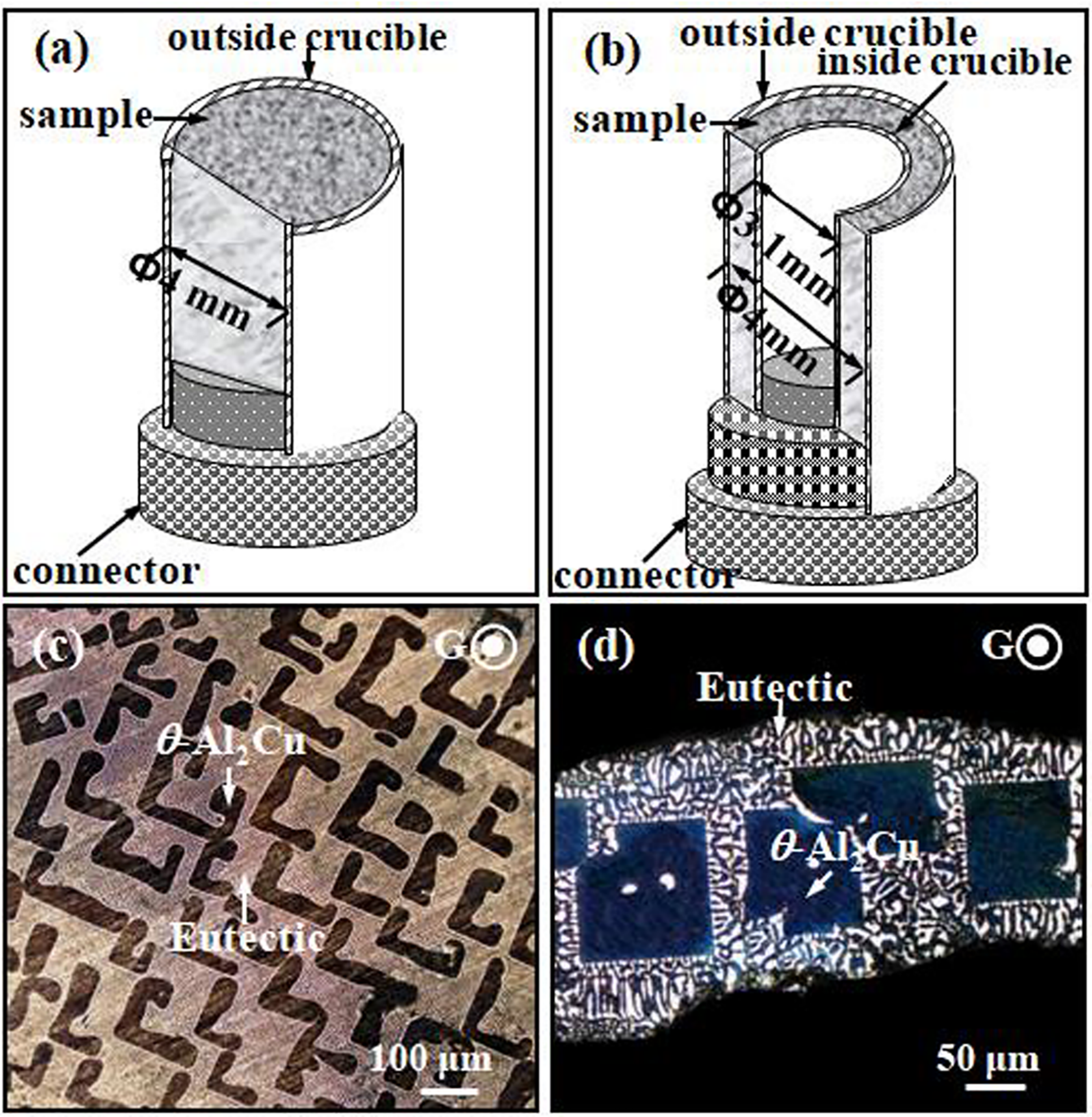

Figure 1. The schematic drawing of different sizes samples under directional solidification: (a) the 4 mm sample, (b) the 0.45 mm sample, transverse microstructures for (c) the 4 mm sample, and (d) the 0.45 mm sample.

the sample was moved downwards at pulling velocity of 10 μm/s. When the directional solidification distance reached 50 mm, the sample was quenched into a liquid Ga-In-Sn pool to keep the S/L interface.

