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Effect of microstructure and γ' precipitate from undercooled DD3 superalloy on mechanical properties

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The mechanical properties of DD3 superalloy solidified at various undercoolings were measured to investigate the effects of γ' precipitate and microstructure on alloy properties. The influence of melt undercooling on the γ' precipitation is also studied. It is found that not only the size of γ' particle, but its distribution in the as-solidified structure is also drastically controlled by the melt undercooling. The analysis indicates that alloy solidified at a low undercooling is brittle, thus leading to a lower toughness and tensile strength. With increasing undercooling, the toughness and strength of the alloy increased accordingly, which may be attributed to the strengthening effect of γ' precipitate and the reduced micro-segregation.

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 temperatures, 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 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 amount of discrete phases at grain boundaries are typical microstructural features in modern advanced cast nickel-base superalloys [3]. Among the microstructural factors, the γ' precipitate morphology plays an important role in influencing the properties of the superalloy.

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 limited, 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 superalloy [7] was performed, which highlighted the dendrite growth and grain refinements occurring with melt undercooling. Unfortunately, the corresponding study in formation of γ'-phase and its effect on alloy's mechanical properties was not involved. It is therefore necessary to understand how formation of γ' precipitate depends on the melt undercooling and, how microstructure influences the alloy's mechanical properties. The aim of this paper is focused on this respect.

2. Experimental procedure

The chemical composition of DD3 superalloy is 9.5Cr-5Co-5.2W-4.2Mo-5.8Al-2.3Ti-Ni Bal. A SiO_2-ZrO_2-B_2O_3 (Si-Zr-B) nucleation inhibitive coating mold [8] ϕ 12 × 100 mm with an inner diameter of ϕ 9 mm was used for preparing the specimen for the mechanical measurements. Here, the Si-Zr-B 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 is found in the experiment that this coating remains amorphous or microcrystalline at high temperature for long times and,

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consequently, prevents premature nucleation of superalloy melt in contact with it, indicating an ideal nucleation inhibition for DD3 superalloy [8].

Prior to melting, the surfaces of the superalloy charges were cleaned mechanically by grinding off the surface oxide layer and chemically by etching in an HCl solution diluted with alcohol. Initially, 60-g alloy charges were first placed in an alumina crucible, and covered with a 5 mm layer of purification agent [9]. Then the vacuum chamber 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. Thereafter, the alloy melt was dropped into the Si-Zr-B coating mold placed right at the bottom of alumina crucible, superheated and held for 1–2 min. Finally, the melt was cooled down. Various microstructures solidified at different undercoolings were obtained by triggering the melt to nucleate using the liquid Ga-In alloy. 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 nucleation inhibitive coating mold and then immersed into the melt in the identical condition. The experimental procedure has been described in more detail elsewhere [7, 10].

The samples for measuring the mechanical properties were machined into standard specimens of $\phi\, 6 \times 30$ mm and then measured in an Instron 1196 multifunction tester with a loading rate of 0.2 mm per min. The fracture of the alloy solidified at different undercoolings and microstructure observation were carried out with an optical microscope, scanning electron microscope (SEM) and transmission electron microscope (TEM). EPMA examination has shown the solute distribution in γ and γ' phases.

3. Results and discussion

3.1. Effect of microstructure on mechanical properties

The solidification process of undercooled DD3 superalloy is as follows. Initially, dendrites are formed at the nucleation site and rapidly propagate through the melt, consisting of γ phase (Ni alloyed with Al, Ti, W, Mo, Co, Cr) [7]. Then the abrupt release of heat of fusion during the dendrite growth leads to rapid recalescence (temperature rising), with possible remelting of the dendrite network. Finally, the remaining interdendritic liquid starts to solidify in the dendritic network at low melt undercooling during post-recalescence. In the relatively long duration of this final stage, diffusional coarsening occurs and γ/γ' eutectic is formed between γ dendrites. During subsequent cooling, γ' precipitates in the γ phase. Therefore, DD3 superalloy melt as similar to single-phase melt can be solidified as a single γ phase during rapid solidification. As illustrated in Fig. 1, the as-solidified microstructure of DD3 superalloy with melt undercooling experiences a transformation from highly branched dendrite (Fig. 1a) to the first granular crystal (Fig. 1b) followed by highly developed fine dendrite (Fig. 1c–f) and then the second granular crystal (Fig. 1g) [7, 11]. The detailed description of microstructure evolution can be seen in [7].

