GRAIN REFINEMENT IN BULK UNDERCOOLED Ni-BASED ALLOY①

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ABSTRACT

Fluxing of 5 g bulk melt Ni77Si13B10 permits high undercoolings to be attained prior to nucleation onset. Investigations of grain refinement in the bulk undercooled alloy as a function of undercooling, recalescence behavior and cooling rate have been reported. A significant inhomogeneity of reduction in grain size of a bulk sample is observed, which is caused by the different solidification conditions: (1) recalescence process, and (2) the followed plateau in which the heat release and extraction rates are equal. It is concluded that the homogeneous refined microstructure can be achieved if the initial undercooling prior to nucleation, or cooling rate after recalescence is further increased.

Key words: Ni-based alloy high undercooling recalescence grain refinement

1 INTRODUCTION

Recent investigations revealed that the solidification morphologies produced by high undercooling essentially resemble those by rapid quenching[1,2]. On the other hand, high undercooling technique makes it possible to fabricate three-dimensional metallic glasses during slow cooling[3]. On basis of the mentioned situation above, science and technology of highly undercooled melts pioneered by Turnbull[4] forty years ago have brought to special notice again. Moreover a remarkable development has been achieved which mainly consists of probing into the solidification microstructure transformations of highly undercooled alloys: from equilibrium to metastable phases, from regular lamellar eutectic to irregular anomalous eutectic, and from coarse dendrites to microcrystalline, such as extremely fine spherical grains of about 1 μm in diameter. Especially, understanding of microstructure refinement in highly undercooled alloy has attracted much attention due to the practical importance of the refinement. The microstructure of some small size samples used in emulsion technique or drop tube is homogeneously refined with the increasing initial undercooling. A sudden grain refinement occurs when the so-called critical undercooling is reached for Ni-based alloys[5,6]. However, the bulk liquid alloys obviously differ from the smaller size samples less than 2 mm in diameter in the undercooling environment, recalescence behavior and their influences upon the resulting microstructure. Therefore studies on grain refinement in bulk undercooled alloy are considered to be meaningful for pushing the undercooling technology into industrial application.

The main purpose of this article is to de-

① Financilly suported by the National Natural Science Foundation of China; manuscript received March 10, 1993

scribe the characteristics of grain refinement in bulk undercooled alloy Ni77Si13B10 both from experimental and theoretical aspects.

2 EXPERIMENTAL METHOD

The master ingots Ni77Si13B10 are prepared by induction melting a mixture of nickel (99.9% Ni), silicon (99.99% Si) and boron (99.999% B) in a fused silica tube under an argon atmosphere. They are later broken into small pieces. For the undercooling experiments a melt fluxing technique has been used in which the bulk melt of 2～5g was embedded into a B_2O_3 flux. The alloy sample was heated and levitated melted by a levitation coil, then it is processed in a mode of the following successive heating cycles: melting — superheating for 2～5min — cooling — solidification. After the high frequency power source was turnned off, the alloy Sample was spontaneously cooled and the cooling curve was measured by an infrared temperature sensing system which is calibrated with a standard PtRh30- PtRh6 thermocouple.

3 EXPERIMENTAL RESULTS

3.1 *Undercooling and Microstructure*

The dependence of solidification microstructure upon the undercooling prior to nucleation can be experimentally observed: bulk undercooled alloy Ni77Si13B10 is considerably refined as a rise in undercooling level, ΔT_r. When ΔT_r = 20K, coarse dendrites Ni_3B of about 20 μm in size are formed. Under the condition of ΔT_r = 82 K, the grain size of dendrites Ni_3B decreases to 5～10 μm. As the initial undercooling ΔT_r increases to 280 K(0.22 T_L), the solidification structure is basically microcrystallized so that it is not identified easily in an optical microscope. Fig. 1 presents the macrograph of the solidified ingot and microstructure along the different positions analyzed by SEM. Dendrites Ni_3B take the shape of granular-crystalline of 1 μm in diameter. The relationship between grain size and undercooling obtained here is in reasonable agreement with the work of Kattamis [7] and Herlach [8] *et al*. However the degree of grain refinement in bulk undercooled alloy differs in various positions.