2.3 Characterization

The directionally solidified samples were sectioned horizontally and vertically, respectively, and etched with the agent of H_2O (46 mL) + HNO_3 (3 mL) + HF (1 mL) to photograph its microstructures by the scanning electron microscopy (SEM, JSM-6390A). The high resolution transmission electron microscopy (HRTEM, Tecnai G^2 F30) was employed to observe the faceted interface of Al_2Cu phase. In addition, the orientations were investigated by means of the X-ray powder diffraction (XRD, D/max-3) and the electron back-scattered diffraction (EBSD) in scanning electron microscopy (SEM, Zeiss Supra 55) equipped with the Channel 5 EBSD system (HKL Technology-Oxford instrument).

In this work, Materialise's interactive medical image control system (Mimics) software and the serial sectioning technique were applied to reconstruct the three-dimensional (3D) microstructure images of the primary Al_2Cu phase. The 3D serial sectioning procedure working principle is similar to the internal structure of the human body analyzed layer by layer by CT in medicine. If we want to obtain the whole microstructure of sample, we should scan it layer by layer and then reconstruct the each layer information by the Mimics system. Firstly, the surface of the sample was milled off with a step-size, then the microstructures of the polished samples were revealed and the first layer information was obtained. Nest repeat the first step and milling off the surface of the sample with the stayed step-size to obtain the second and more other layers information by the serial sectioning technique. After obtaining the all layers information of sample, finally, the obtained images and information were transferred into Materialise's interactive medical image control system, then fixed position, edited, and reconstructed into three-dimensional models.

3. Results and Discussions

3.1 The temperature gradient measured in different sizes samples

In this experimental section, the temperature gradient (*G*) was measured using the NiCr-NiSi thermocouple at the pulling velocity of 10 μm/s. Figure 2 shows the schematic of the temperature gradient measurement and the experimental date in different size samples. The NiCr-NiSi thermocouple was embedded inside the crucible of 4 mm in Figure 2(a) and the inner crucible with a diameter of 3.1 mm in Figure 2(b), respectively. Under directional solidification process, the sample was preheated by a graphite heater at 700 ºC for

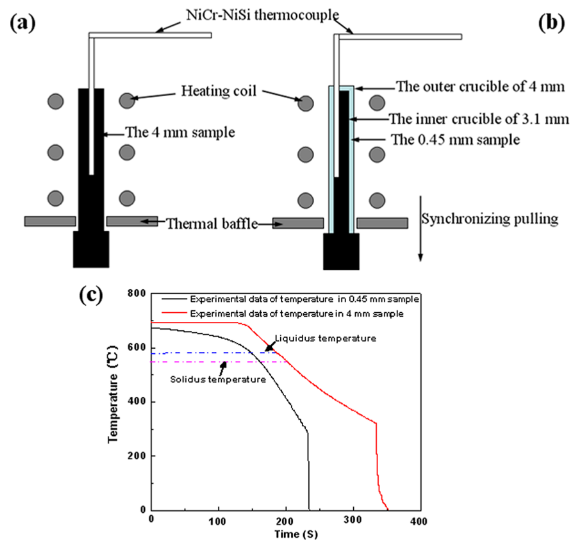

Figure 2. The schematic of the temperature gradient (*G*) measurement in different sizes samples: (a) the 4 mm sample, (b) the 0.45 mm sample, and (c) the experimental date of temperature in different sizes samples.

