Single Crystal Solidification of Undercooled Single-phase Alloys

Guang Sheng Song^{1,2*}, Min Ha Lee¹, Won Tae Kim¹, Do Hyang Kim¹,
Zhen Zhong Zhang², Xin Lin², Gen Cang Yang² and Yao He Zhou²

¹Center for Noncrystalline Materials, Department of Metallurgical Engineering, Yonsei University, Seoul, Korea

²State Key Laboratory of Solidification Processing, Northwestern Polytechnical University,
Xi'an, People's Republic of China

The correlation between dendritic microstructure and melt undercooling is investigated to present a new technique for rapid single crystal growing, or high undercooling directional solidification (HUDS). In a certain range of undercooling for stable dendrite growth in a negative temperature gradient, this new technique is employed to prepare single crystal Ni₅₀Cu₅₀ bars of approximately 10 mm in diameter and 65 mm in length. Optical metallography and X-ray diffraction experiments indicate that the resulting single crystals in the directionally solidified bars are composed of dendrites approximately parallel to each other and growing mainly in the $\langle 100 \rangle$ directions. The formation process and growth velocity of single crystals in an undercooled liquid are analyzed according to the obtained results and calculated by a current dendrite growth theory, respectively. A comparison of the HUDS technique with the as-proposed autonomous directional solidification (ADS) process is made also in the present paper.

(Received March 30, 2000; Accepted September 18, 2000)

Keywords: directional solidification, high undercooling, single crystal, nickel-copper alloy, crystal growth

1. Introduction

Bridgman technique is the most commonly used method for directional solidification (DS) and in particular single crystal (SC) solidification of alloys such as semiconductors and turbine blades. In the case of Bridgman directional growth, unidirectional heat flow is imposed in order to maintain the required positive temperature gradient at the ahead of the interface. Since the cooling rate is mainly limited by the thermal conductivity of the solid, the growth velocity is relatively slow, resulting in the dissipation of time and energy. In order to develop an alternative method for DS, Lux *et al.*⁽¹⁾ proposed the DS of an undercooled melt for the first time, and described the difference between their method and conventional DS. Later, the improvement of this method resulted in the so-called autonomous directional solidification (ADS) technique^(2,3) for producing SC superalloy turbine blades. For the SC blade production, the ADS technique seems to be still complicated in that some operating conditions need to be controlled carefully, including the preparation of the shell mould, setting a longitudinal positive temperature gradient within the undercooled melt, and controlling the undercooling less than the limit 30 K in order to prevent the appearance of equiaxed grains. Nevertheless, the basic idea of this process is noteworthy.

Ni-Cu alloys have been widely studied in laboratory because of their good undercoolability. Several techniques such as levitation, glass flux, and drop tube, can be used to make them attain a high undercooling. In these processed samples, an important microstructural effect of undercooling has been demonstrated in the form of the so-called grain refinement.⁽⁴⁻⁸⁾ Usually, there are two critical undercooling temperatures ΔT_1^* and ΔT_2^* necessary for grain refinement, and somewhat they depend on the alloy composition and cool-

ing rate. The microstructures are grain-refined with dendritic fragments for $\Delta T < \Delta T_1^*$, oriented dendritic for $\Delta T_1^* < \Delta T < \Delta T_2^*$ and grain-refined for $\Delta T > \Delta T_2^*$. Recently Schwarz *et al.*⁽⁹⁾ have proposed a surface energy driven fragmentation model to account for the grain refinement at both low and high undercooling. Mullis and Cochrane⁽¹⁰⁾ showed that dendritic growth can be stable in the undercooling range $\Delta T_1^* < \Delta T < \Delta T_2^*$. However, very little is known about the possibility to prepare SC by correlating directional solidification with high undercooling in the stable region of dendritic growth. From a practical point of view, such a successful combination may become a new technology of undercooling for rapid SC growth.

From the previous investigations on the DS of undercooled superalloy melt, the essential conditions required for the DS can be summarized as follows: (1) creation of an undercooled melt, and (2) formation of an array of oriented dendrites. Obviously the two conditions can be met for the single-phase Ni-Cu alloys. For this reason, a specific composition in the same alloy system is chosen for investigations on SC solidification. A significant part of this work is to relate the oriented dendritic feature of directional solidification to its undercooling to produce a Ni₅₀Cu₅₀ SC from its undercooled melt. Elucidating the SC formation process and growth velocity of the obtained SC is also the focus of our work.

