JOURNAL OF MATERIALS SCIENCE **36** (2001) 3623–3627

γ' Formation and morphology evolution in the undercooled structure of DD3 Single crystal superalloy

FENG LIU*, GENCANG YANG, XUEFENG GUO
State Key Laboratory of Solidification Processing, Xi'an Shaanxi, 710072, People's Republic of China
E-mail: caoyang77@263.net

An investigation of the γ' formation and its morphology evolution in the bulk undercooled DD3 single crystal superalloy is performed. The application of a molten salt denucleating technique combined with thermal cycle enables such investigation over a wide range of undercooling up to 210 K. The microstructure formation has been respectively discussed with respect to undercooling, nucleation and solute segregation during solidification and post-solidification, by employing the classical nucleation theory. Furthermore, TEM and SEM technique are adopted to reveal the γ' microscopy and to illustrate other factors correlated to the γ' precipitation. It is found that the size, fraction, and distribution of precipitated γ' in as-solidified DD3 single crystal superalloy are all influenced by melt undercooling. *© 2001 Kluwer Academic Publishers*

1. Introduction

Over the past years, significant advances have been made in the development of new superalloys which are capable of operating at high service temperature, thus enabling higher engine efficiencies to be realized. In order to function satisfactorily in more severe environments, superalloys must possess properties such as outstanding high temperature strength, creep and fatigue resistance, excellent ductility, good impact resistance and adequate resistance to hot corrosion [1].

Cast nickel-base superalloys are typically composed of high volume fractions of γ'-phase, coherently precipitated in a face-centered cubic (FCC) matrix, together with eutectic phase and one or more carbide phases. The desired properties and resistance to microstructure changes at high temperature in these alloys are obtained by all phases with suitable structure, shape, size, and distribution [2]. It is widely recognized nowadays that coarse grains with serrated grain boundaries, homogeneous composition with uniform cubic γ–γ' microstructures and small discrete phases at grain boundaries are typical microstructural features in modern advanced nickel-base cast superalloys [3]. Among all the microstructural factors, the γ' precipitate morphology plays an important role in influencing the properties of nickel-base superalloy. Therefore, how to produce the desirable γ' precipitate morphology is essential for the development of new types of superalloys.

Interest in solidification behavior of undercooled melts has been heightened in recent years, partly due to the technical and scientific interest in rapid solidification processing. Undercooling plays a major role in determining the structure observed in many rapid solidification processes. However, research in the undercooling of superalloys is very few, except that directional solidification from undercooled melts as proposed by Lux *et al.* [4], was picked up and has been advanced resulting in a new technique for the rapid production of single-crystal superalloy turbine blades [5] during the previous years. Subsequent work in this area resulted in the development of a shell mold system, which enabled efficient thermal melt undercooling of several Nickel-base superalloys [6]. Nowadays, a systematic investigation in structure evolution with undercooling of DD3 single crystal superalloy [7], was performed, which highlighted the dendrite growth and grain refinements occurring with melt undercooling, but unfortunately, the corresponding study in γ'-phase was not involved. It is therefore necessary to understand how formation of γ' precipitate depends on the melt undercooling condition and, how its morphology evolves with the increasing of melt undercooling. The aim of this paper is focused on this respect.

2. Experimental procedure

Commercial DD3 single crystal superalloy [8] (Table I) was chosen in the bulk undercooling experiment, which was established by the application of molten salt covering, denucleating and high frequency induction heating under the protection of argon atmosphere. Prior to melting, the surfaces of the metal charges were cleaned

---

* Author to whom all correspondence should be addressed.

