Research Article

Effect of the Third Element Ni on the Solidification Microstructure of Undercooled Cu-40 wt.% Pb Monotectic Alloy Melt

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In this paper, the evolution of solidification microstructure of Cu-40 wt.% Pb monotectic alloy of the third element Ni pair under deep undercooling conditions was studied. By comparing the phenomena of liquid phase separation during deep undercooling and rapid solidification of Cu-40 wt.% Pb monotectic alloy, the melt of the alloy increases with the undercooling, and the solidification structure appears uneven or even stratified. With the addition of the third element Ni, the liquid phase separation can be effectively inhibited by the change of interfacial energy. The solidified structure undergoes the transformation from coarse dendrite to the first kind of granular and refined dendrite in a wide undercooling range. When the undercooling reaches 143 K, the structure begins to show an inhomogeneous trend.

1. Introduction

Cu-Pb monotectic alloys have broad application prospects because of their excellent properties such as strong impact resistance, high fatigue strength, and high thermal conductivity. They have been widely used in many fields. Due to their excellent wear resistance, they have been widely used in self-lubricating antifriction materials [1–3]. From the thermodynamic point of view, the solidification process of the Cu-Pb monotectic alloy is two-phase separation. Under the conventional solidification conditions, it is decomposed into two liquid phases with different compositions. Because of the density difference between the two liquid phases, segregation is easy to occur. Even more, there will be a phenomenon of component stratification [4,5], which makes it difficult to directly prepare homogeneous monotectic alloy materials by conventional solidification methods, thereby limiting the application of monotectic alloys in industrial fields.

In order to obtain a solidified structure of a monotectic alloy having a uniform dispersed phase structure, a preparation method for homogenizing a plurality of monotectic alloys has been studied [6,7], A liquid phase preparation technique that has been successful both in theory and in practice has not yet been found. The quenching rapid solidification technique in many preparation techniques [8], although only suitable for the preparation of low-dimensional homogeneous monotectic alloys, gives us an inspiration: if the solidification of the bulk alloy melt passes through the liquid phase immiscible zone as soon as possible, when the second phase does not have enough time to complete the dynamic process of liquid phase separation, a monotectic alloy in which the second phase is uniformly distributed to the matrix can be obtained (Figure 1). In
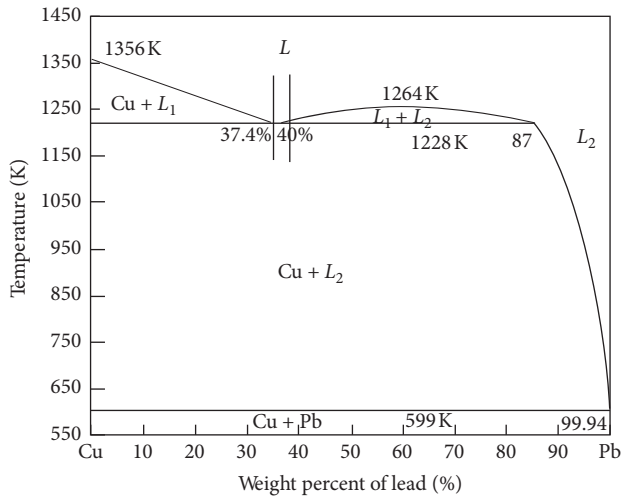
FIGURE 1: Immiscible alloy equilibrium phase diagram: Cu-Pb monotectic alloy.

addition, it is also an effective method to add the third component to change the solidification structure of the alloy [9–12]. In this paper, the deep undercooling method was used to add the third component Ni to the overperformed Cu-40 wt.% Pb monotectic alloy. The third element is the solidification structure and solidification behavior of the alloy of the component.

