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Liquid-liquid phase separation in highly undercooled Ni-Pb hypermonotectic alloys

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Abstract: Liquid-liquid phase separation in the undercooled Ni-20%Pb(mole fraction, the same below if not mentioned) hypermonotectic melts was investigated by the observation of the water-quenched structure and DTA analysis. The results indicate that the number of spherical cells in the water-quenched microstructure increases with dropping temperature, and the cells gather and grow up obviously. The spherical cell origins from L_1 phase separated from homogeneous melt, and is the product of monotectic reaction. Both results of the water-quenched structures and DTA analysis prove that liquid phase separation still occurs in the highly undercooled Ni-Pb hypermonotectic alloy melts, and liquid phase separation in the immiscible gap can not be fully inhibited by high undercooling and rapid solidification.

Key words: Ni-Pb hypermonotectic alloy; monotectic cell; high undercooling; liquid-liquid phase separation; water-quenched microstructure

1 Introduction

Hypermonotectic alloys with homogeneous structure have good physical and chemical properties and can be used as self-lubricating materials, electrical contact materials and superconducting materials, and so on [1,2]. However, it is very difficult to fabricate homogeneous hypermonotectic alloys by employing conventional casting, because the parent liquid will decompose into two distinct immiscible liquid phases in a few seconds when it passes through the immiscibility gap[3−5]. The problem has delayed the utilization of monotectic alloys as industrial materials[6−8].

If the hypermonotectic melts pass through the immiscibility gap at an extremely rapid solidification rate by the method of chilling rapid solidification, the process of liquid-liquid phase separation may be fully inhibited and a homogeneous structure can be acquired[9]. It hence gives us an important edification whether the homogeneous hypermonotectic alloy can be prepared by high undercooling and rapid solidification technology. In fact, it is more effective for high undercooling technique to inhibit the nucleation of solid phases from alloy melts, make bulk alloy melts solidify at a higher speed and obtain homogeneous microstructure with nearly no solution segregation[10−12]. But up to now, there is no literature which reports whether the liquid-liquid separation behavior in the immiscibility gap can be inhibited by high undercooling technique.

Since, the aim of this paper is to investigate the liquid-liquid separation behavior of the undercooled hypermonotectic alloy melt under the condition of high undercooling and rapid solidification, and provide guidance for the industrial application of the immiscible alloys.

2 Experimental

The solid line shown in Fig.1 denotes the selected composition of Ni-Pb binary alloy. The undercooling experiments were completed with high-frequency induction furnace. Ni-20%Pb hypermonotectic alloys, which were prepared by in-situ alloying from 99.99%

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(mass fraction) pure Ni and 99.75%(mass fraction) pure Pb, was melted in a quartz crucible under the atmosphere condition, covered and purified with the complex glass agent (30%B_2O_3+70%NaCaAlSiB, China). The superheating temperature was 150 K above the liquidus temperature of the alloy, which ensures complete mixing of the two components in liquid state, and the superheating time was 3-5 min. The thermal history of Ni-Pb hypermonotectic melt was monitored by using an infrared pyrometer, which was calibrated with a standard PtRh30-PtRh60 thermocouple, and possesses a relative accuracy of ±5 K and the response time less than 1 ms.

Several superheating cycles were conducted till the undercooling (>200 K) of melt became stable.

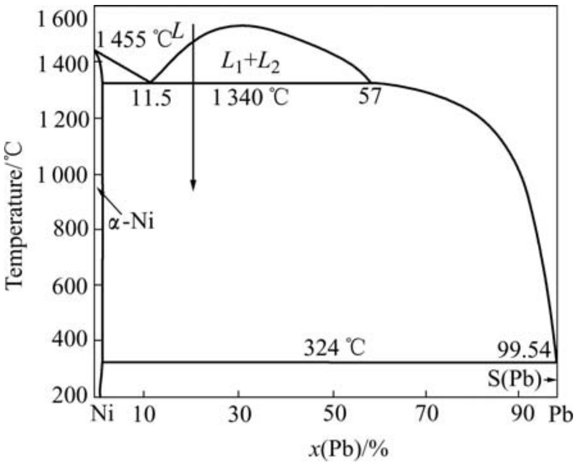

Fig.1 Equilibrium phase diagram of Ni-Pb binary alloy[13]