TABLE I Nominal composition of the DD3 single crystal superalloy [8]

Element	Cr	Al	Ti	W	Co	Mo	Ni
Wt%	9.5	5.9	2.2	5.2	5	3.8	Balance

mechanically by grinding off the surface oxide layer and chemically by etching in HCl solution diluted by alcohol. When beginning experiment, the alloy charges were placed in a cleaned and dried non-catalytic coating mold [9], and covered with a 5 mm layer of salt granules. Then the mold was sealed, evacuated and subsequently back-filled with 99.999% argon gas. Each sample was melted, superheated and solidified several times, i.e. it was processed in a mode of superheating-cooling cycle, in order to obtain large undercoolings. Here, this non-catalytic coating mold is a kind of shell mold (composed of 79 SiO_2, 18 ZrO_2, and 3 B_2O_3, wt%), over whose inner surface a glass coating with the same composition is covered. It was found in the experiment that, this coating mold can keep amorphous or less-crystalline at high temperature for a long time, and consequently, prevent premature nucleation of superalloy melt in contact with it, indicating an ideal non-catalytic nucleation inhibition for DD3 single crystal superalloy [9]. After experiment, the composition analysis, performed on the inner surface of coating mold and in the alloy samples achieved, declared that no chemical reaction occurred between the alloy melt and the mold materials and the salt granules. So the composition of the resultant as-solidified specimens was taken to be the same as the original composition. The thermal behavior of samples was monitored by an infrared pyrometer with an absolute accuracy, relative accuracy, and response time of less than 10 K, 3 K, and 5 ms, respectively. The cooling curve was calibrated with a standard PtRh30-PtRh6 thermal couple, which was encapsulated in a tube composed of the same material as the non-catalytic coating mold and then immersed into the melt in the identical condition. The melting temperature and the undercooling of the alloy melt in the cooling curves could be read after the comparison with the absolute temperature recorded by the standard thermal couple. Each of the samples, which had a weight of 10–15 g and a diameter of 8–12 mm, was sectioned through the triggering spot, and polished, then etched with an aqueous solution of $FeCl_3$ and HCl. Structure observation was carried out with optical microscope, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively.

3. Results and discussion

The constituents of DD3 single crystal superalloy have been classified as solid solution and/or precipitate formers, inferring that two phases, matrix (γ) and strengthening phases (γ') predominantly exist in the as-cast structure. It is also shown in reference [10] that the Ni-Cr-Al-Mo system is of particular interest in representing the equilibria among γ (nickel-rich solid solution), γ' (based on Ni_3Al) and σ phases, and that the Ni-Cr-Al-Mo systems consist of single phase γ–Ni (Al, Cr, Mo) solid solution above 800°C, if correspondingly having the same Al, Cr, Mo content as that in DD3 single crystal superalloy. In addition, Machlin and Shao [11] have proposed the extension of the Ni-Cr-Al-Mo quaternary to higher order alloys by adopting the scheme of equivalents (Ni, Co, Fe) : Cr : (Al, Ti) : (Mo, W, Nb, V, Ta, Hf). It then follows that similarity exists in the solidification characterization between the Ni-Cr-Al-Mo system and DD3 single crystal superalloy, which can solidify as single- phase γ-solid solution in the dendritic rapid solidification process. The detailed solidification process of undercooled DD3 single crystal superalloy is as follows. Dendrites, firstly, are formed at the nucleation point and rapidly propagate through the volume of the melt, in which only single phase γ-solid solution Ni (Al, Ti, W, Mo, Co, Cr) is obtained [8]. Then the rapid release of heat of fusion during dendrite growth results in rapid recalescence and, the dendritic network remelting occurs. Finally, the remaining inter-dendritic melt starts to solidify onto the dendritic network at low melt undercooling in post-recalescence. Furthermore, during the relatively long duration of this stage, coarsening by Ostwald ripening may occur, and γ/γ' eutectic (1 volume pct in the cross-section of the sample) is formed over the boundaries of crystal grains at the end of this stage. After that, phase transformation of diffusional precipitation takes place and γ' phase continuously precipitates in the cooling process.

$$\gamma_1 \to \gamma_2 + \gamma' \tag{1}$$

where γ_1 and γ_2 are respectively the solid solutions with different composition. Based on the classical nucleation theory [12], the driving force for precipitation of γ' phase from γ matrix is the Gibbs free energy difference ΔG_V between γ and γ' states. However, γ' precipitation is also associated with a strain energy change, ΔG_ε. Therefore, the critical work ΔG^* for the formation of a critical nucleus is given as follows.

