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Directional solidification of monocrystal superalloy by electron beam floating zone-melting

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With the development of the aircraft engine, the monocrystal superalloy with homogeneous microstructure, low segregation and high purity is desired. This can be achieved by increasing the cooling rate under high vacuum condition to obtain the dendritic microstructure with superfine primary arm spacing. Using the electron beam floating zone-melting (EBFZ) technique, the single crystals of DD3 superalloy, having alternately planar, cellular and dendritic S/L interface, have been prepared by the seed crystal method in this paper. The misorientation between the single crystal's [100] crystallographic direction and the crystal growth direction is less than 10°. The interface morphology evolution is investigated. It can be seen that, when the zone melting rate is 100 μm/s, the primary dendrite arm spacing is five times smaller than that of the original seed. Meanwhile, the γ' phase and the γ/γ' eutectic are all fined and the microsegregation of the alloy elements decreased. The technical experiments show that, with carefully regulating the heating power and the zone melting rate, the melting zone can be kept stable. When the zone melting rate is small, the heating power can be increased in order to increase the temperature gradient. Whereas, when the zone melting rate is large, the heating power must be decreased in order to keep the growth processing steady.

1. Introduction

Since PWA 1480 monocrystal superalloy was used for the high-pressure turbine blade of PWA2037 aircraft engine in 1982, the R&D of the monocrystal superalloy gets into a flourishing stage. Now the monocrystal superalloy with homogeneous microstructure, low segregation and high purity is desired in order to upgrade the comprehensive property. This can be achieved by improving the solidification and heat-treatment techniques. An extremely effective way is to increase the cooling rate under high vacuum condition during the directional solidification to obtain the dendritic microstructure with superfine primary arm spacing. Thus it is very important to increase the temperature gradient especially the liquidus thermal gradient just before the S/L interface. It is also very important to adopt high-vacuum melting technology eliminating the impurity and gas in the alloy to the utmost.

The monocrystal preparation methods can be classified into two kinds according to the form of the melting zone, i.e., the normal method including the Bridgman and the Czochralski method, and the zone-melting method including the horizontal and the floating zone-melting method. The electron beam floating zone-melting (EBFZ) technique was first proposed by Calverkey *et al.* [1, 2] in 1956. Since then, this technique has mainly been successfully applied to the purification and the single crystal growth of the refractory and the reactive metals (or alloys), such as W, Mo, Ta, Nb and their alloys [3, 4]. It has the following advantages: (1) The energy density of the electron beam is ten thousand times as high as that of the electric arc. (2) Because of the crucibleless and high-vacuum ($\sim 10^{-6}$ mbar) melting, the metal melt gets very high purity. (3) The melting zone is so narrow that the temperature gradient in front of the S/L interface can be very large. Glebovsky [5] gave out that the temperature gradient in front of the S/L interface was 1450 K/cm during the single crystal growth of W by this method. (4) The solidification processing can be easily and precisely controlled by adjusting the state of the electron beam, for example, the strength, the moving rate and the focus state. Today, as the electron beam cold hearth remelting (EBCHR) technique has become the best method for melting the superalloy, it is believed that the EBFZ technique is more suitable for the monocrystal superalloy [6].

In this paper, the monocrystal superalloy with different solidification microstructure is prepared by the EBFZ technique. The technical parameters and their relationship with the microstructure morphology are investigated. The distribution of the γ' and the eutectic,

TABLE I Nominal alloy composition of DD3 (wt %)

C	Cr	Co	W	Mo	Al	Ti	Ni	B	Zr
0.006	9.5	5	5.2	4.2	5.7	2.3	Bal.	Trace	<0.005

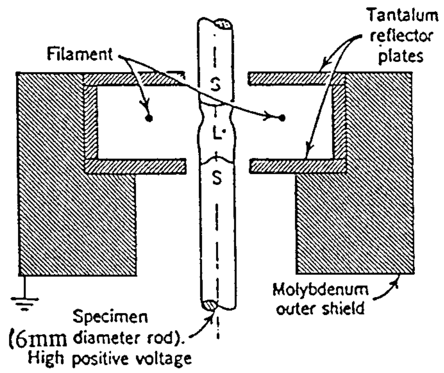

Figure 1 Schematic diagram of monocrystal growth by electron beam floating zone-melting.

the segregation of the alloy elements, and the crystallographic misorientation of the single crystal are studied.

