

# Microstructure of directionally solidified Cu-Cr composites<sup>①</sup>

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**Abstract:** Cu-Cr composites were prepared by self-made directional solidification equipment with the high temperature gradient and double zone heating. The microstructural evolution was investigated during the directional solidification with the different solidification rate for Cu-1.0% Cr, Cu-1.7% Cr and Cu-5.6% Cr alloys, respectively. It is shown that for the hypoeutectic Cu-1.0% Cr alloy, the general microstructures consist of primary  $\alpha$ (Cu) phase and the rod-like or needle-like ( $\alpha$ + $\beta$ ) eutectics, and for the hypereutectic Cu-1.7% Cr and Cu-5.6% Cr alloys,  $\alpha$ (Cu) phase, primary  $\beta$ (Cr) phase and ( $\alpha$ + $\beta$ ) eutectics coexist. With the increase of the solidification rate, the morphology evolution of every phase is that, 1st cellular(dendrite) of  $\alpha$ (Cu) phase thins and cellular(dendrite) spacing shortens gradually, ( $\alpha$ + $\beta$ ) eutectics set in  $\alpha$ (Cu) cellular or dendrite, and primary  $\beta$ (Cr) phase distributes unevenly on  $\alpha$ (Cu) matrix, whose morphology undergoes the change from dendrite to particle.

**Key words:** directional solidification; Cu-Cr alloy; composite

**CLC number:** TB 331; TG 113

**Document code:** A

Directional solidification is an important method to manufacture composites<sup>[1]</sup>. Cu-Cr composite is an important Cu-based engineering material, which utilizes the strengthening effect of compound structure and possesses high conductivity, and shows an important application background in contact cable<sup>[2-5]</sup>. It should be indicated that most of the previous researches focus on the hypoeutectic Cu-Cr alloys, meanwhile, they mainly investigate the effect of the microstructure of the directionally solidified Cu-Cr alloys on conductivity<sup>[6,7]</sup>, but the evolving characteristics of microstructure with the different component is reported little. In this paper, by employing the self-made directional solidification equipment with high temperature gradient and double zone heating, the microstructure evolution of Cu-1.0% Cr, Cu-1.7% Cr and Cu-5.6% Cr under the condition of different solidification rate was studied.

## 1 EXPERIMENTAL

The binary Cu-Cr alloy was smelted from the Cu-25% Cr master alloy and electrolytic pure Cu (99.94%) in a MBD-3M middle-frequency vacuum induction furnace of 25 kg capacity by using a high-purity graphite crucible. Then, the original rods (gauge of 8 mm  $\times$  100 mm) were made by investment casting.

Specimen rods of the composites were prepared by directional solidification experiment on the self-made equipment<sup>[8]</sup>, which can realize the high vacuum and high temperature gradient. The drawing velocity can be continuously adjusted within very large range and processing parameters are easily regulated and controlled by this equipment. By using thermocouples<sup>[9]</sup>, the cooling curves of the specimens can be recorded by a function recording instrument, and the temperature gradient ahead of the solid/liquid interface can be obtained and controlled. In present work, the temperature gradient is about 200 K/cm.

In order to systematically study the influence of the alloy components and solidification conditions on the microstructure, the three component alloys of near eutectic point (hypoeutectic Cu-1.0% Cr and hypereutectic Cu-1.7% Cr) and far from eutectic point (hypereutectic Cu-5.6% Cr) were selected. The solidification rate adopted in this paper was 60, 100, 200, and 400  $\mu\text{m/s}$  in order to review the variation law of microstructure under different solidification conditions.

The specimens were incised along the axial line through line incising technique, then polished, etched, microphotographed on the Neophot microscope and SEM.

① **Foundation item:** Project(2000CQ0404) supported by the Visitor Fund of the Ministry of Education

**Received date:** 2003 - 03 - 25; **Accepted date:** 2003 - 06 - 12

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## 2 RESULTS AND DISCUSSION

The typical directionally solidified microstructure of three kinds of alloys were presented in this paper, and the evolution characteristics of microstructure were chiefly analyzed.

