Peritectic phase growth in directionally solidified Cu-70% Sn alloy

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The growth mechanism of the peritectic η phase involving the peritectic reaction and peritectic transformation in Cu-70%Sn alloy was investigated under directional solidification. The results show that a major growth mechanism in thickening of the peritectic η -layer is not the peritectic reaction but the peritectic transformation. The transformation temperature and isothermal time play crucial roles in determining the volume fraction and the thickness of the peritectic η phase. With the increase of the temperature and isothermal time, the volume fraction of the peritectic η phase increases. The regressed data show that the relationship between the thickness of η phase (Δx) and the transformation temperature (T) meets the following equation

$\ln \Delta x = 6.5 - 1673 \frac{1}{T}$. Additionally, there exists a relationship between the thickness of

the η phase (Δx) and the isothermal time (t) at the 9 mm solidification distance below the peritectic reaction interface, $\Delta x = 0.72t^{1/2}$, which is consistent with the theoretical model.

Cu-70%Sn peritectic alloy, peritectic reaction, peritectic transformation, directional solidification

Many peritectic alloys, such as Fe-C, Ti-Al, stainless steel Fe-Cr-Ni and permanent magnetic materials Nd-Fe-B, have been extensively applied in industry field. Peritectic alloy solidification involves nucleation and growth of the primary phase and peritectic phase. As a result, a wide variety of possible microstructures have occurred, for example, alternating banded microstructures between the primary phase and peritectic phase with different interface morphologies, island-like microstructures and simultaneous coupled growth microstructures, etc.^[1-7]. In recent years, the researches on the peritectic alloy solidification mainly focus on two aspects: one is that the phase/microstructure selection map in peritectic alloys is developed to obtain the relationship between the solidified microstructures and solidification conditions; the other is that the investigation of the growth mechanism of peritectic phase is carried out in different solidification proc-

Received February 11, 2007; accepted April 29, 2007

doi: 10.1007/s11433-007-0095-x

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Supported by the National Natural Science Foundation of China (Grant No. 50395102)

esses. However, there is a limited understanding of the solidification behavior of peritectic alloys compared with that of eutectic alloys.

In this paper, Cu-70%Sn peritectic alloy was used to study the growth mechanism of the peritectic η phase, which is grown as an intermetallic compound in directional solidification. The control of the growth of an intermetallic compound is very difficult, because of its strong anisotropy. In addition, the volume fraction and the size of the peritectic phase in this type alloy can dramatically influence the properties of the material, for instance, in NdFeB permanent magnetic materials, the peritectic T_1 phase ($\text{Nd}_2\text{Fe}_{14}\text{B}$) is also grown as an intermetallic compound. When the volume fraction of T_1 phase reaches 95% in the solidified microstructures, the relatively good magnetic properties can be obtained^[8]. Thus it is necessary to study the growth mechanism and kinetics of the intermetallic compound peritectic phase in order to control its size and interface morphologies effectively to optimize processing conditions.

In directional solidification of Cu-70%Sn peritectic alloy, the thickness of peritectic η phase formed by peritectic reaction and peritectic transformation was theoretically analyzed and compared with the experimental results. The effects of solidification temperature and time on the growth of peritectic η phase have been discussed.

1 Experimental process

The master alloy was obtained by melting 99.9% purity tin and 99.99% purity copper by means of resistance heating, and then cast into the rods of 8 mm in diameter and 120 mm in length. The as-cast rod was machined to be 100 mm in length and 7.1 mm in diameter and put in a high purity alumina crucible which is 115 mm long and 7.2 mm in inner diameter. Directional solidification experiments were carried out using a Bridgman vertical vacuum furnace described elsewhere^[9].

In the directional solidification process, the sample was heated and melted by a graphite heater. Subsequently, the sample was pulled downwards by two types of solidification processes. One type is that the sample withdrew at various constant growth velocities of 5, 10, 30, 50 and 100 $\mu\text{m/s}$, respectively. After the solidified distance reached 50 mm, the sample was quenched into liquid Ga-25wt%In-13wt%Sn alloy to obtain the interface growth morphology. The other type is that the sample withdrew down firstly at 10 $\mu\text{m/s}$ with the solidification distance of 50 mm, and then stopped for various times, which are 15 min, 30 min, 1 h and 2 h, respectively. In addition, the temperature gradient was measured using a NiCr-NiSi thermocouple and the values were 219, 200 and 167 K/cm at 10, 50 and 100 $\mu\text{m/s}$, respectively.

The quenched samples were sectioned both in longitudinal and transverse sections. The microstructures of the polished specimens were revealed with the agent of 5 g FeCl_3 +10 mL HCl +100 mL H_2O . Microstructures were observed by light microscope Leica DM4000M, and the volume fraction and the thickness of each phase in Cu-70%Sn peritectic alloy were measured by SISC IAS V8.0 analysis software.

