Microstructure evolution of directionally solidified Sn-16%Sb hyperperitectic alloy

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Abstract: The directionally solidified microstructure of Sn-16%Sb hyperperitectic alloy has been investigated at various solidification rates using a high-thermal gradient directional solidification apparatus. The results indicate that the solidification microstructure consists of hard primary intermetallic SnSb phase embedded in a matrix of soft peritectic β-Sn phase. The primary SnSb phase exhibits faceted growth with tetragonal or trigonal shapes. At the same time, the primary SnSb phase is refined with an increase in the solidification rate and dispersed more uniformly in the matrix of β-Sn phase. The volume fraction of the SnSb phase firstly decreases and then increases when the solidification rate increases in directionally solidification of Sn-16%Sb hyperperitectic alloy.

Key words: Sn-16%Sb hyperperitectic alloy; directional solidification; primary phase; morphological size; volume fraction

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Peritectic systems are usual alloys and apply to many kinds of industrial fields, such as Ni-based superalloy [1], Ti-Al alloy [2-3], stainless steel Fe-Cr-Ni alloy [4], permanent magnetic Nd-Fe-B material [5-6] and superconducting Y-Ba-Cu-O alloy [7]. Recently, increasing interest has been attracted in investigating the peritectic solidification, especially introducing the method of directional solidification into this aspect. There are some microstructures which are different to the microstructures of single phase or eutectic phase, including the banded microstructure in which the two phases (primary phase and peritectic phase) alternately form perpendicular to the growth direction [8-9], the coupled growth of two phases which are parallel to the growth direction [10-13], microstructure which consists of primary phase distributed in a matrix of peritectic phase, etc [14,18]. In this research, the Sn-Sb alloy was used as the study material: it is a common peritectic alloy and is called babbit alloy. It is usually applied in industry as a sliding material, such as the bearing babbit alloy. The Sn-Sb peritectic alloy has widespread applications, and is valuable in industry [15].

The Sn-Sb binary system is a typical peritectic alloy; the phase diagram for the Sn-Sb system is shown in Fig.1 [15]. As mentioned above, the alloy is a bearing babbit alloy, thus its property of resisting wear is very important. That property is related to the amount and morphological size of the primary SnSb phase. When there is more of the SnSb phase and the SnSb phase is well refined, the wear resistance of the alloy is enhanced. Therefore, it is necessary to study the volume fraction and morphological size of the primary phase in directionally solidified Sn-Sb peritectic alloy. The primary SnSb peritectic phase can be well refined through super-cooling or rapid cooling technology; and the macro-segregation in the sample is reduced compared with conventional casting [15]. A. P. Titchener and J. A. Spittle obtained the banded structure, perpendicular to the growth direction, in directionally solidified Sn-Sb peritectic alloy under high G/V ratio in 1974 [16]. Through rapid solidification and modification in Sn-Sb alloy, fine-grained microstructure was observed and its mechanical properties were reinforced [17].

The microstructure of directionally solidified Sn-Sb peritectic alloy consists of the primary SnSb inter-metallic phase distributed in a matrix of the peritectic β-Sn solid solution.

One of the aims of this study is to investigate how to obtain fine-grained SnSb inter-metallic phase distributed with high homogeneity in the matrix of β-phase; at the same time, the anticorrosion of Sn-Sb alloy with that microstructure is enhanced. Another is to study the distributional pattern in the matrix of Sn-Sb alloy.
the peritectic β phase and the morphological size of the primary SnSb phase in directionally solidified Sn-16%Sb hyperperitectic alloy with different solidification rates, by investigating the microstructures under different growth conditions.

1 Experimental procedure

The Sn-16%Sb (mass%) binary alloy is selected to be the master alloy. It has the hyperperitectic composition. The phase diagram of this master alloy is shown in Fig. 1.

The master alloy was prepared using 99.9% purity tin and 99.99% purity antimony. Appropriate quantities of the pure metals were melted in a graphite crucible, which was heated by a resistance furnace; the whole process was done in an Ar atmosphere. After initial melting and holding at 873 K for 20 minutes, the alloy was stirred and then cast into the cylindrical metal mold, 45 mm in diameter and 100 mm in length. The as-cast ingot was machined to be 3.9 mm in diameter and 80 mm in length. The ingot was chemically analyzed by inductively-coupled plasma (ICP) to determine the composition of the master alloy, which was found to be 15.81% Sb.