2. Experimental

The experimental material is Cu-40 wt.% Pb monotectic alloy. The sample weighs about 15 g. The crucible is made of pure quartz with 99.99% purity of electrolytic pure Cu and 99.75% Pb, 99.9% purity of the third element of Ni, and 5% addition of total mass. The experimental method of deep undercooling is purification of molten glass and cyclic superheating. Deep undercooling experiment was carried out on GP30W-G7, a high-frequency induction heating device. The output power of the high-frequency generator is 30 kW, and the working frequency is 300–50 KHz. The specific experimental process is as follows: firstly, about 2/3 of the weight of glass purifier and Cu are added to the quartz crucible, and then after the complete melting of copper, lead, Ni, and the remaining glass purifier are added in turn; secondly, under the protection of molten glass, the alloys with the above components are melted in situ, and the alloys are superheated cyclically. The superheated temperature is 1500 K, and the superheated time is 5 minutes. When the air bubbles are completely eliminated, the power supply is cut off to make the sample cool naturally. A CIT-2M K_{2H} infrared thermometer is used in the heating and cooling process. Its temperature range is 623 K-2323 K and response time is 1 ms. The glass purifier is B_2O_3 and Na-Ca-Si glass, and the addition amount is 20% of the sample weight. Metallographic specimens were intercepted on fully solidified specimens. Microstructure and composition of the samples were analyzed by SS-550 Shimadzu scanning electron microscopy, a PHoenix EDAX-2000 energy dispersive spectrometer, and X-ray diffraction (6000X). The

schematic diagram of the specific test device is shown in Figure 2.

3. Results and Discussion

3.1. Solidification Behavior of Cu-40 wt.% Pb Monotectic Alloy and Cu-40 wt.% Pb-5 wt.% Ni. The schematic diagram of melt cooling curve of hypermonotectic Cu-40 wt.% Pb alloy is shown in Figure 3 [13]. T_L is the liquidus temperature of Cu-Pb alloy and T_N is the monotectic reaction temperature of Cu-Pb alloy. As can be seen from the figure, when the melt temperature of the alloy is lower than the equilibrium liquidus temperature and falls to T, the first inflection point appears on the cooling curve, and then the temperature rises back to T_r', that is, the first reglow occurs, and then the temperature decreases. When the temperature falls to T_n, the second inflection point appears on the cooling curve, and then the temperature rises back to T_r and the second reglow occurs, and then no reglow occurs. The alloy system enters the natural solidification stage until it is cooled to room temperature, and the solidification process of the sample is completed. During the whole solidification process, the alloy melt reglow twice, and the liquid phase separation of the alloy must occur during the cooling process.

The cooling curve diagram of the melt solidification process of undercooled Cu-40 wt.% Pb-5 wt.% Ni alloy shown in Figure 4 shows that the dotted line in Figure 4 is a monotectic reaction line. The solidification process can be divided into three stages:

(i) In Figure 4(a), only one reglow was detected, so it can be inferred that no liquid phase separation occurred at low undercooling. At deep undercooling, there is a slight reglow process on the cooling curve due to liquid nucleation, as shown in Figure 4(b), which is the phase of liquid phase separation before melt solidification, that is, $T_n' \longrightarrow T_r'$ stage in Figure 4.

(ii) Once solid phase nucleation occurs in the melt, the crystals grow rapidly to the undercooled melt at a very fast speed. The free-growing solid phase crystals can instantly grow over the whole sample, which results in the obvious reglow phenomenon of the melt. Therefore, this stage is the rapid solidification stage in the initial stage of the melt, that is, $T_n \longrightarrow T_r$ stage in Figure 4.

(iii) After re-glow, the alloy system enters a slow solidification stage with natural cooling at furnace temperature.

It can be seen that the solidification behavior of Cu-40 wt.% monotectic Pb alloy is changed within a certain undercooling range after the addition of the third element Ni.