Subsequently, the melt was imbibed into a 0.8 mm inner diameter quartz tube and quenched rapidly into water as soon as possible at various temperatures (or undercooling) in the immiscible gap. The metallographic samples were sectioned through longitudinal section, then polished and etched with 8 g $FeCl_3$+20 mL HCl +100 mL H_2O solution. The microstructure observation was completed by using optical microscope and Amray-1000B scanning electronic microscope.

In order to investigate the effect of undercooling on liquid phase separation, DTA analysis was employed to study the phase transition of the undercooled Ni-20%Pb melt in the course of cooling. After being pre-alloyed, each sample was contained in an quartz crucible covered with NaCaAlSiB glass as denucleant and fluxing agent, and then was placed in a differential thermal analyzer. The samples were heated up to 1 773 K. After an isothermal period of 5 min, the samples were cooled at a constant rate down to 1 300 K, at which solidification had been completed. The heating and cooling cycles were performed for each sample at the rates of 20 and −20 K/min, respectively. The melting point of pure Ni was used to calibrate the temperature scale of the facility to an accuracy of better than ±1.5 K.

3 Results and discussion

Fig.2 presents the water-quenched microstructure of the undercooled Ni-20%Pb alloy melt at different

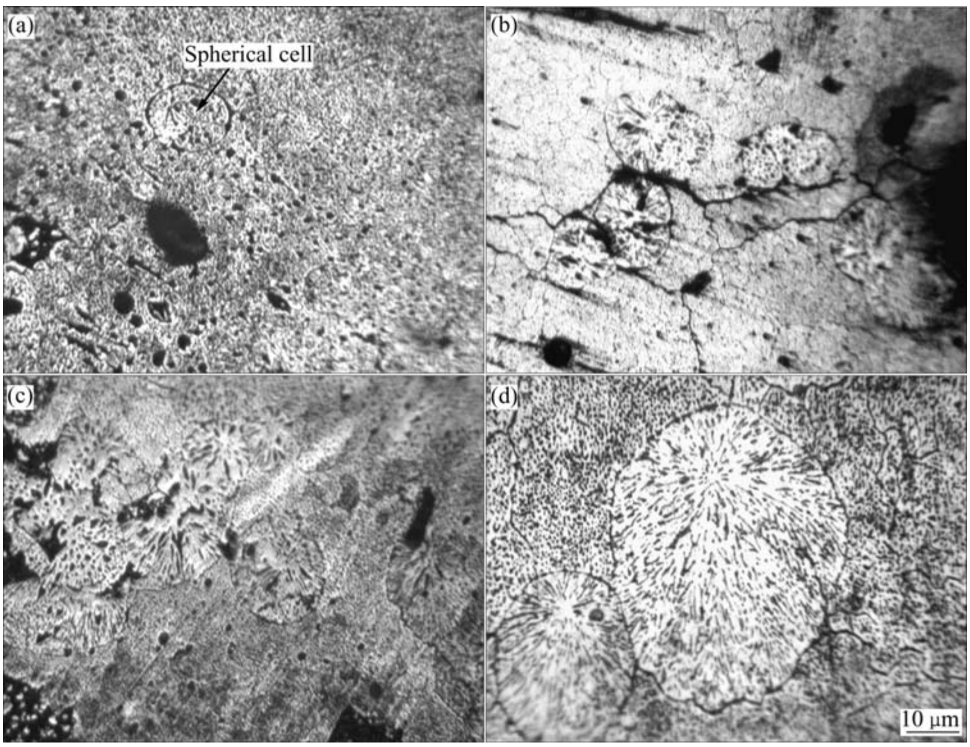

Fig.2 Water-quenched structures of Ni-20%Pb hypermonotectic melts in immiscible gap at different temperatures: (a) 1 770 K; (b) 1 663 K; (c) 1 650 K; (d) 1 603 K

temperatures respectively. When the temperature of the undercooled melt reaches 1 770 K, spherical cell can be found in the quenched structure, and its dimension is about 15 μm in diameter. Comparatively, the number of spherical cells increases obviously with the dropping temperature, the cells gather and their dimension is about 20-30 μm (Figs.2(b) and (c)). When the temperature is down to 1 603 K, the cells grow up obviously and the maximum size is about 50 μm (Fig.2(d)).