TABLE I Relationship between the recalescence temperature and undercooling of the DD3 superalloy

Parameter	Value							
ΔT (K)	25	30	44	66	78	120	140	153
Recalescence temperature (°C)	1355	1358	1365	1348	1338	1330	1322	1320

Now, we would like to focus on the mechanical properties of the superalloy solidified at various undercoolings. Fig. 2 shows the relationship of the tensile strength and the toughness of the alloy solidified at various undercoolings. Fig. 3 (a–f) exhibits the corresponding morphology of the failure fracture of the DD3 superalloy sample solidified at undercooling of 20 K, 45 K, 80 K, 110 K, 130 K, and 145 K, respectively. Table I presents the relationship between recalescence temperature and undercooling. From Fig. 1a, we can tell that the grain size is rather large. The lower undercooling leads to little solid product crystallizing during recalescence, which will, undoubtedly, leave much remaining liquid after the primary phase has been produced (Table I). Consequently, the solidification interval after recalescence for the sample to crystallize completely is much longer than that at high undercoolings, resulting in substantial dendrite ripening. In the meanwhile, solute redistribution will unavoidably occur during the following slow solidification, thus producing considerable solute segregation. Both the large ripened grains and the segregation can result in very low mechanical properties. Fig. 3a provides a catastrophic failure mode owing to inter-crystalline fracture, in which even the coarse dendrite can be seen. For the sample solidified at undercooling of 45 K, the overall cross-section is occupied by refined grains with a diameter of 50–70 μm (see Fig. 1b). Although the dendrite remelting is most serious in this undercooling range (Table I), the grain boundary segregation in this refined structure is much less than that in the aforementioned coarse dendrite [12]. So, the deleterious effect on the mechanical properties is correspondingly reduced. From Fig. 3b, we can find a mixing failure mode including inter-crystalline fracture and inner-crystalline fracture. It then follows that the mechanical properties are slightly improved, especially the toughness (Fig. 2).

In the undercooling range of 78–150 K, compared with that achieved in 20 K (Fig. 1a), a fine dendritic structure (Fig. 1c–f) is formed as a result of heterogeneous nucleation occurring in the highly undercooled liquid alloy [7]. Once the nucleus forms from the triggering site, dendrite will grow radially and rapidly into the undercooled liquid. In order to elucidate the influence of the process conditions on the growth behavior, Boettinger *et al.* proposed a model (BCT) for the undercooled melt [13]. According to the BCT model, the effect of thermal diffusion on the dendrite growth