$$\Delta G^* = \frac{16\pi\sigma^3_{\gamma-\gamma'}}{3(\Delta G_V - \Delta G_\varepsilon)^2} \tag{2}$$

where $\sigma_{\gamma-\gamma'}$ is the interfacial free energy of the γ–γ' interface, which can be classified into two parts

$$\sigma_{\gamma-\gamma'} = \sigma_c + \sigma_s \tag{3}$$

where σ_c and σ_s denote the γ–γ' interfacial free energy induced by the change in chemical bonds and crystal structure, respectively. Due to the same structure and similar lattice constant between γ and γ' phase, the value of σ_s tends to be zero and, thus definitely make the value of $\sigma_{\gamma-\gamma'}$ very small. In connection with Equation 2, the critical work ΔG^* is therefore so modest that it is in favor of the γ' precipitation process. The calculation of ΔG^* for the formation of a critical nucleus in as-solidified undercooled DD3 single crystal superalloy makes it possible to predict the nucleation rate of γ'

phase. The steady state homogeneous nucleation rate I can be expressed as follows.

$$I = A \cdot \mathrm{EXP}\left(-\frac{Q}{KT}\right) \cdot \mathrm{EXP}\left(-\frac{\Delta G^*}{KT}\right) \quad (4)$$

Under conventional directional solidification conditions with solidification velocity being controlled by cooling rate, the ratio of the temperature gradient in front of the liquid/solid interface (G_L) to the growth rate (R) seems to play a predominant role for the interface morphology [13], thus drastically influencing the γ' precipitation peculiarity. Moreover, we can infer from Equation 2 that ΔG_ε and ΔG_V are respectively in proportion to ΔV^2, ΔT or ΔX, in which ΔV, ΔT, and ΔX respectively denote the volume change in γ' precipitation, the γ' precipitation undercooling and the solute super-saturation of the supersaturated γ solid solution. With the increment of cooling rate, the corresponding ΔT and ΔX will be consequently increased and, thus obviously enlarges the nucleation rate of γ' phase. Whereas the diffusional process is progressively inhibited, inferring that growth velocity of γ' precipitate diminishes. Therefore, the higher the cooling rate, the more the precipitation sites, and the smaller the precipitate size. Whilst in the undercooled solidification controlled by negative thermal gradient, the morphology, size, distribution, and fraction of γ' precipitate are bound to be determined by melt undercooling instead.

Under various solidification conditions with different melt undercooling, the typical morphology of as-solidified structure and γ' precipitate in the DD3 single crystal superalloy are those respectively illustrated in Fig. 1, Fig. 2 and Fig. 3. Here, no efficient way is adopted to accelerate the cooling process after recalescence, and the cooling rate should therefore be constant in every melt undercooling experiment run, indicating that the undercooling for γ' precipitation is always invariable. However, the size of typical γ' precipitate substantially drops as the melt undercooling increases. Fig. 4 gives the corresponding γ' particle size as a function of melt undercooling.

As illustrated in Fig. 1, the as-solidified structure of DD3 single crystal superalloy with melt undercooling experiences a transformation from highly branched dendrite to the first granular crystal, and to largely developed fine dendrite, then to the second granular crystal [9], indicating a predominant role of melt undercooling in structure evolution. As a result of high-velocity growth after large melt undercooling, a high energy content of the first-formed structure also can be expected to be built in, in the form of a high population of crystalline defects, such as dislocation, vacancy, and (low-angle) grain boundary (Fig. 5), which subsequently act as precipitate nucleation sites. The higher the melt undercooling, the more the defects. The existence of these non-equilibrium defects is beneficial to the nucleation on these defects of γ' precipitate owing to the reduced critical work [14].