2. Experiment

In this paper, the ESZ1.5/5 electron beam floating zone-melting furnace is used to prepare the single crystal of DD3 superalloy by the seed method. DD3 is the first generation of Chinese monocrystal superalloy series, which has equivalent mechanical property to that of PWA1480, CMSX-2 and SRR99. Its solidus temperature is 1325 °C and the liquidus temperature is 1370 °C. The nominal alloy composition is shown as Table I.

The sample is $\phi 6 \times 100$ mm. The seed is $\phi 7 \times 20$ mm and its crystallographic orientation is [100]. The seed is put below the sample and partially remelted to initiate the crystal growth. With the electron gun, consisting of the cathode filament and the focussing system, moving upward, the sample is zone-melted and directionally solidified. The principle of the experiment is shown as Fig. 1. In this paper, the zone-melting rate varies between 0.1–6.0 mm/min, the vacuum in the chamber is 5×10^{-6} mbar, and the heating power lies in $90 \sim 110$ W. The S/L interface is obtained by means of shutting down the cathode current suddenly. The sample is etched with the corrodent consisting of HCl and $FeCl_3$. The morphology evolution is observed with NEOPHOT-1 and Quaintmet 500 metaloscopes and AMRAY100B SEM. The segregation of the element is measured with SX-macro electron probe. The orientation of the single crystal is determined with D/max-3c X-ray diffractometer.

3. Result and discussion

3.1. Technical research

To ensure the success of single crystal growth by the EBFZ technique, the melting zone must be kept stable during the directional solidification processing. The length of the melting zone is determined by the strength and the section size of the focused electron beam. In our experiment, the diameter of the DD3 sample is fixed, so the section size of the focused electron beam is decided with the focussing system unchanged. Therefore, the length of the melting zone depends upon the heating power and the zone-melting rate. The experiment result shows that the length of the melting zone increases with the increase of the heating power and the zone-melting rate. Thus, it is very important to give coordination of the heating power and the zone-melting rate.

It is also found that along with the experiment progressing, the length of the melting zone increases and the necking phenomenon becomes serious even though the heating power and the zone-melting rate remain unchanged. The reason is that as the length and temperature of the solidified crystal continuously increase, the temperature gradient in the solidified crystal decreases but the heat-conduction passage lengthens. If the heating power is unchanged, the solidification rate R becomes smaller than the zone-melting rate and the melting zone becomes longer and longer. At this time, in order to maintain the crystal growth stable, the heating power must be reduced to shorten the melting zone. On the other hand, the critical length of the stable melting zone is directly proportional to the square root of the ratio of the surface tension γ to the density ρ of the molten sample [2], namely $(\gamma/\rho)^{1/2}$. Therefore, properly reducing the heating power can reduce the superheating of the molten sample and raise its surface tension, which is helpful to eliminate the necking phenomenon.

3.2. Interface morphology and microstructure evolution

As the solidification character of superalloy can be described by the model of the single phase alloy crystalline system [7], the morphology of the solidified subunit, namely the usually called S/L interface, is determined by the constitutional supercooling. Thus, for a definite superalloy, the S/L interface morphology is mainly determined by the cooling rate, which is the product of the solidification rate R and the temperature gradient G_L in the liquid phase just in front of the S/L interface. Meanwhile, the primary dendritic arm spacing λ_1 is also decided by the cooling rate. Since the zone-melting rate and the solidification rate under steady state growth are approximately equal, namely the moving rate of the electron gun, the experimental result shows that: when $R < 0.3$ mm/min (5.0 μm/s), the S/L interface is planar; when $R = 0.3$–0.5 mm/min (5.0–8.3 μm/s), the S/L interface is cellular; and when $R > 0.5$ mm/min (8.3 μm/s), the S/L interface becomes dendritic. With the zone-melting rate further increasing, the primary dendritic arm spacing gradually decreases. The interface morphology and the microstructure evolution is shown as Fig. 2 and Table II. It can be seen that the primary dendritic arm spacing of the single crystal with fine dendrite is over five times smaller than that of the seed, which shows the feasibility and potential of preparing the monocrystal superalloy with the superfine microstructure by the EBFZ technique.