3.2 *Inhomogeneity of Grain Refinement*

Fig. 1 clearly displays the recalescence behavior and microstructure along the distance within the undercooled cylindrical specimen (max. *d* 8mm × 18mm) when the undercooling is 280 K. Apparently the recalescence starts from a single point on the upper surface which is defined as the original point of distance (z = 0), furthermore radiates to the whole specimen from this nucleation point. The extremely fine ternary eutectic (αNi — Ni_3B — Ni_6Si_2B) of 0.1～0.5 μm lamellar spacing is found when the distance z is less than 10mm, as shown in Fig. 1(a). The crystal growth during recalescence proceeds with the eutectic cluster. As the temperature at the recalescence front increases, a variety of morphologies may be solidified along the distance z. The residual liquid among the recalescence beams is transformed to dendrites Ni_3B. Hence Fig. 1(b) and Fig. 1(c) manifest the dendrite structure among the eutectic colony and interface morphology of eutectic/dendrite when z ranges from 10 to 30 mm. At z = 42 mm, a very pronounced dendritic microstructure of Ni_3B phase which grows in different directions emerges from the residual liquid (Fig. 1 (d)). The temperature in the region of z = 80～90 mm greatly increases, so the residu al liquid after the completion of recalescence produces the results as shown in Fig. 1 (e) and (f) at slow crystal growth. Compared with the fine ternary eutectic, the grain size at the specimen bottom is coarsened by an order of magnitude.

4 THEORETICAL ANALYSES

4.1 *Correlation of Inhomogeneous Refinement with Undercooling Behavior*

Three types of cooling curves of highly undercooled alloy Ni77Si13B10 are depicted in Fig. 2 in which the arbitrary time during continuous cooling process is chosen as the time original point ($t = 0$). These curves comprise four distinct stages: undercooling (nn_1), recalescence (n_1t_1), isothermal plateau (t_1t_3) which only appears on curve