20 minutes. Then the NiCr-NiSi thermocouple and the sample were moved downwards synchronously. At the same time, the temperature curve was measured by the thermometric instruments shown in Figure 2(c). The thermal gradient was calculated by the Eq. (1)[9]:

$$G = \frac{T_L - T_S}{V \cdot t} \tag{1}$$

where T_L is the liquidus temperature, T_S is the solidus temperature, V is the pulling rate, and t is the time of the melt cooling from the liquidus temperature to the solidus temperature. Through calculating, the thermal gradient in 4 mm sample was about 236 K/cm, which was less than the value of 255 K/cm in 0.45 mm sample. This result proves that when the thickness of sample is thinner, its thermal gradient is higher. However, the difference value of thermal gradient measured between different sizes samples is least (i. e. to about 8.5% of the thermal gradient in 4 mm sample). It can be deduced that the effect of the samples size (thickness) decreasing on the temperature gradient during directional solidification is small.

In fact, the minimal changes about the temperature gradient in different sizes samples could not result in more effects on the morphology evolution. Trivedi *et al.*[10] found that with the diameter of Al-4%Cu alloy sample decreasing, the crystal morphology had little differences only the size decreased. It indicates that the temperature gradient may only affect the characteristic size of microstructure, such as the dendrite arm spacing, eutectic spacing and so on. On the other hand, a large number of previous works[11-13] were investigated the preferred orientation of the super alloys during directional solidification process. The preferred orientation was the [001] direction, which had not been changed whether in higher or lower temperature gradient. The effect of thermal gradient on dendrite orientation may be also small. This means that the growth changes of the Al_2Cu phase caused by the changing of thermal gradient can be neglected in this work.

3.2 Directionally solidified microstructures (2D and 3D) in different sizes samples

Figure 1(c) and (d) show the growth patterns (2D) of Al-40%Cu alloy in different size samples under directional solidification. It is well known that the solidification microstructures of the alloy consist of primary intermetallic θ-Al_2Cu and eutectic (Al/Al_2Cu) based on the Al-Cu phase diagram. In 4 mm sample, the primary Al_2Cu phase crystal could be clearly distinguished from the eutectic in Figure 1(c). The Al_2Cu phase displayed regular faceted L-shaped and I-shaped patterns[14] in the transverse section.

When sample size decreased to 0.45 mm, the primary Al_2Cu crystals were regularly aligned in single layer and exhibited faceted rectangular patterns[15] shown in Figure 1(d), which is different from the microstructures in Figure 1(c). Moreover, the size of the Al_2Cu crystal was smaller than that in 4 mm sample. By using the serial sectioning technique[16,17], the three-dimensional (3D) microstructure of the primary Al_2Cu phase in 0.45 mm sample was reconstructed during directional solidification shown in Figure 3, which provides a novel way to deeply understand the crystal growth of the solidified phases. The Al_2Cu phase crystal was observed rectangular parallelepiped in 0.45 mm sample and grew along the pulling direction. The 2D morphologies of Al_2Cu phase in transverse section displayed the rectangular patterns by cutting the 3D microstructure along transverse section shown in Figure 3, which is consisting with the result in Figure 1(d).

Interestingly, there were some smooth holes in the three-dimensional microstructures of Al_2Cu phase crystal shown in Figure 3. Different with the forming reason about re-melting of solidification front or dissolving of the local crystal surface in the presence of impurities[18], these smooth holes were eutectic microstructures transformed from remaining liquid in the centre of the rectangle pattern of the Al_2Cu phase crystal. Actually, these holes filled by eutectic microstructures were also found in the two-dimensional microstructures in Figure 1(d). The above results indicated that the Al_2Cu phase crystal displayed different microstructures solidified under the different conditions, for example in different size samples.

3.3 Faceted interface of Al_2Cu phase determined in different sizes samples

We employed TEM to investigation the facets of Al_2Cu phase in different size samples. the L-shape and I-shaped patterns in 4 mm sample were observed in Figure 1(c). The two patterns of Al_2Cu phase were also bounded by faceted planes. Figure 4(b) is an TEM image of the microstructure of red region and Figure 4(c) is a selected-area electron diffraction pattern (SAED) from the Al_2Cu phase in Figure 4(b). The (001) zone axis was paralleled with the direction of electron beam. By indexing the diffraction patterns, the four diffraction patterns in Figure 4(c) can be identified to be the {110} facets of Al_2Cu phase. The relationship between {110} facets and surface of L-shape morphology can be identified in Figure 4(d).