Directional solidification experiments were carried out using a MDS-1 apparatus which is a Bridgman vertical vacuum furnace described elsewhere [20]. The sample was put in a high purity aluminum crucible which is 100 mm long and 4 mm in inner diameter. Then it was heated and melted by a graphite heater, which was heated by a high frequency induction coil. The temperature of the graphite heater was maintained at 750 K for 20 minutes to ensure a uniform concentration of alloy and a steady temperature field. Subsequently, the sample was pulled downwards at various constant velocities of 0.3, 1, 2, 5, 10, 30, 50, 100 and 500 µm/s. After the solidified distance reached 50 mm, the sample was quenched in liquid Ga-25wt%In-13wt%Sn alloy. The experiments were done under Ar atmosphere to avoid the components (Sn and Sb) in the sample oxidizing and evaporating. The thermal gradient, measured using a NiCr-NiSi thermocouple and LR4100 functional recording instrument, was 18 K/mm.

The directionally solidified samples were polished and then etched using a 2% nital solution. Microstructures were observed using an optical microscope, Leica DM4000M. The volume fraction and morphological size of the primary phase in Sn-16%Sb hyperperitectic alloy under different solidification rates were measured using SISCIASV8.0 analysis software.

2 Results and discussion

2.1 Microstructures in equilibrium solidification of Sn-16%Sb peritectic alloy

According to the Sn-Sb alloy phase diagram (Fig.1), the Sn-16%Sb alloy has the hyperperitectic composition. This alloy should firstly solidify as the intermetallic SnSb phase below the temperature of 581 K in equilibrium solidification, and then a peritectic reaction occurs between the SnSb phase and liquid to form peritectic phase β-Sn, if the temperature reaches peritectic temperature (523 K), the reaction is simply given by

\[ \text{SnSb} + \text{Liquid} \rightarrow \beta\text{-Sn} \quad (1) \]

Where β phase is a Sn-rich solid solution. Considering the solidification pattern of hyperperitectic alloy, the peritectic reaction between the primary phase and liquid is not complete, so the solidification microstructure consists of remaining primary SnSb phase which is distributed in a matrix of peritectic β phase.

2.2 Effect of the solidification rate on the directionally solidified microstructures

In the directional solidification process, the samples were pulled at various velocities. Figure 2 and Fig. 3 show longitudinal sections of the Sn-16%Sb alloy for different solidification velocities. They indicate that at all solidification rates, the microstructures consist of primary SnSb phase (white phase) and peritectic β phase (gray phase), with the primary SnSb phase distributed in a matrix of peritectic β solid solution. When the pulling velocity is lower than 10 µm/s, the primary SnSb phase grows with triangular, tetragonal or polygonal shapes, and its size is large, as shown in Fig. 2(a) to Fig. 2(d). There are macro-segregation in the samples which were pulled with low velocities, as shown by analyzing the microstructure of the different parts of samples. These microstructures are quite different compared to the results of the rapid solidification (where \( V \geq 10 \mu m/s \)). The reason leading to segregation is because that there is a gravity segregation during solidification of the primary SnSb phase with low velocities. In that situation, the SnSb phase is assembled locally. When the pulling velocity is 10 µm/s or higher, the SnSb phase is finer and is homogeneously distributed in the matrix of the β phase solid solution; the macro-segregation in the sample is reduced or eliminated, as shown in Fig. 3(a) to Fig. 3(e). The SnSb phase also grow with triangular, tetragonal or polygonal shapes; in addition, Fig. 4(a) indicates that the SnSb phase is changed into snowflake shape or tiny graininess from sharp triangular or tetragonal shapes. The corner angle of the SnSb phase becomes blunt with an increase in velocity, especially when the pulling velocity is 500 µm/s the SnSb phase can grow with tiny polygonal shapes, even spherical shapes and distributed with high homogeneity, as shown in Fig. 4(b).

