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Peritectic transformation and primary α-dendrite dissolution in directionally solidified Pb–26%Bi alloy

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ABSTRACT

Peritectic transformation is one of the main mechanisms during solidification of peritectic alloys, and accompanied with dissolution of primary phase. In the present work, the effect of solidification temperature on the peritectic transformation and dissolution of primary α-dendrite was investigated during directional solidification of Pb–26wt%Bi peritectic alloy. The resulting microstructures of the alloy in consideration of different solidification temperature have been investigated using optical microscopy. The volume fraction of peritectic β-phase and the average size of α-dendrite core were measured using image analyzing software SISC IAS V8.0. These results show that the increment in β-phase volume fraction and decrement in size of α-dendrite core first increase, then decrease with falling solidification temperature. These results can be explained from the viewpoint of a reduced solidification temperature leading to the rate of peritectic transformation first increases to a maximum, and then decreases.

1. Introduction

Peritectic solidification has drawn huge attention since it is not only encountered in structural materials [1–6], but also in the production of superconductors such as YBCO [7], YBaCuO [8] and magnetic materials such as Co–Sm–Cu [9] and Nd–Fe–B [2]. Three kinds of growth mechanism have been reported for peritectic alloys [1]. The first one is the 'peritectic reaction' which is processed by solute diffusion in the liquid phase at the triple phase junctions [10]. The second one is the 'peritectic transformation' which is controlled by solute diffusion through the peritectic β envelope around the primary α phase [11–13]. It's well known that the peritectic transformation is accompanied by dissolution of primary α phase, and the transformation rate is equal to the dissolution rate. The last one is the direct solidification of peritectic β phase. Generally speaking, the amount of peritectic β phase formed by peritectic reaction can be ignored. That is because the rapid peritectic reaction rate resulting in a short reaction time, the amount of β formed during this stage is generally a small fraction of the total. The amount of peritectic β phase is assumed to depend mainly on the extent of the peritectic transformation and direct solidification. In some peritectic alloys, the total volume fraction of peritectic phase plays an important role to properties of materials, such as the Nd–Fe–B magnetic alloy [14]. Thus the detailed investigations on the peritectic transformation are necessary.

In this paper, the effect of solidification temperature on the peritectic transformation and the dissolution of primary α-dendrite was investigated during directional solidification of Pb–26%Bi peritectic alloy.

2. Experimental procedure

The phase diagram of Pb–Bi system is shown in Fig. 1a. The master alloy was prepared by melting 99.95% purity lead and 99.99% purity bismuth using a resistance furnace. The sample with diameter of 6.9 mm and length of 100 mm was machined from the as-cast ingot. The sample was put into a high purity alumina crucible which is 115 mm long and 7 mm in inner diameter. Directional solidification (DS) experiment was carried out in an improved Bridgman vertical vacuum furnace described elsewhere [15]. The temperature of the melted alloy was heated to about 375 °C and stabilized for 30 min, subsequently, the sample was withdrawn downward at a constant growth velocity of 10 μm/s for 60 mm in length.

The temperature in the sample was measured with K-type 0.25 mm in diameter insulated two thermocouples which were fixed within the sample with spacing of 10 mm. In the present work, a 2.0 mm OD × 1.0 mm ID alumina tube was used to insulate the thermocouples from the melt. All the thermocouple's ends were then connected the measurement apparatus containing a data-logger. When the solid/liquid interface was at the second thermocouple, the temperature difference between the first and second thermocouples (ΔT) was read from the data-logger record. The temperature gradient ($G = \Delta T/\Delta X$) in the liquid phase was determined using the measure values of ΔT and ΔX. The time taken for the solid/liquid interface passes the thermocouples separated by known distances was read from data-logger record. Thus the growth velocity ($V = \Delta X/\Delta t$) was determined using the measured value of Δt and known value of ΔX. The measured values of G and V are 20 K/mm and 10 μm/s, respectively.

The DS sample was sectioned longitudinally and transversely. The transverse sections were taken every 500 μm, starting from the peritectic β-front, as shown in Fig. 2. After polishing, they were etched in a solution of 100 ml distilled water (H_2O), 10 ml of nitric acid (HNO_3) and 4 g of ammonium molybdate ($(NH_4)_6MO_7O_{24}\cdot 4H_2O$). The volume fraction of the peritectic β phase and the size of the primary α-dendrite core (seen in Fig. 3) were measured by SISC IAS V8.0 analyzing software, respectively.