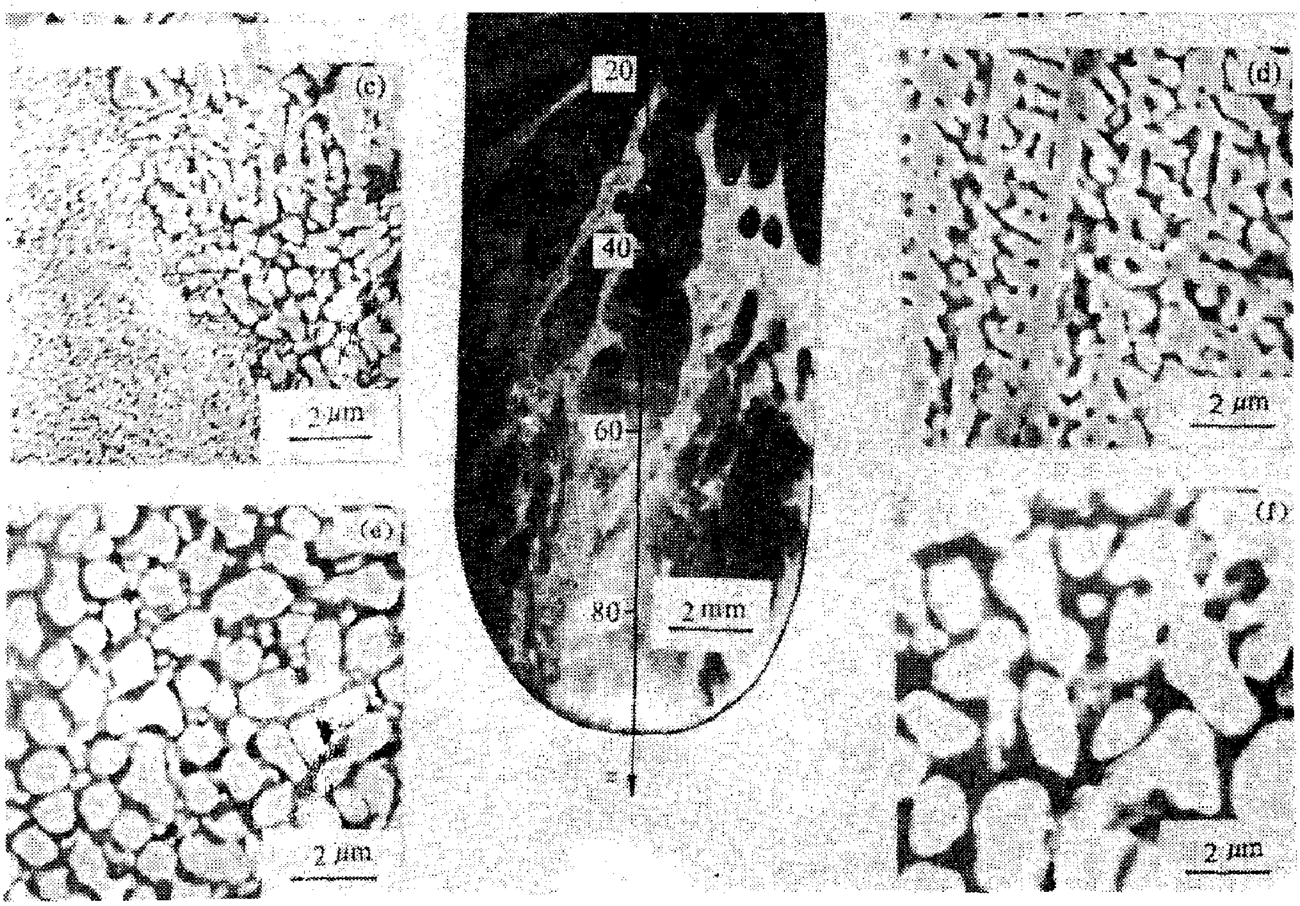

Fig. 1 Recalescence morphology and microstructure along the distance, z.

B, and lastly a continuous cooling (t_3f). The total solidification time is equal to the sum of recalescence time and the plateau period. For slightly undercooled melts of $\Delta T_r < 200$ K which does not far depart from the equilibrium condition, the slow recalescence corresponding to curve A leads to formation of homogeneous coarse structure. When ΔT_r is over 330 K, the isothermal plateau on the cooling curve disappears. So curve C indicates that the whole solidification is completed in the rapid recalescence event, which gives rise to rapidly solidified microcrystalline in the entire specimen. The curve B of $\Delta T_r = 280$ K is found to be a very typical cooling curve of the undercooled alloy Ni77Si13B10. To analyze the solidification process, the transient undercooling, ΔT_c, is introduced, and:

$$\Delta T_c = T_L - T(t) \qquad (1)$$

where T_L is the liquidus temperature, and $T(t)$ a transient temperature during recalescence. Since the liquid is situated at the

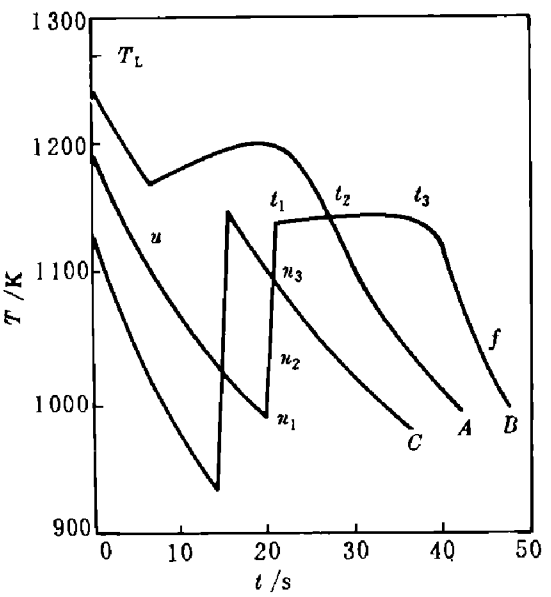

Fig. 2 **Three typical cooling curves of undercooled Ni-based alloy.**
Undercooling: A—100 K; B—280 K; C—335 K

