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Non-equilibrium solidification of undercooled Ni-31.44%Pb monotectic alloy melts ①

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[Abstract] By using the method of molten glass denucleating combined with superheating cycling, solidification behavior of the bulk undercooled Ni-31.44% Pb monotectic alloy melts was systematically investigated. The results indicated that the undercooled monotectic alloy solidifies in form of dendrite essentially during the stage of rapid solidification and after recalescence, the residual melts between the dendrites solidify in the equilibrium mode. Within the achieved undercooling range, the solidification structures are classified into three categories. When the undercooling is less than 50 K, the structures are composed of coarse dendrites and interdendritic lead phase. With the undercooling increasing into the range of 70 ~ 232 K, the dendrite clusters are refined and fine lead particles separate out from the supersaturated primary dendrite arms because of solute trapping. When the undercooling exceeds 242 K, the granular grains form and fine lead particles homogeneously distribute in the whole sample. Based on the observation of the solidification structures and the calculated results with BCT model, it is found that the granulation mechanism of the granular grains is owing to the primary dendrite disintegration and recrystallization.

[Key words] high undercooling; Ni-Pb monotectic alloy; structural evolution; granulation mechanism
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1 INTRODUCTION

The solidification of the undercooled alloy melts has been the subjects of extensive study for over 30 a. As an important way to study modern solidification theories, high undercooling technique has become one of focus in materials science and engineering field[1]. The interest in the microstructure evolution and phase selection of the undercooled melts has been heightened in recent years, largely due to the technical and scientific interest in rapid solidification processing. Up to now, the solidification behavior of the undercooled melts has been well studied in different systems including eutectic[2, 3], peritectic[4, 5], metallic compound[6] and solid solution[7, 8] alloys. Compared with other alloy systems, the solidification behavior of the undercooled monotectic[9, 10] alloys has never been studied further and recently, the monotectic alloys have become important engineering materials due to their unique potential applications, which include bearing materials, catalysts, permanent magnets and fine particle superconductors and so on[11], so the structural evolution and phase selection of undercooled monotectic alloys should be studied systematically, it was therefore decided to study the effect of undercooling on the structures and analyze the solidification behavior of undercooled monotectic alloys.

For the Ni-Pb system, some important thermodynamic parameters have been measured by means of experiments and a lot of undercooling studies have been conducted in many kinds of Ni base alloys, so the Ni-31.44% Pb alloy was considered to be an ideal monotectic alloy in this undercooling experiment. The present article describes the results of an experimental investigation of the solidification behavior of the undercooled Ni-31.44% Pb monotectic alloy melts.

2 EXPERIMENTAL

The alloy used in this experiment is Ni-31.44% Pb monotectic alloy. Prior to melting, the surfaces of the metal charges were cleaned mechanically by grinding off the surface oxide layer and chemically by etching in HCl solution diluted by alcohol. The experiments were performed in a high-frequency induction-heating furnace. Firstly, borosilicate glass purifier was put into a cleaned quartz glass tube and then heated into liquid. Then the nickel and lead charges with purities higher than 99.99% were dropped into the bottom of the tube, and melted *in-situ* to obtain an alloy with a composition of Ni-31.44% Pb. Several superheating cycles were conducted till undercooling of the alloy melt became stable, and subsequently the nucleation of the melt was stimulated at the predetermined undercooling.

The cooling curves of the melts were measured by an infrared pyrometer, which was calibrated with

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a standard PtRh30-PtRh60 thermocouple, and possesses a relative accuracy of 5 K, and a response time less than 1 ms.

Each sample had a mass of 8~ 10 g and a diameter of 8~ 12 mm, and was sectioned through the nucleation spot, then polished, and etched with 5% $FeCl_3$ aqueous solution. The structure observation was carried out with a Neophot-1 optical microscope.

3 RESULTS

3. 1 Cooling curve

Fig. 1 shows the typical cooling curve of the undercooled Ni-31. 44% Pb monotectic alloy. When the melts was cooled to the nucleation temperature T_n, the sample nucleated quickly and grew, then the solid phase released the latent heat and the sample temperature rose to T_R, that is so-called recalescence. After recalescence, the sample cooled down slowly. Within the achieved undercooling range, there is only one recalescence in all of cooling curves. The notation, T_m, stands for the monotectic reaction temperature.

