Formation mechanism of primary phases and eutectic structures within undercooled Pb-Sb-Sn ternary alloys

WANG WeiLi, DAI FuPing & WEI BingBo[†]

Department of Applied Physics, Northwestern Polytechnical University, Xi'an 710072, China

The solidification characteristics of three types of Pb-Sb-Sn ternary alloys with different primary phases were studied under substantial undercooling conditions. The experimental results show that primary (Pb) and SbSn phases grow in the dendritic mode, whereas primary (Sb) phase exhibits faceted growth in the form of polygonal blocks and long strips. (Pb) solid solution phase displays strong affinity with SbSn intermetallic compound so that they produce various morphologies of pseudobinary eutectics, but it can only grow in the divorced eutectic mode together with (Sb) phase. Although (Sb) solid solution phase and SbSn intermetallic compound may grow cooperatively within ternary eutectic microstructures, they seldom form pseudobinary eutectics independently. The (Pb)+(Sb)+SbSn ternary eutectic structure usually shows lamellar morphology, but appears as anomalous eutectic when its volume fraction becomes small. EDS analyses reveal that all of the three primary (Pb), (Sb) and SbSn phases exhibit conspicuous solute trapping effect during rapid solidification, which results in the remarkable extension of solute solubility.

undercooling, dendritic growth, eutectic growth, ternary eutectic, solute trapping

The solidification of eutectic alloys, which involves the competitive nucleation and cooperative growth of two or more eutectic phases from one liquid phase, is an important research subject in the field of material physics. For the binary eutectic growth, there have been sufficient investigations which lay the foundation of successful theoretical models^[1]. In contrast, the solidification process of ternary eutectic alloys is very complicated^[1–12], which requires further profound investigations. Most of the recent research on ternary eutectic solidification pays more attention to the extension of the classic JH model, the evolution of solidification structure, and the properties of ternary alloys under equilibrium or quasi-equilibrium conditions. Himemiya et al.^[5] extended JH model to the coupled growth of three phases in ternary eutectic alloys. Souza et al.^[6] studied the growth

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[†]Corresponding author (email: bbwei@nwpu.edu.cn)

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mechanism of the primary phase and the evolution of eutectic microstructure in Al-Cr-Nb ternary eutectic alloy under directional solidification conditions. Witusiewicz et al.^[7–9] analyzed the phase equilibrium and growth mechanism of lamellar eutectic for ternary eutectic alloys.

The Pb-Sb-Sn ternary alloys form a typical eutectic system, which exhibits three primary phase regions in its equilibrium phase diagram. The primary phase and the eutectic morphology are quite different in these three phase zones. (Pb) phase is a non-faceted solid solution phase, (Sb) phase is a classic faceted phase, and SbSn phase is an intermetallic compound. Owing to great difference in the lattice structure and growth mode among these three phases, their coupled growth and structural morphology are extremely complicated. Although some work has been done on the solidification microstructures and physical properties of Pb-Sb-Sn ternary alloys at near-equilibrium state^[12–15], there are few investigations on the rapid solidification of highly undercooled Pb-Sb-Sn alloys.

An alloy melt can be substantially undercooled to temperatures well below its equilibrium freezing point by eliminating the intrinsic heterogeneous nuclei. The glass fluxing method is an efficient approach to removing heterogeneous nuclei and achieving bulk undercooling, which is applicable to Pb-Sb-Sn ternary alloys. The objective of this work is to investigate the nucleation mechanism of primary and eutectic phases, reveal the microstructural evolution and solidification routes and explore the solute redistribution characteristics under substantial undercooling conditions.

1 Experimental procedure

The experiments were performed by the glass fluxing method. Pb-Sb-Sn ternary alloy samples were prepared from pure Pb(99.999%), Sb(99.95%) and Sn(99.9%). Each sample had the mass of 1 g and was contained in an 8 ID×10 OD×12 mm alumina crucible. The sample was covered by 0.2 g B₂O₃ glass as the fluxing agent and melted in a resistance furnace. After being superheated by 200 K for several minutes, the sample was cooled at a rate of 46–73 K/min by rapidly moving the crucible away from the heating source. The process of heating and cooling was repeated for 2 to 5 times. The sample temperature was monitored by a NiCr-NiSi thermocouple and recorded by a 3066 type three-pen recorder.

After experiment, the solidified samples were sectioned and polished. At first, the sample was etched with a solution of 10%HCl for 2 min, and subsequently etched with 10 g FeCl₃+2 mL HCl+97 mL H₂O for 20 s. The thermodynamic properties were determined with TA Modulated DSC 2910 differential scanning calorimetry analyzer. Its phase constitution was examined with Rigaku D/max 2500 X-ray diffractometer. Microstructural morphologies were analyzed with FEI Sirion 200 scanning electron microscope and Zeiss Axiovert 200MAT optical microscope, and solute distributions were examined with INCA Energy 300 energy dispersive spectrometer.