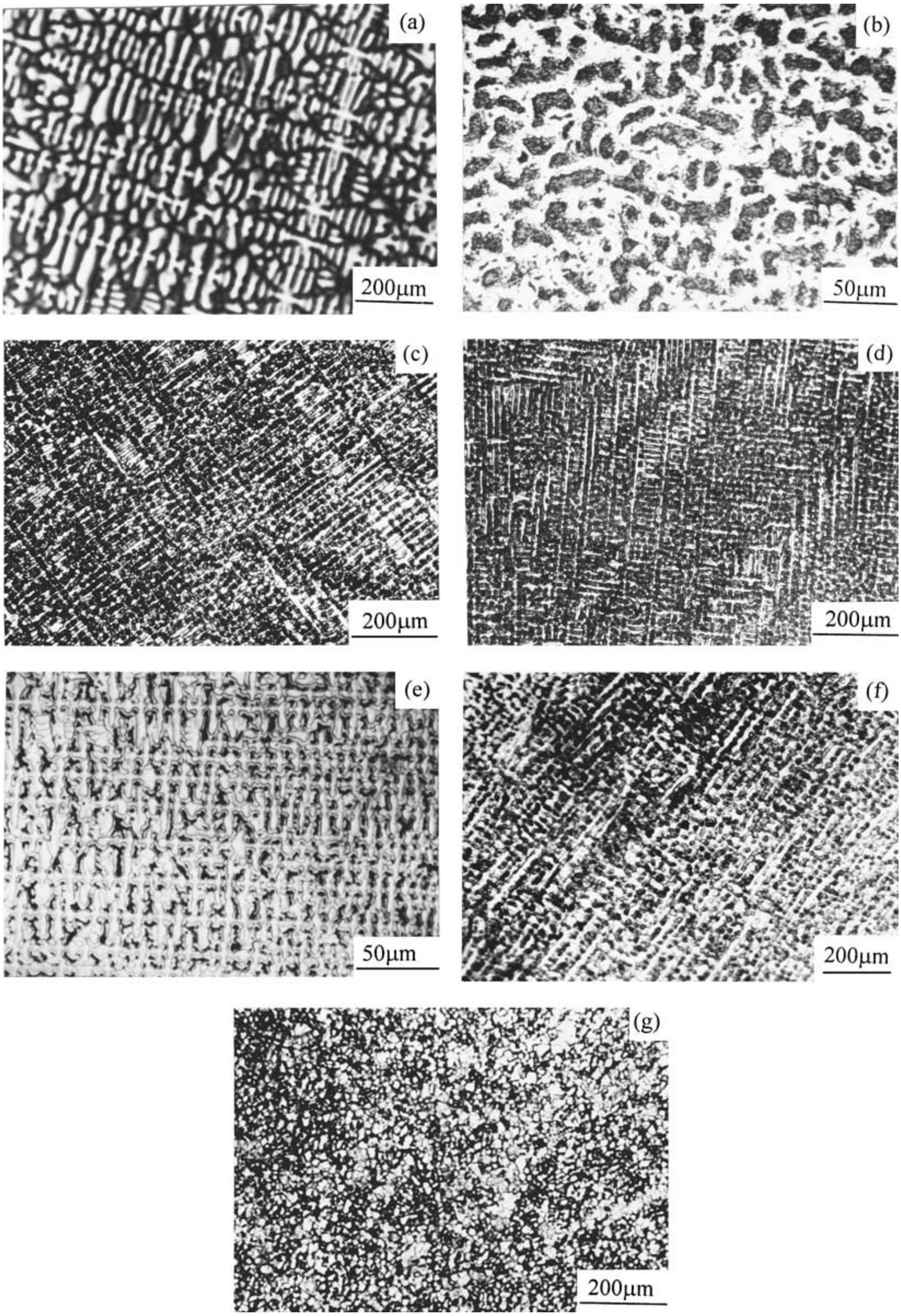

Figure 1 Microstructure evolution of DD3 superalloy with melt undercooling: (a) $\Delta T = 20$ K, (b) $\Delta T = 45$ K, (c) $\Delta T = 80$ K, (d) $\Delta T = 110$ K, (e) $\Delta T = 130$ K, (f) $\Delta T = 145$ K, (g) $\Delta T = 250$ K.

becomes strong with increasing undercooling. Solute diffusion is consequently substituted by thermal diffusion to control the dendrite growth, resulting in a transition from the equilibrium solidification by the solute gradient to a thermally controlled growth by a relaxation of diffusional equilibrium at the solid-liquid interface. With increasing undercooling, dendrite will be finer and finer, i.e. the resultant primary and secondary arm spacing is substantially reduced (Fig. 1e and f) and segregation can be suppressed. As illustrated in Table I, the maximum recalescence temperature, in the undercooling range of 78–150, decreases with increasing undercooling, indicating that dendrite remelting is still serious near 80 K (Fig. 1c) [12]. When on load, inter-crystalline fracture will probably happen to some remelted dendrite, thus resulting in the fracture

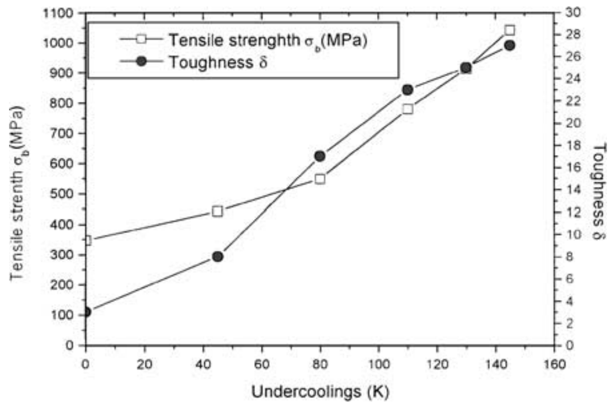

Figure 2 The tensile strength (σ_b) and toughness (δ) of DD3 superalloy solidified at different undercoolings.