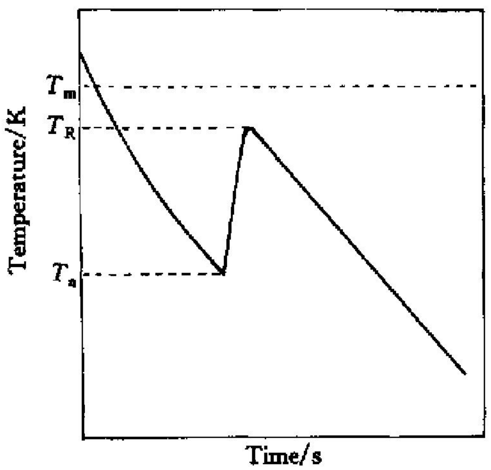

Fig. 1 Typical cooling curve of undercooled Ni-31. 44% Pb monotectic alloy

3. 2 Solidification structures under different undercoolings

A high undercooling up to 286 K was achieved in the Ni-31. 44% Pb monotectic alloy. Within the achieved undercooling range, the solidification structures are classified three categories. When the undercooling is less than 50 K, the structures are composed of common coarse dendrites and interdendritic lead phase (Fig. 2(a) and (b)). Within the undercooling range of 70 to 232 K, the dendrites are refined, fine lead particles can be found in dendrite arms and with the increase of undercooling, the lead particles distributes more and more homogeneously (Fig. 2(c) ~ (f)). When the undercooling exceeded 242 K, the granular grains form, Fig. 2(g) shows the dendrite substructure appears in this kind of grain. Fig. 2(h) shows fine lead particles homogeneously distribute in the whole sample undercooled up to 286 K.

4 DISCUSSION

4. 1 Analysis of cooling curve

The cooling curve of monotectic resembles that of the undercooled single-phase alloy and there is only one recalescence in the achieved undercooling range, so we conclude that during the stage of rapid solidification, the melts have been in the single-phase α(Ni) metastable zone, the α(Ni) dendrites form firstly, and after recalescence the residual melts solidify in the equilibrium mode with liquid separation and monotectic reaction.

4. 2 Solidification behavior of undercooled monotectic alloy

When the undercooling was less than 50 K, in theory, the melts solidify by monotectic reaction firstly, however, in view of the final structures, it's obvious that the undercooled melts solidified in the form of dendrites during the stage of rapid solidification and formed the dendrites skeleton. After recalescence, the residual melts solidified with common liquid separation and monotectic reaction, that is, $L \rightarrow L_1 + L_2$ and $L_1 \rightarrow \alpha + L_2$. The process of monotectic reaction resembles divorced eutectic, namely, the α(Ni) phase grew by means of primary α dendrites, formed divorced monotectic. At the eutectic temperature (597 K), the second liquid phase (L_2) solidified into eutectic, that is, $L_2 \rightarrow \alpha + (Pb)$, so the final solidification microstructures were composed of common α dendrites and interdendritic lead phase.

Within the undercooling range of 70 to 232 K, the initial nucleation temperature of the melts is far below the monotectic temperature (1 615 K). According to the equilibrium solidification theory, the melts should solidify by monotectic reaction firstly. However, the solidification structures far from equilibrium were similar to the dendrite structures of the undercooled single-phase alloy, so we conclude that the solidification behavior is same with that of small undercooling.

Under middle undercooling, with the increase of undercooling, the driving force of solid/ liquid phase transition and the dendrite tip growth velocity increase quickly, and the solute trapping becomes more and more serious, so that the supersaturated α dendrites formed. During the following cooling process, lead particles separated out from the primary dendrites. Comparing the structures in this undercooling range with that of 50 K, the fine lead particles can be observed obviously in the dendrite arms and the primary dendrite spacing was more smaller.

When the undercooling exceeds a critical value, the solidification structures after rapid solidification should be the supersaturated dendrites plus a little liqu-

Fig. 2 Solidification mirostructures of Ni-31.44% Pb monotectic alloy under different undercoolings
(a) $-\Delta T=10$ K; (b) $-\Delta T=50$ K; (c) $-\Delta T=70$ K; (d) $-\Delta T=110$ K; (e) $-\Delta T=154$ K; (f) $-\Delta T=203$ K; (g) $-\Delta T=243$ K; (h) $-\Delta T=286$ K

id phase. In this experiment, the critical value of undercooling is 242 K. Over the critical undercooling, an abrupt transformation from dendrites to granular grains occurred.