2 Results and discussion

The three alloy compositions chosen for the experimental research are Pb-5%Sb-4%Sn, Pb-20%Sb-4%Sn and Pb-14%Sb-10%Sn, which correspond to the three primary phase regions of (Pb), (Sb) and SbSn, respectively. Their locations in the Pb-Sb-Sn ternary phase diagram are designated as points *A*, *B* and *C* in Figure 1, where Figure 1(a) is the Pb-rich corner of liquidus pro-

fection and Figure 1(b) is the vertical section along the M - M line in Figure 1(a)^[13–15]. The maximum undercoolings obtained in this work are 82 K(0.15 T_L), 87 K(0.15 T_L) and 68 K(0.12 T_L), respectively, for these three alloys.

Figure 1 Schematic of three solidification routes. (a) Pb-rich corner of liquidus projection; (b) M - M vertical section.

2.1 Rapid solidification of undercooled Pb-5%Sb-4%Sn ternary alloy

(i) Thermal analysis and phase constitution. The thermal analysis of Pb-5%Sb-4%Sn ternary alloy was carried out by differential scanning calorimetry (DSC). A sample with the mass of 2.49 mg was heated and cooled at a rate of 5 K/min during the experiment. Its total melting enthalpy is determined as 22.34 J/g, and the DSC curve is illustrated in Figure 2(a). Apparently, this alloy exhibits two melting peaks and two solidification peaks. The first melting peak takes place at a temperature of 514 K, while the second one appears as a small peak at 550 K. There exist two sharp crystallization peaks at 544 and 510 K, respectively, in the cooling process. The DSC analysis shows that the liquidus temperature is 558 K, and the solidus temperature is 514 K.

The X-ray diffraction (XRD) analyses were performed on the solidified samples with various undercoolings in the range of 10–82 K. XRD patterns are presented in Figure 2(b), which indi-

Figure 2 Thermal analysis and X-ray diffraction of Pb-5%Sb-4%Sn ternary alloy. (a) DSC thermogram; (b) XRD patterns.

cates that the solidification microstructures obtained within this undercooling range are all composed of (Pb) solid solution phase and SbSn intermetallic compound phase.

(ii) Structural characteristics of primary (Pb) phase. Pb-5%Sb-4%Sn alloy is located within the primary (Pb) phase region, and its solidification microstructures consist mainly of primary (Pb) phase and eutectic structure. As seen in Figure 2(a), the primary (Pb) phase begins to nucleate when the temperature reduces to 544 K, and the latent heat of crystallization is 7.74 J/g. The temperature interval between the first and the second exothermic peaks is 34 K, which means that a lot of primary (Pb) phases form in this ternary alloy.

(1) Dendritic microstructures. An evident transition occurs in the microstructure of primary (Pb) phase with the enhancement of undercooling. Figure 3 presents the microstructural variation of Pb-5%Sb-4%Sn ternary alloy as undercooling increases, where the black phase is the primary (Pb) phase and the white part is the pseudobinary (Pb)+SbSn eutectic microstructure. When undercooling is small, the (Pb) phase is characterized by coarse and well-developed dendrites. As undercooling increases, the microstructures are significantly refined. If undercooling exceeds a value of about 61 K, the primary (Pb) phase is found to form small equiaxed dendrites. The dendritic structures become homogeneous and equiaxed fragments when the alloy melt is undercooled by 82 K. A measurement has been done to establish the relationship between the average grain size of primary (Pb) phase and undercooling. Figure 4(a) shows the measured results. Evidently, the average grain size of primary (Pb) phase decreases dramatically with undercooling. Figure 3 and Figure 4(a) reveal some characteristics of dendritic fragmentation, indicating that the refinement of microstructures is caused by remelting and ripening of primary dendrites. At small undercoolings, the latent heat of crystallization is efficiently released through the liquid alloy and its surroundings, and the primary (Pb) phase grows directly into coarse dendrites. Once undercooling exceeds 39 K, the rapid release of latent heat results in a strong recalescence effect, which brings about remelting and fragmentation of rapidly growing dendrites. Clearly, the grain structure is refined under rapid solidification and high undercooling conditions.

Figure 3 Solidification microstructures of Pb-5%Sb-4%Sn alloy at different undercoolings.

Figure 4 Grain size (a) and solute content (b) versus undercooling.