The SEM image of the water-quenched Ni-20%Pb melt at 1 770 K is shown in Fig.3. The energy spectrum analysis shows Pb content of the spherical cell in Fig.2(a) and Fig.3 is 15.40%, corresponding to that of L_1 phase in the equilibrium phase diagram at 1 758 K[13]. This indicates that the spherical cell origins from L_1 phase which is separated from homogeneous melt, and is the product of monotectic reaction. The same spherical morphology has been reported as monotectic cell in the undirectionally solidification of Cu-Pb and Al-Pb monotectic melts by KAMIO et al[14]. The formation mechanism of the spherical cells can be described as follows.

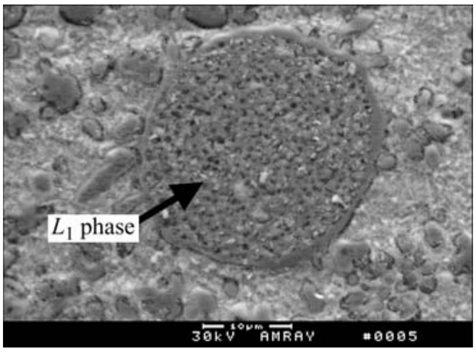

Fig.3 SEM image of water-quenched Ni-20%Pb melt at 1 770 K

When the homogeneous Ni-20%Pb melt passes through immiscibility gap, liquid-liquid phase separation occurs because there is nearly no limit of the undercooling, and so the melt separates into two liquid phases L_1 (Ni-rich phase) and L_2 (Pb-rich phase) in the immiscible gap. With the dropping temperature, the monotectic reaction $L_1 \rightarrow \alpha$-Ni+ L_2'(Pb) occurs. As shown in Figs.4 and 5, the calculation results of the critical nucleation energy and the nucleation rate, which is detailed in Ref.[15], indicate that L_2'(Pb) phase acts as the prior phase in the L_1 liquid phase. In case of nucleation of L_2'(Pb) from L_1 phase, subsequently α-Ni solid phase begins to crystallize. The formation and growth of α-Ni results in a centripetal arrangement of solid α-Ni and liquid L_2'(Pb) towards α-Ni crystalline centre, and spherical cells form as a monotectic reaction product. Up to now, it is not certain that under high undercooling condition, whether or not L_2'(Pb) phase morphology in the monotectic cell is mainly controlled by surface energy of itself, growth velocity of α-Ni phase or cooling rate.

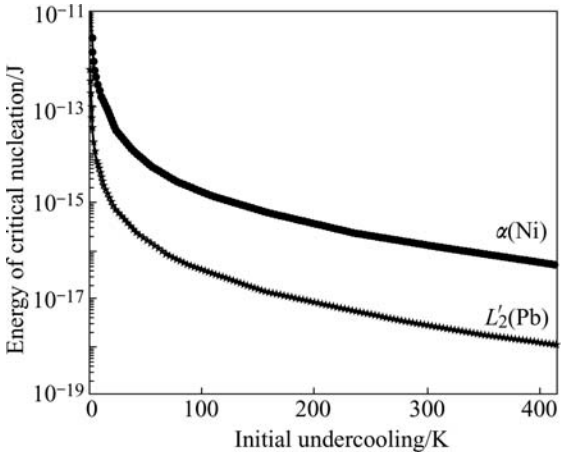

Fig.4 Critical nucleation energy of α-Ni and L_2'(Pb) phases vs initial undercooling in Ni-Pb melts

