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# Microstructures and evolution mechanism of highly undercooled Ni-Pb hypermonotectic alloy①

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**Abstract:** The microstructures and evolution mechanism of the undercooled Ni-20% Pb(molar fraction) alloy were investigated systematically by high undercooling solidification technique. The experiment results indicate that the morphology of α-Ni phase and the distribution of Pb element in undercooled Ni-20% Pb alloys change with the increase of undercooling. The main evolution mechanisms of α-Ni are dendrite remelting and recrystallization. Pb phase in the microstructure of Ni-20% Pb hypermonotectic alloy originates from $L_2$ phase separated from the parent melt during the cooling process through immiscible gap and $L'_2$ phase formed at the temperature of monotectic transformation. The solubility of Pb element in α-Ni phase under high undercooling condition is up to 5.83% which is obviously higher than that under equilibrium solidification condition. The real reason that causes the solubility difference is distinct solute trapping.

**Key words:** high undercooling; Ni-Pb hypermonotectic alloy; structural evolution; dendrites remelting; recrystallization
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## 1 INTRODUCTION

Monotectic system alloys possess excellent physical and chemical properties, and they can be used as self-lubricating materials, electrical contact materials, superconducting materials, etc[1-3]. However, it is very difficult to prepare homogeneous hypermonotectic alloy by employing conventional casting, because the parent liquid will decompose into two distinct immiscible liquids in a few seconds when it passes through the immiscibility gap[4-6]. In the past several decades, the development of aerospace science and technology aroused fresh interest in studying solidification behavior of hypermonotectic alloys, but there are still some problems which have not been solved[7-9]. High undercooling technique can make bulk metal melts solidify at a high velocity under large undercooling and produce homogeneous microstructure with almost no solution segregation[10, 11]. Therefore, the aim of the present work is to undercool Ni-20% Pb hypermonotectic alloy to a significant extent and investigate solidification microstructure and its evolutional mechanism within a large undercooling range.

## 2 EXPERIMENTAL

The undercooling experiments were performed by the method of molten glass fluxing and recycle superheating with a high-frequency induction furnace. The samples were prepared by in-situ alloying procedure from 99.99% pure Ni and 99.75% pure Pb. After ground off the surface oxide and etched in HCl solution diluted by alcohol, the alloy was immersed into a pool of molten glass in a quartz crucible, then melt and superheated to 1 923 K which is above the consolute temperature (1 773 K) of the immiscibility gap to ensure homogeneous alloying. The superheating time of the samples was 3-5 min. Several superheating cycles were conducted till the undercooling became stable, and subsequently nucleation was triggered at the predetermined undercooling using a nickel needle. The thermal behavior of samples was monitored by using an infrared pyrometer, which was calibrated with a standard PtRh30-PtRh60 thermocouple, with a relative accuracy of 5 K and a response time less than 1 ms. Each of the samples had a mass of 6-8 g and a diameter of 12 mm, and was sectioned through the triggering spot, then polished and etched with 8 g $FeCl_3$ + 20 mL HCl + 100 mL $H_2O$

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solution. The structure observation was completed by using a Nephot-1 optical microscope and Amray-1000B SEM.

## 3 RESULTS AND DISCUSSION

Ni-20% Pb hypermonotectic alloy is located at the left side of immiscibility gap on Ni-Pb phase diagram, as shown in Fig. 1. Under the equilibrium solidification conditions, both $L_1$(Ni) and $L_2$(Pb) liquid phases start to separate from the parent liquid phase, $L \rightarrow L_1(\mathrm{Ni}) + L_2(\mathrm{Pb})$, as soon as the temperature falls below 1 773 K. The composition of $L_1$(Ni) and $L_2$(Pb) phases changes along the bindle curve in the immiscibility gap. Immediately after the monotectic transformation $L_1(\mathrm{Ni}) \rightarrow \alpha\text{-Ni} + L'_2(\mathrm{Pb})$ at 1 615 K, the microstructure is composed of 1.02% α-Ni and 57% $L'_2$(Pb). The $L'_2$(Pb) phase diminishes gradually as the temperature drops down and is completely consumed by the eutectic transformation of $L'_2(\mathrm{Pb}) \rightarrow \alpha\text{-Ni} + \mathrm{Pb(s)}$ at 600 K.