maximum transient undercooling, the microstructure solidified at the period of recalescence onset is significantly refined. The fraction of residual liquid increases with decreasing the transient undercooling and recalescence rate. The points n_2 and n_3 during the recalescence stage correspond to the mixed microstructure of eutectic and dendrite, see Fig. 1(b) and (c). The remaining liquid in the plateau characterized by points t_1, t_2 and t_3 is suitable for growth of dendrites Ni_3B owing to the smaller transient undercooling at the end of recalescence. Therefore points t_1, t_2 and t_3 qualitatively represent the solidification conditions of the microstructure as illustrated in Fig. 1(d), (e) and (f).

4.2 *Crystal Growth in Undercooled Liquid*

In the light of two extreme types of kinetic behavior at the solid - liquid interface: diffusion- limited and collision- limited, Greer[9] calculated the change in some parameters such as nucleation frequency and growth rate with undercooling for Ni-based alloys at the idealized isothermal transformation as seen in Fig. 3. If latent heat release during solidification is ignored, isothermal transformation is possible, and the resulting grain size d is related to the growth rate U and bulk nucleation frequency I, i. e.

$$d = (U / I)^{1/4} \qquad (2)$$

Fig. 3 demonstrates considerable refinement at high undercooling. This refinement will be observed only if recalescence during growth does not stifle further nucleation. For a bulk undercooled alloy, the latent heat release rate can become equal or greater than an external heat extraction rate, characterized by the cooling rate $\dot{T}$. The time t^* at which the heat release and extraction rates are equal is

$$t^* = \left(\frac{d^5 C_L \dot{T}}{24 U^3 L} \right)^{1/2} \qquad (3)$$

where C_L and L are the liquid heat capacity and the latent heat per unit volume. We can conclude that the effects of latent heat release are not important if the solidification time meets the condition

$$\frac{d}{2U} < \frac{3L}{C_L \dot{T}} \quad (4)$$

Contours of $(3L/C_L\dot{T})$ are plotted on Fig. 3 for comparison with the solidification time for the collision-limited and diffusion-limited cases. The cooling rates in Ks^{-1} are marked on these lines. If the solidification time falls below the horizontal lines, recalescence will preclude grain refinement and the

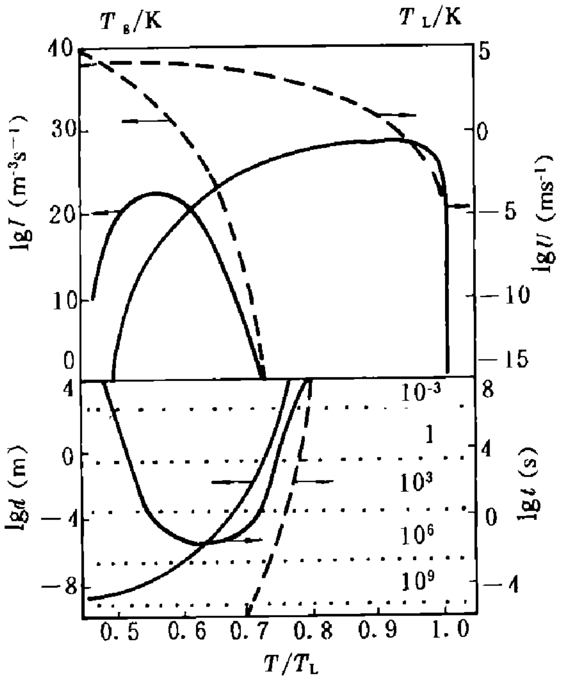

Fig. 3 Calculated interface kinetics for diffusion-limited (solid lines) and collision-limited (dashed lines)