3.2. Comparison of Solidified Microstructures of Cu-40 wt.% Pb Monotectic Alloy and Cu-40 wt.% Pb-5 wt.% Ni. Figure 5 shows the solidification structure of Cu-40 wt.% Pb monotectic alloy at different degrees of undercooling. In the
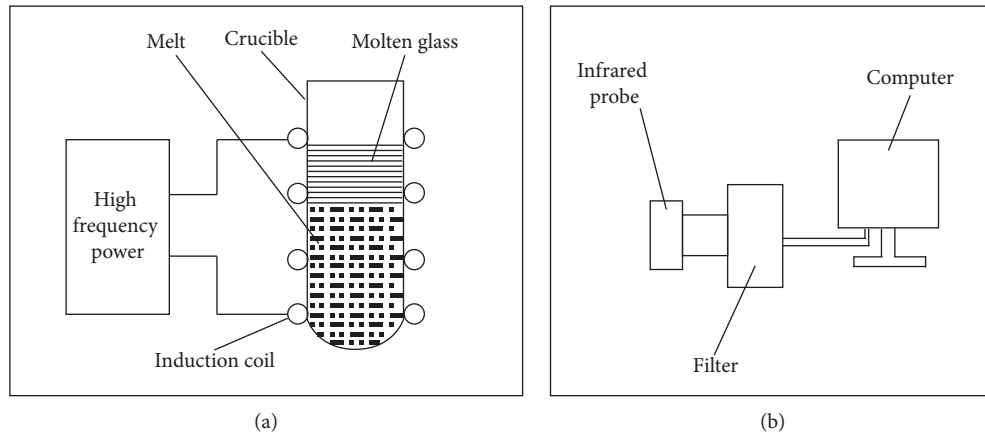
(a)

(b)

FIGURE 2: Combined melting glass purification and cyclic superheating experimental equipment schematic.
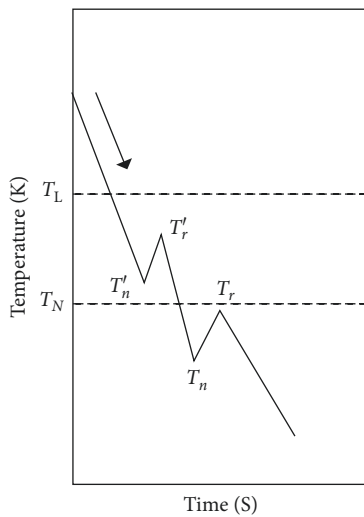

FIGURE 3: Cooling curves of the undercooled Cu-40 wt.% Pb alloy melt after quenching with copper mold.
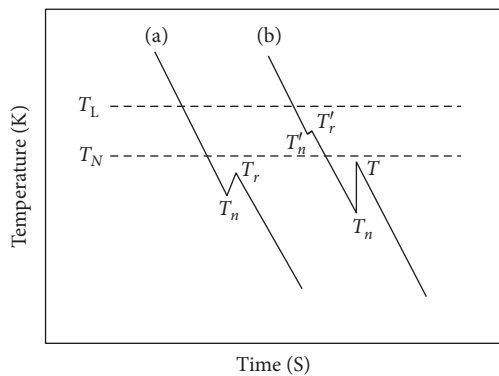

FIGURE 4: Schematic diagram of the cooling curve of the Cu-40 wt.% Pb-5 wt.% Ni alloy melt under different degrees of undercooling: (a) $\Delta T < 143$ K and (b) $\Delta T > 143$ K.

low undercooling range of 40 K $\leq \Delta T \leq 75$ K, according to the cooling curve of the alloy, liquid phase separation occurs inside the alloy melt. At this time, a few phase L_2 (Pb) liquid phases distribute in the matrix L_1 (Cu) liquid phase. From the monotectic reaction $L_1 \longrightarrow L_2 + \alpha$ (Cu), it can be seen that the monotectic reaction first takes place in the droplets of the matrix phase. During the rapid solidification stage, because the monotectic cells always grow along the direction of exothermic heat, the phase dendrites formed by the reaction grow rapidly in the radial direction around them, so that the L phase concentrating around the L phase disperses and distributes among them. At the same time, the L_2 formed by the monotectic reaction distributes equally among the fibers α (Cu). The chrysanthemum-like monomorphic cell structure is formed between the two forms [14]. When the temperature is further cooled to 599 K, eutectic reaction occurs in the L_2 phase. The L_2 (Pb) phase is dispersed on the S (Cu) substrate in a fibrous or granular form, as shown in Figure 5(a). With the deepening of undercooling, the number of monotectic cells in the alloy melt increases. In addition, higher undercooling increases the growth rate of monotectic cells, increases the probability of collision and adhesion between adjacent monotectic cells, enlarges the undercooling zone, and eventually leads to the formation of irregular monotectic cells in the alloy system, as shown in Figure 5(b). When the undercooling degree increases to 80 K, the macrosegregation of L_2 phase appears obviously in the solidified structure of the alloy, and the undercooling zone increases further, as shown in Figure 5(c). As the undercooling deepens, the solidified structure of the alloy eventually delaminates, as shown in Figure 5(d) [15, 16].