2. Experimental Procedures

The experimental work was carried out in a high frequency induction furnace under air atmosphere. Prior to the DS experiment, the apparatus was first used to produce a series of small bulk samples with the aim of studying the microstructural evolution as a function of the liquid undercooling. Samples with 20 g in weight and composition of Ni-50 at%Cu (Ni₅₀Cu₅₀) were *in-situ* prepared in fused silica crucibles. The largest undercooling of up to 300 K was achieved by combining the glass flux technique with superheating-cooling cycles.

*Corresponding author: E-mail: gssong@bubble.yonsei.ac.kr

The used glass flux was a mixture of B_2O_3 and soda lime glass. At selected undercooling temperatures, solidification was externally triggered with a needle. Microstructural examination was carried out to search for a critical undercooling ΔT^* corresponding to the transition between grain-refined and dendritic microstructures.

In the light of the obtained microstructure-undercooling relationship, the undercoolings needed for the appearance of stable dendritic microstructure were chosen as precondition of the DS experiment. In order to inhibit the lateral heat extraction and strengthen high temperature endurance of the fused silica tube, it was necessary that these tubes (13 mm OD $\times$ 120 mm L in size) be surface coated with a protective material. For the DS experiment, a two-step process was employed to minimize gas content in alloy melt weighing 70 g. Firstly, an appropriate amount of glass flux with non-electrical conductivity was melted in a fused silica tube with the aid of a graphite susceptor heated by eddy currents induced by an alternating electromagnetic field. To enhance the temperature of the molten glass, it was necessary to add some weighted pieces of Ni and Cu in the molten glass. As soon as these metal pieces were melted completely, the graphite susceptor was promptly removed from the furnace. Subsequently, the rest of the weighted charge was put into the crucible in the form of step feed. Each piece of Ni or Cu was alternatively immersed in the molten glass and held at a temperature of approximately 1400°C until the gas bubbles in the liquid were fully released, and then another piece was added. After the remaining pieces had been exhausted in this way, the temperature of the furnace was raised to achieve the superheat of the melt. Large volume of melt, cycled by superheating-cooling operation, could be undercooled by as much as 250 K. At pre-determined undercooling temperatures, directional solidification was initiated by touching the top central part of the sample surface with a needle. The size of the obtained DS bars was 10 mm in diameter and 65 mm in length.

The temperature of the samples was monitored by using an infrared pyrometer with a relative accuracy of less than 3 K and a response time of 5 ms. The measured undercoolings were calibrated with a standard thermocouple. In order to eliminate the influence of glass flux on the measurement accuracy, the observable window was prepared on the side of the crucible. The micro- and macro-structures of as-solidified samples were revealed by optical metallography. For DS samples, the growth orientation was analysed by X-ray diffraction (XRD) utilizing the monochromatic Cu- K_α radiation, and the growth velocity was estimated by the current theory of dendrite growth into an undercooled melt.¹¹⁾

3. Results

The internal microstructure of the fluxed samples is grain-refined for both low and high undercoolings ($\Delta T < 100$ K and $\Delta T > 200$ K) reached prior to nucleation, but is coarse and dendritic for intermediate undercoolings ($100 \text{ K} < \Delta T < 200 \text{ K}$). Representative microstructures corresponding to individual undercooling regions are shown in Figs. 1(a)–(c). For the grain-refined microstructures produced at low and

high undercoolings, the former contains dendrite fragments, whereas the latter contains no dendrite fragments and many of the grains are separated by high-angle grain boundaries. For the dendritic microstructure formed at intermediate undercoolings, the most frequently observed is in the form of multiple dendrites forming a network, each dendrite growing in a preferential direction but its branches being out of the perpendicular. On the basis of such observations, it is possible to identify two microstructural transitions: from grain-refined to coarse dendritic up to ΔT_1^* , and back to grain-refined after ΔT_2^* as illustrated schematically in Fig. 1(d). For an alloy of $Ni_{50}Cu_{50}$ composition, the two critical undercooling temperatures are 100 and 200 K, respectively, with an error of about ± 10 K, reflecting the range over which the transition takes place. If we associate the oriented dendritic structure with directional solidification of the undercooled melt, this DS experiment should be carried out in the undercooling range 100–200 K needed for stable dendritic growth.