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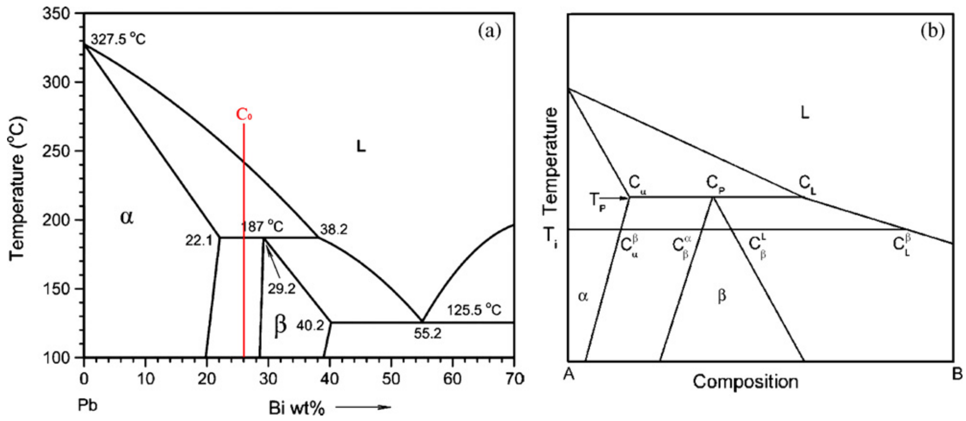

Fig. 1. (a) Phase diagram of Pb–Bi system [11]; (b) a schematic diagram in a peritectic system, showing symbols used for phased, compositions and temperatures. C^{α}_{β} and C^{β}_{α} are the compositions of the β phase in equilibrium with the α phase and vice versa. C^{L}_{β} and C^{β}_{L} are the compositions of the β phase in equilibrium with the liquid phase and vice versa.

3. Results and discussion

Fig. 2b shows the longitudinal section of the sample which was solidified at the growth rate of 10 μm/s. The black part in Fig. 2b represents the primary α phase, and the white part represents the peritectic β phase. It is clearly seen that the primary α phase precipitated firstly and the secondary peritectic β phase started forming on the periphery of the primary phase at a lower temperature. The α phase grew as dendrite embedded in peritectic β phase. Fig. 4 shows the microstructures of the corresponding transverse sections of sample in Fig. 2. As temperature falling, an increase in the volume fraction of β phase and a dissolution of primary α-dendrite can be observed simultaneously.

The data points in Fig. 5 show the results obtained from image analysis. Fig. 5a shows that the volume fraction of peritectic β phase increases with decreased temperature. Further detail is gained that the volume fraction of β phase first increases sharply at high temperature stage and then increases smoothly at low temperature stage. That is to say that the increment in the volume fraction of β phase first increases, then decreases with falling temperature. That is similar to the results in Ag–Sn peritectic system [16]. Fig. 5b shows the size of α-dendrite core with different solid-