$$\Delta G^* = \frac{16\pi\sigma^3_{\gamma-\gamma'}}{3(\Delta G_V - \Delta G_\varepsilon)^2} - \Delta G_d \quad (5)$$

where ΔG_d is the energy essentially required to eliminate these defects. Therefore, the γ' nucleation rate is improved, which indicates that the nucleation sites in

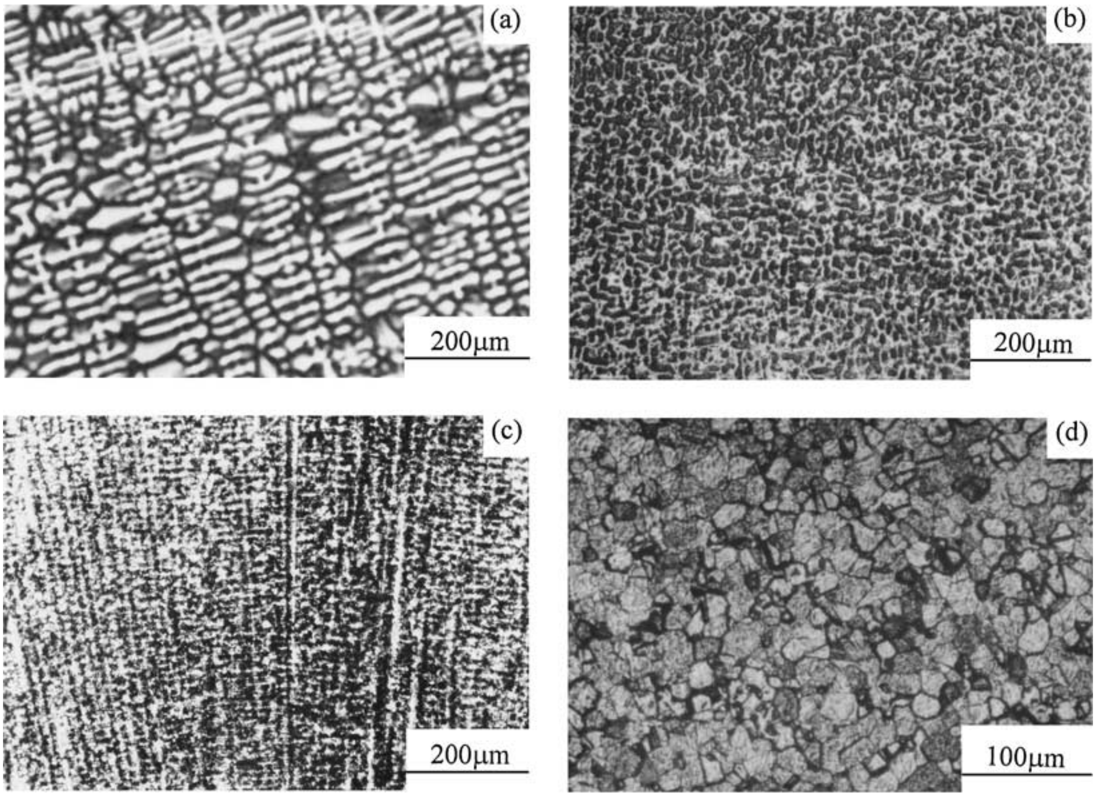

Figure 1 Structure evolution of DD3 single crystal superalloy with melt undercooling (a) $\Delta T = 25$ K, (b) $\Delta T = 50$ K, (c) $\Delta T = 130$ K, and (d) $\Delta T = 200$ K.