### 2.1 Directionally solidified structure of Cu-1.0% Cr alloy

The typical solidified structures of Cu-1.0% Cr alloy under different solidification rates are shown in Fig. 1.

Based on the phase diagram in Fig. 2<sup>[10]</sup> and the analysis of spectrograph (EDS spectra are shown in Fig. 3). Fig. 1 shows that the white region is the primary  $\alpha$ (Cu) phase, and the black one is the ( $\alpha$ + $\beta$ ) eutectics. At the low solidification rate, much of the 2nd dendrite of primary  $\alpha$  phase is observed and the 1st dendrite arm is thicker, which still shows directional tendency. With the increase of the solidification rate, the 2nd dendrite decreases, the 1st dendrite thins, and cellular (dendrite) spacing shortens gently. As a result, the observed 1st dendrite becomes more and the directional tendency of  $\alpha$  phase comes to be obvious. It can be seen that when the growth rate is above 200  $\mu\text{m/s}$ , the morphology of primary  $\alpha$  phase with the increase of the solidification rate inclines to cellular, the evolving law of which answers

for the theory that dendrite arm changes with the variety of the solidification rate<sup>[11]</sup>.

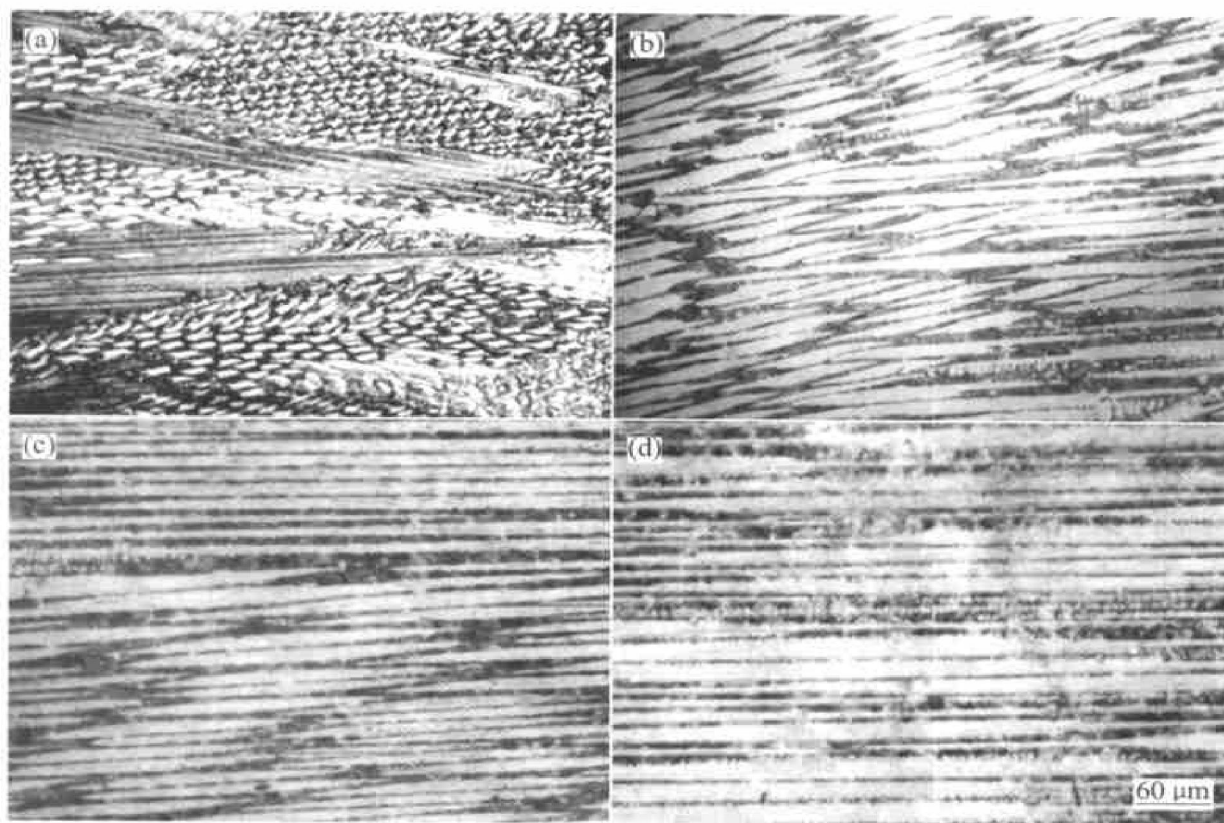
Whereas magnifying rate of optical microscopy is very low, scanning electronic microscopy is adopted to analyze the solidified structure (Fig. 3). From Fig. 1, it can be seen that, due to the influence of primary  $\alpha$ , ( $\alpha$ + $\beta$ ) eutectics are distributed directionally and orderly as a whole between the primary  $\alpha$  cellular (dendrite). But from Fig. 3, it can be seen that  $\alpha$  phase and  $\beta$  phase in ( $\alpha$ + $\beta$ ) eutectics arrange locally disorder, the morphologies of which are rod-like or needle-like. Thereby, the compound structures generally consist of  $\alpha$  matrix and ( $\alpha$ + $\beta$ ) eutectics, which are even each other and regular along the directional orientation.