Since the electron beam has very high energy density, the floating melting-zone can be kept stable under high temperature gradient with carefully imposing the heating power and the moving rate of the electron

TABLE II Relationship between zone-melting rate and primary dendritic arm spacing

Zone-melting rate (mm/min)	Seed	0.1	0.3	0.5	1.0	3.0	4.0	5.0	6.0
Interface morphology	Coarse dendrite	Plan	Cell	Cell-dendrite	Coarse dendrite	Dendrite	Dendrite	Dendrite	Fine dendrite
Primary dendritic arm spacing (μm)	500		207	164	197	169	154	139	94

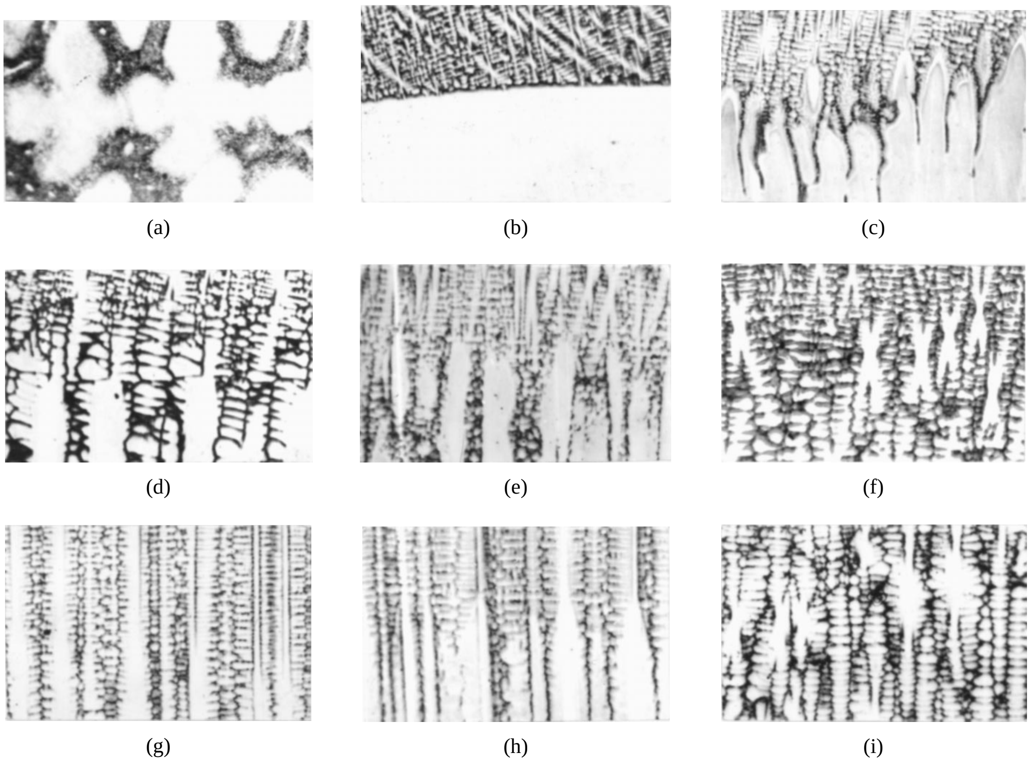

Figure 2 Interface morphology and microstructure evolution with different zone-melting rate: (a) seed, (b) $R = 0.1$ mm/min, (c) $R = 0.3$ mm/min, (d) $R = 0.5$ mm/min, (e) $R = 1.0$ mm/min, (f) $R = 3.0$ mm/min, (g) $R = 4.0$ mm/min, (h) $R = 5.0$ mm/min, (i) $R = 6.0$ mm/min.

gun during the experiment processing. With the heating power unchanged, the temperature gradient G_L is constant. The theoretical calculation and the experimental research [8] show that G_L is about 460 K/cm during the stable growth of DD3 by the EBFZ method. Therefore, with the increase of the moving rate of the electron gun, the cooling rate increases and the S/L interface morphology evolves from plan to cell and then to dendrite. According to Kurz and Fisher [9], $\lambda_1 \propto R^{-1/4} G_L^{-1/2}$, which means that the primary dendritic arm spacing decreases with the increase of the moving rate of the electron gun.

3.3. Growth pattern of γ' phase

Generally speaking, monocrystal superalloy can be considered as a dual-phase system consisting of γ and γ' phases. γ' phase is the main precipitation-strengthening phase, which precipitates during the cooling processing after the solidification of γ solid solution. The growth pattern including the morphology and distribution of γ' phase depends to a large extent on the solidification condition. Fig. 3 shows the morphology of γ' phase in different areas of the single crystal solidified under different zone-melting rate. Fig. 4 gives out the relationship between the size of γ' phase and the zone-melting rate.