Figure 6 shows the solidification structure of ternary Cu-40 wt.% Pb-5 wt.% Ni alloy at different undercooling. It can be seen from the graph that the solidification structure of the alloy becomes finer and finer with the increase of the undercooling degree when the melt undercooling degree is $\Delta T < 143$ K. At that time, when the alloy melt has a degree of undercooling $\Delta T > 143$ K, with the increase of the undercooling degree, the size of the second phase particles in the solidification structure of the alloy increases gradually until the appearance of the final stratification phenomenon. In this paper, the $\Delta T < 143$ K undercooled zone is called the homogenized undercooled zone of the alloy melt. In the homogenized undercooling zone, the second phase S (Pb) is
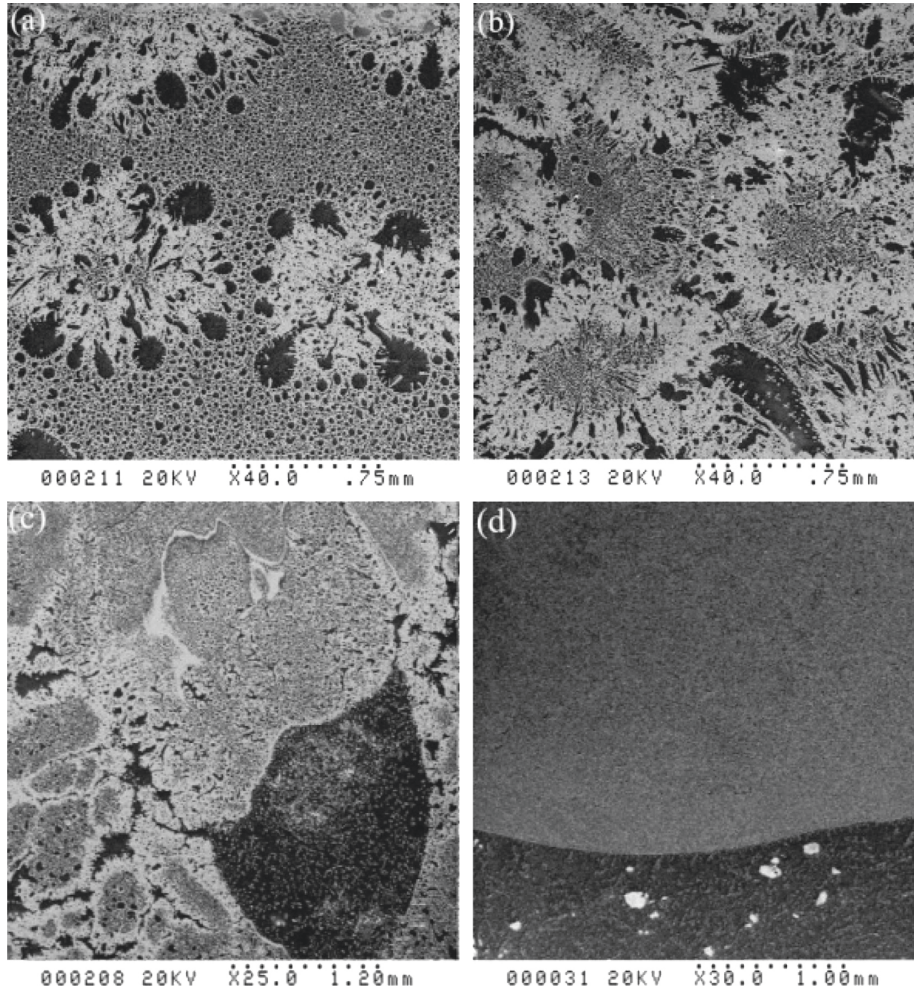
FIGURE 5: Microstructures of Cu-40 wt.% Pb hypermonotectic alloy under different undercoolings: (a) $\Delta T = 42$ K; (b) $\Delta T = 65$ K; (c) $\Delta T = 80$ K; and (d) $\Delta T = 142$ K.