Thus the solidification structures of the hypoeutectic Cu-1.0% Cr alloy consist of primary  $\alpha$  phase and rod-like or needle-like ( $\alpha$ + $\beta$ ) eutectics. With the increase of the solidification rate, primary  $\alpha$  phase thins gently and ( $\alpha$ + $\beta$ ) eutectics as the reinforcing phase set in the primary  $\alpha$  cellular or dendrite evenly and orderly.

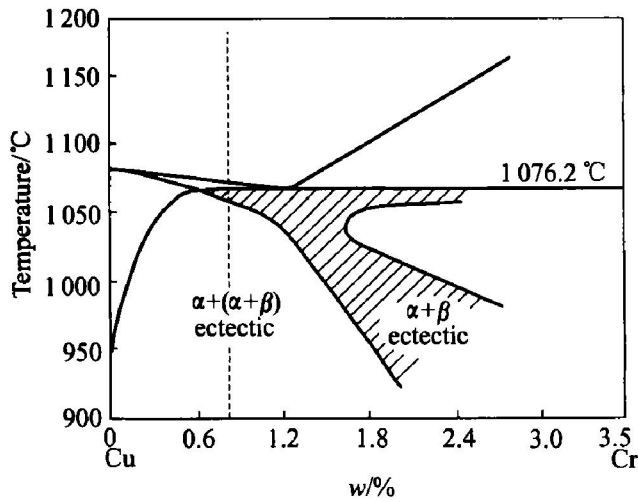
### 2.2 Directionally solidified structure of Cu-1.7% Cr alloy

Typical solidified structures of Cu-1.7% Cr alloy under different solidification rates are shown in Fig. 4.

From Fig. 4, it can be seen that the solidified structures of Cu-1.7% Cr alloy still consist of white



**Fig. 1** Microstructures from longitudinal section of Cu-1.0% Cr alloy ( $G_1 = 200 \text{ K/mm}$ )  
(a)  $-R = 60 \mu\text{m/s}$ ; (b)  $-R = 100 \mu\text{m/s}$ ; (c)  $-R = 200 \mu\text{m/s}$ ; (d)  $-R = 400 \mu\text{m/s}$



**Fig. 2** Phase diagram of Cu-Cr alloy under non-equilibrium solidification (Cu-rich corner)

$\alpha$  phase and black ( $\alpha + \beta$ ) eutectics. At the low solidification rate, the observed 2nd dendrite of  $\alpha$  phase is still more and 1st dendrite arm shows thick, which still shows directional tendency. With the increase of the solidification rate, the observed 2nd dendrite decreases, 1st cellular (dendrite) spacing shortens, cellular (dendrite) thins, and the directional tendency becomes obvious. The morphological evolution of  $\alpha$  phase in Cu-1.7% Cr alloy with the variety of the solidification rate is similar to that in the Cu-1.0% Cr alloy. It can be seen that the morphological change of  $\alpha$  phase comes slower above 200  $\mu\text{m/s}$  than that of below 200  $\mu\text{m/s}$ .