2 Results and discussion

According to Cu-Sn alloy phase diagram^[10], the equilibrium solidification microstructures of Cu-70%Sn hyperperitectic alloy only consist of peritectic η phase and eutectic (η +Sn) without primary ε phase. Since the directional solidification is a non-equilibrium solidification process and the earlier experiment^[11] showed that the primary ε phase still exists in the directionally solidified

microstructures of Cu-70%Sn, it means that the volume fraction and growth behavior of peritectic η phase cannot be predicted by the alloy phase diagram.

The variation of the volume fraction of peritectic η phase, resulting from peritectic reaction and peritectic transformation in Cu-70%Sn peritectic alloy, is difficult to be accurately measured in the experiment. Thus theoretical analysis is needed to confirm the main growth mechanism of peritectic η phase and its influencing factors.

2.1 The thickness of peritectic η phase formed by peritectic reaction

Peritectic reaction takes place at ε/L interface and leads to the growth of peritectic η phase in directional solidification of Cu-70%Sn alloy. Fredriksson et al.^[12] firstly developed a model to calculate the peritectic reaction rate based on the maximum growth rate assumption. It showed that a plate-shape η phase with a radius r grows along the phase boundary between the primary ε phase and the liquid phase L. The growth velocity V , i.e., the peritectic reaction rate, was described as a function of the supersaturation Ω , which can be presented by

$$V = (9/8\pi)(D_L/r)\Omega'^2, \quad (1)$$

$$\Omega' = \Omega/[1 - (2\Omega/\pi) - (\Omega^2/2\pi)], \quad (2)$$

$$\Omega = (C_L^\eta - C_L^\varepsilon)/(C_L^\eta - C_\eta^L), \quad (3)$$

where D_L is the diffusion coefficient of solute in liquid; C_L^η , C_L^ε and C_η^L are the liquid concentration at the η/L boundary, liquid concentration at the ε/L boundary and the peritectic η phase concentration at the η/L boundary, respectively, as shown in Figure 1.

Figure 1 Schematic peritectic alloy phase diagram for different phase concentrations at undercooling ΔT .

For Cu-70%Sn alloy, both the concentration differences $(C_L^\eta - C_L^\varepsilon)$ and $(C_L^\eta - C_\eta^L)$ reported from the previous result^[12] are described as

$$C_L^\eta - C_L^\varepsilon = 1.73 \times 10^{-4} \Delta T, \quad (4)$$

$$C_L^\eta - C_\eta^L = 0.43 + 1.19 \times 10^{-3} \Delta T, \quad (5)$$

where ΔT is the peritectic nucleation undercooling, which is usually small in most peritectic al-

loys, since the peritectic phase nucleation and growth can occur at the presence of substance of the primary phase during the directional solidification process. Assume that ΔT is equal to 1, 10 and 30 K, respectively, and $D_L=5\times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$, the variation of the peritectic η layer thickness ($2r$) with the growth rate V has been calculated for Cu-70%Sn alloy using eqs. (1)–(5), as illustrated in Figure 2. It can be seen that the thickness of peritectic η phase decreases as V increases.

In order to obtain the η phase layer thickness formed by the peritectic reaction, the peritectic reaction rate is needed. Shibata H, et al.^[13,14] have successfully *in-situ* observed the solidification processes of Fe-C and Fe-Ni peritectic alloys. The results showed that the peritectic reaction rate ranged from 20 to 145 $\mu\text{m/s}$ for Fe-Ni peritectic alloy and 1.5 to 5.5 mm/s for Fe-C peritectic alloy. Since the diffusion of Sn atom in Cu-70%Sn peritectic alloy may be much slower than that of C atom in the Fe-C alloy, the peritectic reaction rate of Cu-70%Sn alloy may be smaller than that of the Fe-C alloy. As shown in Figure 2, when the reaction rate changes within 5 $\mu\text{m/s}$ –1 mm/s in directional solidification of Cu-70%Sn alloy, the maximum thickness of the peritectic η phase is only 0.045 μm . The value is about two orders of magnitude smaller than that of the total thickness of η phase measured in the experiment (Figure 3). This indicates that the amount of η phase

Figure 2 The relationship of thickness $2r$ of peritectic η phase layer formed by the peritectic reaction and the reaction rate V .

Figure 3 The relationship of the measured thickness of the peritectic η phase layer and the cooling rate in directional solidification of Cu-70%Sn alloy.

formed by the peritectic reaction is very small. Consequently, the peritectic reaction is not a major growth mechanism for thickening peritectic η phase to increase its volume fraction in directional solidification of Cu-70%Sn alloy.