dispersed between the dendrites of α(Cu), and with the increase of undercooling degree, the dendrites of α(Cu) become finer and the distribution of the second phase S (Pb) becomes more uniform. When the undercooling of the alloy melt occurs at $\Delta T = 143$ K, a small amount of Pb-rich phase flocculation appears in the solidified structure and disperses in the matrix, which means that the radius of L_2 Pb-rich phase droplets increases continuously with the prolongation of separation time until its volume fraction approaches (or reaches) the critical value of homogenization. Before that, fast solidified dendrites of α(Cu) play a role in the continuous growth of the volume fraction of the second-phase Obvious Inhibition, as shown in Figure 6(e). When the undercooling degree is $\Delta T > 143$ K, it can be judged from the cooling curve that the liquid phase separation occurs in the alloy melt. With the increase of the undercooling degree, the volume fraction of the second phase increases, which results in the increase in the size of the Pb-rich phase flocs distributed between the dendrites of α(Cu) and the decrease in the uniformity of the distribution. When the undercooling degree is $\Delta T > 160$ K, the second phase appears in the alloy structure under the action of Stokes motion Layered.

3.3. Effect of Third Component Ni on Interface Energy of Cu-40 wt.% Pb Alloy.

According to Chadwick's [17] viewpoint of interfacial energy balance between solid phase S, liquid phase L_1, and liquid phase L_2 in the alloy melt, the formation mechanism of the monotectic alloy structure can be expressed as follows:

$$\gamma_{SL_2} > \gamma_{SL_1} + \gamma_{L_1L_2}. \tag{1}$$

γ_{SL_2}, γ_{SL_1}, and $\gamma_{L_1L_2}$ in the formula represent the interfacial energy between solid S and liquid L_2, solid S and liquid L_1, and liquid L_1 and liquid $L_{2,\text{ respectively}}$. Chadwick [17] believed that if the melt interface could satisfy equation (1) during the monotectic reaction, the liquid phase of L_2 would not wet the solid phase of S through the monotectic reaction. Because $\gamma_{SL_2} = 310 \pm 10$ mJm^{-2}, $\gamma_{SL_1} = 254 \pm 26$ mJm^{-2}, and $\gamma_{L_1L_2} = 6 \pm 2$ mJm^{-2} in Cu-40 wt.% Pb monotectic alloy, the liquid phase of L_2 in Cu-40 wt.% Pb hypermonotectic alloy will not wet with solid phase S.