4.3 Granulation mechanism of granular grains in undercooled melts

According to the above mentioned discussion, Ni-31.44% Pb monotectic alloy solidified in the form of dendrites essentially during the stage of rapid solidification and after recalescence, the residual melts nucleated and grew between the primary dendrite clusters. The final structural morphology was mainly determined by the evolution of primary dendrites with the undercooling of the melts. The dendrite growth behavior during the stage of rapid solidification can be described by BCT model[12], the initial undercooling at the dendrite tip consists of four contributions, see Fig. 5

$$\Delta T = \Delta T_t + \Delta T_c + \Delta T_r + \Delta T_k \quad (1)$$

where ΔT_t, ΔT_c, ΔT_r and ΔT_k are thermal undercooling, constitutional undercooling, curvature undercooling and kinetic undercooling, respectively. The expression for each kind of undercooling can be found in Ref. [12].

The solute (lead) concentration of the liquid and solid at the dendrite tip, C_L^* and C_S^*, can be written as

$$C_L^* = C_0/[1-(1-k)Iv(P_c)] \quad (2)$$

$$C_S^* = kC_0/[1-(1-k)Iv(P_c)] \quad (3)$$

where C_0 is the nominal composition of the alloy, $Iv(P_c)$ is Ivantsov function of solute Peclet number P_c, and k is non-equilibrium solute partition coefficient that can be used to evaluate the level of solute trapping[13]

$$k = \frac{k_0 + (a_0/D)v}{1+(a_0/D)v} \quad (4)$$

where k_0, D, and a_0 are equilibrium solute partition coefficient, solute diffusivity, and characteristic length of solute diffusion in the liquid alloy, respectively; v is the denrite growth velocity.

Here we assume Ni-31. 44% Pb alloy as ideal melt, the solid/liquid phase transition velocity, $Q_L - Q_S$, under different undercoolings can be written as[14]

$$Q_L - Q_S = \frac{4}{3}\pi \frac{C_L^* - C_0}{C_L^*(1-k)} \left| \frac{\Delta Q_m}{1+\Delta Q_m} \right| \cdot v^3 \quad (5)$$

$$\Delta Q_m = (1 - C_S^*)\Delta Q_{Ni} + C_S^* \Delta Q_{Pb} \quad (6)$$

where ΔQ_{Ni} and ΔQ_{Pb} are the volume change rate of pure nickel and lead, respectively. Using the foregoing equations and the thermodynamical parameters of the Ni-31. 44% Pb monotectic alloy listed in Table 1, the non-equilibrium solute partition coefficient, the dendrite tip growth velocity, the solid/liquid phase transition velocity and the undercooling contributions at different initial undercoolings of the melts can be calculated (Figs. 3~ 5).

When the undercooling exceeded the critical value, 242 K, the thermal undercooling has been much higher than the constitutional undercooling in front of the dendrite tip. Thermal diffusion controlled the dendrite growth process predominantly and the kinetic undercooling increased strikingly.

From Eq. (5), it's known that $(Q_L - Q_S) \propto v^3$ and $v \propto T^b$, here b is a constant[16] to be independent of undercooling. Therefore, when the undercooling exceeded 242 K, the solid/liquid phase transition velocity increases rapidly. Comparing $(Q_L - Q_S)$ under the undercooling of 55 K with that of 242 K, the latter improves eight orders of magnitude (Fig. 5), which will lead to inner stress increase sharply because of the unbalanced shrinkage of solid phase, and led to a complete disintegration, formed the dendrite fragments as shown in Fig. 2(g). The emission of the sound heard in the experiment is a consequence of the stress relaxation through the deforma-

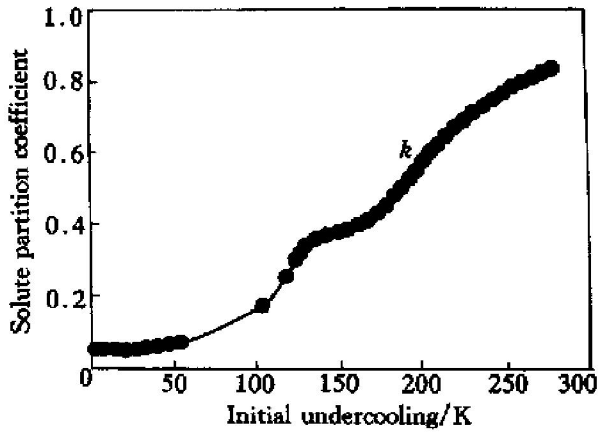

Fig. 3 Non-equilibrium solute partition coefficient vs initial undercooling of melts