(2) Solute trapping effect. EDS analysis indicates that remarkable solute trapping occurs during the rapid solidification of Pb-5%Sb-4%Sn ternary alloy. The contents of solute Sb and Sn in (Pb) phase at its grain center are illustrated in Figure 4(b). Obviously, the solute contents increase with undercooling. When alloy undercooling is below 39 K, the contents of Sb and Sn are less than the original alloy concentration. However, at the undercooling of 82 K, the solubilities of Sb and Sn exceed the original alloy concentration, and they rise up to 6.96% and 4.59%, respectively. It is apparent that the solute solubility of primary (Pb) phase is effectively extended under rapid solidification and high undercooling conditions.

(iii) Pseudobinary eutectic structures. When the temperature of Pb-5%Sb-4%Sn alloy falls to 510 K in the process of solidification, the (Pb)+SbSn pseudobinary eutectic microstructures grow from the liquid phase whose composition reaches the pseudobinary eutectic line in Pb-Sb-Sn ternary phase diagram. Since the liquid phase has completely solidified before it attains the ternary eutectic point, no ternary eutectic microstructures are produced in Pb-5%Sb-4%Sn alloy. The microstructural morphologies of (Pb)+SbSn pseudobinary eutectic are shown in Figure 3(c), where lamellar eutectics mainly appear around the primary (Pb) phase.

The phase constitution and the solute distribution of (Pb)+SbSn lamellar eutectic are determined by EDS scanning analyses, as shown in Figure 5, where the dark phase is (Pb) solid solution, and the white one is SbSn intermetallic compound. (Pb) and SbSn phases grow cooperatively in a lamellar way. As is obvious in Figure 5(b) and (c), the solubility of Sb is higher than that of Sn in SbSn intermetallic compound.

Figure 6 presents the relationship of (Pb+SbSn) pseudobinary eutectic and undercooling. As undercooling increases, the volume fraction of pseudobinary eutectic decreases, which follows a linear relation:

$$f_{\text{BE}} = 0.57 - 0.0084\Delta T. \quad (1)$$

(iv) Nucleation mechanism and solidification route. The (Pb+SbSn) pseudobinary eutectic structures appear around the primary (Pb) phase, and the edge of (Pb) dendrites grows smoothly. It is obvious that primary (Pb) phase is not an effective heterogeneous nucleus for the intermetallic compound SbSn phase, just as shown in Figure 3. By comparing Figure 4(b) with Figure 6, it can be clearly seen that the solubility of Sb increases but the volume fraction of (Pb+SbSn) pseudobinary eutectic decreases with undercooling, which keeps the mass conservation of Pb-5%Sb-4%Sn ternary alloy.

Figure 5 Solute distribution of (Pb)+SbSn pseudobinary eutectic structure. (a) EDS scanning line; (b) profile of Sb content; (c) profile of Sn content.

Figure 6 Volume fraction of (Pb+SbSn) pseudobinary eutectic structure at different undercoolings.

The solidification route is illustrated in Figure 1(a), which shows that the concentration and temperature of Pb-5%Sb-4%Sn ternary alloy change along line *Aa*. The (Pb+SbSn) eutectic

structure starts to grow when the concentration and temperature of remnant liquid phase reach the pseudobinary eutectic line. Subsequently this kind of pseudobinary eutectic grows continuously. The solidification process is completely finished before the concentration and temperature arrive at the ternary eutectic point, which explains why no ternary eutectics form in the undercooled Pb-5%Sb-4%Sn ternary alloy.

2.2 Primary phase and eutectic structure of Pb-20%Sb-4%Sn ternary alloy

(i) Thermodynamic property and phase constitution. Differential scanning calorimetry (DSC) was applied to investigating the thermodynamic property of Pb-20%Sb-4%Sn ternary alloy. The sample has the mass of 2.49 mg, which was heated and cooled at a rate of 5 K/min during the experiment. As shown in Figure 7, the melting-cooling curves show three melting and three crystallization peaks, indicating that the phase transformation occurs three times. Clearly, the melting temperatures are 512, 514 and 519 K, respectively, and the total heat of fusion is 35.78 J/g. In the cooling process, the crystallizing temperatures are 570, 513 and 510 K, respectively, and the third exothermal peak is very sharp. The liquidus temperature of the Pb-20%Sb-4%Sn ternary alloy is determined as 570 K, while the solidus temperature is 512 K.

Figure 7 Thermal analysis and X-ray diffraction of Pb-20%Sb-4%Sn ternary alloy. (a) DSC thermogram; (b) enlarged part of DSC curve; (c) XRD pattern.

In order to explore the phase constitution of Pb-20%Sb-4%Sn ternary alloy, XRD diffraction analyses have been accomplished. Figure 7(c) presents the XRD patterns of several samples with different undercoolings. It is evident that solidification microstructures always consist of (Pb) solid solution, (Sb) solid solution and SbSn intermetallic compound.