The optical metallograph illustrating the characteristic microstructure of Ni-20% Pb alloy is shown in Fig. 2, where the white phase is α-Ni solid solution and the black one Pb phase. As seen in Fig. 2, it can be found that α-Ni grows in dendrite mode and the morphology of α-Ni phase changes with the undercooling increasing. The structural evolution mechanisms of Ni-20% Pb alloy are introduced as follows.

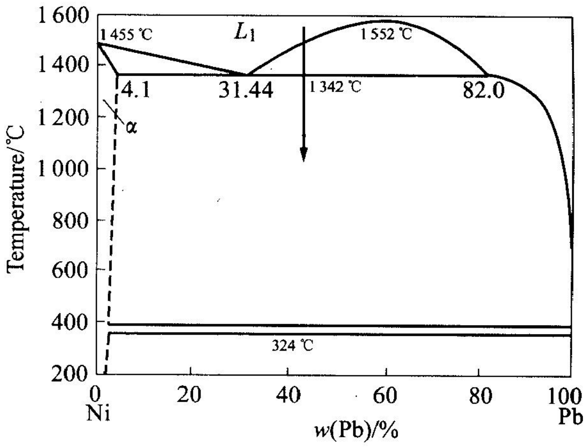


**Fig. 1** Equilibrium phase diagram of Ni-Pb binary alloy

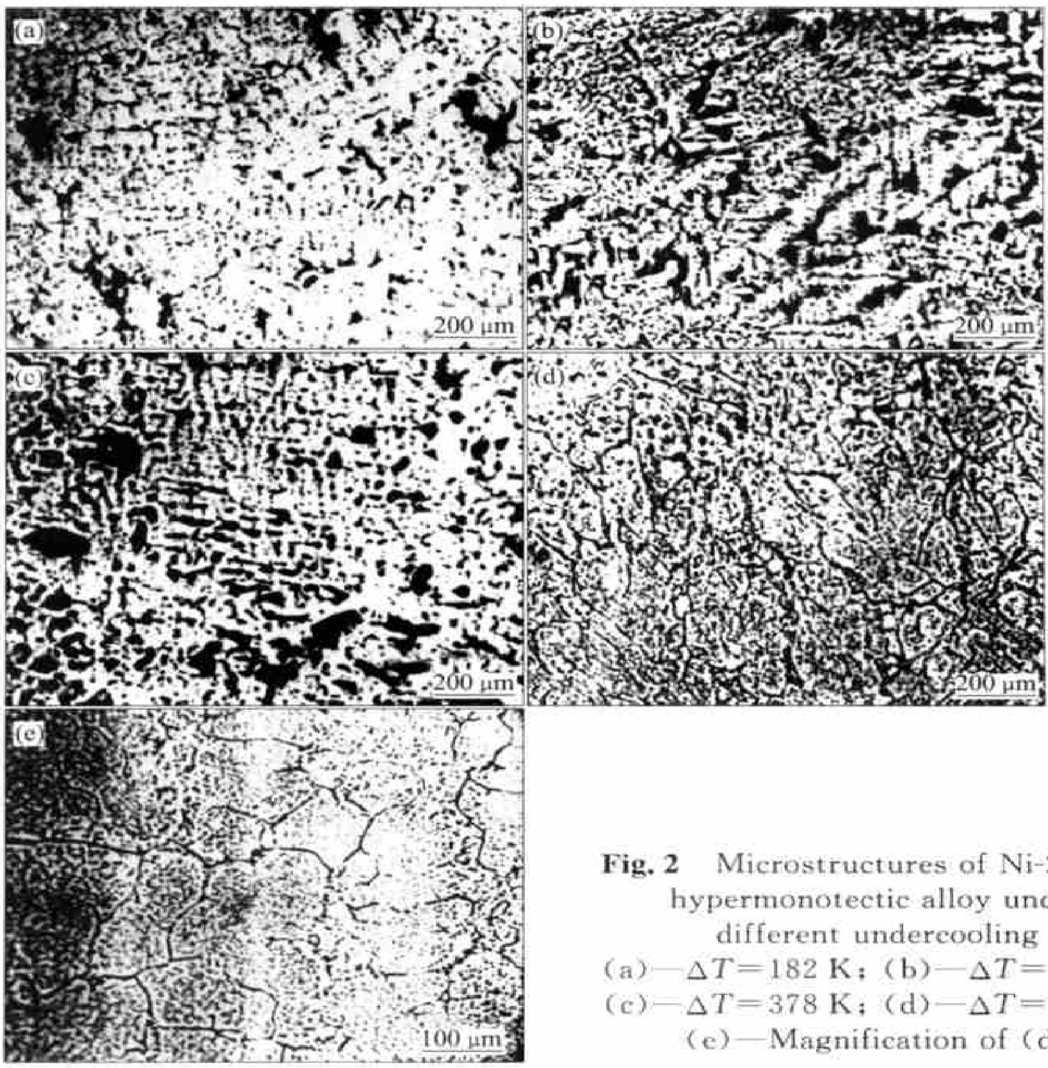


**Fig. 2** Microstructures of Ni-20%Pb hypermonotectic alloy under different undercooling
(a)—$\Delta T$=182 K; (b)—$\Delta T$=242 K; (c)—$\Delta T$=378 K; (d)—$\Delta T$=418 K; (e)—Magnification of (d)

For small undercooling range less than 242 K, the typical character of $\alpha$-Ni is rough dendrite. The similar experiment results have been reported in our previous work[12]. In this undercooling range, the growth of $\alpha$-Ni is mainly controlled by solution diffusion. At the same time, the latent heat is also in a smaller magnitude and is not enough to remelt dendrite entirely. So a lot of integrated dendrites exist in the final solidification structure.

Within the undercooling range from 242 K to 378 K, the dendrite character of $\alpha$-Ni vanishes. Solute diffusion is replaced by the thermal diffusion which predominantly controls the dendrite growth process, so the growth of $\alpha$-Ni is mainly controlled by thermal diffusion. At this stage, the dendrite tip radius is in smaller range, the recalescence superheating and the remelting fraction of dendrites are all in the largest range[12], which leads the dendrite framework formed during the course of solidification to be in serious superheating state, and finally partial dendrites remelt. Thus dendrite remelting is the main mechanism for the morphology evolution at small undercooling range from 242 K to 378 K.