Although the interface of most monotectic alloys can satisfy formula (1), the corresponding size of $\gamma_{L_1L_2}$ different alloys has a great influence on the solidification structure of
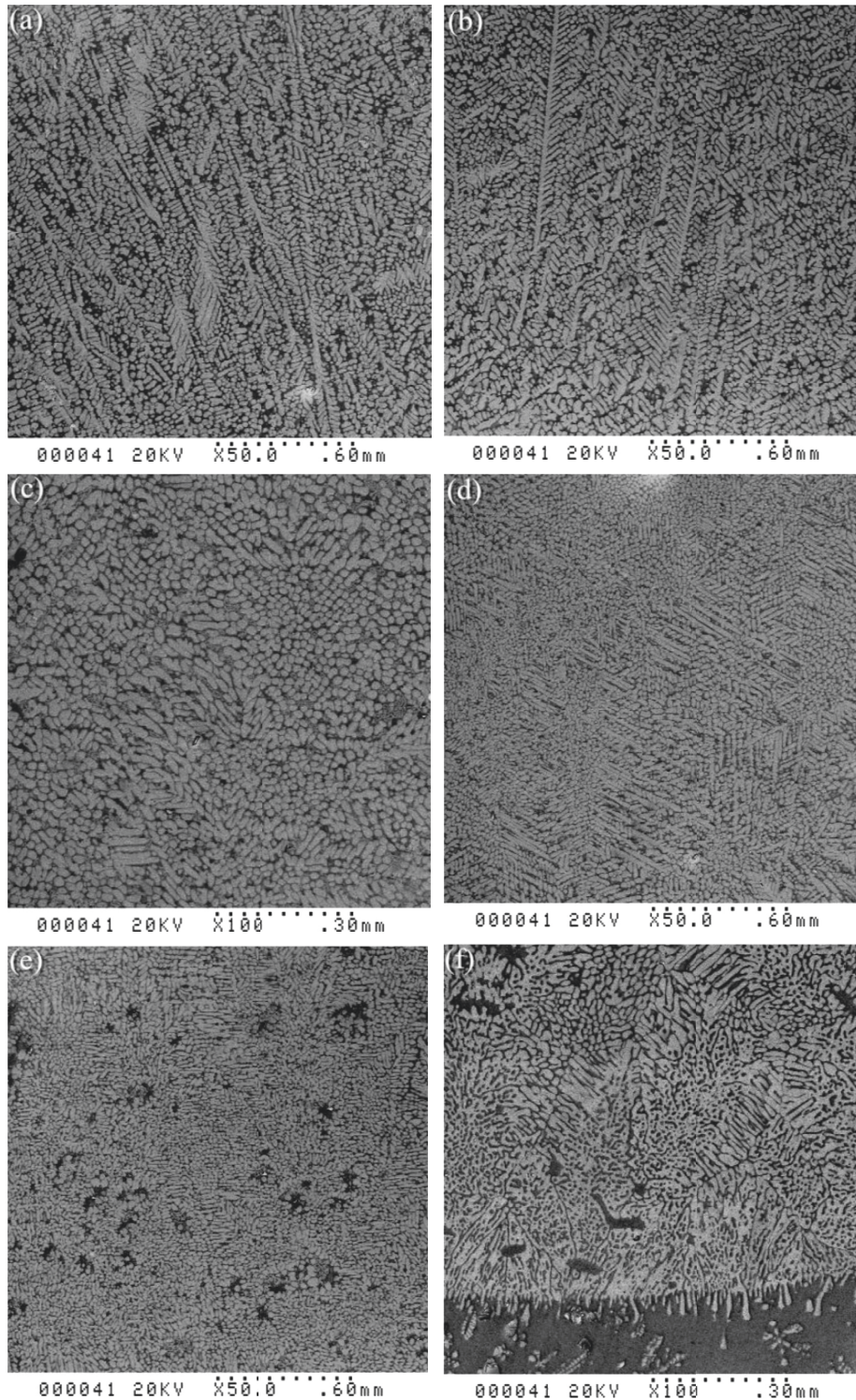
Figure 6: Microstructure of Cu-40 wt.% Pb-5 wt%Ni with different undercoolings: (a) $\Delta T = 58$ K; (b) $\Delta T = 75$ K; (c) $\Delta T = 98$ K; (d) $\Delta T = 120$ K; (e) $\Delta T = 143$ K; and (f) $\Delta T = 160$ K.

the alloys. The larger the value of $\gamma_{L_1 L_2}$, the greater the barrier to form the second phase, the smaller the volume fraction of the separated second phase, and the more difficult it is for the second phase droplets to accumulate. The increase of the volume fraction of the second phase in the undercooled melt takes a longer time, which lays a foundation for improving

the undercooling degree of homogenized solidification. The size of the immiscible zone in the liquid phase has a direct influence on $\gamma_{L_1 L_2}$. $\gamma_{L_1 L_2}$ is shown in Table 1.

The addition of Al in Cu-Pb monotectic alloys enlarges the immiscible zone of the two phases and shifts the monotectic point to the direction of low concentration of

TABLE 1: Monotectic point and miscibility gap in some monotectic alloys.

Alloy	Monotectic point (K)	Miscibility gap (K)
Cu-Pb	1228	36
Al-Pb	931	769
Ni-Pb	1651	210

TABLE 2: $\gamma_{L_1 L_2}$ and miscibility gap in some monotectic alloys.