2.2 The thickness of peritectic η phase formed by peritectic transformation

Once peritectic η phase is formed, further growth of the η phase occurs via peritectic transformation controlled by the solid diffusion. At the transformation temperature T_i below the peritectic temperature T_p , St John and Hogan^[15] proposed that the thickness Δx of the layer of peritectic phase would follow the equation:

$$\Delta x^2 = 2t\gamma(C_\eta^L - C_\eta^\varepsilon)\bar{D}, \quad (6)$$

where $\bar{D}$ is the average interdiffusion coefficient in the peritectic phase, t is the time of isothermal annealing, the concentration difference $(C_\eta^L - C_\eta^\varepsilon)$ is the driving force for the peritectic transformation, and the factor γ is defined as

$$\gamma = \frac{C_L^\eta - C_\varepsilon^\eta}{(C_L^\eta - C_\eta^\eta)(C_\eta^\eta - C_\varepsilon^\eta)}, \quad (7)$$

where $C_\eta = \frac{1}{2}(C_\eta^\varepsilon + C_\eta^L)$. Eq. (7) shows that γ is only dependent on the peritectic alloy diagram (Figure 1). Also, eq. (6) predicts that the rapid peritectic transformation will occur if the composition range of the η phase is large and the term $(C_L^\eta - C_\eta^\eta)(C_\eta^\eta - C_\varepsilon^\eta)$ is small. For Cu-70%Sn alloy, since the composition range of the η phase is small, the peritectic transformation rate of η phase may be very slow.

In addition, the transformation time in eq. (6) can be calculated as $t = (T_p - T_i)/(GV)$ (G is the temperature gradient and V is the growth rate) during the directional solidification process. When the temperature drops from T_p to T_i , the thickness of peritectic η phase via the peritectic transformation can be given by

$$\Delta x^2 = \frac{2\gamma\bar{D}(T_p - T_i)(C_\eta^L - C_\eta^\varepsilon)}{GV}. \quad (8)$$

As indicated in eq. (8), the thickness of peritectic η phase layer is inversely proportional to the square root of the cooling rate (GV). The thickness of the η phase measured in the experiment is given in Figure 3, which shows that the peritectic η phase thickness decreases as the cooling rate increases. The regressed data fit the relationship $\Delta x = 13.3/(GV)^{1/2}$, which is in agreement with the prediction of the theoretical model.

Using the regressed curve, and combined with eq. (8), the diffusion coefficient $\bar{D}$ is calculated to be $3.49 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ when the values $\gamma=7.1$, $T_p - T_i = T_p - T_e = 188 \text{ K}$, and $C_\eta^L - C_\eta^\varepsilon = 1.9\%$. This value is smaller than the data of Cu-78%Sn peritectic alloy given by Ha et al.^[16] and the change may be attributed to their different compositions.

Furthermore, it can be seen that the thickness of peritectic η phase calculated by eq. (8) is in good agreement with the experiment results. This indicates that the growth mechanism for thickening η phase is mainly the peritectic transformation, not the peritectic reaction. Therefore, we

further investigated the effect of solidification time and the temperature in eqs. (6) and (8) on the solidified microstructures of Cu-70%Sn alloy during directional solidification.

2.3 Effect of the solidification temperature on the solidified microstructures

Figure 4 shows that the peritectic reaction interface of the sample was solidified at the growth rate of 10 $\mu\text{m/s}$ for about 50 mm and then stopped for 1 h. It could be seen that most of the grey primary ε phases had transformed to the white peritectic η phases behind the peritectic reaction interface.

Figure 4 Schematic of peritectic reaction interface and temperature distribution in the solidifying sample stopped for 1 h in directional solidification of Cu-70%Sn alloy.

In the microstructure of longitudinal sections, it was also observed that the volume fractions of the primary ε phase and peritectic η phase vary with the solidification position behind the peritectic reaction interface (see Figure 4). So, the volume fractions of phases were measured in the experiment and plotted in Figure 5. This process was undertaken by polishing the sample gradually and etching the solidified microstructures from the peritectic reaction interface in transverse cross sections. Due to the solidification position of the sample representing the temperature distribution in directional solidification, we can obtain the solidified microstructures with respect to their solidification temperature, T_i , or undercooling ($\Delta T = T_p - T_i$) as shown in Figure 5. It can be seen that the volume fraction of peritectic η phase gradually decreases as the solidification temperature decreases, which means that the peritectic transformation for the growth of peritectic η phase becomes more difficult. The cause may be ascribed to the difficult diffusion in peritectic transformation at lower solidification temperature.