of other dendrites in advance (Fig. 3c). Fig. 3 (c–f) shows the morphology of semi-tenacious or tenacious fracture mode of dendrite sample undercooled by 80 K, 110 K, 130 K, and 145 K, respectively. In connection with Fig. 1 (c–f), only after achieving a sufficient undercooling, the dendrite perfection can be maintained, thus leading to the complete plastic deformation of the primary arm spacing before fracture. As shown in Fig. 3 (e and f), large amount of slipping bands can be clearly observed in tenacious pits after serious plastic slipping, indicating that the tensile strength and toughness are substantially improved (Fig. 2).

As shown in [7], the critical undercooling for the second grain refinement in DD3 superalloy is 180 K, beyond which the equiaxed fine microstructure (Fig. 1g),

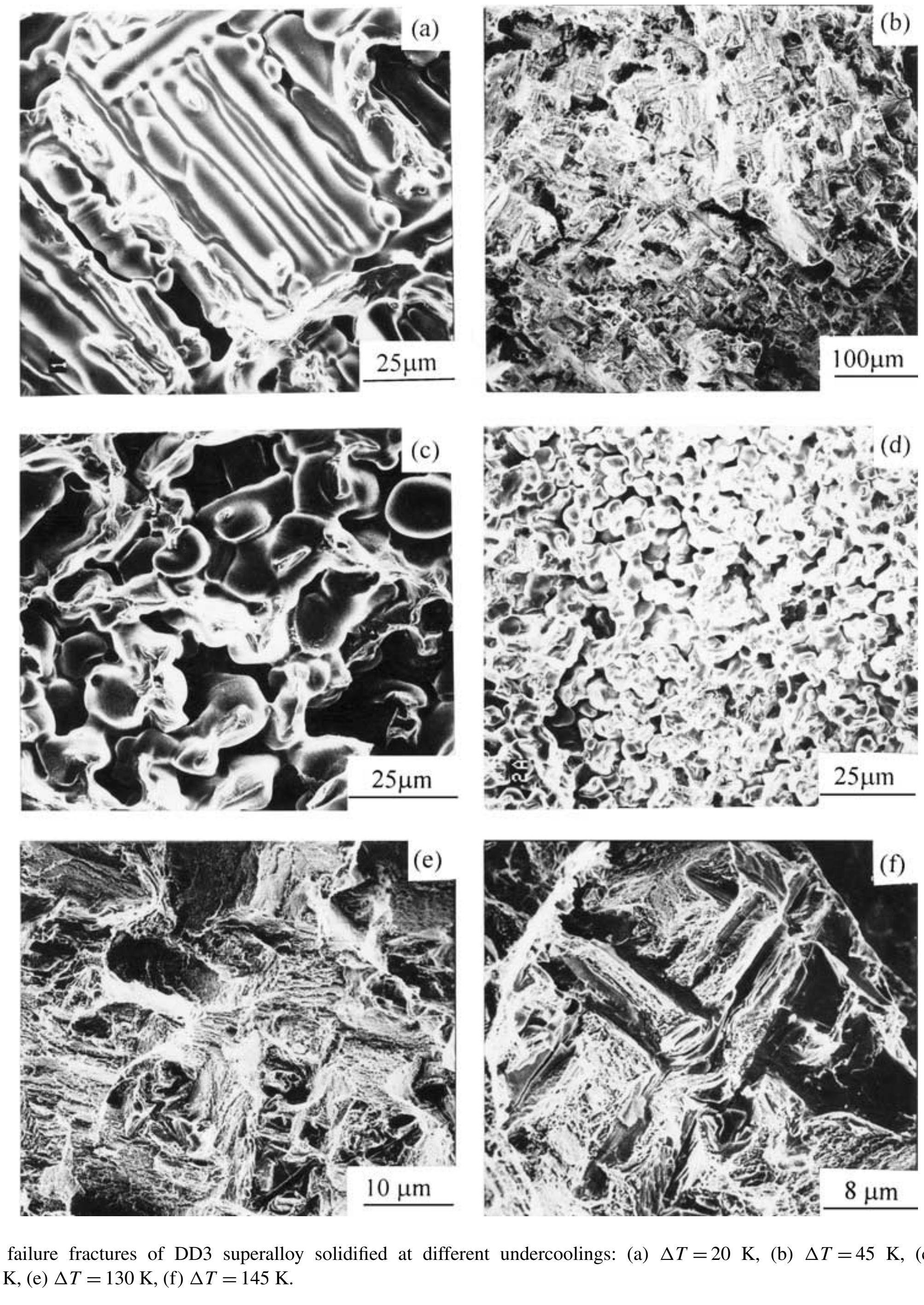

Figure 3 The failure fractures of DD3 superalloy solidified at different undercoolings: (a) $\Delta T = 20$ K, (b) $\Delta T = 45$ K, (c) $\Delta T = 80$ K, (d) $\Delta T = 110$ K, (e) $\Delta T = 130$ K, (f) $\Delta T = 145$ K.