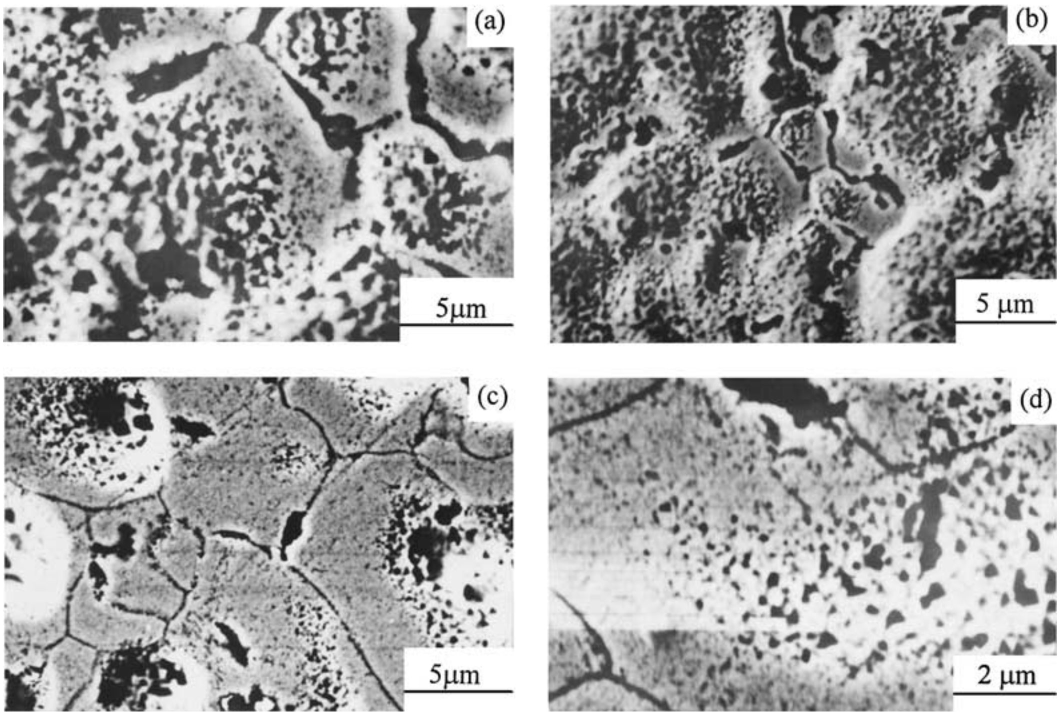

Figure 2 SEM microscopy of γ' matrix precipitation in DD3 single crystal superalloy respectively solidified at undercooling of (a) 45 K, (b) 120 K, (c) 180 K, and (d) 210 K.

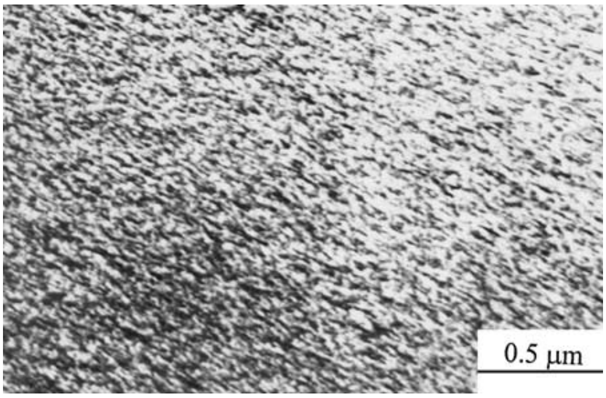

Figure 3 Typical γ' morphology (TEM) in DD3 single crystal superalloy solidified at undercooling of 250 K.

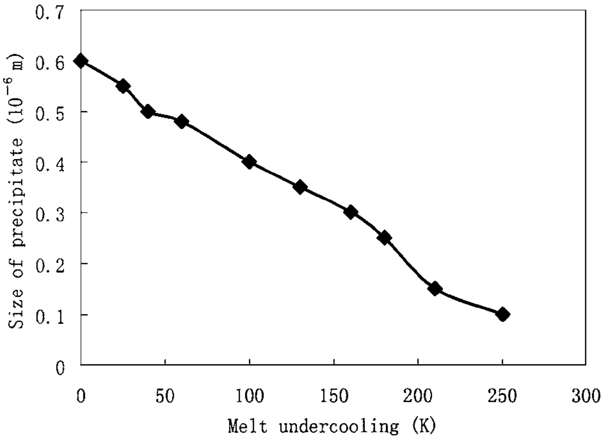

Figure 4 Variation of γ' precipitate size as a function of the melt undercooling of DD3 single crystal superalloy.