In eq. (6), the diffusion coefficient $\bar{D}$ can be usually expressed as a function of the temperature and composition, that is

$$\bar{D} = D_0 \exp(-Q/RT), \quad (9)$$

where D_0 is a physical constant depending on the alloy composition, R is gas constant, and Q is activation enthalpy, respectively. Substituting eq. (9) into eq. (6) yields

$$\ln \Delta x = A - \frac{Q}{2R} \times \frac{1}{T}, \quad (10)$$

where A is constant. Eq. (10) indicates that the thickness of the peritectic phase layer Δx decreases with the decrease of the solidification temperature.

Figure 5 Dependence of volume fractions of the primary ε phase and peritectic η phase on the solidification temperature in directional solidification of Cu-70%Sn alloy at $V=10\ \mu\text{m/s}$ and the time of 1 h.

Figure 6 shows the measured thickness of η -layer is a decreasing function of the solidification temperature below T_p . The regressed line shows that the relationship between the experimental thicknesses of η phase (Δx) and the solidification temperature (T) satisfies $\ln \Delta x = 6.5 - 1673 \frac{1}{T}$.

The result matches well with eq. (10). According to eq. (10) and the regressed data, the activation enthalpy of the Cu-70%Sn peritectic alloy can be estimated as 28 kJ/mol, which is close to the value (28.9 kJ/mol) presented by Takenaka^[17]. Thus, the investigation of the layer thickness of the peritectic phase by the peritectic transformation may be an effective method to obtain the activation enthalpy of peritectic alloys during the solidification process.

Additionally, due to the higher temperature, the diffusion coefficient is larger, so that the peritectic transformation rate increases. As a result, the increase in the volume fraction of the η peritectic phase takes place as shown in Figure 5.

2.4 Effect of the isothermal time on the solidified microstructures

Figure 7 shows the transverse microstructures of Cu-70%Sn peritectic alloy at $10\ \mu\text{m/s}$, which

Figure 6 The relationship of the measured thickness of η -layer and the solidification temperature below T_p .

stops for 15 min, 30 min, 1 h and 2 h, respectively. The solidified microstructures were taken at the solidification position of 9 mm behind the peritectic reaction interface. It can be seen that as the isothermal time increases, the primary ε phase has been gradually dissolved and the remaining liquid becomes smaller with the growth of the peritectic η phase. After holding the isothermal time for 2 h, the peritectic η phase has almost occupied all the space between ε and L. The volume fraction of the peritectic η phase has reached 80%, so the isothermal time required for completely depleted primary ε phase should be larger than 2 h.

Figure 7 The effect of the isothermal time on the peritectic transformation in Cu-70wt%Sn alloy at $V=10 \mu\text{m/s}$. (a) 15 min; (b) 30 min; (c) 1 h; (d) 2 h.

For isothermal transformation at a given temperature T_i below T_p , according to eq. (6), the thickness Δx of the peritectic phase layer is proportional to the square root of the annealing time t , which can be described as

$$\Delta x = B(T_i)t^{1/2}, \quad (11)$$

where $B(T_i)$ depends on the temperature and alloy composition.

The experimental thickness of peritectic η phase as a function of the isothermal time is illustrated in Figure 8. It indicates that the thickness of the η phase varies with the isothermal time with the relationship of $\Delta x = 0.92t^{1/2}$ and $\Delta x = 0.72t^{1/2}$ at the solidification distance of 5 mm and 9 mm below the peritectic reaction interface, respectively. The regressed data are in agreement with the calculated results of eq. (11). But at higher temperature, the measured values depart from the relationship $\Delta x = 0.92t^{1/2}$. This may be caused by the peritectic transformation at higher temperature being controlled not only by the solid diffusion, but also by other diffusion ways, such as grain boundary diffusion, etc.

3 Conclusions

- (1) The major growth mechanism in thickening of the peritectic η -layer is not the peritectic reaction but the peritectic transformation in directional solidification of Cu-70%Sn alloy.
- (2) The relationship between the thickness of η phase (Δx) and the solidification temperature (T)

Figure 8 The relationship of the measured thickness of η -phase with the isothermal time for Cu-70wt%Sn alloy.

satisfies $\ln \Delta x = 6.5 - 1673 \frac{1}{T}$, in agreement with the predicted theoretical model. The diffusion activation enthalpy is estimated as 28 kJ/mol in Cu-70%Sn peritectic alloy.

(3) During directional solidification of Cu-70%Sn peritectic alloy, the thickness of the η phase and the isothermal time t have the relationship as follows: $\Delta x = 0.92t^{1/2}$ and $\Delta x = 0.72t^{1/2}$ at the solidification distance of 5 mm and 9 mm below the peritectic reaction interface, which fits the theoretical analysis results.

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