From the three-dimensional (3D) microstructures, the primary Al_2Cu phase crystal displayed regularly rectangular parallelepiped and had obviously faceted characterization in 0.45 mm sample. The smooth hole was filled by eutectic microstructures shown in Figure 5(a), which was introduced before in this paper. Figure 4(b) is an enlarged HRTEM

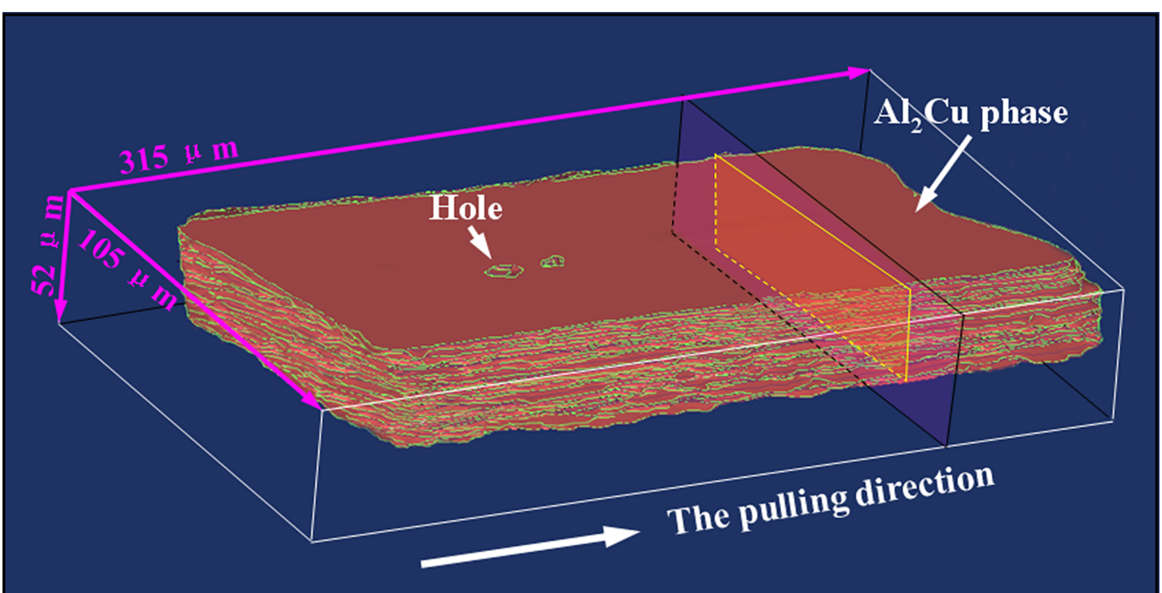

Figure 3. The 3D microstructure of primary Al_2Cu phases crystal in 0.45 mm sample during directional solidification.

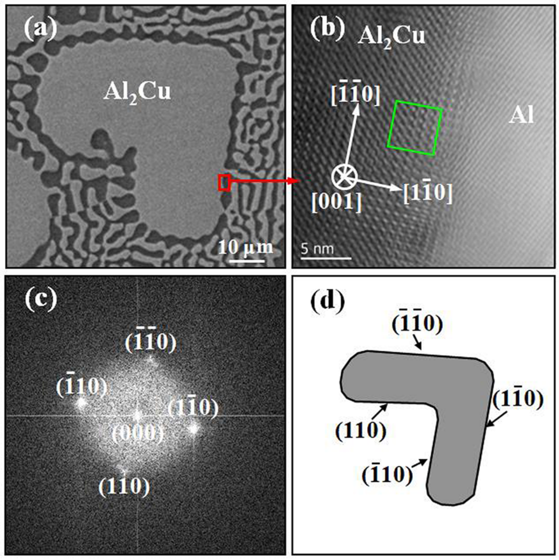

Figure 4. (a) Transverse-section SEM image of rectangle pattern about Al_2Cu phase crystal in 4 mm sample, (b) the HRTEM image of the red region from (a), (c) the selected-area electron diffraction pattern (SAED) from (b): [001] crystal, and (d) {110} facets image.