When the undercooling is higher than 378 K, distinct granulation of the grain occurs in the final solidification structure (Fig. 2(d) and (e)). Under large undercooling, the superheating of $\alpha$-Ni dendrite will be at a lower level because partial heat has been absorbed by the undercooled melt. Therefore, dendrite remelting can't really cause granular grain to form. Nevertheless, with the increase of undercooling, high growth velocity and the unbalanced shrinkage of solid phase will lead the inner stress and defects to increase strikingly[13], which makes dendrites break into small pieces. Finally, driven by the interfacial energy, the recrystallization takes place and leads to the formation of anomalous granular grain.

Accompanying with $\alpha$-Ni morphology evolution, the distribution of Pb also changes with undercooling increasing. For small undercooling range less than 242 K, Pb element mainly exists in the interdendritic zone. Within the undercooling range from 242 K to 378 K, a small quantity of Pb particles appear in the intra-dendritic besides those in the interdendritic zone. When the undercooling is higher than 378 K, Pb particles in the grain increase obviously(Fig. 3(b)).

In the present work, Pb phase in the microstructure of Ni-20% Pb hypermonotectic alloy originates from $L_2$ phase separated from the parent melt in immiscible gap, and $L'_2$ phase formed at the temperature of monotectic transformation. Previously it was indistinct whether $L_2$ phase separates from the parent liquid under high undercooling conditions or not. Fig. 4 shows the quenching structures of the undercooled Ni-20% Pb melt through immiscible gap, where the black phase is $\alpha$-Ni phase (Fig. 4(a)) and the white one Pb-rich phase (Fig. 4 (b)). It can be undoubtedly illuminated that liquid-liquid separation has been occurred. In case of $L_2$ phase separation from the parent melt, $L_2$ phase grows up and deposits. The appearance of $\alpha$-Ni dendrites, which is formed after the formation of $L_2$ phase, will affect the distribution of $L_2$ phase. When the undercooling is small, the growth of $\alpha$-Ni dendrites pushes $L_2$(Pb) to the interdendrite and causes the massive Pb lumqs to form in the interdendrite. When the undercooling is less than 242 K, the dimension of Pb lumps decreases and the dendrite becomes minute with the increase of the undercooling. For the undercooling more than 242 K, Pb particles appear in the intradendrite with distinct solute trapping[14], besides those in the interdendritic zone.