(ii) Structural morphology of primary (Sb) phase. Pb-20%Sb-4%Sn ternary alloy is selected from the primary (Sb) phase region in the Pb-Sb-Sn ternary phase diagram. When the sample

temperature decreases to 570 K, the primary (Sb) phase grows in the faceted mode as the preceding nucleation phase, and the latent heat of crystallization is 4.21 J/g. The temperature interval is 57 K between the first and the second exothermic peaks, indicating that a lot of primary phases (Sb) form in Pb-20%Sb-4%Sn ternary alloy.

(1) Structural characteristics. Figure 8(a) and (b) presents the structural morphology of faceted (Sb) phase. The primary phase grows into either faceted polygonal blocks or faceted long strips and appears as the white structures in optical micrographs. Figure 9 demonstrates the relationship between the volume fraction of polygonal faceted (Sb) blocks and undercooling. It indicates that the volume fraction of polygonal faceted (Sb) phase decreases with undercooling. The polygonal faceted (Sb) phase occupies 15% volume in the solidified structures when undercooling is 53 K, and grows at the upper part of the sample. Usually, there are also some polygonal (Sb) blocks attached to the faceted (Sb) strips. However, the volume fraction of polygonal faceted (Sb) phase becomes only 3.03% when undercooling increases to 87 K. It is evident that the high undercooling condition suppresses the growth of polygonal faceted (Sb) phase and promotes the formation of faceted (Sb) strips. With the increase of undercooling, the volume fraction of polygonal faceted (Sb) phase decreases according to the following relation:

$$f_{(Sb)} = 0.67 - 0.01\Delta T + 8.13 \times 10^{-5} \Delta T^2. \quad (2)$$

Figure 8 Structural morphologies of Pb-20%Sb-4%Sn ternary alloy. (a) Low magnification structure; (b) primary phases; (c) ternary eutectic structure.

(2) Solute trapping effect. EDS line scan analysis shows that the solubility of Sn is larger than that of Pb in the primary polygonal (Sb) blocks, just as shown in Figure 10. The actual contents of both solutes Sn and Pb in primary (Sb) phase are also determined and the results are shown in

Figure 9 Volume fraction of polygonal primary (Sb) blocks versus undercooling.

Figure 10 Solute distribution of primary (Sb) phase. (a) EDS scanning line; (b) Sn distribution; (c) Pb distribution.

Figure 11. It is apparent that the solute contents of primary (Sb) phase increase with undercooling. According to the Pb-Sb and Pb-Sn binary phase diagrams, the maximum solubilities of Pb and Sn inside (Sb) phase are 3.24% and 9%, respectively. At undercooling of 53 K, the Pb content in primary (Sb) phase is 2.83%. This solute content becomes 3.64% when undercooling rises up to 81 K. At the large undercooling of 87 K, the solubility of Pb inside the primary (Sb) phase is ex-

Figure 11 Solute contents of primary (Sb) phase as a function of undercooling. (a) Solute Pb; (b) solute Sn.

tended to 4.25%. Similarly, the Sn content in primary (Sb) phase also exhibits an obvious increasing tendency. In the sample undercooled by 53 K, the primary (Sb) phase contains 9.28% Sn. But the Sn content of (Sb) phase increases to 10.52% when the ternary alloy is undercooled by 87 K. These measured results of EDS analyses have shown that the rapid solidification induced by high undercooling leads to the remarkable extension of solute solubilities within primary (Sb) phase.

(iii) Pseudobinary eutectic morphology. Figures 8(a) and (b) show that Pb phase grows around the primary (Sb) phase. The white and dark phases are the solid solution (Sb) and (Pb) phases respectively in these two optical micrographs. Since the primary (Sb) phase has a rather large solidification temperature range and it consumes large quantities of Sb atoms to grow up, Pb atoms become enriched in the liquid phase surrounding the primary (Sb) phase. Once temperature drops down to 513 K, the liquid phase concentration attains the (Pb+Sb) pseudobinary eutectic line. In such a case, (Pb) phase nucleates independently and grows in a dendritic way in the vicinity of primary (Sb) phase, resulting in the formation of (Pb)+(Sb) divorced eutectic. This is quite different from the prediction of Figure 1(b) that (Sb)+SbSn pseudobinary eutectic should have formed under the equilibrium condition. The direct reason is that the extremely nonequilibrium condition produced by substantial undercooling has drastically changed the actual solidification route of Pb-20%Sb-4%Sn ternary alloy.