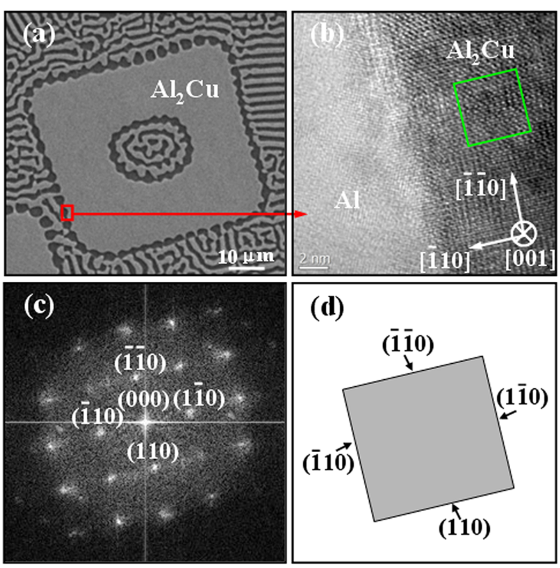

Figure 5. (a) Transverse-section SEM image of rectangle pattern about Al_2Cu phase crystal in 0.45 mm sample, (b) the HRTEM image of the red region from (a), (c) the selected-area electron diffraction pattern (SAED) from (b): [001] crystal, and (d) {110} facets image.

image of the microstructure of red region. The black area structure can be identified as Al_2Cu phase in Figure 5(b). A selected-area electron diffraction pattern of Al_2Cu phase is shown in Figure 5(c). By indexing the diffraction patterns, the {110} facets of Al_2Cu phase in Figure 5(c) can be clearly identified, which is identical to the previous work[18]. Moreover, this diffraction patterns show the faceted characteristic as the rectangle pattern in Figure 5(d). The bounded surfaces of regular rectangle pattern about Al_2Cu phase crystal were {110} facets.

In addition, Hamar *et al.*[19] obtained the growth morphology of Al_2Cu crystal assuming the growth rates to be proportional to the attachment energy. Basing on their works, it could be also inferred that the regular rectangle pattern of Al_2Cu phase crystal was bounded by {110} facets in transverse section.

3.4 Orientations in different sizes samples

With sample size decreasing, Al_2Cu phase crystal patterns became more regular and uniformly arranged; seen from Figure 1(d). The growth behaviour may be also responsible for those regular microstructures. For clarifying the crystallographic characteristic of the Al_2Cu phase crystal, XRD was used to measure its growth orientation, as reported by Huang *et al.*[20]. Generally, Al_2Cu phase crystal grew freely from various crystal planes (110), (310), (200), (211), (112), (202), and (420) [21, 22]. Only two peaks of the phase, (330) and (004), appeared in 4 mm sample, as shown in Figure 6(a). When sample size was further decreased to 0.45 mm, the crystal plane (330) disappeared and only the diffraction intensity of the peak (004) increased in Figure 6(d), which was higher than that in 4 mm sample. Apparently, Al_2Cu phase had a strong and single preferred orientation at (004) direction. The single preferred orientation was consistent with the regular rectangular patterns of the phase in Figure 1(d) and Figure 3.

Further, the crystal orientations of the primary Al_2Cu phase in different sizes samples were investigated by the EBSD analysis. Figure 6(b)-(c) and 6(e)-(f) show the EBSD results in the transverse section and corresponding (100)-pole figures of the Al_2Cu phase in different sizes samples, respectively. The L-shaped pattern and rectangular pattern could be observed in Figure 6(b) and (e), respectively. From the pole figure, it is easy to deduced that both for 4 mm and 0.45 mm samples, the application of directional solidification had oriented the primary Al_2Cu phase with the [001]-crystal direction, which was along the heat flow direction. Moreover, with the sample size decreasing, the orientation of Al_2Cu phase was further concentrated to the heat flow direction, which agrees well with the XRD results in Figure 6(a) and (d). The above results proved that a regular microstructure with a single growth direction might be obtained in small size sample.