For the DS bars triggered at pre-determined undercoolings ranging over 100–200 K, longitudinal sections of each bars were taken to identify the macrostructure. The optical macrographs for these samples are shown in Fig. 2. In all DS bars, the trigger point position located in the top central region of the sample is clearly demonstrated due to recognizable needle-like trace. Also it can be seen that grains grow in radial direction from the trigger point, forming the spread of orientations about the bar axis. Such growth favors only grains aligned along the axis direction of the bar. Below a certain position from the trigger point, the growth is approximately unidirectional. For the DS samples triggered at undercoolings of 105, 122 and 137 K, the axial distance of non-directional growth zone between the trigger point and the starting of directionality is almost the same, nearly equal to 1/9 the size of the whole sample (Figs. 2(a)–(c)), whereas for the DS sample triggered at $\Delta T = 160$ K the distance is much shorter (Fig. 2(d)). In addition, the size and number of these grains change as the axial distance from the trigger point increases. In the initial stage of the growth, many small oriented grains are observed around the trigger point; while in the later stage of the growth, a few large grains are observed along the main growth direction parallel to the bar axis, as illustrated in Figs. 2(a)–(c). Notably, Fig. 2(d) illustrates a macrostructure with one grain visible, and this grain originates from a few small oriented grains at the trigger point.

The variation of grain orientation scattering with axial distance can be found by analyzing the changes in the intensity and number of diffraction peaks. As an example, Fig. 3 shows XRD patterns obtained at several transversal sections, marked by A, B, C and D in Fig. 2(c), perpendicular to the axis of the DS bar triggered at $\Delta T = 137$ K. It can be seen that the relative intensity and number of diffraction peaks changed from a normal distribution for the section A to an abnormal distribution for the section D, suggesting a change of grain orientation distribution with the axial distance of the sample. In fact, the result reflects a change of dendritic orientation since the substructure within one grain, formed in the undercooling range 100–200 K, is dendritic. XRD trace from the section A, shown in Fig. 3(a), shows all reflections corresponding to the planes (111), (200), (220) and (311) in the diffraction range

Fig. 1 Representative optical micrographs of three types of microstructures in as-solidified $\text{Ni}_{50}\text{Cu}_{50}$ samples obtained from differently undercooled liquid: (a) low undercooling $\Delta T = 50$ K, (b) intermediate undercooling $\Delta T = 168$ K, (c) high undercooling $\Delta T = 275$ K, and (d) schematic diagram showing variation of microstructure as a function of undercooling.

40–100°, and the corresponding diffraction peak intensity values are consistent with the standard data given by the JCPDS card. This indicates that the orientations of the initial dendrites are almost randomly distributed along the bar axis. As the axial distance increases, the (200) reflection peak becomes abnormally strong, the (111) reflection weak and others absent (Figs. 3(b)–(d)). From the experimental results, it is possible to conclude that the (100) plane becomes more dominant as the axial distance increases from the nucleation triggered point and below the section D, the preferred dendritic orientation occurs mostly as a single $\langle 100 \rangle$ growth texture. This suggests that only the preferentially oriented dendrites can survive in the later stage of solidification to form a dendritic SC and to have a main $\langle 100 \rangle$ direction parallel, or nearly parallel, to the bar axis. For cubic crystals, it is well known that dendrites are characterized by growth of the trunks and branches along preferred crystallographic $\langle 100 \rangle$ directions. This is a usual dendritic solidification behavior. In the case of high undercooling directional solidification, however, the appearance of the accompanying weak (111) reflection may be associated with the fact that dendrite branches growing in the $\langle 100 \rangle$ direction are not always orthogonally arranged (see Fig. 1(b)).

