[Article ID] 1003 - 6326(2000)04 - 0430 - 05

Isothermal solidification behavior of typical Ni_3Al base superalloy IC6 ①

WANG Xiao-ping(汪小平), ZHENG Yun-rong(郑运荣), XIAO Cheng-bo(肖程波), WANG Bei-lei(王蓓蕾), HAN Ya-fang(韩雅芳)
(Beijing Institute of Aeronautical Materials, Beijing 100095, P.R.China)

[Abstract] Solidification sequence of a typical Ni_3Al base superalloy IC6 was studied by isothermal solidification method. The results show that the liquidus, solidus, melting point of the boride and secondary γ' precipitation temperature of the IC6 alloy are notably higher than those of conventional nickel base superalloys because of its higher Mo content. There is no eutectic γ' precipitation during the solidification of the alloy, but a kind of Mo-rich δ-$Ni_{0.76}Mo_{1.24}$ primary phase precipitates together with γ phase by eutectic reaction $L' \rightarrow \delta + \gamma + L''$ in the temperature range of 1 573 ~ 1 553 K, this δ-$Ni_{0.76}Mo_{1.24}$ phase has a primitive orthorhombic structure with a = 0.9178 nm, b = 0.9142 nm and c = 0.8828 nm. Moreover, Al element of the alloy segregates in dendritic areas during isothermal solidification process, which causes secondary γ' phase precipitate in the order of precedence from dendrites to interdendrites.

[Key words] Ni_3Al base superalloys; solidification process; microstructures; δ-$Ni_{0.76}Mo_{1.24}$ phase
[CLC number] 132.3$^+$2 **[Document code]** A

1 INTRODUCTION

In recent years, many studies have been carried out focusing on the solidification process and liquid phase transformation of casting nickel base superalloys[1~8]. These investigations are of great value in understanding the solidification sequence of the alloys, explaining the effects of trace element and assessing the castability of the casting nickel base superalloys.

Ni-Al-Mo-B system directional solidification (DS) Ni_3Al base alloy IC6 is a new type of γ'-Ni_3Al based superalloy, it shows better mechanical properties than most of the present commercial Ni and Ni_3Al base DS cast superalloys at higher temperatures[9,10]. In this article, the solidification sequence and solidification transformation of a typical IC6 alloy are determined by isothermal solidification method.

2 EXPERIMENTAL

The nominal composition of IC6 alloy is Ni-(13.5 ~ 15.0) Mo-(7.4 ~ 8.5) Al-(0.02 ~ 0.10) B (mass fraction, %). The chemical composition of IC6 alloy used in this article is Ni-14.0 Mo-7.9 Al-0.04B (mass fraction, %). The isothermal solidification experiments were carried out as follows: the as-cast specimens were first plastered with alumina grit adhered by silica gel, then were embedded in the drilling holes of graphitic blocks. After desiccation, they were heat-treated in the high-temperature furnace with silicon-carbide heating element. When the specimens were heat-treated, they were all first heated up to the temperature of 20 ~ 30 ℃ above the liquidus of IC6 alloy, and kept 10 min for melting, then they were cooled down to the isothermal solidification temperature, staying for 15 min followed by water quenching.

Pure Pt was selected as the reference specimen of DTA experiments, and the rates of raising or lowering temperature were controlled at 10 ℃/min. The microstructures and phase transformation of the specimens after isothermal solidification at different temperatures were analyzed by means of optical microscopy, SEM, EDX, EPMA, TEM and X-ray diffraction methods, whereas, the volume fraction of residual liquids at each temperature were measured by area measurement method under quantitative optical microscope.

3 RESULTS AND DISCUSSION

3.1 As-cast microstructure

Three phases of γ'-$Ni_3(Al, Mo)$, γ and boride-Mo_2NiB_2 exist in the alloy, as typically shown in Fig. 1. It reveals that the as-cast microstructure of the alloy mainly consists of two different areas of $\gamma + \gamma'$, fine γ' precipitates (about 0.3 μm) in interdendritic area A, and coarse γ' precipitates in dendritic area B, combined with some boride and eutectic single γ' phase in interdendritic areas. The quantitative image measurement showed that the total volume fraction of γ' phase was about 80 % ~ 85 % in this alloy.