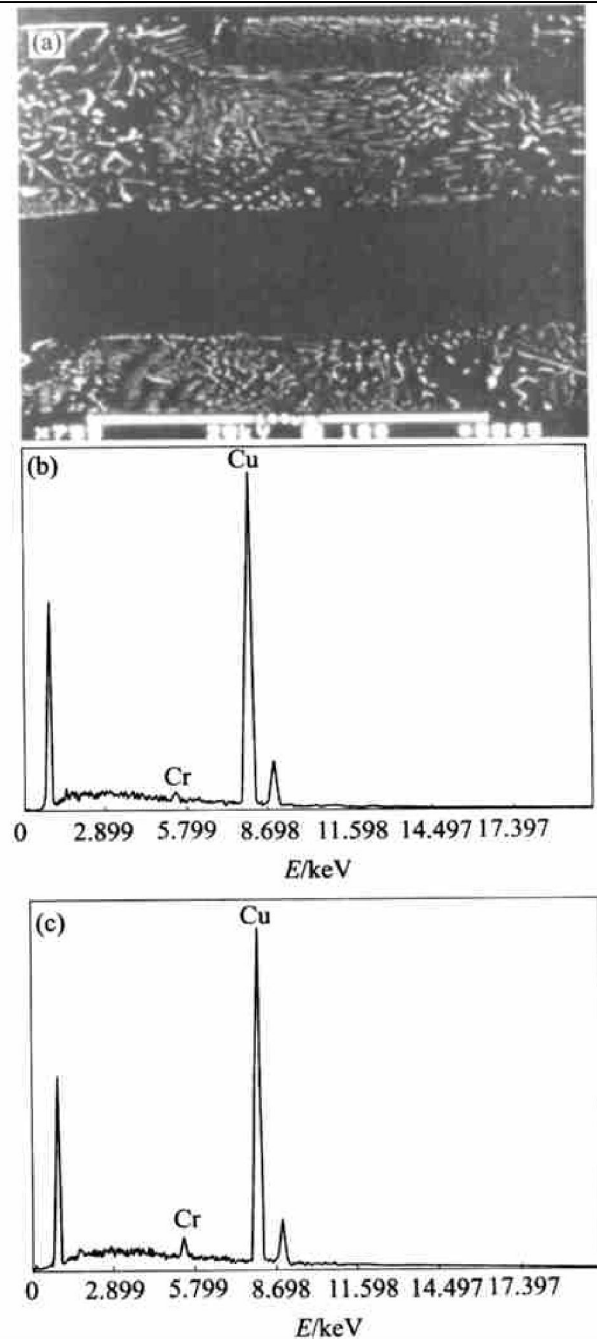
The microstructure of Cu-1.7% Cr alloy is also analyzed by SEM (Fig. 5).

Fig. 5 shows that there are some particles in  $\alpha$  matrix, besides white  $\alpha$  phase and black ( $\alpha + \beta$ ) eutectics. These particle structures are confirmed to be primary  $\beta$ (Cr) phase through the analysis of spectrograph.

When the solidification rate is higher, directional solidification takes place on the condition of far from equilibrium state, and the degree of far from equilibrium lies on the undercooling ahead of the solid/liquid interface and crystal solidification rate. For binary eutectic alloy, to achieve stable liquid/solid interface, the following formula needs to be met with [12]

$$G/v \geq [-m_1(C_e - C_0)]/D_1 \quad (1)$$

where  $G$  is temperature gradient;  $v$  is solidification rate;  $m_1$  is relevant liquidus slope;  $C_0$  is initial composition;  $C_e$  is eutectic composition;  $D_1$  is diffused coefficient of the solute in the liquid phase. If the unstable single phase is thought to happen on the boundary of the coupled zone of the growth interface, it is