(iv) Ternary eutectic microstructure. As seen in Figure 7(a), (Pb)+(Sb)+SbSn ternary eutectic structures start to form when the temperature reduces to 510 K. The ternary eutectic transformation has aroused a sharp exothermal peak, and the latent heat of crystallization is 31.64 J/g, which indicates that a large amount of ternary eutectic structures are produced in Pb-20%Sb-4%Sn ternary alloy. Figure 8(c) is the back scattering electron micrograph of the (Pb)+(Sb)+SbSn ternary eutectics distributed within the interspacings of (Pb)+(Sb) pseudobinary eutectics shown in Figure 8(a). Here the white phase is (Pb) phase, the dark grey phase is SbSn intermetallic compound, and the bright grey phase is (Sb) phase. It is apparent that (Sb) and SbSn phases have nucleated and grown dependently. Figure 8(a) also shows that there are a lot of ternary eutectic microstructures between the (Pb)+(Sb) pseudobinary eutectic colonies, which agrees well with the DSC experiment of Figure 7(a). The alternating nucleation and cooperative growth of (Pb), (Sb) and SbSn phases results in the formation of lamellar ternary eutectics.

Figure 12 gives the volume fraction of ternary eutectics at different undercoolings. It can be seen that the volume fraction of (Pb)+(Sb)+SbSn eutectics increases dramatically with undercooling. This is because a large number of primary polygonal (Sb) blocks are formed together with lots of

(Pb) phase under a small undercooling condition, and consequently there remain few interspaces for ternary eutectics. As shown in Figure 13, the primary (Sb) strips increase their interspacings when the primary polygonal (Sb) blocks reduce their volume fraction at large undercoolings. Therefore, more ternary eutectics can form accordingly. The volume fraction of ternary eutectics varies with undercooling according to the following relation:

$$f_{TE} = -0.94 + 0.03\Delta T - 1.81 \times 10^{-4} \Delta T^2. \quad (3)$$

(v) Nucleaion characteristics and solidification route. In the solidification process of Pb-20%Sb-4%Sn ternary alloy, the primary (Sb) phase nucleates preferentially in alloy melt and grows into faceted strips and polygonal blocks. Meanwhile, (Pb) phase also nucleates independently and grows up in the surroundings of primary (Sb) phase. There are no traces of attached or dependent nucleation at the smooth edges of both (Sb) and (Pb) phase. This means that they are not effective heterogeneous nucleus for each other. On the other hand, (Pb)+(Sb)+SbSn ternary eutectics have formed in the interspaces of (Pb)+(Sb) pseudobinary eutectic colonies, suggesting that primary (Sb) phase should not be an efficient heterogeneous nucleant for SbSn phase either. In addition, the rapid solidification of this undercooled ternary alloy yields (Pb)+(Sb) rather than (Sb)+SbSn pseudobinary eutectic microstructures.

Figure 12 Volume fraction of ternary eutectics in Pb-20%Sb-4%Sn alloy at different undercoolings.

Figure 13 Interspacing of primary (Sb) strips versus undercooling.

The solidification route of Pb-20%Sb-4%Sn ternary alloy is schematically presented in Figure 1(a). When the alloy temperature falls to 570 K, primary (Sb) phase precipitates from alloy melt and its solidification route proceeds along the *Bb* line. As soon as the concentration and temperature arrive at point *b* of the (Pb)+(Sb) pseudobinary eutectic line, (Pb) phase begins to nucleate and divorced eutectics come into being. Later on, the solidification process continues along line *bE* until the ternary eutectic point *E*, where (Pb)+(Sb)+SbSn ternary eutectics form and put an end to solidification.

It should be pointed out that there is a great difference between the equilibrium solidification route and the actual solidification route of undercooled Pb-20%Sb-4%Sn ternary alloy. At equilibrium state, (Sb)+SbSn pseudobinary eutectics are usually formed, because the concentration and temperature will attain the (Sb)+SbSn pseudobinary eutectic line. However, the substantial undercooling causes the extremely nonequilibrium condition. This makes the concentration and

temperature vary in such a way that they reach the (Pb)+(Sb) pseudobinary eutectic line, leading to the formation of (Pb)+(Sb) eutectic microstructures.

2.3 Microstructure and macrosegregation of Pb-14%Sb-10%Sn ternary alloy

(i) Thermodynamic property and phase constitution. Pb-14%Sb-10%Sn ternary alloy is located in the primary SbSn phase region. A sample of 2.92 mg is employed for DSC analysis. The heating and cooling rates are both 5 K/min. DSC curves are presented in Figure 14(a) and (b). There are three endothermic peaks and four exothermic peaks, showing the complexity of the alloy microstructure. The first two endothermic peaks are not separated, the second endothermic peak corresponds to the melting of main structures, whereas the third peak is only a weak melting process initiated at 518 K. The total enthalpy of the whole melting process is 38.68 J/g. In the solidification process, the starting temperatures of the four exothermic peaks are 525, 514, 513 and 509 K, respectively. Obviously, the third crystallizing peak coincides with the formation of major solidification microstructures. According to these DSC analyses, the liquidus and solidus temperature of this ternary alloy are determined to be 543 and 512 K.