about two magnitudes of order lower than that in usual casting, can be observed [11]. For the industrial usage of superalloy, such as turbine blades, however, the equiaxed fine microstructure is not our aim, so the corresponding investigation in the mechanical properties is omitted.

3.2. Effect of γ' precipitate on the mechanical properties

Under various solidification conditions with different melt undercooling, the typical morphology of as-solidified microstructure and γ' precipitate in the DD3 superalloy are illustrated in Figs 1 and 4, respectively. It is found that the size of typical γ' precipitate was substantially refined as the melt undercooling increases. However, the rapid solidified γ' morphology is not homogeneous, compared with heat-treated one. It is reasonable to assume the geometry of γ' precipitate to be nearly spherical from Fig. 4. After complex calculation from substantial SEM and TEM observations, the γ' size change as a function of melt undercooling was obtained, as shown in Fig. 5.

When melt undercooling reaches and surpasses the critical value (ΔT^*), the volume variation rate in rapid

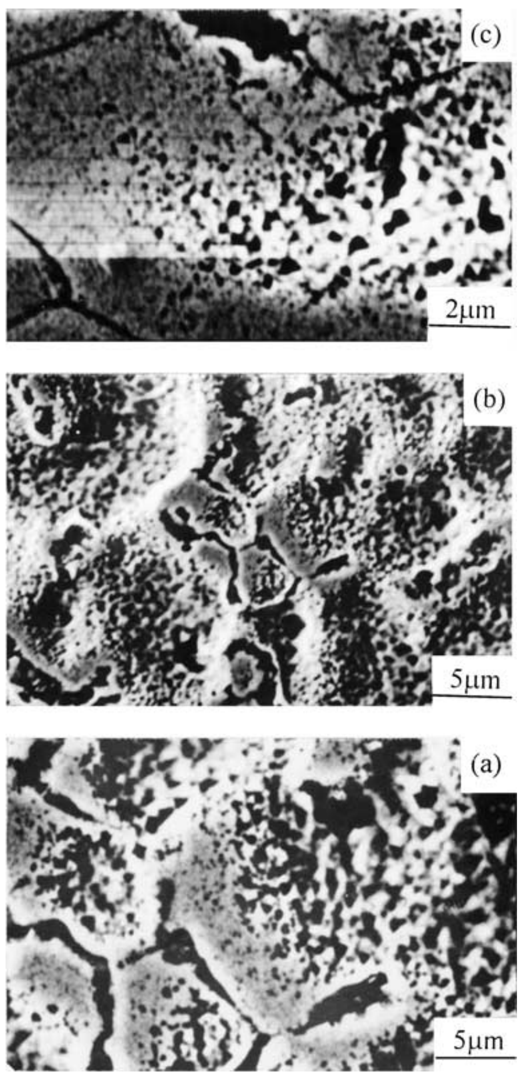

Figure 4 SEM microphotos of γ' matrix precipitation in DD3 superalloy solidified at undercooling of: (a) 45 K, (b) 125 K, and (c) 200 K, respectively.