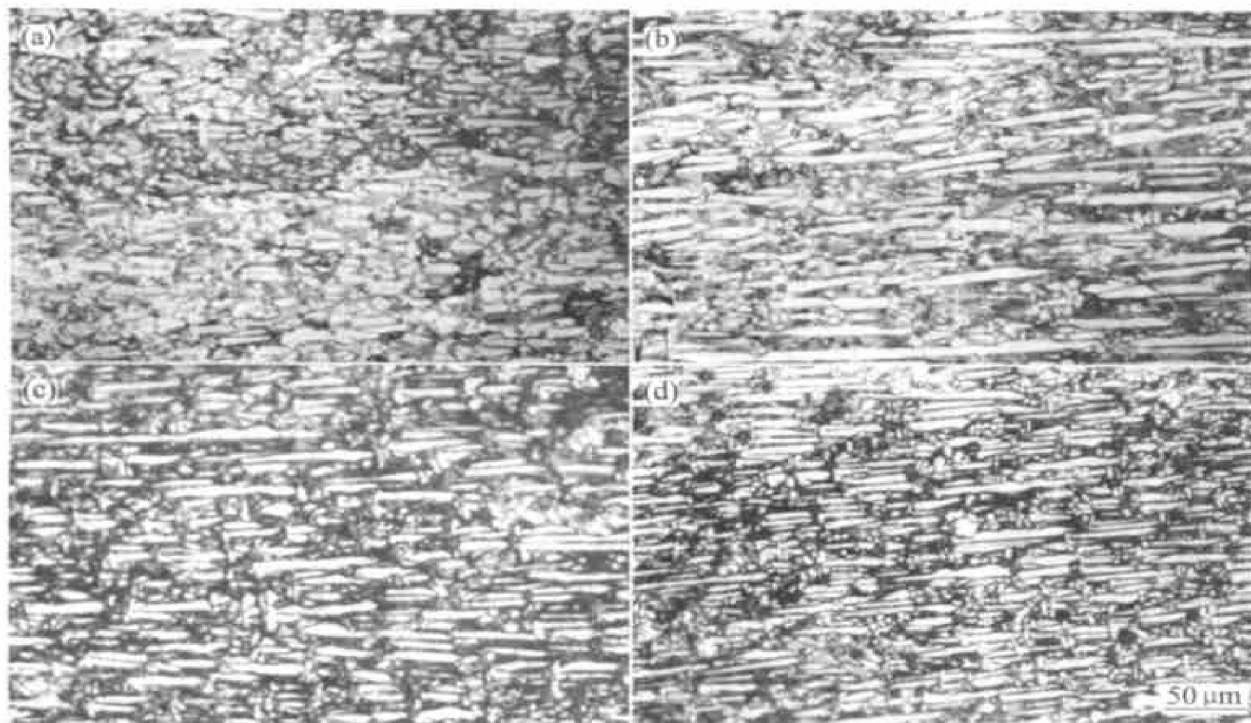


**Fig. 3** SEM photograph of Cu-1.0% Cr and EDS spectra

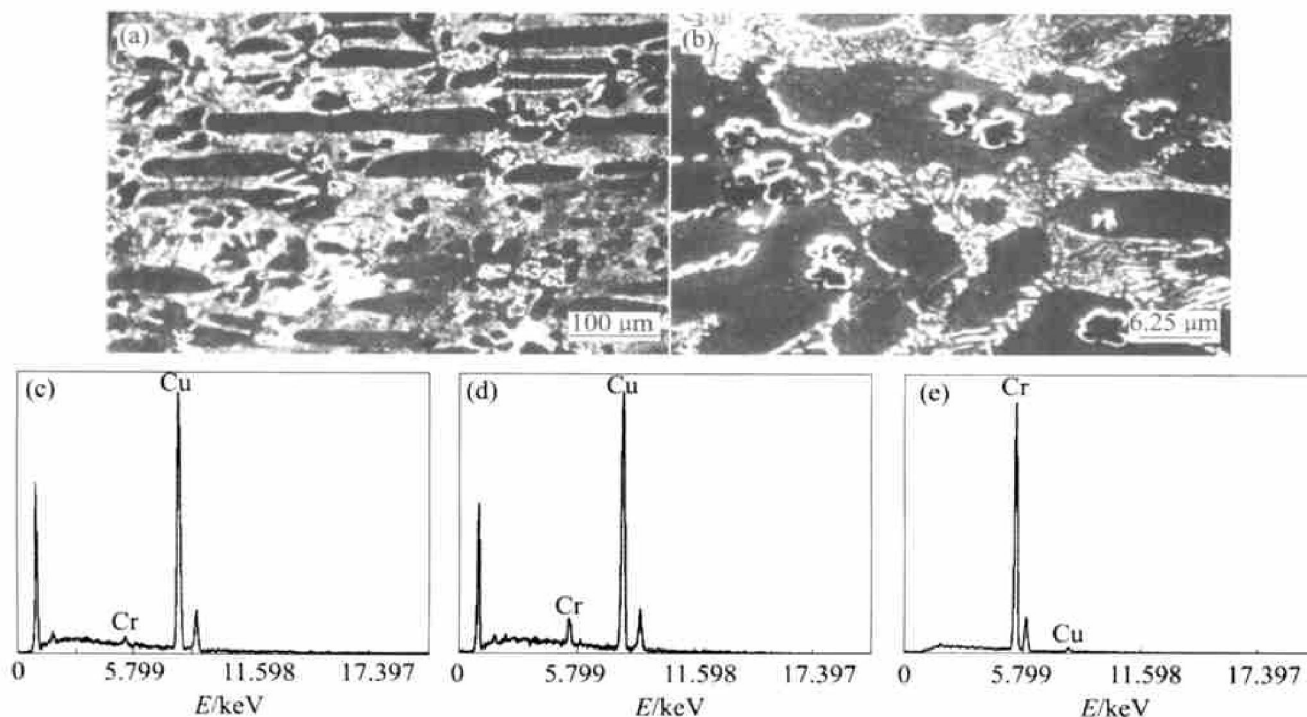
(a) —Primary  $\alpha$ (Cu); (b) —( $\alpha + \beta$ ) eutectics

known from Eqn. 1 that when the temperature gradient is certain, the critical components of the coupled zone boundary will decrease with the increase of solidification rate. Based on the phase diagram of Cu-Cr alloy, the value of  $m_1$  in the hyper-eutectic zone is larger than that in the hypoeutectic zone. So the solidification rate has greater influence on the left boundary of the coupled zone of Cu-Cr alloys, but smaller on the right, thus the coupled zone deflects to the hyper-eutectic zone.

For the binary Cu-Cr eutectic system, because the melting entropy of  $\alpha$  phase is less than that of  $\beta$  phase and the component difference between  $\alpha$  phase and the alloy is also smaller than the one between  $\beta$  phase and the alloy, the growth of  $\alpha$  phase is faster so that the left boundary of the coupled zone of Cu-Cr



**Fig. 4** Microstructures from longitudinal section of Cu-1.7%Cr alloy ( $G_1 = 200$  K/mm)  
(a)  $-R = 60 \mu\text{m/s}$ ; (b)  $-R = 100 \mu\text{m/s}$ ; (c)  $-R = 200 \mu\text{m/s}$ ; (d)  $-R = 400 \mu\text{m/s}$