Figure 14 Thermal analysis and XRD diffraction of Pb-14%Sn-10%Sn ternary alloy. (a) DSC thermogram; (b) enlarged part of DSC curve; (c) XRD patterns.

The XRD experimental results are shown in Figure 14(c). It is concluded that the solidification structures of Pb-14%Sb-10%Sn ternary alloy consist of SbSn intermetallic compound, (Pb) and (Sb) solid solution phases under various undercooling conditions.

(ii) Microstructural morphology of primary SbSn phase. It is known from the DSC curves of Figure 14(a) that primary SbSn phase begins to nucleate when the temperature of

Pb-14%Sb-10%Sn ternary alloy falls to 525 K. The latent heat is 4.27 J/g for this primary phase. Because the temperature interval is only 11 K between the first and second exothermic peaks, there should not be a large amount of primary SbSn intermetallic compounds.

(1) Morphology of solidified microstructures. The microstructures of Pb-14%Sb-10%Sn ternary alloy display serious macrosegregation, and primary SbSn phase grows in different manners at the upper and lower parts of an undercooled sample as illustrated in Figure 15(a). At the upper part, primary SbSn phase appears as coarse dendrites and polygonal faceted blocks. The polygonal faceted SbSn blocks are so arranged that they form a sort of discontinuous dendrites, with their interspacings filled with (Pb) phase. At the lower part of the undercooled sample, the primary SbSn phase takes the shape of triangular stars. Some of these triangular stars are connected in such a way that they look like fish bones, which is evident in Figure 15(a).

Figure 15 Solidification microstructure of Pb-14%Sb-10%Sn ternary alloy. (a) Macrosegregation; (b) pseudobinary eutectic; (c) ternary eutectic.

(2) Solute trapping effect. The EDS measurement results show that the Pb content in primary SbSn phase exhibits an ascending tendency with the increase of undercooling (Figure 16). From the equilibrium Pb-Sb and Pb-Sn phase diagrams, it is inferred that the maximum Pb solubility in (Sb) and (Sn) phases is 3.24% and 2.5%, respectively. The primary SbSn phase is an intermetallic compound with a stable crystalline structure and cannot dissolve too much solute under the equilibrium condition. However, Pb element can be efficiently dissolved into primary SbSn phase during high undercooling and rapid solidification. When undercooling is 12 K, the Pb content is 10.26%. As undercooling increases to 68 K, the Pb content attains 12.06%. It is apparent that the solute solubility of primary SbSn phase can be extended under rapid solidification conditions.

(iii) Macrosegregation of SbSn phase. The densities of the three solid phases and one liquid

Figure 16 Pb content of primary SbSn phase at different undercoolings.

Figure 17 Macrosegregation versus undercooling.

phase in solidifying Pb-14%Sb-10%Sn ternary alloy are quite different from each other. SbSn phase is the lightest one among them. It floats to the upper part of the solidifying sample and causes macrosegregation during solidification. The macrosegregation of this ternary alloy is characterized by the inhomogeneous variation of microstructures along the vertical direction. There is a visible boundary between the two segregated parts: the upper part is enriched with SbSn phase; whereas the lower part is depleted of SbSn phase.

For the convenience of theoretical analyses, the ratio S_d of the upper segregated part height h to sample height H is defined as the degree of macrosegregation, i.e. $S_d = h/H$. The relationship between S_d and undercooling is illustrated in Figure 17. It can be seen that the degree of macrosegregation decreases with the increase of undercooling. In the case of small undercoolings, the primary SbSn phase has smaller density because of its less Pb solubility and floats to the sample top by Stokes motion to form coarse dendritic structures there. At large undercoolings, the dendrite fragmentation occurs in primary SbSn phase owing to the rapid recalescence effect. Meanwhile, the Pb solubility in SbSn phase is extended and results in the reduction of density difference between primary SbSn phase and its surrounding liquid phase. Some of the SbSn dendritic fragments exist at the middle and lower parts of alloy sample to form the triangular star microstructures. The macrosegregation degree is consequently reduced. This indicates that the rapid solidification at substantial undercoolings may facilitate the suppression of macrosegregation.