a definite space volume after high melt undercooling are much more than those after low melt undercooling. Furthermore, if the growth is too great to permit complete diffusion of solute out of the melt in contact with the advancing dendrite tip, effective solute trapping may take place in the solid [15]. Increase in the terminal solid solubility of additions (for example, Al, Ti) can consequently be obtained in undercooled rapid solidification. This provides higher volume fractions of γ' precipitate in γ matrix. Accordingly, the size of γ' precipitate declines with the rising of melt undercooling (Figs 2–4).

Segregation of alloying elements severely influences the shape, size, and distribution of γ' precipitate [16]. With reference to Fig. 2, γ' precipitate is of regular shape and small size at dendritic arms or in the crystal grains, whereas it is of irregular shape and relatively large size at the inter-dendritic sections or at the crystal grain boundaries. This non-homogeneous condition is due to solute segregation occurring in solidification. When in solidification process with low velocity, i.e. low melt undercooling, dendrite segregation will cause considerable aggregation of γ' forming elements (Al, Ti) in the inter-dendritic section, and corresponding deficiency at dendritic arms, thus certainly resulting in the aforementioned shape and size of γ' precipitate.

As we all know, large melt undercoolings enable the liquid-solid interface to move at a relatively high velocity. From Fig. 1, it can be found that the as-solidified structure subject to the ascending melt undercooling is continuously refined. Thus the resultant secondary arm spacing is often less than 25 μm (Fig. 1c) and, in the extreme, segregation can totally be suppressed. When the melt undercooling is enhanced, solidification velocity is therefore heightened, and the composition difference between dendritic arm and inter-dendritic section, or between inner grain and grain boundaries is