**Fig. 5** SEM photographs of Cu-1.7% and EDS spectra  
(a)  $-\alpha$  phase; (b)  $-(\alpha + \beta)$  eutectics

alloys deflects to the hypereutectic zone. During the directional solidification of Cu-1.7%Cr alloy, higher Cr concentration in liquid ahead of the solid/liquid interface results in the nucleating and growing of primary  $\beta$  phase so that the environmental concentration is close to eutectic components. Around the primary  $\beta$  phase, Cu-rich environment leads the nucleating of  $\alpha$  phase, which grows so faster than primary  $\beta$  phase

that primary  $\beta$  is enwrapped. At the end, primary  $\beta$  sets in the  $\alpha$  phase, and  $(\alpha + \beta)$  eutectics still distributes between the  $\alpha$  cellular (dendrite). It is obvious that non-equilibrium effect of directional solidification induces that solidification structure makeup of hypereutectic alloys inclines to the one of hypoeutectic alloys. So the directional solidification structures of hypereutectic Cu-1.7%Cr alloys consist of primary  $\beta$



phase,  $\alpha$  phase and ( $\alpha + \beta$ ) eutectics. With the increase of the solidification rate,  $\alpha$  phase thins gently, ( $\alpha + \beta$ ) eutectics still set in  $\alpha$  cellular or dendrite, and primary  $\beta$  as particles unevenly distributes on  $\alpha$  matrix.