Basing on the above results, the growth mode of Al_2Cu phase crystal under different growth conditions is proposed. Al_2Cu phase crystal belongs to tetragonal crystal system and possesses anisotropy. Normally, Al_2Cu phase will grow along disorder direction depended on the interfacial energy (surface energy, boundary kinetics, etc) under free solidification as shown in Figure 7(a). Then it will be formed various microstructure morphologies without any special orientation. Actually, its growth directions are directionless pointed to the surrounding. In directional solidification, solidified microstructure can be well controlled and the orientation was selected well resulted from the convection

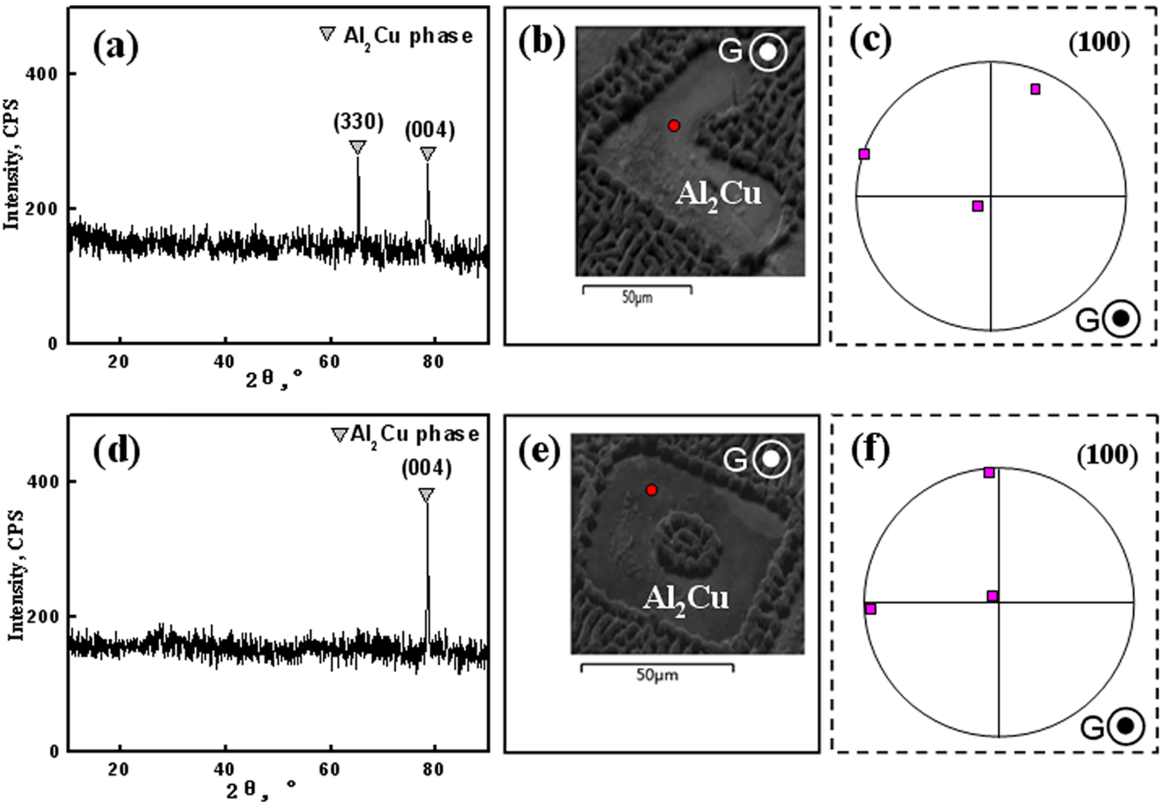

Figure 6. The 4 mm sample under directionally solidified in transverse section: (a) XRD patterns, (b) the position of EBSD testing, and (c) (100)-pole figure of Al_2Cu phase; the 0.45 mm sample under directionally solidified in transverse section: (d) XRD patterns, (e) the position of EBSD testing, and (f) (100)-pole figure of Al_2Cu phase.