(iv) Evolution of pseudobinary eutectics. Because Pb atoms are expelled from the growing SbSn dendrites or blocks, they become accumulated ahead of the solid/liquid interface of primary SbSn phase. When the alloy temperature decreases to 514 K, (Pb) phase nucleates from the liquid phase with a favourable concentration and grows dendritically. Although it does not form by coupled growth together with SbSn phase, (Pb) phase depends on SbSn phase to acquire the desirable concentration condition. The divorced (Pb)+SbSn pseudobinary eutectics result from this sort of weakly dependent growth of these two phases. At the temperature of 513 K, the liquid concentration arrives at (Pb)+SbSn pseudobinary eutectic line. According to the DSC curves of Figure 14(a), the corresponding exothermic peak is very sharp and strong, indicating that a great number of (Pb)+SbSn eutectic structures have been produced. The measured solidification temperature range is 4 K, while the heat of fusion is 34.68 J/g. As seen in Figure 15, at the upper segregated part of the alloy sample, lamellar (Pb)+SbSn eutectics usually form inside the interspaces between divorced

(Pb)+SbSn eutectic colonies. In contrast, (Pb)+SbSn eutectics frequently grow in a radiative way from the edge of SbSn phase at the lower part of the alloy sample. The (Pb)+SbSn eutectic microstructures occupy a large volume fraction and display various kinds of interesting morphologies.

(1) Morphology of solidified microstructures. Figure 18 presents various morphologies of (Pb)+SbSn eutectics at different locations of a Pb-14%Sb-10%Sn ternary alloy sample under-cooled by 68 K. The bright phase is SbSn intermetallic compound, and the dark phase is (Pb) solid solution. At the upper part of this segregated sample, there are two different kinds of (Pb)+SbSn eutectics: divorced eutectic and lamellar eutectic, which proceed in different growth temperatures. When alloy temperature drops to 514 K, (Pb) dendrites precipitate from the liquid phase surrounding primary SbSn dendrites and blocks, resulting in the formation of divorced (Pb)+SbSn eutectic structures. At temperatures below 513 K, a large quantity of lamellar (Pb)+SbSn eutectics form within the interspaces of divorced eutectic colonies. Figure 18(a) is a labyrinth-like eutectic structure formed by the alternating nucleation and coupled growth of (Pb) and SbSn phases. Figure 18(b) shows a two-phase dendritic morphology of (Pb) +SbSn eutectics. Regular lamellar eutectics grow from the tips of this sort of two-phase composite dendrites. There are also lots of feather-like (Pb)+SbSn eutectics originating from the primary SbSn phase in these composite dendrites. At the lower part of the alloy sample, the (Pb)+SbSn eutectic colonies frequently take the shape of triangular stars. Lamellar (Pb)+SbSn structures originate from the primary axes of triangular SbSn phase and grow in radiative directions. As demonstrated in Figure 18(c), many triangular stars of

Figure 18 Structural morphology of (Pb+SbSn) pseudobinary eutectic. (a) Labyrinth-like structure; (b) dendritic morphology; (c) fishbone shaped structure; (d) lamellar structure.

(Pb)+SbSn eutectics are so connected that they produce a kind of fishbone-like microstructure. Figure 18(d) gives the regular lamellar eutectics which form at the tails of those triangular stars mentioned above.

(2) Lamellar spacing and solute distribution. Figure 19 presents the interlamellar spacing of (Pb)+SbSn eutectics versus undercooling at upper and lower parts of undercooled Pb-14%Sb-10%Sn ternary alloy samples. At small undercooling of 12 K, serious macrosegregation and coarse SbSn dendrites are formed. In such a case, (Pb)+SbSn eutectics grow slowly and exhibit large interlamellar spacings. The eutectic growth velocity increases with undercooling, which results in reduced interlamellar spacings and refined microstructures. This structural refinement effect is quite conspicuous during the rapid solidification of undercooled Pb-14%Sb-10%Sn ternary alloy.

Figure 19 Interlamellar spacing of (Pb+SbSn) pseudobinary eutectic versus undercooling.

EDS scan analyses are conducted to explore the solute distribution profiles of (Pb)+SbSn eutectics in Pb-14%Sb-10%Sn ternary alloy. As seen in Figure 20, the white phase is SbSn intermetallic compound, and the dark phase is (Pb) solid solution. The lamellar structures result from the alternating and cooperative growth of SbSn and (Pb) phases. Figure 20(b) presents the Sb distribution profile, while Figure 20(c) gives the distribution curve of Sn content.

(v) Growth of ternary eutectics. In the light of DSC curves in Figure 14(a), (Pb)+(Sb)+SbSn ternary eutectics start to form when alloy temperature decreases to 509 K and alloy composition attains the ternary eutectic point. It is found by metallographic analyses that ternary eutectic microstructures only appear at the lower part of the alloy sample and exist in the interspaces between (Pb)+SbSn eutectic colonies. The ternary eutectics occupy only a small volume fraction, which agrees well with the fact that the fourth exothermic peak of Figure 14(a) is very weak.