### 2.3 Directional solidified structure of Cu-5.6% Cr alloy

Fig. 6 shows the typical solidified structures of Cu-5.6% Cr alloy under different solidification rate.

From Fig. 6, it can be seen that the solidification structures of hypereutectic Cu-5.6% Cr alloys are the mixture of primary  $\beta$  phase,  $\alpha$  phase and ( $\alpha + \beta$ ) eutectics. On account of the augment of initial Cr component, the volume fraction of primary  $\beta$  phase increases accordingly. So the primary  $\beta$  phase is easier to be observed on optical microscopy with the same magnifying rate as the Cu-1.7% Cr alloy. Compared with the solidified structure characteristics of Cu-1.7% Cr alloy, Cu-5.6% Cr alloy has the following differences:

1) Due to the variety of alloy component, primary  $\beta$  phase increases accordingly. At low solidification rate, the observed 2nd dendrite of primary  $\beta$  phase becomes more, the morphology of which shows strong dendrite. Due to the higher Cr content than the eutectic point, primary  $\beta$  phase of Cu-5.6% Cr alloy may nucleate and grow directly in liquid ahead of crystallization. Meanwhile, due to slow solidification rate, Cr atoms have so long time to diffuse in liquid phase that the 2nd or more index dendrite may adequately develop in the preferred growth direction.

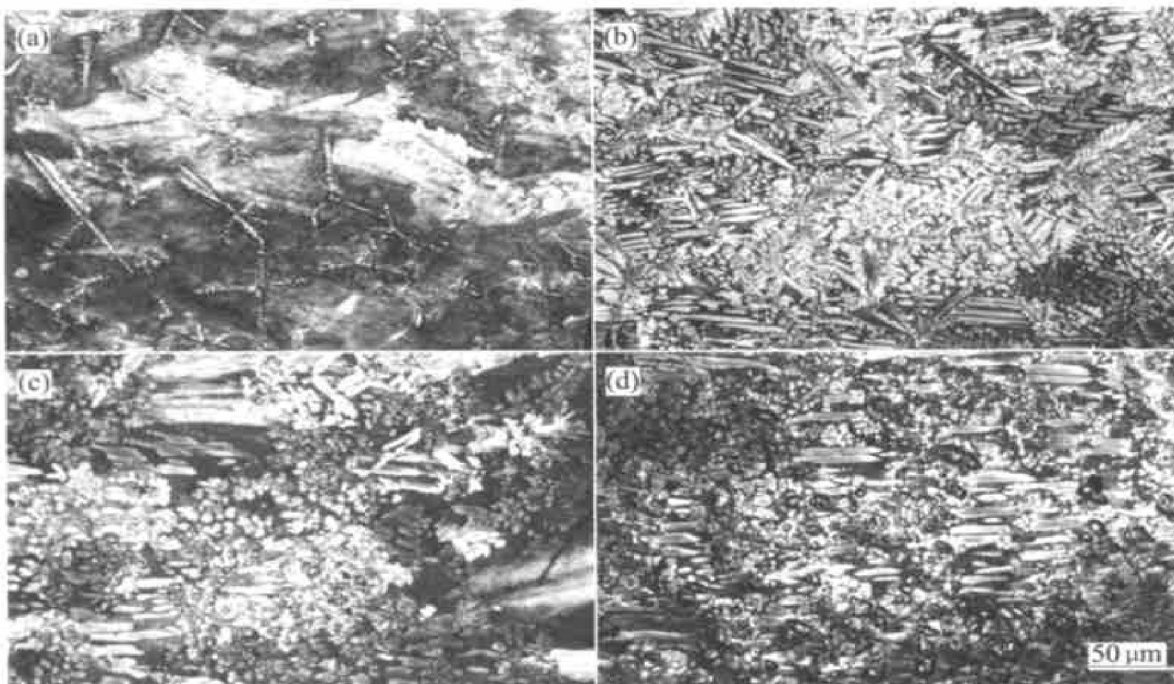
Therefore, the directional tendency of  $\alpha$  phase appears poorer and 1st cellular (dendrite) of  $\alpha$  phase shows bulky relatively.