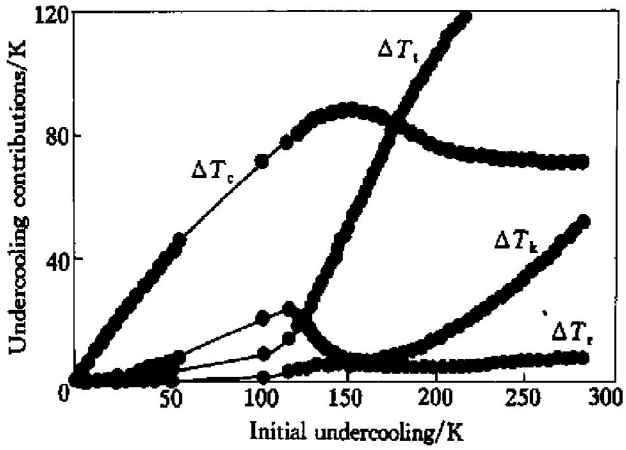

Fig. 4 Undercooling contributions vs initial undercooling of melts

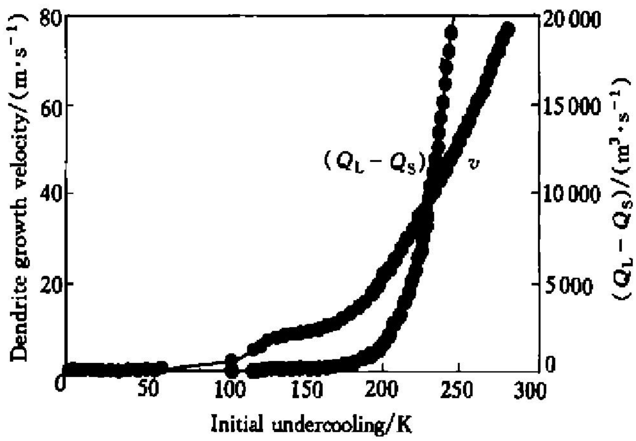

Fig. 5 $(Q_L - Q_S)$ and dendrite growth velocity vs initial undercooling of melts

Table 1 Thermodynamic parameters of Ni-31.44% Pb monotectic alloy[15]

Parameter	Value	Parameter	Value
Heat of fusion ΔH / (J·m^{-3})	2.055×10^{9}	Solute diffusivity D / (m^2·s^{-1})	6.0×10^{-9}
Specific heat C_p / (J·m^{-3}·K^{-1})	6.362×10^{6}	Partition coefficient k_0	0.053
Interfacial tension σ / (J·m^{-2})	0.240	Diffusion length a_0 / m	3.5×10^{-10}
Liquidus slope m_L / K^{-1} (mole fraction, %)	−2.887	Liquidus temperature T_L / K	1615
Sound speed in liquid v_0 / (m·s^{-1})	2000	S/L volume change of nickel ΔQ_{Ni} / %	4.5
Thermal diffusivity α / (m^2·s^{-1})	3.0×10^{-6}	S/L volume change of lead ΔQ_{Pb} / %	3.5

tion of the dendrites. On the other hand, considering the rapid increase of dendrite growth velocity from 0.2751 m/s to 45.9480 m/s, the dendrite defects increase strikingly[17]. The dendrite disintegration will give rise to an increase in system surface energy, which combined with the strain energy, drives the dendrite fragments to merge into final granular structures. Some of them merged during the high temperature stage and formed the granular grains. The boundaries migrate and grow so quickly that it's even possible to form the twins in final solidification structure. It's well known that the migration at high temperature could be a recrystallization process, thus the granulation mechanism of the granular grains should be due to dendrite disintegration and the subsequent recrystallization, resembling the second kind of granular grains formed in the undercooled single-phase alloys[14].

5 CONCLUSIONS

1) With glass purification and superheating cycling, bulk Ni-31.44% Pb monotectic alloy was undercooled up to 286 K. The undercooled Ni-31.44% Pb monotectic alloy solidifies in the form of dendrites essentially during the stage of rapid solidification and after recalescence, the residual melts between the dendrites solidify in the equilibrium mode.

2) Within the achieved undercooling range, the solidification structures of Ni-31.44% Pb monotectic alloy are classified three categories. When the undercooling is less than 50 K, the structures consist of common coarse dendrites and interdendritic lead phase. Within the undercooling range of 70~232 K, the primary dendrite spacing is smaller and fine lead particles separate out from the primary supersaturated dendrites. When the undercooling exceeds 242 K, the granular grains form.

3) The granulation mechanism of the granular grains is due to the dendrite disintegration owing to the extremely high stress of the uneven contraction during solidification, and the migration of the boundary at high temperature.

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