4. Discussion

4.1 Single crystal formation process

The present research has shown that it is possible to produce a single grain by combining directional solidification with the undercooling at which nucleation is triggered. The optical metallograph and XRD analysis are helpful to gain understanding of the SC formation process. Of particular interest in the present work is that the dendritic microstructures produced for $\Delta T_1^* < \Delta T < \Delta T_2^*$ have clearly preferred orientation and dendrites grow mainly along the $\langle 100 \rangle$ crystallographic direction, confirming results reported for Cu–30 at%Ni¹²⁾ and Cu–2 wt%Sn.¹³⁾ During dendrite growth in the undercooled melt, because the heat extraction through the undercooling melt is isotropic and thus sets up a negative temperature gradient ahead of the interface, dendrites radiating in the $\langle 100 \rangle$ direction at the trigger point grow along all of the available orientations at the same velocity. By following this mode various orientation grains spread out in a radial fashion around the trigger point, leading to the divergence of the $\langle 100 \rangle$ orientations relative to the bar axis and thus forming a nearly

Fig. 2 Optical micrographs of longitudinal-section macrostructure in the DS bars triggered at undercooling temperatures of (a) 105, (b) 122, (c) 137 and (d) 160 K. Lines A through D in Fig. 2(c) indicate cross-sectional cuts. Their corresponding distances from the trigger point at the top of the sample are 3, 6, 10 and 20 mm, respectively.

Fig. 3 XRD patterns obtained from the cross sections A, B, C and D perpendicular to the axis of the sample indicated on Fig. 2(c): (a) 3, (b) 6, (c) 10 and (d) 20 mm.

random distribution of $\langle 100 \rangle$ orientation. The larger the divergent angle between the $\langle 100 \rangle$ orientation of individual grains and the bar axis, the more unfavorable the crystal orientation for growth and, consequently, the unfavoured grains stop growing readily due to the crucible obstacle to the growth orientation deviation from the bar axis. However, those dendrites which grow nearly parallel to the bar axis can survive the initial stages of solidification and continue to progress because no barrier inhibits the growth ahead of the interface. Other orientations tend to impinge on the crucible wall, resulting in the interruption of their growth. Beyond a certain stage in the development of the divergent growth, some of the initially randomly oriented grains enter a directional stage. Such orientation competition of crystals leads to grain selection, unlike Bridgman-type DS process for which the grain selection is caused by competitive growth velocity. The former is at-

Fig. 4 Schematic diagram of single-crystal formation process showing an evolution of the initial random-orientation grains from divergent growth to directional growth zone. Arrows indicate the different directions of the $\langle 100 \rangle$ orientation relative to the sample axis and the curved line is regarded as the envelope of individual crystal growth front.

tributed to a space constraint, whereas the latter is attributed to a unidirectional heat extraction constraint

The formation of such a SC can be understood with the aid of Fig. 4. At the initial stage of growth, grains nucleated at the trigger point grow in the radial direction, forming a divergent growth zone. When the divergent growth zone has progressed to some distance from the trigger point, only an orientation of grains parallel to the path of the crucible becomes most favourable in space due to the crucible obstacle to departure of the growth orientation from the sample axis. As a result, only one grain can continue getting bigger until it is restricted by the bottom of the crucible and form a SC bar containing a single columnar grain structure. In the divergent growth zone, the projection of each grain length along the $\langle 100 \rangle$ orientation on the longitudinal boundaries of the bar, defined as the divergent height (H), depends on the bar diameter (d) and the divergent angle θ . The expression for the relation is $H = d/2 \cot \theta$. For a given diameter of the DS bar, the greater the divergent angle, the shorter the divergent height. Clearly, a much shorter divergent growth zone is very important in order to obtain a larger size SC bar in the subsequent directional growth zone. The action of the crucible itself on the initial divergent growth is regarded as an orientation filter. The so-called filter acts as a natural (but not an artificial) single crystal selector. Unlike the Bridgman process of monograin selection, this process does not require a complicated artificial selector and controllable heat flow device, and so is easier to control only by the imposed undercooling.