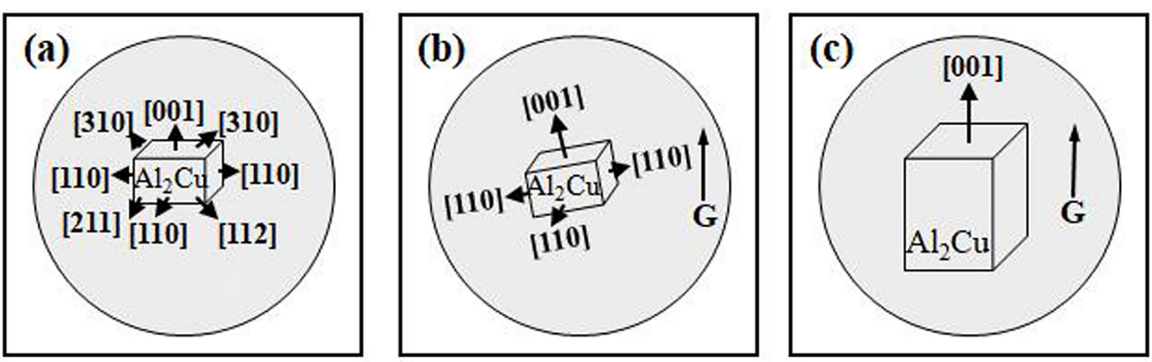

Figure 7. Growing schematic illustration of Al_2Cu phase crystal: (a) under free solidification, (b) in 4 mm sample under directional solidification, and (c) in 0.45 mm sample under directional solidification.

influence. The convection caused the change of atomic stacking direction and velocity at the interface, resulting in the interfacial energy changing. So some growth directions were disappeared. Similar with the super alloys growth during directional solidification, the directional heat flow becomes the dominant factor affecting the crystal growth[11-13]. The [001] and [110] directions were the preferred growth directions, but there were perpendicular directions. The [001] direction was the c-axis direction closing the heat flow direction and [110] direction was the normal direction of side boundary surrounding. So the Al_2Cu phase crystal growth process was including two almost simultaneous actions, such as growing taller along [001] direction nearly the heat flow direction and growing in width direction along [110] direction in Figure 7(b). However, due to the [110] direction not so concentrate to the heat flow direction shown in Figure 6(c) and not be perpendicular to the solid/liquid interface, Al_2Cu phase grew slightly tilted. Then the part of crystal was re-melted and formed the L and I-shaped patterns not the regular rectangular pattern. When the sample size decreased, there has the diffusion environment. Due to the interfacial energy of Al_2Cu phase [19], the preferred growth direction will be along the crystal plane direction with highest attachment energy and the [001] direction will be the dominant one. And in our work, the preferred orientation of Al_2Cu phase crystal was only [001] direction and it would further concentrate to the heat flow direction in Figure 7(c). The [001] growth direction in the 0.45mm was more isotropic and growth along this direction was to be faster. The phase morphology would be more regular, which is corresponding with the three-dimensional (3D) microstructures in Figure 3. The regular microstructure with a single orientation can be achieved by reducing the sample size.

In this study, a 0.45 mm thickness sample was adopted to prepare, and the regular faceted Al_2Cu phase crystal growth in Al-40%Cu hypereutectic alloy was investigated. The three-dimensional (3D) microstructures of Al_2Cu phase in small size sample became more concentrative. The results show that the solidified microstructure and the orientation selection can be well controlled in a much smaller sample under directional solidification.

4. Conclusions

The microstructures and orientations of intermetallic Al_2Cu phase crystal in directionally solidified Al-40%Cu hypereutectic alloy with different size crucibles were investigated. With the sample size ranging from 4 mm to 0.45 mm, the primary Al_2Cu phase crystal in transverse section changed from L-shaped patterns to faceted regular rectangular patterns. By using the serial sectioning technique, the three-dimensional (3D) microstructures of Al_2Cu phase in 0.45 mm sample was observed as rectangular parallelepiped. The faceted interface of Al_2Cu phase dendrite was {110} planes. The orientation of Al_2Cu phase became more concentrative and was along the heat flow direction. A single preferred orientation at (001) was obtained.

5. Acknowledgments

This work was financially supported by the fund of the Key of Scientific Research Project of Henan Provincial (No.162102210241) and the Higher Education of Henan Provincial (No.17A430007).

6. References

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