It can be seen that: γ' phase in the planar interface monocrystal is coarse and irregular; in the cellular or dendritic interface monocrystal, γ' phase in the cell or dendrite trunk is smaller than that in the inter-cell or inter-dendrite area. Meanwhile, γ' phase is relatively regular cubic and round in the cell or dendrite trunk, but is much irregular in the inter-cell or inter-dendrite area. With the increase of the solidification rate, γ' phase is fined accompaning the dendrite fining.

The formation of γ' phase is a kind of solid phase transformation. The driving force of the transformation is proportional to the supercooling degree and the supersaturation degree of the solid solution [10]. With the increase of the solidification rate, the phase transformation driving force increases due to the growing supercooling degree, which leads to the raise of nucleation rate. In the meantime, as the local solidification time is shortened, the γ' nucleus has not enough time to grow up. Thus, a lot of fine γ' phase is observed in the solidified microstructure. On the other hand, due to the microsegregation, the γ' phase formation elements such as Al and Ti are enriched in the inter-cell or inter-dendrite area, which raises the supersaturation degree in the inter-cell or inter-dendrite area. Therefore, the phase transformation driving force and the phase growth driving force increase. This leads to the result

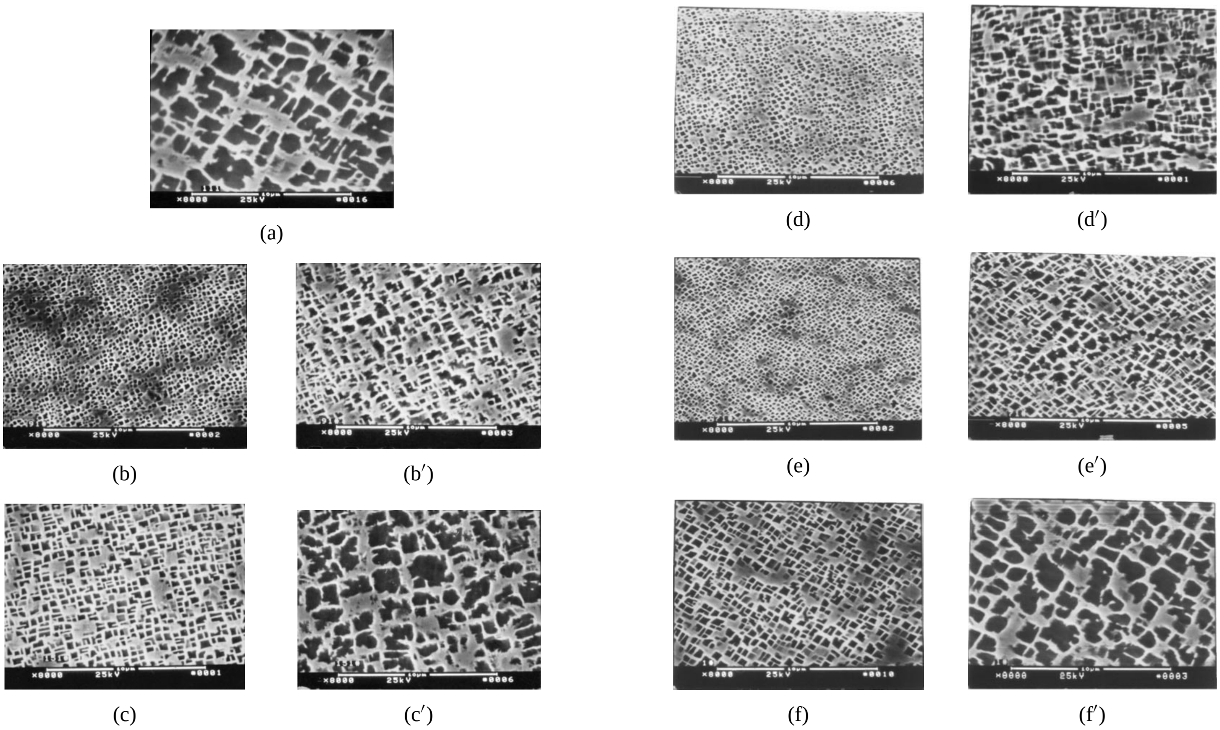

Figure 3 γ' Phase morphology under different zone-melting rate: (a) $R = 0.2$ mm/min, (b, b′) $R = 0.3$ mm/min, (c, c′) $R = 1.0$ mm/min, (d, d′) $R = 4.0$ mm/min, (e, e′) $R = 6.0$ mm/min, (f, f′) seed.