3.2 DTA analysis

DTA analysis of the as-cast alloy in Fig.2

① [Received date] 1999 - 07 - 19; [Accepted date] 1999 - 11 - 14

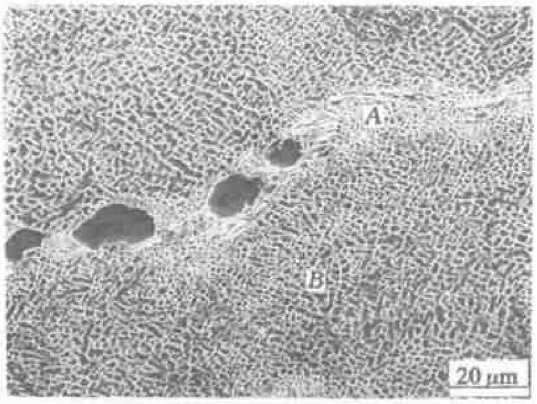

Fig.1 Typical microstructure of IC6 alloy(as-cast)

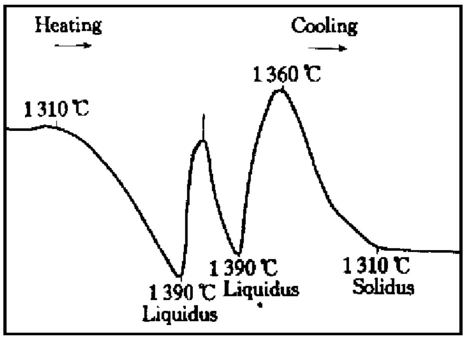

Fig.2 DTA curve of IC6 alloy

showed that the liquidus and solidus of the alloy were about 1 390 ℃ and 1 310 ℃ respectively, and most of the primary grains formed at the temperature about 1 360 ℃. Although there existed certain amount of eutectic phases and borides in the alloy, no corresponding melting or solidification peaks were observed in the DTA curve, and this may be attributed to the relatively less amount of γ' phase and borides in the alloy.

3.3 Isothermal solidification analysis

The alloy was as-liquid when it was heated to 1 390 ℃, but primary γ phase with volume fraction of about 62 % formed during isothermal solidification at 1 380 ℃, as shown in Fig.3(a). The content of primary γ phase increased greatly and that of the residual liquids in interdendrites of the alloy decreased quickly with decreasing of temperature, for example, the content of residual liquids in interdendrites measured about 14.9 %, 9.7 % and 6.8 % (volume fraction) when the alloy solidified at 1 370 ℃, 1 360 ℃ and 1 340 ℃, respectively. As a result, less and less residual liquids were contained in interdendritic areas of the alloy with decreasing of temperature, and the liquid-supplement between interdendrites gradually became more and more difficult. Fig.3(b) showed the optical micrograph of the alloy after solidification at 1 320 ℃, it can be seen that most of the interdendritic residual liquids of the alloy were isolated at this temperature, and whose the volume fraction was about 3.9 %.

When the alloy was thermally solidified at 1 300 ℃, a kind of irregular, strip or block like white phases precipitated near the interdendritic residual liquid pools, as typically shown by the arrow in Fig.4 (a). Besides, the optical micrograph of the alloy after isothermal solidification at 1 280 ℃ is shown in Fig.4 (b), which indicates that large amount of these white phases were precipitated at this temperature, and it can be estimated from this figure that the size of these white phases is about 3 ~ 8 μm.

Chemical composition of these white phases was determined by EPMA, the results show that the white phases are Ni-Mo phases, that is, it only contained Ni and Mo elements, whereas no Al or B element exists in these phases, and the exact chemical composition of these phases is about 38 %Ni and 62 % Mo(mole fraction). Further studies from X-ray powder diffraction spectrum of the specimen after solidifi-

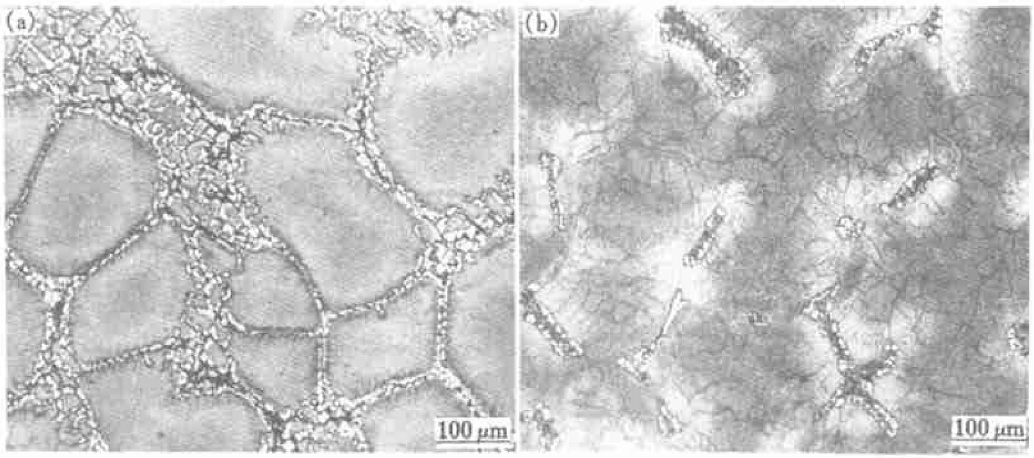

Fig.3 Microstructures of IC6 alloy after isothermal solidification
(a) —1 380 ℃; (b) —1 320 ℃

