High rate directional solidification and its application in single crystal superalloys

Hengzhi Fu*, Xingguo Geng

State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, People's Republic of China

Received 14 June 1999

Abstract

In the present paper there are two parts contributing to the discussion of high rate directional solidification and its application. The first part aims to characterize the high rate directional solidification of various kinds of alloys. It was found that the relevant cooling rate of the high rate directional solidification is defined to be within $1 \times 10^7$ K/s (solidification rate is $10^{-3} \sim 10^{-1}$ m/s as $G_L = 100$ K/cm) and that it is located in the region between the near-equilibrium slow growth rate and the rapid solidification rate beyond the equilibrium condition, whilst at the same time there occurs a series of turning effects of interface stability and morphologies. With the increase in the growth velocity the interface with the plane front evolves to cells and dendrites at the stage of near-equilibrium and with a further increase in growth rate they transformed reversibly from dendrites to cell structure and then to the absolute stability of a planar interface. The change of solute segregation reveals the same from a low segregation, then increased and finally reduced again. An explanation based on effective constitutional supercooling about the evolution of interface morphologies with respect to the changes of growth rate is proposed.

The second part is devoted to introducing experimental results for single crystal superalloys using the rate directional solidification principle. It is shown that the single crystal superalloys CMSX-2 and NASAIR 100 exhibit significant improvement in microstructure segregation and mechanical properties at high temperature both in the as-cast and after-heat-treatment conditions with the high rate directional solidification technique. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: High rate directional solidification; Single crystal superalloys; Effective constitutional supercooling; Improvement in mechanical properties

1. Characteristics of high rate directional solidification

1.1. Introduction

As a milestone in quantitative solidification science, the constitutional supercooling theory of Tiller and Chalmers was established and verified for single phase alloys by a series of experimental results of directional solidification at a low growth rate. The interface stability theory of Mullins and Sekerka from the aspects of dynamics, with consideration of influence of temperature gradient of solid phase and curvature effect, successfully predicted and explained the phenomenon of absolute stability at high growth rate.

Examination of the solidification process shows that there exists a considerable difference in the relationship between the solidification structure and the response parameters at low and high growth rate. The significant difference in solidification characteristics between these two extreme conditions reflects the different effects of the environmental and essential parameters governing the solidification process. It also shows that the influence of those parameters might reveal a positive or reverse effect on the interface morphology stability and their microstructure, while the growth velocity passes through the range from low to high level, which is called the near rapid or sub-high rate solidification corresponding to the range of the cooling rate of about $10^0 \sim 10^7$ K/s (a growth rate of around $10^{-3} \sim 10$ cm/s for $G_L = 100$ K/cm). For example, the solidification system is considered near equilibrium and the interface can be treated with local equilibrium principles at low growth rate. However at high growth rate there might occur diffusionless solidification, with even an amorphous structure appearing as a complete non-equilibrium feature. At near equilibrium conditions, interface morphologies transform from planar to cellular, then to dendrite with the increase of growth rate, whereas during high growth rate these change from dendrite to fine cellular, and then to plane front reversibly. Moreover the solute diffusion effect increases the interface stability at low growth rate, whereas, at high growth rate it decreases the stability, and so on.
Fig. 1 generally describes the appropriate problems concerned with near rapid directional solidification for single direction heat flow. It demonstrates microstructure transition and growth behaviour during directional solidification. It should be emphasized that the microstructure characteristics, the coupling effects of temperature and solute field, and the interface stability during transition to absolute stability still remain not completely clear. The mechanism of diffusionless solidification, solute trapping, planar front and its structure of absolute stability, and the formations of metastable phase, are considered to be of great interest for investigation in the region of rapid solidification.

1.2. Effective constitutional supercooling and dendrite–cell transition

So far there have only been a few investigations contributing to near rapid directional solidification (DS) because the current popularly-used DS furnace, which constrains the maximum cooling rate for DS to only about 1 K/s, cannot provide enough growth velocity. Thus the crystal growth is within the dendrite growth range, and the solidification retains the near equilibrium solidification characteristics, which cannot express the near rapid solidification features.