According to the KGT model [22], the under-cooling of the interface during directional solidification consists of constitutional under-cooling, curvature under-cooling, and kinetic under-cooling. The kinetic under-cooling can usually be ignored because the solidification rate is much lower than the rapid solidification rate. Thus the under-cooling can be written as

\[ \Delta T = \Delta T_c + \Delta T_r \quad (2) \]

Where \( \Delta T_c \) is the constitutional under-cooling of the interface, which can be written as

\[ \Delta T_c = m (C_l - C_r^*) \quad (3) \]

Where \( m \), \( C_l \) and \( C_r^* \) are the liquidus slope, initial composition of the master alloy and the liquid composition at the interface, respectively. \( \Delta T_r \) is curvature under-cooling.
which can be obtained as

$$\Delta T_r = \frac{2}{R}$$  

Where $\Gamma$ is the Gibbs-Thomson coefficient, $R$ is the radius of the dendrite tip, and $C_l^*$ can be evaluated from the Ivatsov solution as

$$C_l^* = \frac{C_e}{(1 - (1 - k_s)I_v [P_c])}$$  

Where $P_c$ is solutal Peclet number, may be obtained as

$$P_c = \frac{RV}{2D_l}$$  

$$R = \frac{2\pi}{mC_e\gamma}$$

Where $D_l$ is the diffusion coefficient of solute in the liquid, $k_s$ is the partition coefficient of solute, and $I_v [P_c]$ is the Ivantsov function.

$P_c$ increases with the increasing solidification rate according to Eq. (6), and the value of $I_v [P_c]$ also increases. $C_l^*$ and $\Delta T_c$ should increase correspondingly according to Eqs. (5) and (3), respectively. In contrast, the radius $R$ decreases as $V$ increases. Subsequently, it can be seen that $\Delta T_r$ increases as $R$ decreases using Eq. (4). Overall, the under-cooling in the liquid ahead of the interface increases with the increasing of the solidification rate $V$, this results in the formation of a lot of primary phase nucleus in liquid. At the same time, as the increasing of solidification rate the time for growth of the primary phase is not sufficient, which leads to the growth of the primary to be suppressed. Thus the primary SnSb phase is refined and distributed homogeneously in $\beta$ phase.

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**Fig. 2** Directional solidified microstructures of Sn-16%Sb peritectic alloy at different solidification rates:
- 0.3 $\mu$m/s ($a_1$–$a_3$);
- 1 $\mu$m/s ($b_1$–$b_3$);
- 2 $\mu$m/s ($c_1$–$c_3$);
- 5 $\mu$m/s ($d_1$–$d_3$)
2.3 The volume fraction of the primary SnSb phase at various solidification rates

The measured volume fraction of the primary phase-SnSb compound at low withdrawal velocities, which are lower than 10 µm/s, is shown in Fig. 5(a). It clearly indicates that the volume fraction of the SnSb phase drastically decreases with increased withdrawal velocity. There is heavy macro-segregation in a sample which is pulled at low velocity, leading to lots of SnSb phase locally floated in some parts of the sample, but other parts have much less of the SnSb phase. Thus there exists an inaccuracy between the measured volume fraction of the SnSb phase and the actual volume fraction; the value of the measured volume fraction of SnSb phase is larger than the actual. Taking into account the inaccuracy, we measure the volume fraction of the SnSb phase in different parts of the sample and take the average value. The measured volume fraction of the SnSb phase for higher \( V \geq 10 \) µm/s pulling velocities is shown in Fig. 5(b). Initially, the volume fraction has no obvious change with the increasing of the pulling rate \( V \); while when \( V \) is higher than 100 µm/s, the volume fraction of SnSb phase increases with the increasing \( V \), but the increase is not as acute as the decrease in low solidification rate.

With the increasing of \( V \), the size of the primary SnSb phase become smaller and it distributed homogeneously in the matrix of \( \beta \) phase. Thus the contact area of primary phase and liquid increases, which promotes the peritectic reaction and...
3 Conclusions

(1) When unidirectional solidified at a temperature gradient up to 1.8 × 10^4 K·m⁻¹, and the pulling velocity was 0.3 μm/s to 500 μm/s, the microstructures of the Sn-16%Sb hyperperitectic alloy are primary SnSb phases embedded in the matrix of peritectic β-Sn phase.

(2) When the withdrawal velocity is lower than 10 μm/s, heavy macro-segregation occurs during slow solidification of the SnSb phase; the SnSb phase concentrated locally and distributed non-homogeneously.

(3) As the solidification rate increases, the primary phase SnSb compound is gradually refined, it becomes homogeneously distributed in the matrix, and the macro-segregation is effectively controlled. The morphology of the SnSb phase changed into snowflake shapes or tiny graininess from sharp triangular or tetragonal shapes.

(4) The volume fraction of the SnSb phase, which is distributed in a matrix of the peritectic β phase, initially decreases, then increases as the solidification rate increases.

References