I —nucleation frequency; U —growth rate; d —grain size; t —solidification time; T_g—glass transition temperature

calculated value of d will not apply. This effect certainly exists in the collision-limited case even for imposed cooling rates greatly in excess of that ($\sim 10^6$ Ks^{-1}) in melt spinning. In the diffusion-limited case, at cooling rate $\geqslant\sim 10^6$ Ks^{-1}, the latent heat release is not important and grain refinement is observable, just as glass formation becomes possible.

4.3 *Origins of Grain Refinement*

A number of theories including heterogeneous or homogeneous copious nucleation, recrystallization and stress mechanism have been proposed to explain the grain refinement in undercooled alloys. But the mechanism of grain refinement remains in doubt. In accordance with recent studies[10], it is claimed that the refinement in highly undercooled melts is due to dendrite disintegration which appears to be associated with the liquid flow arising from temperature gradient and solidification shrinkage. With regard to the experimental results of this work, to say the least the theory of dendrite disintegration does not conform to the mechanism of grain refinement in bulk undercooled Ni-based alloys. Fig. 1 shows powerful evidence that rapid solidification during recalescence gives rise to considerable grain refinement in bulk undercooled alloys. Since the effect of latent heat will prevent melts from being further refined for the rapid solidification kinetic system, dendrite growth and remelting, i.e. disintegration may occur during the later period. It is believed that grain refinement in highly undercooled alloys is attributed to rapid solidification of melts far from the equilibrium condition, whereas slow crystal growth in the isothermal plateau is a key reason of inhomogeneous grain refinement in a bulk sample. Naturally if the plateau is eliminated by the following possible steps: further increasing the initial undercooling or cooling rate at the end of recalescence, the bulk undercooled alloy can be homogeneously refined. To increase undercooling levels is a more effective approach to improve the homogeneity of grain refinement, especially for large volume melts.

5 CONCLUSIONS

(1) A significant reduction in average grain size can be achieved with increasing initial undercooling.

(2) Recalescence process originates from a single point on the surface when the undercooling ΔT_i is equal to 280 K. The microstructure of the bulk undercooled Ni77Si13B10 specimen changes along the distance from the nucleation point to the inside. Accordingly a fine ternary eutectic of about 0.1 μm lamellar spacing is firstly solidified during recalescence, while the remaining liquid at the completion of recalescence corresponds to the growth of dendrite Ni_3B of 1～5 μm in grain size.

(3) Considerable grain refinement in bulk undercooled alloys can be explained by rapid solidification during recalescence. Subsequently slow crystal growth in the isothermal plateau is considered to be the essential reason of inhomogeneous grain refinement within a bulk sample. Homogeneous great grain refinement can be attained if the undercooling or cooling rate further increase as to remove the influence of latent heat.

REFERENCES

1 Caesar, C *et al*. Mater Sci Eng, 1988, 98 (2): 339.

2 Li, Delin *et al*. Chinese J of Aeronautics, 1992, 5(3): 143.

3 Kui, H W *et al*. Appl Phys Lett, 1984, 45 (6): 615.

4 Turnbull, D *et al*. J Appl Phys, 1950, 21 (8): 801.

5 Mueller, B A. Microstructure Development in Highly Undercooled Aluminum Alloys: Doctoral Thesis. USA: University of Wisconsin-Madison. 1986.

6 Abbaschian, G J. AD-A120770, 1982.

7 Kattamis, T Z *et al*. Rapidly Quenched Metals V, Vol. 1. North-Holland: Elsevier Science Publishers, 1985. 51.

8 Cochrane, R F *et al*. Mater Sci Eng, 1991, A133(3): 706.

9 Greer, A L. Mater Sci Eng, 1991, A133(3): 16.

10 Flemings, M C *et al*. Mater Sci Eng, 1984, 65(4): 157.