4.2 Single crystal growth velocity

In the case of the directional growth of single-phase alloy

dendrites, dendrites can grow freely due to the imposed negative temperature gradient. Therefore, the dendrite growth velocity can be described by the theory of free growth model. Considering that each columnar grain consists of dendrites parallel to each other, the growth velocity of a single dendrite can be regarded as that of a single crystal. According the BCT dendrite growth theory,¹¹⁾ the dendrite growth velocity, V , as a function of undercooling, ΔT , is uniquely determined by the following two coupled equations:

$$\Delta T = \frac{\Delta H_f}{C_p^L} I_v(P_t) + \frac{2\Gamma}{R} + \frac{V}{\mu} + m_1 c_0 \left(1 - \frac{m_1/m_l}{1 - (1-k)I_v(P_c)} \right) \quad (1)$$

$$R = \frac{\Gamma/\sigma^*}{\frac{\Delta H_f P_t}{C_p^L} \xi_t - \frac{2m_1 c_0 (1-k) P_c}{1 - (1-k)I_v(P_c)} \xi_c} \quad (2)$$

where $P_t = VR/2\alpha$ is the thermal Peclet number, R the radius at dendrite tip, α the thermal diffusivity, $P_c = VR/2D$ the solute Peclet number, and D the solute diffusion coefficient. The meanings of the other notations are the same as that described in the BCT model. Equation (1) gives the correlation between the bulk undercooling ΔT and the product VR in terms of the Peclet numbers. Equation (1) together with eq. (2) can give the V - ΔT relationship.

Using the physical properties of the alloy as given in Table 1, the dependence of the growth velocity, V , on bulk undercooling, ΔT , has been calculated as shown in Fig. 5. In the range of undercooling ($\Delta T_1^* < \Delta T < \Delta T_2^*$) necessary for the directional growth, the dendrite growth velocity varies from 2 to 30 m/s, showing the rapidity of the dendrite growth into the undercooled melt. For the DS bar triggered at $\Delta T = 106$ K, the dendrite growth velocity is about 10 m/s. This means that the SC grows from the trigger point at a velocity of 10 m/s. In other words, for the bar 65 mm in length, the time taken for the solidification front to sweep across the bar surface is about 6.5×10^{-3} s, indicating the formation of a dendritic-columnar grain in a very short time. Consequently, the SC grows to its full size quickly after nucleation. The full length of a columnar grain is determined by the given crucible size. For the conventional DS process, however, such a high growth velocity is absolutely impossible to reach. Normally, the Bridgman-type DS proceeds with a growth velocity in the

Table 1 Physical parameters used in the calculation of dendrite growth velocity for $\text{Ni}_{50}\text{Cu}_{50}$ alloy.

Liquidus temperature	T_L (K)	1585
Latent heat of fusion	ΔH_f (J/m ³)	2.211×10^9
Specific heat of liquid	C_p^L (J/m ³ K)	5.234×10^6
Liquidus slope	m_L (K/wt%)	-3.151
Interfacial tension	σ (J/m ²)	0.374
Equilibrium partition coefficient	R_E	0.791
Diffusion length	a_0 (m)	3.0×10^{-10}
Sound velocity in Ciquid	V_0 (m/s)	2000
Thermal diffusivity	α (m ² /s)	3.0×10^{-6}
Solute diffusion coefficient	D (m ² /s)	6.0×10^9

Fig. 5 Calculated values of growth velocity as a function of undercooling for $\text{Ni}_{50}\text{Cu}_{50}$ alloy. The black dot represents a growth velocity of a single crystal at an undercooling of 160 K.

order of about a few $\mu\text{m/s}$.

As far as the credibility of the model is concerned, the comparison of the measured growth velocities for Ni and $\text{Cu}_{70}\text{Ni}_{30}$ with the theoretical calculations has been presented by many authors such as Willnecker *et al.*¹⁴⁾ and Li *et al.*¹⁵⁾ Their results have revealed that at undercooling temperatures below ΔT_2^* , growth velocity can be adequately represented by the current dendritic growth model but above ΔT_2^* , the velocity-undercooling relationship deviates from the model. Therefore, for the DS bars investigated in the undercooling range $\Delta T_1^* < \Delta T < \Delta T_2^*$, the model can predict their growth velocities correctly without the available velocity data for the $\text{Ni}_{50}\text{Cu}_{50}$ alloy solidified in the stable dendritic region.

4.3 Comparison between the ADS and HUDS techniques

The ADS process exhibits two main advantages compared with the conventional DS technologies: (1) the complicated equipment of the Bridgman process can be simplified because of no requirements of the withdrawal device and relative motion between the sample and the heater; (2) the relatively rapid solidification leads to reductions in both the processing times and microsegregation. Nevertheless, in order to ensure the growth of single crystals, the ADS process still needs an artificial SC selector and a longitudinal positive temperature gradient within the undercooled melts. For the HUDS, however, the growth of single crystals is solely controlled via the undercooling required prior to nucleation. Thus this process is cheaper and easier to control than the ADS process. In addition, the HUDS technique can bring more rapid growth of single crystals, thus leading to a finer dendritic microstructure and lower microsegregation throughout the samples. The detail comparison between the two techniques is listed in Table 2.