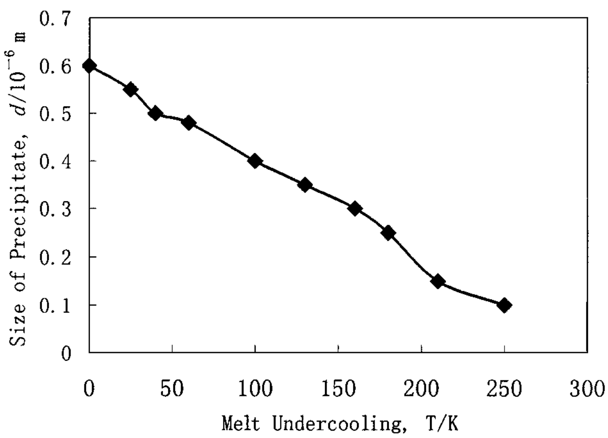

Figure 5 Variation of γ' precipitate size as a function of the melt undercooling of DD3 superalloy.

solidification becomes to 300–500 m^3/s approximately, and stress is generated by the impediment of the static liquid to the contraction of the rapidly growing dendrite. This inevitably causes solidification contraction strain energy (SCSE) to expand so that primary dendrites formed in the rapid solidification are distorted and disintegrated into subgrain or small new grain [11]. While a high density of defects such as vacancies, dislocations, and grain boundaries or sub-boundaries are also produced (Fig. 6) [11]. The higher the undercooling, the more defects could be induced. On the other hand, the incorporation of the various alloying elements into the crystal lattice must cause solute trapping effect [14] at high undercooling. Consequently, the formation of large magnitude of crystalline defects combined with the incorporation of solute atoms will induce the deviation of atoms from their equilibrium lattice sites (lattice distortion). Both the lattice distortion energy (LDE) and the SCSE can be temporarily stored in the aforementioned distorted dendrite fragments. This indicates that the distorted fragments must be in a "state of unstable condition". The existence of these non-equilibrium defects is beneficial to the nucleation of γ' precipitate on these defects owing to the reduced critical work ΔG^* [15]. So the γ' nucleation rate increases substantially with melt undercooling. Furthermore, effective solute trapping in the solid leads to a break-through of the terminal solid solubility of additions (for example, Al, Ti) in rapid solidified structure. This provides higher volume fractions of γ' precipitate in γ matrix. Accordingly, γ' precipitate is progressively refined with melt undercooling (Figs 4 and 5). If we define the ratio between the maximum solute content in the grain boundary and the minimum one in the inner-grain as segregation rate (S), Fig. 7 provides the corresponding value of S with undercooling, by using EPMA technique. In connection with Figs 1 and 4, we can find that the resultant secondary arm spacing is often less than 25 μm and, in the extreme, segregation can totally be suppressed. In the meantime, the composition difference between dendritic arm and inter-dendritic section, or between inner grain and grain boundaries is hencely 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