In the authors’ laboratory, the interface morphology and its microstructure evolution of various alloys solidified directionally from low to sub-high rate, has been investigated with high (<250 K/cm) and super-high (<1300 K/cm) temperature gradient DS apparatus. Fig. 2 shows the interface microstructure of Ni-based superalloys during the transition of Cell–Dendrite–Cell (C–D–C). It can be seen that the primary spacing after the D–C transition is very small. It can also be seen that the sidebranch passes through a transition from development to degeneration and then to disappearance. This means that with the increase of the growth velocity there must be a maximum development of sidebranch during the transition, which should correspond to the maximum effective constitutional supercooling.

Fig. 2. Directionally solidified microstructures of Ni base alloy: (a) $V = 5.5 \, \mu m/s$, $G_L = 200 \, K/cm$; (b) $V = 13.3 \, \mu m/s$, $G_L = 200 \, K/cm$; (c) $V = 100 \, \mu m/s$, $G_L = 200 \, K/cm$; (d) $V = 100 \, \mu m/s$, $G_L = 1000 \, K/cm$. 
Fig. 3. $W_{CS}$ and $R$ (KGTC’s model) [4] vs. growth rate $V$.  

(1) From the MS theory [1], the planar interface stability criterion is:

$$-G_L + mG_C \xi_C - \Gamma \omega^2 = 0 \quad (1.1)$$

where $G_L$ and $G_C$ are the temperature and concentration gradients respectively; $\xi_C$ is a function related to the diffusion coefficient $D_L$, solute redistribution coefficient $k$, growth velocity $V$ and disturbed frequency $\omega$; and can be simplified as:

$$\xi_C = 1 - 2k/[1 + (2\omega D_L/V)^{1/2} - 1 + 2k] \approx D_L^2 \omega^2/(V^2 k)$$

$$\omega = 2\pi/\lambda$$

Let $W_{CS} = mG_C = V \Delta T/D_L$, and $W_{LS} = \Gamma \omega^2/\xi_C \approx \Delta \lambda \nu V^2/D_L$, for the marginal stability ($G_L = 0$), $(W_{CS} - W_{LS})$ can be called effective constitutional supercooling, i.e. the lenticular enclosed part in Fig. 3. Thus, the maximum effective constitutional supercooling can be obtained as $dW_{CS}/dV = dW_{LS}/dV$, which is expressed as $V = D_L \Delta T/(2\Gamma k)$.  

When $V < D_L \Delta T/(2\Gamma k)$, the effective constitutional supercooling increases with $V$; and when $V > D_L \Delta T/(2\Gamma k)$, the effective constitutional supercooling decreases with $V$.

The effect of the growth velocity on the change of interface stability occurs at $V = D_L \Delta T/(2\Gamma k)$, which can be defined as the transition growth velocity $V_T$. The maximum effective constitutional supercooling corresponding to $V_T$ may be considered as the fully developed dendrite sidebranch and the maximum micro-segregation.

(2) The C–D and the D–C transitions are in fact the generation and the degradation of the sidebranches during the columnar crystal growth. From the stability criterion for cylindrical surface proposed by Kotler and Tiller [2] and Trivedi [3]:

$$-G_L + mG_C \xi(j) \leq \Gamma \nu^{-2} L(j)$$

$$L(j) = j(j + 1) + j(j + 1)K_S K_L^{-1}$$

$$\xi(j) = (j + K_S K_L^{-1})(j - 2P(1 - k))^{-1}$$

where $j$ is the symmetric parameter determined by the crystal morphology, $K_S$ and $K_L$ are the thermal conductivity of the solid and liquid phases, respectively, $\Gamma = \gamma T_0 \Delta T^{-1}$ is the Gibbs–Thomson coefficient, $R$ is the cylinder radius, $P = VR/(2D_L)$ is the Peclet number, and $k$ is the solute distribution coefficient ($k < 1$).

From Eq. (1.2), it can be seen that when $\xi(j) < 0$, the cylindrical interface is stable and there will be no secondary branch near the tip part. The dendrites will be degenerated to cells. Thus:

$$V_{DC} \geq [J \sigma^2/(1 - k)^2] (\Delta T \nu L/\Gamma)$$

is the D–C transition velocity for the binary alloy solidified at sub-high rate.