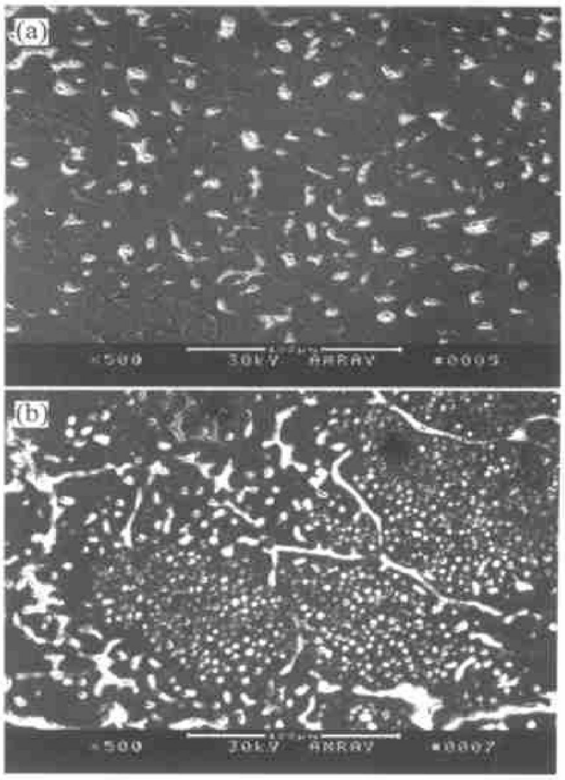


**Fig. 3** SEM photographs of sample undercooled by $\Delta T =$ 242 K(a) and $\Delta T =$ 418 K(b)

In addition, the maximum solid solubility of Pb was investigated. It is well known that the maximum solid solubility of Pb in $\alpha$-Ni is 1.02% under the equilibrium solidification condition[15]. Table 1 shows that the solubility of Pb in $\alpha$-Ni phase is 3.38% in a sample undercooled by 242 K, and 5.83% by 418 K. The real reason that causes the solid solubility difference between the equilibrium and non-equilibrium condition is distinct solute trapping.

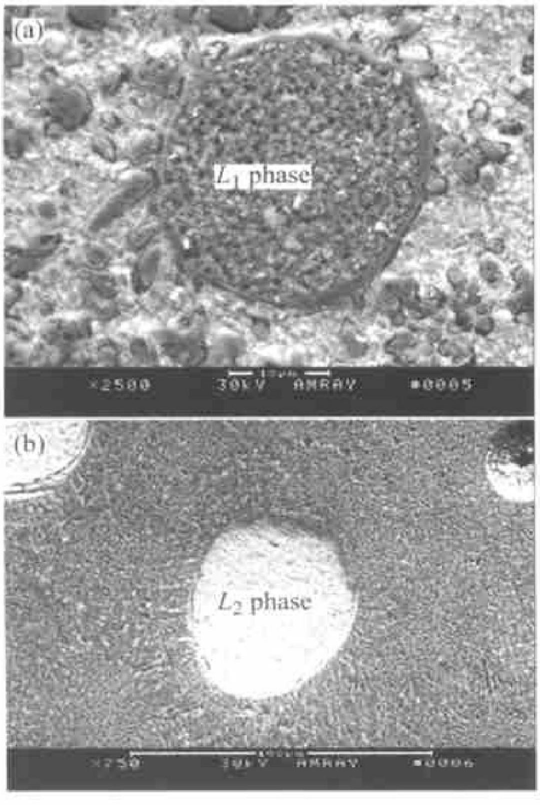


**Fig. 4** SEM images of water-quenching Ni-20% Pb alloy at 1 770 K

**Table 1** Pb content in α-Ni grains

| Undercooling/ K | Pb | |
|---|---|---|
| | $x$ % | $w$ % |
| 242 | 3.38 | 10.94 |
| 418 | 5.83 | 17.83 |

## 4 CONCLUSIONS

1) The morphology of α-Ni phase in the undercooled Ni-20% Pb alloys changes with the increase of undercooling. For small undercooling range less than 242 K, the growth of α-Ni is mainly controlled by solution diffusion. In the small undercooling range from 242 K to 378 K, dendrite remelting is the main mechanism. When the undercooling is higher than 378 K, recrystallization is the decisive mechanism.

2) Accompanying with α-Ni morphology evolution, the distribution of Pb also changes with the increase of undercooling. Pb phase in the microstructure of Ni-20% Pb hypermonotectic alloy originates from $L_2$ phase separated from the parent liquid through immiscible gap, and $L'_2$ phase formed at the temperature of monotectic transformation.

3) The solubility of Pb in α-Ni phase under high undercooling condition is obviously higher than that under equilibrium solidification condition. The real reason that causes the solid solubility difference between the equilibrium and non-equilibrium condition is distinct solute trapping.

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