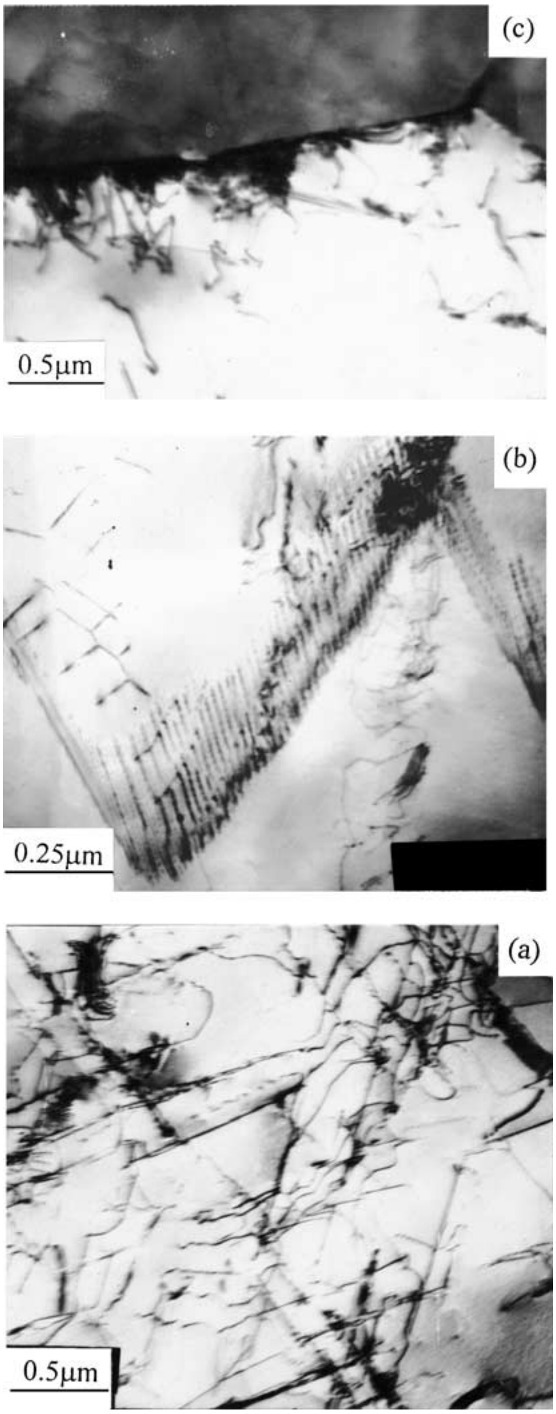

Figure 6 TEM microscopy of formation of dislocation at (a) inner grain, (b) sub-boundary, and (c) grain boundary in DD3 superalloy.

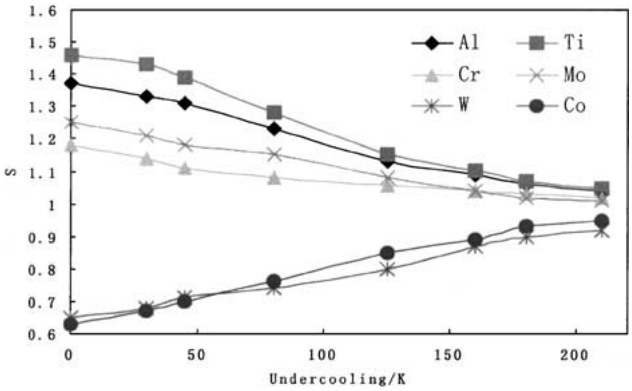

Figure 7 Variation of segregation ratio of alloying elements with undercooling.

cube in the inter-dendritic section or at grain boundaries (Fig. 4).

Now, we should focus on the contribution of γ' precipitate to the mechanical properties of the superalloy. From Fig. 2, the tensile strength and toughness of DD3 superalloy are significantly heightened with undercooling. Besides the microstructure difference as abovementioned, this may be also attributed to the following reasons. Firstly, such high resistance to plastic deformation may arise from the higher volume fraction of γ' precipitate due to the high contents of γ' phase forming elements, Al, Ti and Mo in highly undercooled solidification. Secondly, the relatively low misfit between γ and γ' phases owing to existence of defects and the entering of more high-melting-point elements, W and Mo, into γ' phase during rapid solidification makes γ' precipitates more stable when on load. Thirdly, the resistance to dislocation shearing and climb during loading mainly depends on the distribution of γ' precipitates. It is considered that the refinement and homogeneous distribution of γ' precipitates originating from rapid solidification will prevent or retard the climb of dislocation and force some mobile dislocation to have to cut γ' particles or γ/γ' interface, which need higher applied stress, and therefore provides higher resistance to dislocation motion.

4. Conclusions

The mechanical properties of the DD3 superalloy solidified at various undercoolings were measured, indicating that the alloy solidified at a rather low undercooling is brittle, thus leading to lower tensile strength and toughness. With increasing undercooling, however, the size, volume fraction and distribution of γ' precipitate in as-solidified DD3 superalloy is refined, increased, and homogenized, respectively. In connection with the refined microstructure and the reduced or suppressed microsegregation, the tensile strength and the toughness of DD3 superalloy are hencely improved.

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