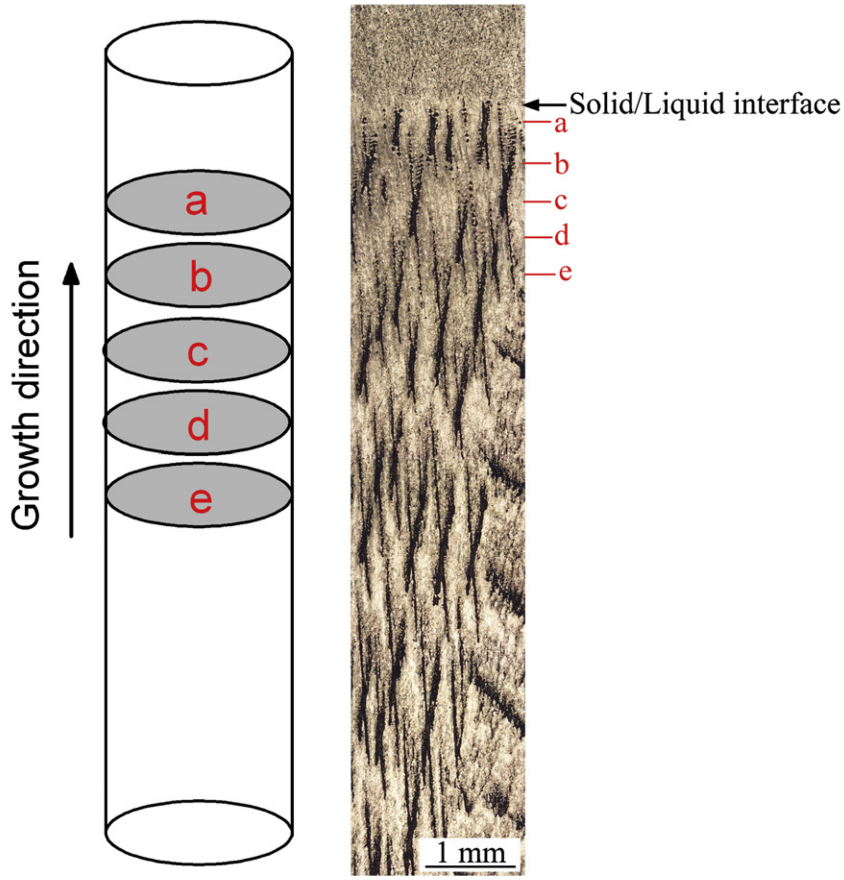

Fig. 2. Longitudinal microstructure of directionally solidified Pb–26%Bi hypoperitectic alloy at $G = 20$ K/mm and $V = 10$ μm/s, a, b, c and d represent the positions of the transverse sections, a is the peritectic β-front.

ification temperature. It is obviously indicated that a reduction in the size of α-dendrite core was observed. And the decrement also first increases and then decreases with falling temperature. In other words, the primary α-dendrite dissolution rate first increases to a maximum, and then decreases with falling solidification temperature.

It is to be expected that the peritectic reaction is normally isothermal, the initial reaction $L + \alpha \rightarrow \beta$ is stifled by formation of an envelope of solid β around the primary α phase. Further growth of β phase then occurs via peritectic transformation controlled by the solute diffusion through the peritectic envelope when temperature falls below the peritectic temperature T_P. Meanwhile, the thickening of the β envelope was accompanied by the dissolution of primary α-dendrite, as shown in Fig. 6. At the solidification temperature T_i (Fig. 1b) below T_P, the β envelope will separate α phase of composition C_{α}^{β} from liquid of composition C_{L}^{β}. The composition of β phase will vary between C_{β}^{α} and C_{β}^{L}.

According to St John and Hogan [11], an equation describes the solute flux through the envelope of peritectic phase was proposed

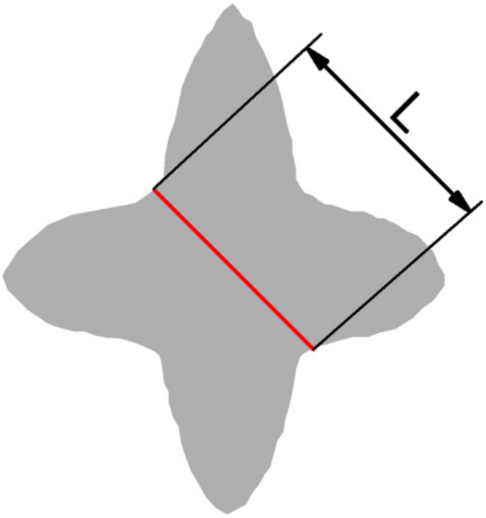

Fig. 3. Schematic drawing for size of primary α-dendrite core.