5. Summary

In the predetermined range of undercoolings needed for stable dendrite growth, the newly developed HUDS process has been utilized successfully to obtain large single crystals of single phase $\text{Ni}_{50}\text{Cu}_{50}$ alloy. This demonstrates that the proper combination of directional solidification and high undercooling opens up possibility for rapid growth of single crystals. As compared with any other single-crystal-growing

Table 2 Comparison of the two techniques ADS and HUDS.

Technique	Undercooling ΔT (K)	SC selector	Solidification conditions
ADS	≤ 30	Yes	$G > 0$ Water-cooled chill plate
HUDS	100–200	No	$G = 0$ Point trigger

G denotes an imposed longitudinal positive temperature gradient within the undercooled melt.

techniques, this process is easier to operate since there are no requirements for grain selector and unidirectional heat flow. In order to obtain a directional SC microstructure, this technique requires only the proper undercooling temperature at which solidification starts. In the process of SC formation, the initial divergent crystal growth whose orientations are deviated from the sample axis is restricted by the side wall of the crucible, and the subsequent growth whose orientations are nearly parallel to the axis of the crucible is the most favorable for the formation of one grain with the preferred (100) orientation. Such orientation selection is generally obtained by a given space constraint. For the DS bar triggered at an undercooling of 160 K, single crystals can be grown in undercooled melt at a velocity of about 10 m/s.

Acknowledgements

We would like to gratefully acknowledge the Creative Research Initiatives of the Korean Ministry of Science and Technology and the Chinese Natural Science Foundation for their financial support.

REFERENCES

- 1) B. Lux, G. Haour and F. Mouard: *Metall.*, **12** (1981), 1235–1239.
- 2) A. Ludwig, I. Wagner, J. Laackmann and P. R. Sahm: *Mater. Sci. Eng.*, **A178** (1994), 299–303.
- 3) L. A. Wagner and P. R. Sahm: *Superalloys*, ed. by R. D. Kissinger, D. J. Deye and D. L. Anton: The Minerals Metals and Materials Society, (1996), pp. 497–501.
- 4) A. Munitz and G. J. Abbaschian: *Undercooled Alloy Phases*, ed. by E. W. Collings and C. C. Koch, The Metall. Soc., Warrendale, (1986), pp. 23–29.
- 5) R. Willnecker, D. M. Herlach and B. Feuerbacher: *Appl. Phys. Lett.*, **56** (1990), 324–326.
- 6) A. L. Greer: *Mater. Sci. Eng.*, **A133** (1991), 16–21.
- 7) J. Z. Xiao, K. K. Leung and H. W. Kui: *J. Mater. Res.*, **12** (1997), 873–876.
- 8) A. F. Norman, K. Eckler and A. Zambon: *Acta Materia.*, **46** (1998), 3355–3370.
- 9) M. Schwarz, K. Kamar, K. Eckler and D. M. Herlach: *Phys. Rev. Lett.*, **73** (1994), 1380–1383.
- 10) A. M. Mullis and R. F. Cochrane: *J. Appl. Phys.*, **82** (1997), 3783–3790.
- 11) W. J. Boettinger, S. R. Coriell and R. Trivedi: *Rapid Solidification Processing: Principles and Technologies IV*, ed. by R. Mehrabian, P. A. Parrish, Claitor's, Baton Rouge, (1988), pp. 13–21.
- 12) F. Gärtner, A. F. Norman and A. L. Greer: *Acta Materia.*, **45** (1997), 51–66.
- 13) A. J. McLeod and L. M. Hogan: *Metall. Trans. A.*, **9A** (1978), 987–998.
- 14) R. Willnecker, D. M. Herlach and B. Feuerbacher: *Phys. Rev. Lett.*, **62** (1989), 2707–2709.
- 15) J. F. Li, Y. H. Zhou and G. C. Yang: *Mater. Sci. Eng.*, **161–168** (2000), 161–168.