Comprehensively, the critical velocities relevant to the morphology transition in the whole solidification range are:

$$V_{CS} = G_L D_L \Delta T = G_L D_L k/[mC_o(k - 1)];$$

$$V_{CD} = G_L D_L \Delta T/(\Delta T k) = G_L D_L k/[mC_o(k - 1)];$$

$$V_T = \Delta T D_L/(2T k) = mC_o(k - 1) D_L/(2T k^2);$$

$$V_{DC} \geq [J \sigma^2/(1 - k)^2] (\Delta T \nu L/\Gamma)$$

$$= J \sigma^2 mC_o D_L/(\Delta T \nu L/\Gamma(k - 1)) \quad (\text{here } J \text{ is constant});$$

$$V_{ab} = \Delta T D_L/(\Gamma k) = mC_o(k - 1) D_L/(\Gamma k^2).$$

1.3. Solidification character near the absolute stability limit

After the transition from dendrites to superfine cells (or microcells), with a further increase in growth velocity the microcells develop to the M.S. absolute stability of planar interface. From the experiments of near absolute stability on Al–1.2 wt% Mn, the following were found.

1. There exists the occurrence of interface morphological transition from coarse deep cells at low growth rate to high rate fine cells, and then again with the increase of growth velocity, to a high rate coarsened cellular structure. The typical morphological evolution of Al–1.2 wt% Mn through this process is shown in Fig. 4. The main features are:

(i) Only cells structure at the various velocities mentioned above are seen and no dendrite structure is observed. (ii) Coarse cell structures are revealed when the growth rate is lower than 200 μm/s. (iii) A fine cell structure is found at the growth rate of 600–5000 μm/s, and the cells spacing is decreased with the increase in velocity; finally the cells have a finer structure with high rate. (iv) When the growth rate is over 5000 μm/s a tendency of coarsening of cells is observed. The change of the cells’ average spacing from coarse to fine and to coarse again shows that there should exist a minimum cells’ spacing with respect to velocity. In the present experiments the
minimum spacing for a velocity of about 5000 μm/s is around 10 μm. It should be noted that the corresponding velocity of turning transition of the cells’ spacing from coarse to fine and to coarse again is just located at half the critical velocity, \(1/2 \, V_{\text{th}}\), of the absolute stability of the M.S. theory.

2. For Al–1.2 wt% Mn alloy when the growth rate is higher than 5000 μm/s, experiments also show that in the case of existing strong disturbance, the cellular structure could abruptly transform to a band or a grain-like structure. The occurrence of the finest cell structure in experiments for Al–Mn alloys can be explained using effective constitutional supercooling. It is shown that the turning transition of effective constitutional supercooling, with respect to growth rate from increase to decrease, can give rise to a change of interface morphology. The change in the effective constitutional supercooling also reflects the instability of the planar interface.

At very low growth velocity, as the instability for a planar interface appears, there will be instability of the planar interface, causing the occurrence of a transition from planar to cellular, to balance the driving force of instability with an increase in interface curvature. When the effective constitutional supercooling reaches the maximum that also corresponds to the maximum interface instability, the interface will then certainly become a form with maximum curvature, so as to increase the interface stability by boundary energy. With the decrease of effective constitutional supercooling the tendency of instability of the related planar interfaces decreases, which leads also to a change of radius of interface curvature.

Accordingly, the relation between curvature radius and growth rate is given in Fig. 3, and shows the consistency of the maximum value of effective constitutional supercooling with a minimum radius of curvature. These results show the consistence of the turning velocity of effective constitutional supercooling from an increase to decrease, and that the critical velocity \(V_{\text{co}}\), corresponding to the minimum value of cellular structure, is in good agreement with the results of experiments: \(V_t \approx V_{\text{th}}/2 \approx V_{\text{co}}\).

As far as the analysis of band structures observed in experiments is concerned, not only the non-equilibrium but also the non-linear effects in a non-equilibrium process should be taken into account.

2. High rate directional solidification of single crystal superalloys

2.1. Nickel-base single crystal superalloys

In recent years Nickel-base single crystal superalloys have been popularly used as turbine blade materials for advanced aircraft engines, and can be characterized as: (i) the complete elimination of grain boundaries (ii) accurate control of the growing crystal orientation; (iii) reasonable reduction of the amount or elimination of the grain boundary
minor element that leads to a rise in solution temperature and a strengthening effect of γ; (iv) considerable improvement in the mechanical properties of the alloys.

However, it should be noted that some problems still exist in microstructures for single crystal superalloys although they have demonstrated considerable achievement in their application: (i) coarse dendrite structure; (ii) very elongated sidebranches of dendrites; (iii) serious segregation and porosity.