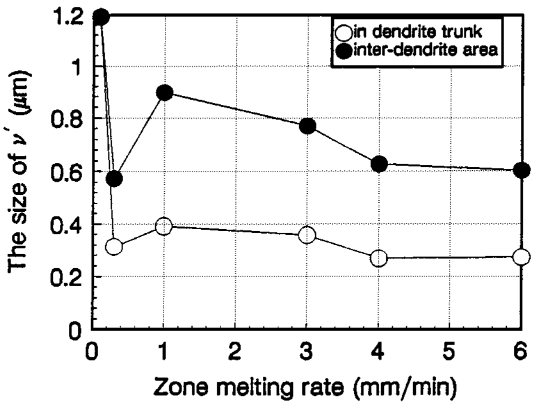

Figure 4 Relationship between γ' phase size and zone-melting rate.

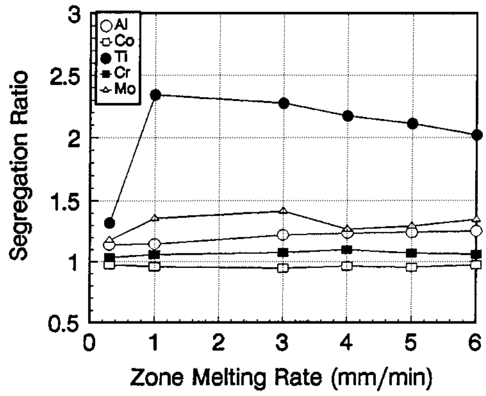

Figure 5 Relationship between segregation ratio and zone-melting rate.

that γ' phase in the cell or dendrite trunk is smaller than that in the inter-cell or inter-dendrite area.

3.4. Alloy element microsegregation and γ/γ' eutectic

The solute redistribution during solidification brings about the alloy element microsegregation, while the solute diffussion reduces the segregation. Due to the alloy element segregation, γ/γ' eutectic is formed in the inter-cell or inter-dendrite area. Fig. 5 shows the relationship between the segregation ratio and the zone-melting rate. Fig. 6 gives out the relationship between the γ/γ' eutectic size and the zone-melting rate. It can be seen that Al, Ti, Mo and Cr are enriched in the inter-cell or inter-dendrite areas, but W and Co are enriched in the cell or dendrite trunks. It can also be seen that the segregation ratios of the alloy elements are all near the unity owing to the high temperature gradient. Meanwhile, the γ/γ' eutectic size decreases with the increased zone-melting rate. This is helpful to raise the solution-treament temperature and rate for upgrading the mechanical property of the monocrystal superalloy.

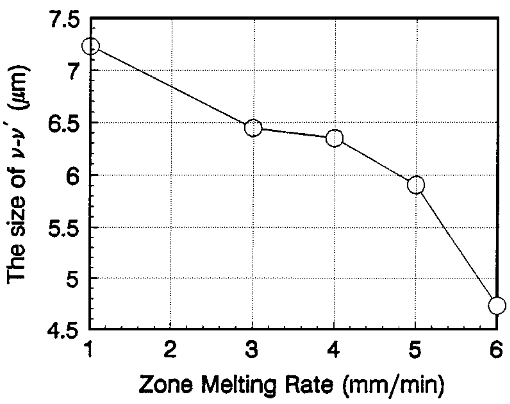

Figure 6 Relationship between γ/γ' eutectic size and zone-melting rate.

3.5. Crystal orientation

During the directional solidification of the monocrystal superalloy, many cellular or dendritic subunit grows up simultaneously. According to Duhl [11], there is very little misorientation between the different subunits,