Alloy	$\gamma_{L_1 L_2}$ (mJm^{-2})	Miscibility gap (K)
Al-Pb	145 ± 30	769
Al-Bi	60	640
Al-In	42 ± 9	306
Cu-Pb	6 ± 2	36

Pb [17]. Comparing the phase diagrams of Al-Pb and Ni-Pb, the immiscible temperature range (Table 2) shows that the immiscible temperature range of the two alloys is much higher than that of the Cu-Pb alloy and the Ni-Pb alloy has the largest solid solubility at the monotectic temperature point. Therefore, the addition of the third element Ni increases the $\gamma_{L_1 L_2}$ of Cu-Pb alloy, weakens the separation of the second phase, and shifts the deviation point to the direction of low concentration of Pb. Therefore, under small undercooling, α(Cu) is expressed as a reglow phenomenon in the cooling curve according to the single-phase solidification mode. With the increase of undercooling, the volume fraction of the separated second phase increases, and the coagulation effect is gradually reflected in the later stage. The cooling curve is reflected in the secondary re-glow, which leads to the deposition of the second phase [15,18,19].

In theory, according to the expression of excess free energy of the ternary free system proposed by L. Ratke [18],

$$G^{E} = X_A X_B \Omega_{AB} + X_B X_C \Omega_{BC} + X_C X_A \Omega_{CA}. \qquad (2)$$

In the formula, $\Omega_{AB} = N_0 Z \omega_{AB}$, N_0 is the Avogadro constant, Z is coordination number, ω_{AB} is interaction coefficient between A and B atoms, $\omega_{AB} = u_{AB} - 1/2(u_{AA} + u_{BB})$, and u_{AB}, u_{AA}, and u_{BB} represent affinity energy between AB, AA, and BB atoms, respectively. When the interaction coefficient ω_{AC} and ω_{BC} of the third component Ni and the Cu-Pb alloy or the second phase are negative, that is, $u_{AC} < 1/2(u_{AA} + u_{CC})$ and $u_{BC} < 1/2(u_{BB} + u_{CC})$, both Ω_{BC} and Ω_{AC} are negative. Combined with formula (2), the free energy of the ternary Cu-Pb-Ni alloy system decreases. The change in the free energy of the system will inevitably have a certain degree of influence on the shape of the liquid phase immiscible region of the monocrystalline alloy system. Therefore, it can be seen from Figure 5 that the addition of the third component Ni leads to an increase in the critical subcooling of the liquid phase separation of the alloy system in the alloy phase diagram, thereby suppressing the growth of the second phase droplets in the alloy melt. Based on the above analysis, the solidification structure of the alloy melt was refined by adding the third element Ni.

4. Conclusion

(i) The addition of the third element Ni increases the amount of Cu-40 wt.% Pb monotectic alloy and the immiscible zone, which leads to the weakening of liquid phase separation. The solidification structure is solidified by single-phase alloy in the range of $T = 58$ K ~ 143 K. With the increase of undercooling, the transition from coarse dendrite to the first kind of granular and fine dendrite occurs.

(ii) The addition of the third component Ni changes the interface energy of Cu-40 wt.% Pb monotectic alloy, which can weaken the liquid phase separation, but cannot completely inhibit it.

(iii) Compared with Cu-40 wt.% Pb monotectic alloy, the addition of the third element Ni decreases the free energy of the alloy system, increases the critical undercooling degree of liquid phase separation, and decreases the volume fraction of L_2 phase separation in the immiscible zone.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.
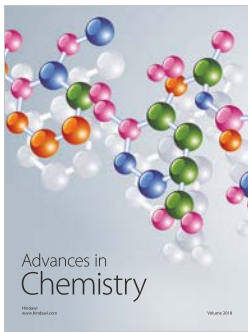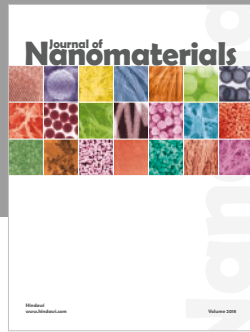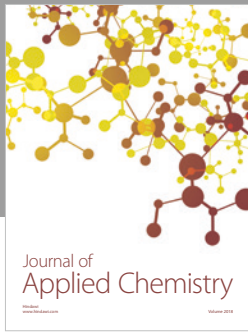
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