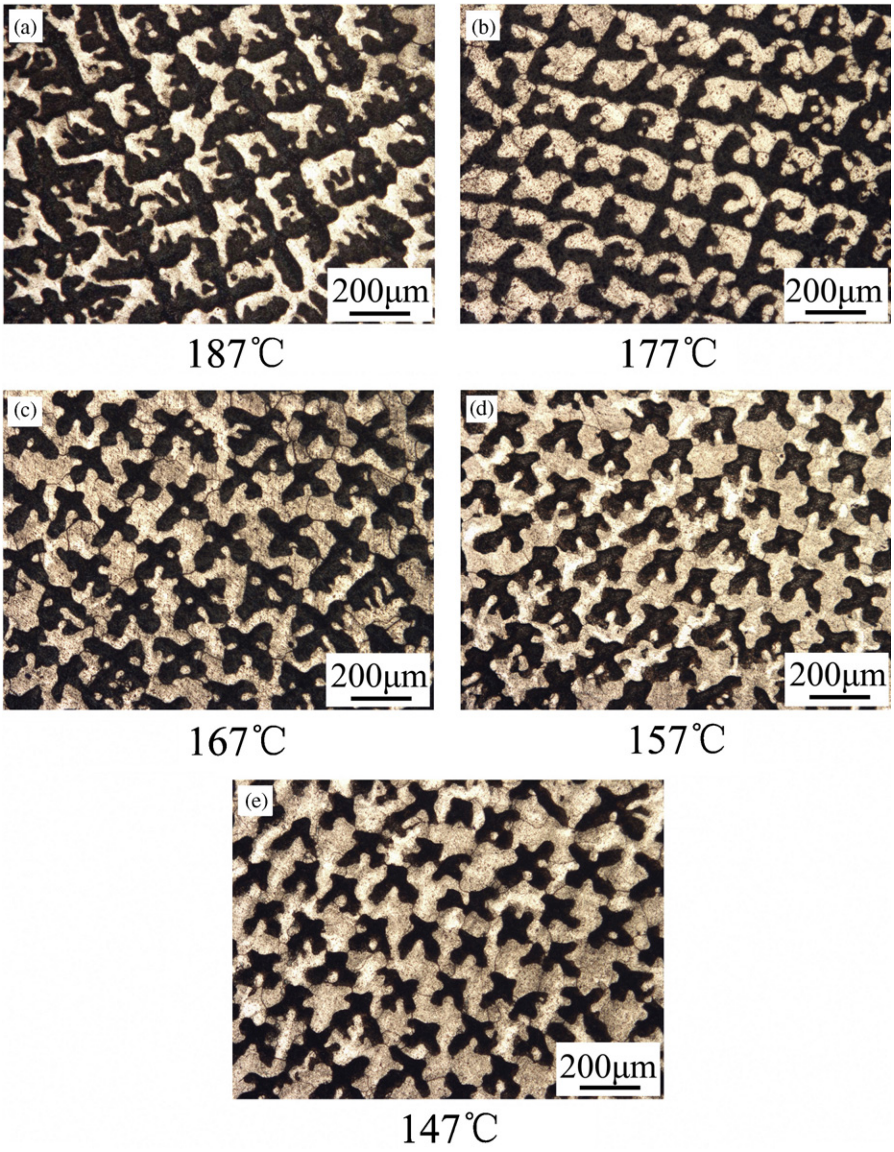

Fig. 4. Transverse microstructures of Pb–26%Bi peritectic alloy at sections of a, b, c, d, and e in Fig. 2.

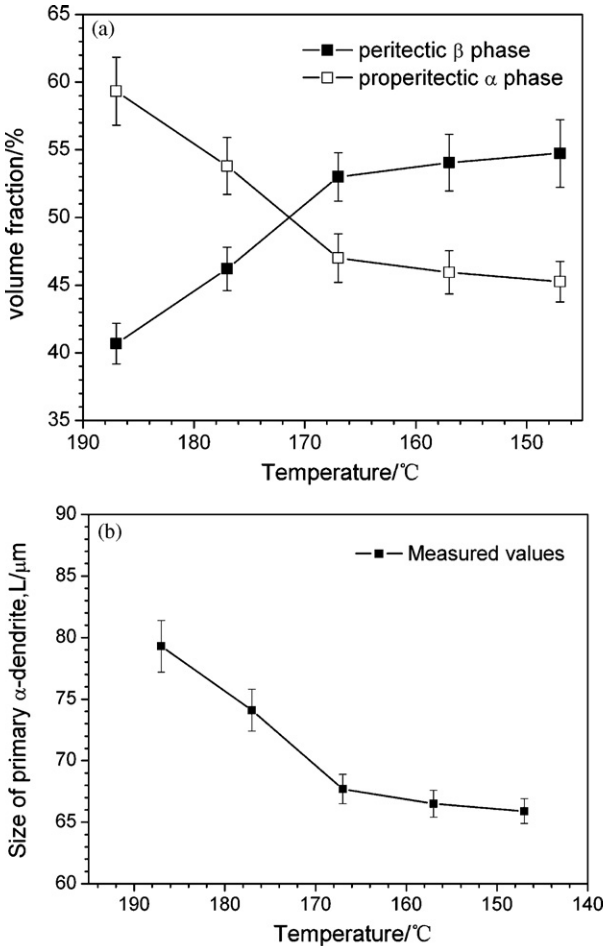

Fig. 5. Variation of the volume fractions of the peritectic and primary phases as the temperature decreases in the Pb–26wt%Bi system.