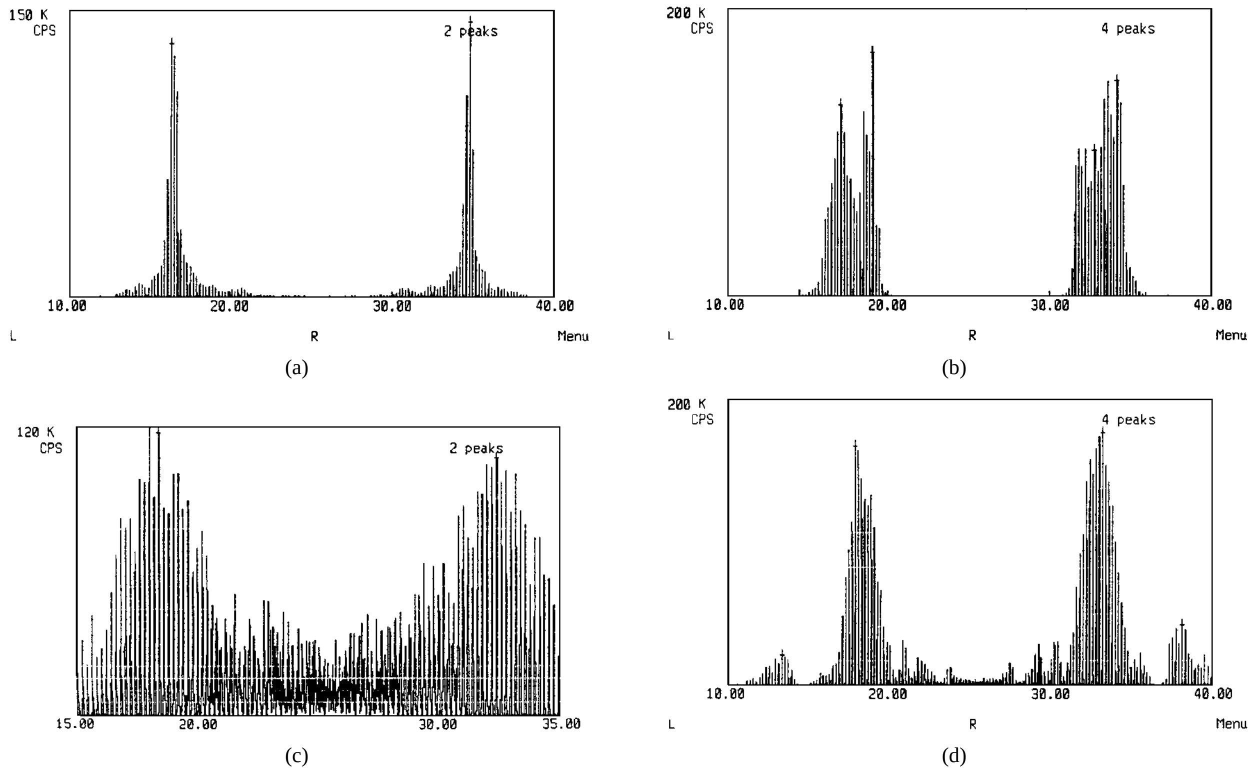

Figure 7 X-ray diffraction curve of DD3 monocrystal superalloy with different microstruture: (a) planar, (b) cellular, (c) coarse dendrite, (d) fine dendrite.

which is 1°–2°, so the monocrystal superalloy can be regarded as a kind of quasi-single crystal consisting of many subunits with very little misorientation. Thus there is deviation between the crystal orientation (i.e., the sample axial direction) and the prior growth direction, namely the crystal misorientation. The prior growth direction of DD3 monocrystal superalloy is [100]. It is shown [12, 13] that for DD3 monocrystal superalloy, the crystal misorientation should be controlled within 10° in order to obtain the excellent high-temperature property. From Fig. 7 which shows the X-ray diffraction curve of DD3 monocrystal superalloy with different microstruture, it can be seen that the crystal misorientations of all the samples prepared by the EBFZ method are smaller than 10°.

4. Conclusion

(1) Using the electron beam floating zone-melting technique, the single crystals of DD3 superalloy, having alternately planar, cellular and dendritic S/L interface, have been prepared by the seed crystal method. The misorientation between the single crystal's [100] crystallographic direction and the crystal growth direction is less than 10°.

(2) When the zone melting rate is 100 μm/s, the primary dendrite arm spacing of the single crystal superalloy is five times smaller than that of the original seed. Meanwhile, with the increase of the zone melting rate, the γ' phase and the γ/γ' eutectic are all fined and the microsegregation of the alloy elements decreased.

(3) With carefully regulating the heating power and the zone melting rate, the melting zone can be kept stable. When the zone melting rate is small, the heating power can be increased in order to increase the temperature gradient. Whereas, when the zone melting rate is large, the heating power must be decreased in order to keep the growth processing steady.

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