The microstructure of (Pb)+(Sb)+SbSn ternary eutectic is illustrated in Figure 15(c), where the white phase is SbSn phase, the black one is (Pb) phase and the grey one is (Sb) phase. It can be seen that the microstructures consist mainly of (Pb) and SbSn phases. (Sb) phase nucleates and grows depending on SbSn phase. When the remnant liquid achieves the temperature and compo-

Figure 20 Solute distribution of (Pb+SbSn) pseudobinary eutectic. (a) EDS scanning line; (b) Sb distribution; (c) Sn distribution.

sition of the ternary eutectic point, the three eutectic phases grow cooperatively and form the anomalous (Pb)+(Sb)+SbSn ternary eutectic.

(vi) Nucleation characteristics and solidification route. From the DSC curve of Figure 14(a), it is known that the temperature interval between the first and second exothermic peaks is 11 K. In solidification microstructures, (Pb)+SbSn pseudobinary eutectics grow radiatively from the primary SbSn faceted phase. This shows that SbSn phase is the effective nucleants for (Pb) and (Sb) phases. Since (Pb) and SbSn phases have strong mutual affinity, they tend to grow cooperatively and produce various kinds of pseudobinary eutectics. (Pb)+(Sb)+SbSn ternary eutectic structures exist inside the interspaces of (Pb)+SbSn eutectic colonies. Although (Sb) and SbSn phases display dependent growth in ternary eutectic structures, they have never formed (Sb)+SbSn pseudobinary eutectics independently.

The solidification route of Pb-14%Sb-10%Sn ternary alloy is shown in Figure 1(a). In the solidification process, primary SbSn phase precipitates from liquid phase at first, when temperature decreases to 525 K. The alloy composition and temperature vary along line Cc. When temperature falls to 514 K and (Pb)+SbSn eutectic line is attained, (Pb) phase nucleates around the SbSn phase and forms the divorced eutectic microstructure. With the further decrease of temperature to 513 K, a large amount of (Pb)+SbSn lamellar eutectics are produced. Later on, the alloy composition

moves ahead along line cE . Once alloy temperature drops to the ternary eutectic point E , all the remnant liquid is solidified into the (Pb)+(Sb)+SbSn ternary eutectic microstructure.

3 Conclusions

(i) Three types of Pb-Sb-Sn ternary alloys selected from different primary phase regions have been investigated by undercooling experiments. The primary (Pb) and SbSn phases grow mainly in a dendritic way, whereas primary (Sb) phase usually displays faceted growth in the form of polygonal blocks and long strips. In the various solidification microstructures, primary SbSn phase frequently produces serious macrosegregation, while primary (Pb) and (Sb) phases are distributed homogeneously. All of the three primary (Pb), (Sb) and SbSn phases are subject to solute trapping effect during rapid solidification, resulting in the remarkable extension of solute solubility under the substantial undercooling condition.

(ii) It is found that (Pb) and SbSn phases possess strong mutual affinity and produce various kinds of (Pb)+SbSn pseudobinary eutectics. (Pb) and (Sb) phases nucleate independently and show a weak cooperative growth tendency, which can only lead to divorced pseudobinary eutectics. Although (Sb) and SbSn phases have not formed pseudobinary eutectics independently, they exhibit dependent growth within (Pb)+(Sb)+SbSn ternary eutectic structures.

(iii) The (Pb)+(Sb)+SbSn ternary eutectic microstructure displays lamellar growth when the alloy composition ensures a large volume fraction for this ternary eutectic. If its volume fraction is small, the ternary eutectic appears as anomalous eutectic. Usually (Pb) and SbSn phases are the major constitution of ternary eutectic, and (Sb) phase composes only a minor part.

(iv) Microstructural analyses indicate that (Pb) phase is not an efficient heterogeneous nucleant for (Sb) and SbSn phases. Similarly, (Sb) phase is not a good nucleant for either (Pb) or SbSn phase. Nevertheless, the SbSn intermetallic compound has acted as the effective nucleant for both (Pb) and (Sb) phases.

(v) The solidification routes of three different types of Pb-Sb-Sn ternary alloys have been determined under the substantial undercooling condition, which is schematically presented in Figure 1. For Pb-5%Sb-4%Sn ternary alloy, its composition and temperature vary along line Aa at first. When point a on the (Pb)+SbSn pseudobinary eutectic line is attained, its solidification proceeds along line aE subsequently. And this solidification process ends up before the ternary eutectic point E is achieved. Similarly, the solidification process of Pb-20%b-4%Sn ternary alloy follows the route “ $Bb \rightarrow bE \rightarrow E$ ”, while that of Pb-14%Sb-10%Sn ternary alloy takes the route “ $Cc \rightarrow cE \rightarrow E$ ”.

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