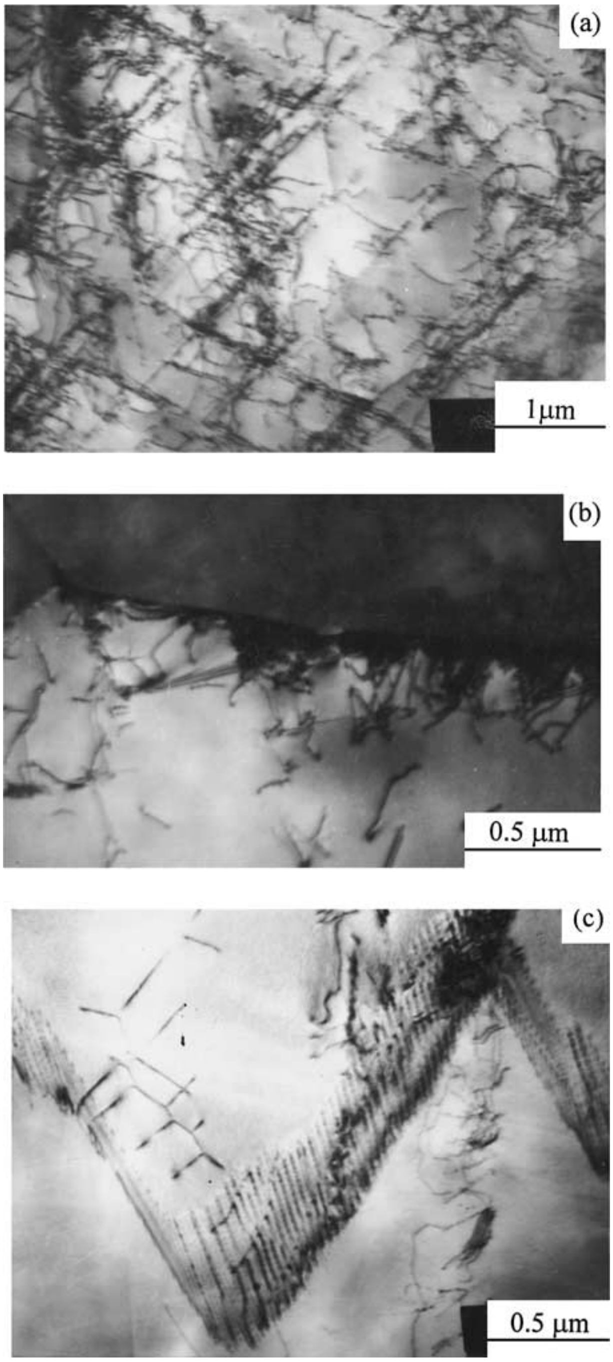

Figure 5 TEM microscopy of formation of dislocation at (a) inner grain, (b) grain boundary, and (c) sub-boundary in DD3 single crystal superalloy.

consequently alleviated, which particularly makes the distribution of alloying elements in γ phase more uniform. In this case, γ' precipitates form a shape of fine sphere at dendritic arm or in inner grain, while regular cube in the inter-dendritic section or at grain boundaries (Fig. 2, Fig. 3, and Fig. 5).

4. Conclusions

1. The size of precipitated γ' in as-solidified DD3 single crystal superalloy is predominantly controlled by melt undercooling. With the increase of melt undercooling in the undercooled rapid solidification process, not only a high population of crystalline defects could be built in the high energy content of first-formed structure to reduce the critical nucleation work, but the increase in terminal solid solubility of γ' forming elements (Al, Ti) may also be obtained to improve the fraction of γ' precipitate. Accordingly, the size of γ' precipitate declines.

2. The non-homogeneous characterization in the morphology and distribution of γ' precipitate owing to solute segregation could be alleviated as a result of rapid solidification after large melt undercooling. This makes γ' precipitate forms a shape of fine sphere at dendritic arm or in inner grain, while regular cube in the inter-dendritic section or at grain boundaries.

Acknowledgements

The authors are grateful to the financial support of the Natural Science Foundation of China (Grant No. 59871041) and the Aeronautical Science Foundation of China (Grant No. 98H53093).

References

1. E. NEMBACH and G. NEITE, *Prog. Mater. Sci.* **29** (1985) 177.
2. G. R. STOECKINGER and J. P. NEUMANN, *J. Appl. Crystallogr.* **3** (1970) 32.
3. P. CARON and T. KHAN, *Mater. Sci. Eng.* **61** (1983) 173.
4. B. LUX, G. HAOUR and F. MOLLARD, *Metall.* **35** (1981) 1235.
5. J. STANESCU and P. R. SAHM, *Ing.-Werkst.* **2** (1990) 64.
6. I. A. WANGER and P. R. SAHM, in "Superalloy 1996," edited by R. D. Kissinger, D. J. Deye, D. L. Anton *et al.* (The Minerals Metals & Materials Society, 1996) p. 497.
7. F. LIU, X. F. GUO and G. C. YANG, *J. Mater. Sci.*, accepted.
8. W. DU, Ph.D. thesis, Northwestern Polytechnical University, 1998.
9. F. LIU, X. F. GUO and G. C. YANG, *Mater. Sci. Eng.*, accepted.
10. S. CHAKRAVORTY and D. R. F. WEST, *J. Mater. Sci.* **19** (1984) 3574.
11. E. S. MACHLIN and J. SHAO, *Met. Trans.* **9A** (1978) 561.
12. D. J. TURNBULL, *Chem. Phys.* **18** (1981) 950.
13. L. LIN, F. SOMMER and H. Z. FU, *Scripta Metall.* **30** (1994) 587.
14. M. J. AZIZ, *Metall. Mater. Trans.* **27A** (1996) 671.
15. X. P. GUO, Ph.D. thesis, Noethwestern Polytechnical University, 1992.
16. D. FURRER and H. FECHT, *Scripta Metall.* **11** (1999) 1215.

Received 24 July 2000
and accepted 12 February 2001