as follow:

$$\int_{C_\beta^\alpha}^{C_\beta^L} D\,dc = \frac{(C_\beta - C_\alpha^\beta)(C_L^\beta - C_\beta)}{C_L^\beta - C_\alpha^\beta}\,\frac{\Delta x^2}{2t} \qquad (1)$$

where D is the interdiffusion coefficient in the β phase for composition C, which is composition in weight percent of B, subscripts are as in Fig. 1b for temperature T_i. In Eq. (1), the expression of C_β is calculated as:

$$C_\beta = \frac{C_\beta^\alpha + C_\beta^L}{2} \qquad (2)$$

Δx is the thickness of the β envelope at time t after its formation, t is the time of isothermal transformation. For directional solidification, t can be obtained as follow:

$$t = \frac{T_\mathrm{P} - T_\mathrm{i}}{GV} \qquad (3)$$

Eq. (1) can be expressed in the form

$$\frac{\Delta x^2}{2t} = \gamma \int_{C_\beta^\alpha}^{C_\beta^L} D\,dc \qquad (4)$$

where the factor γ is defined as

$$\gamma = \frac{C_L^\beta - C_\alpha^\beta}{(C_\beta - C_\alpha^\beta)(C_L^\beta - C_\beta)} \qquad (5)$$

where γ is depended only on the form of the phase diagram. The Eq. (1) can also be expressed as

$$\int_{C_\beta^\alpha}^{C_\beta^L} D\,dc = (C_\beta^L - C_\beta^\alpha)\overline{D}_\mathrm{av} \qquad (6)$$

where $\overline{D}_\mathrm{av}$ is the average interdiffusion coefficient in the β phase. Substituting Eq. (6) into Eq. (4):

$$\frac{\Delta x^2}{2t} = \gamma (C_\beta^L - C_\beta^\alpha)\overline{D}_\mathrm{av} \qquad (7)$$

According to the schematic phase diagram, as shown in Fig. 1b, these compositions can be written as:

$$C_\alpha^\beta = C_\alpha - \frac{T_\mathrm{P} - T_i}{m_\alpha^\beta} \qquad (8)$$

$$C_\beta^\alpha = C_\mathrm{P} - \frac{T_\mathrm{P} - T_i}{m_\beta^\alpha} \qquad (9)$$

$$C_\beta^L = C_\mathrm{P} + \frac{T_\mathrm{P} - T_i}{m_\beta^L} \qquad (10)$$

$$C_L^\beta = C_L + \frac{T_\mathrm{P} - T_i}{m_\beta} \qquad (11)$$

where m_α^β, m_β^α, m_β^L and m_β are the slopes of solid solubility lines for β phase in α phase, α phase in β phase, solidus and liquidus of β phase, respectively. The values of these parameters in Pb–Bi peritectic system are shown in Table 1.

In Eq. (7), the diffusion coefficient $\overline{D}_\mathrm{av}$ can be usually expressed as a function of the temperature and composition, that is

$$\overline{D}_{av} = D_0 \exp\left(\frac{-Q}{R_a T}\right) \qquad (12)$$

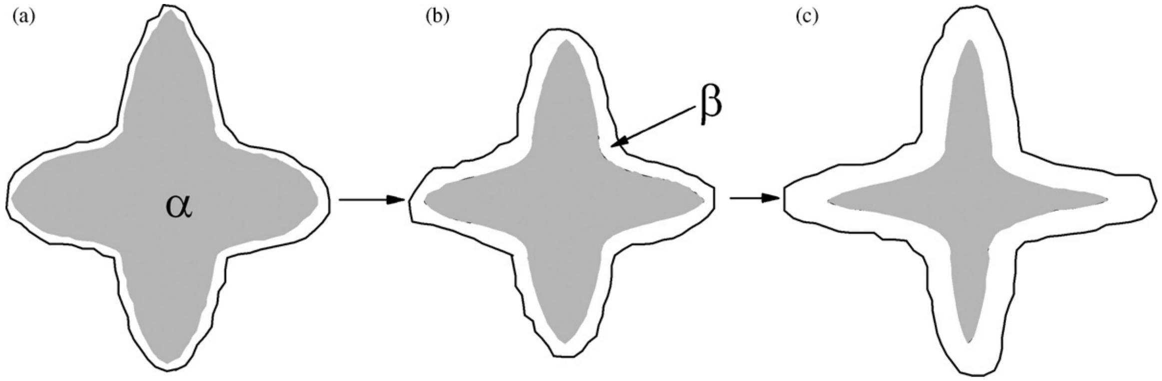

Fig. 6. Schematic diagram for dissolution of primary α-dendrite resulted from peritectic transformation.