Fig. 5(a) is the typical microstructure of a nickel-base...
single crystal superalloy with developed sidebranches, its primary dendrite spacing being about 300–400 μm in average, which gives rise to a limit in the use potential of the materials. Thus, it is considered that there are probably two ways to improve the microstructure and mechanical properties further: (i) structure refinement; (ii) degeneration and elimination of dendrite sidebranches (cells structure).

In experiments, NASAIR 100, Rene N-4, CMSX-2 and DD3 superalloys were selected for investigation, their nominal chemical composition being as follows:

|     | Cr | Co | Mo | W  | Ta | Nb | Al | Ti | Ni |
|-----|----|----|----|----|----|----|----|----|----|
| NASAIR 100 | 8.5 | 1  | 10 | 3.3 | 5.8 | 1.2 |     |    | Bal.|
| Rene N-4   | 9  | 8  | 2  | 6  | 4  | 0.5 | 3.7 | 4.2 | Bal.|
| CMSX-2     | 8  | 5  | 0.6| 8  | 6  | 5.6 | 1.0 | Bal.|
| DD3        | 9.5| 5  | 3.8| 5.2 |    |    |    |    |    |

Experiments were carried out using HRS, LMC, ZMLMC and EBM directional solidification furnaces with temperature gradients of 50, 250, 460 and 1000 K/cm, the maximum \(G_t\) being about 10 times that of the popularly used HRS technique.

The single crystals of alloys with various S/L interface morphologies were obtained using a ‘seed’ technique for which the seed orientation is [001].

2.2. Results and discussion

Various interface morphologies from planar, cellular, dendritic and superfine cellular at different temperature gradients \(G(30–1000 \text{ K/cm})\) and solidification rates \(V\) (0.13–1000 μm/s) were obtained. The summary of the morphologies of single crystal superalloys versus \(G\) and \(V\) is shown in Fig. 5(b). Some of their solidification microstructures are shown in Fig. 2. The following may be noted.

1. The solidification microstructure tends to be refined with the increase of \((G.V)\), as shown in Fig. 6.

2. The interface morphology changes from dendrite to cellular and then to a planar structure as \((G/V)\) increases, and it changes in the reverse direction as \((G/V)\) decreases.

3. At a lower \(G\), the increases of \(V\) causes a breakdown of the D.S. condition, which leads to the occurrence of an equiaxed structure.

4. For the dendrite structure, a degeneration of sidebranches appears at a higher \((G.V)\), further increase of \((G.V)\) giving rise to dendrites suffering from fine cell transition to become a superfine cellular structure.

5. The temperature gradient and solidification rate of single crystal superalloys for a turbine blade produced by the conventional HRS technique are located in the dark area in Fig. 5(b). Its cooling rate is about 0.1–2 K/s, the appropriate microstructure corresponding to the coarse dendrite with developed sidebranches, as shown in Fig. 5(a). Experiments indicate that increase of the solidification cooling rate leads not only to a change of interface morphologies but also to a refinement of \(\gamma'\) precipitates in the alloys.

6. Fig. 7 shows [5] the effect of cooling rate on the size of \(\gamma'\) of as-cast NASAIR 100. The average \(\gamma'\) size decreases from the cellular structure to fine dendrite with the increase of \((G.V)\).

7. Increase of the solidification cooling rate leads to a decrease of segregation and the amount of \(\gamma/\gamma'\) eutectic during solidification.

8. Because of the microstructure refinement of single crystal superalloys by increased solidification cooling rate, an improvement in the mechanical properties of the alloys can be expected. Fig. 8 shows the relationship between the stress rupture life of single crystal superalloy NASAIR 100 and the solidification cooling rate and their different solidification morphologies. It is seen that a higher rupture life for specimens with superfine dendrite or cellular structure was obtained both in the as-cast condition and after heat treatment. Similar results can be seen for superalloy CMSX-2 at 1050°C and 160 MPa test conditions (Fig. 9).
Fig. 7. The change of γ size with G.V.

Fig. 8. Stress rupture lives at 1050°C and 160 MPa and their corresponding initial microstructure of NASAIR 100.
The results of the present investigation indicate that refinement of dendrite and cellular structure by means of a high thermal gradient furnace and increasing the solidification rate should be considered as an effective way to improve the microstructure and the mechanical properties of single crystal superalloys, so as to further increase the potential of single crystal superalloys for applications.

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