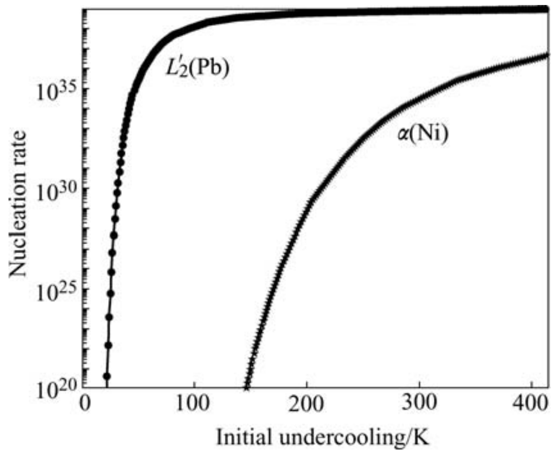

Fig.5 Nucleation rates of α-Ni and L_2'(Pb) phases vs initial undercooling in undercooled Ni-Pb melts

Fig.6 shows the typical DTA curves of Ni-20%Pb alloy sample. On the cooling curve, with the dropping temperature, the DTA curve show the same trend as mentioned above. When the temperature is down to 1 764.51 K, an obvious inflexion appears on the temperature difference curve, corresponding to release of the abundant latent heat, which indicates that a certain phase transformation must have taken place. Combined with the Ni-Pb binary phase diagram, the alloy melt at 1 764.51 K has entered into the immiscibility gap, the remarkable temperature difference inflexion on the DTA curve is only related with liquid-liquid phase separation in the immiscibility gap. At the same time, it can also be found from the DTA cooling curve that the process of liquid-liquid phase separation occurs mainly in the temperature range from 1 764.51 K to 1 680.27 K, where the temperature difference is small and the latent heat is released slowly and continuously. When the temperature is down below 1 680.27 K, the DTA cooling curve shows a continuous temperature drop and a sharp peak occurs at 1 597.14 K, correspond- ing to the formation of α-Ni phase from the melt.

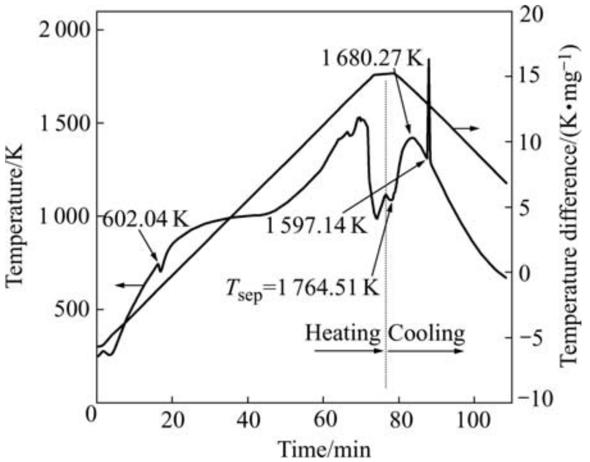

Fig.6 DTA curve of undercooled Ni-20%Pb alloy

The above-mentioned results indicate that liquid-liquid phase separation in the immiscibility gap still takes place under the condition of high undercooling and rapid solidification technology. The temperature, at which liquid-liquid phase separation occurs in the undercooled Ni-20%Pb melt, is 1 764.51 K, and 10 K smaller than the experimental data of MILLER et al [13], determined from the Fe-Pb-Ni, Fe-Ni-C and Fe-Ni-Pb-C by chemical analysis. Therefore, liquid-liquid phase separation in the undercooled melt can be inhibited to a certain extent, but not fully.

4 Conclusions

1) With the dropping temperature, the number of the spherical cells in the water-quenched structure increases, the cells gather and grow up obviously. The spherical cells origin from the L_1 phase separated from the homogeneous melt and is the product of monotectic reaction.

2) Liquid phase separation in the immiscible gap can not be fully inhibited by high undercooling and rapid solidification.

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