Table 1
Parameters of Pb–Bi phase diagram.

Parameters	Values	Units
m_{α}^{β}	20.56	°C/wt%
m_{β}^{α}	41.11	°C/wt%
$m_{\beta}{}^{L}$	5.6	°C/wt%
m_{β}	2.17	°C/wt%

where D_0 is a physical constant depending on the alloy composition, R_a is gas constant, and Q is the activation enthalpy, respectively. In Pb–Bi peritectic system, the physical constant $D_0 = 1 \times 10^{-4}\,\mathrm{m^2/s}$, the activation enthalpy $Q = 108960\,\mathrm{J/mol}$ [17], and the gas constant $R_a = 8.314\,\mathrm{J/mol\,K}$.

After combining Eqs. (2), (5) and (7)–(12), making appropriate rearrangements, we obtain:

$$\frac{\Delta x^2}{2t} = \frac{C_L - C_\alpha + (T_P - T_i)(1/m_\beta + 1/m_\alpha^\beta)}{(C_P - C_\alpha + (T_P - T_i/2)(1/m_\beta^L - 1/m_\beta^\alpha + 2/m_\alpha^\beta))(C_L - C_P + (T_P - T_i/2)(2/m_\beta + 1/m_\beta^\alpha - 1/m_\beta^L))} \tag{13}$$
$$(T_P - T_i)(1/m_\beta^L + 1/m_\beta^\alpha) D_0 \exp(-Q/R_a(T_i + 273))$$

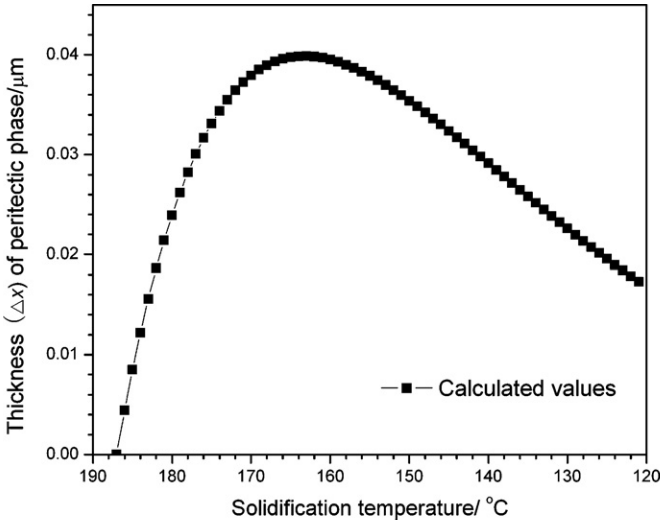

Fig. 7. The thickness of peritectic phase formed through peritectic transformation under different temperature.

Taking into account the data from Table 1, Eqs. (3) and (13), the thickness of peritectic β envelope was calculated with different solidification temperature T_i, as shown in Fig. 7. It is clearly indicated that the peritectic transformation rate first increased with decreasing temperature to a maximum, and then decreased with further decrease in temperature. There could be two competing factors governing the effect of solidification temperature on the peritectic transformation rate and dissolution rate of primary α phase in peritectic solidification. One is the compositional difference $(C_\beta^L - C_\beta^\alpha)$ across the β envelope, which tends to increase with falling temperature resulting in peritectic transformation rate increasing with decreasing temperature. The second is the average interdiffusion coefficient $\overline{D}_{av}$, which will decrease with falling temperature leading to the peritectic transformation rate decreasing with decreasing temperature. Thus the combined effect of these two factors results in the peritectic transformation rate first increasing, and then decreasing with falling temperature.

4. Conclusion

In summary, since peritectic transformation is strongly depended on solute diffusion in peritectic β phase. Two factors are responsible to solute diffusion, one is the compositional difference $(C_\beta^L - C_\beta^\alpha)$ which is the driving force for the peritectic transformation, and other is the average interdiffusion coefficient $\overline{D}_{av}$ in the β phase. Both factors are directly dependent on solidification temperature, the former increases while the latter decreases with falling temperature. Basing on the combined effect of the two factors, the thickness of the peritectic β envelope with different solidification temperature was calculated. The calculated results showed that the peritectic transformation rate first increased to a maximum, and then decreased with falling solidification temperature. The experimental results about the volume fraction of peritectic β phase and the size of primary α-dendrite core are in good agreement with the calculated results.

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