2) With the increase of the solidification rate, primary  $\beta$  phase as particles distributes on  $\alpha$  matrix disorderly and unevenly. In virtue of the improvement of the solidification rate, 2nd or more index dendrite growth of primary  $\beta$  phase is restrained so that 2nd dendrite of primary  $\beta$  phase weakens. So the directional tendency of  $\alpha$  phase appears clear; 1st cellular (dendrite) of  $\alpha$  phase thins, and cellular (dendrite) spacing decreases.

3) Because the crystallizing temperature interval of Cu-5.6% Cr alloy is larger than that of Cu-1.7% Cr alloys, two-phase solidification zone becomes wide so that primary  $\beta$  phase increases. During the solidification of Cu-5.6% Cr alloy, there is the morphology change of not only  $\alpha$  phase but also primary  $\beta$  phase. The morphology change of primary  $\beta$  phase throws bigger influence on the directional tendency of  $\alpha$  phase. Although  $\alpha$  phase of Cu-5.6% Cr alloy thins gently with the increase of the solidification rate, the morphology change becomes slow according to Cu-1.7% Cr alloy.

SEM results of the microstructure of Cu-5.6% Cr alloy are shown in Fig. 7. From Fig. 7, it can be seen that the structure morphology of Cu-5.6% Cr alloy changes under the condition of different solidification rate. The primary  $\beta$  phase grows as dendrite at low rate, as particles at high rate, and all distributes on the  $\alpha$  matrix.

So the directionally solidified structures of hy -



**Fig. 6** Microstructures from longitudinal section of Cu-5.6% Cr alloy(  $G_1 = 200$  K/mm)

(a)  $-R = 60 \mu\text{m/s}$ ; (b)  $-R = 100 \mu\text{m/s}$ ; (c)  $-R = 200 \mu\text{m/s}$ ; (d)  $-R = 400 \mu\text{m/s}$



**Fig. 7** SEM photographs of Cu-5.6% Cr  
(a) — $R = 60 \mu\text{m/s}$ ; (b) — $R = 200 \mu\text{m/s}$

hypereutectic Cu-5.6% Cr alloy consist of primary  $\beta$  phase,  $\alpha$  phase and ( $\alpha + \beta$ ) eutectics. With the increase of the solidification rate, the morphology of primary  $\beta$  phase undergoes the change from dendrite to particle,  $\alpha$  phase thins gently, and ( $\alpha + \beta$ ) eutectics still set in  $\alpha$  cellular or dendrite,

### 3 CONCLUSIONS

The directional solidification structures of Cu-Cr alloys were observed by optical microscopy and SEM, the evolution laws and change trend of the structures are as follows:

1) The solidification structure of hypoeutectic Cu-1.0% Cr alloy consists of primary  $\alpha$  phase and rod-like or needle-like ( $\alpha + \beta$ ) eutectics. With the increase of the solidification rate, the directional tendency of  $\alpha$  phase appears clear, 1st cellular (dendrite) thins gently, and cellular (dendrite) spacing decreases. The ( $\alpha + \beta$ ) eutectics as the reinforcement phase set in  $\alpha$  cellular or dendrite evenly,

orderly and directionally, thus the composites are formed.

2) The directional solidification structures of the hypereutectic Cu-1.7% Cr alloy and Cu-5.6% Cr alloys consist of primary  $\beta$ (Cr),  $\alpha$  phase and eutectic ( $\alpha + \beta$ ). The  $\alpha$  phase thins gently with the increase of the solidification rate and ( $\alpha + \beta$ ) eutectics set in  $\alpha$  cellular or dendrite. The primary  $\beta$  phase unevenly distributes on the  $\alpha$  matrix, which grows as particles in the Cu-1.7% Cr alloy and undergoes the change from dendrite to particle in the Cu-5.6% Cr alloy.

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(Edited by LI Xiang-qun)