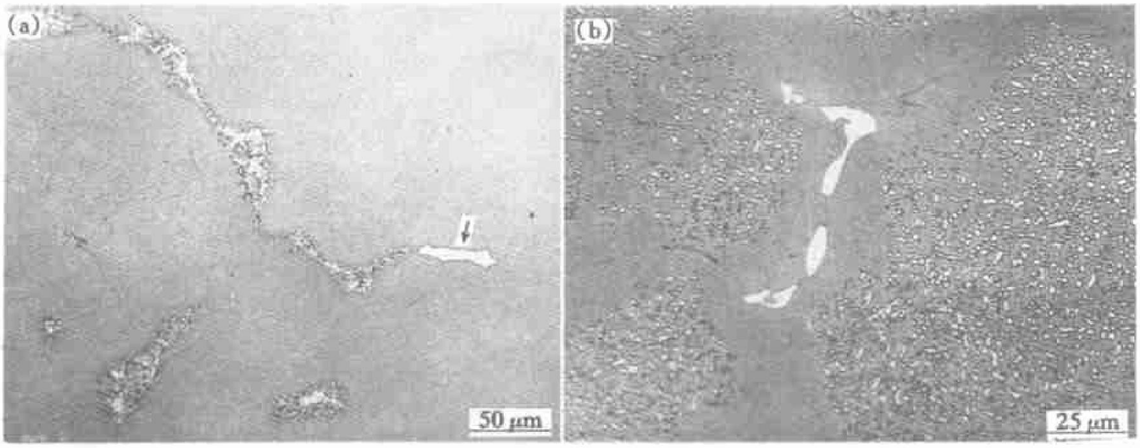

Fig.4 Morphologies of primary δ $Ni_{0.76}Mo_{1.24}$ phases precipitated during isothermal solidification
(a) —1 300 ℃; (b) —1 280 ℃

cation at 1 280 ℃ suggested that there exists a kind of δ $Ni_{0.76}Mo_{1.24}$ phase in the alloy, which has a primitive orthorhombic structure with $a = 0.9178$ nm, $b = 0.9142$ nm, $c = 0.8828$ nm, as shown in Fig.5. Besides, the thin foils of the specimen after solidification at 1 280 ℃ were also examined by TEM. The selected-area electron diffraction patterns of these Ni-Mo phases are shown in Fig.6, which confirmed that these phases are δ $Ni_{0.76}Mo_{1.24}$ phases. Therefore, combined with the results by EPMA, X-ray powder diffraction spectrum and the Ni-Mo binary phase diagram, it can be concluded that these white phases are δ $Ni_{0.76}Mo_{1.24}$ phases, and they are precipitated by the eutectic reaction of $L' \rightarrow \delta + \gamma + L''$, where L', L'' represent the residual liquids before and after the reaction respectively.

When the alloy solidified at 1 260 ℃, it was found that a large amount of borides (Mo_2NiB_2 phases) precipitated at the interdendrites of the alloy, as shown in Fig.7. Simultaneously, the residual liquids in the alloy decreased quickly with the precipitation of these borides, and its volume fraction is about 0.1%. It can be determined from Fig.4(b) and Fig.7 that a large amount of secondary γ' phases precipitated at 1 280 ℃ and 1 260 ℃ respectively. The precipitation order of secondary γ' phases is from dendrites to interdendrites, which is opposite to that of most commercial nickel base superalloys. It can be explained by the negative-segregation of Al element of the alloy.

Average chemical compositions at both dendrites and interdendrites of the as-cast alloy and the alloys after isothermal solidification at 1 380 ℃ and 1 320 ℃ are listed in Table 1. It shows that Mo element in the alloy tends to segregate at the interdendrites during the solidification process, while Al element segregates at the dendrites due to the higher Mo content in the alloy. Similar results have also been obtained in former researches[1~4], it has been found that the Al element in nickel base superalloy often segregates at interdendritic regions of the alloy, as well as Mo element. On the contrary, when the alloy enriches in Mo or Cr element, the Al element usually segregates in the dendritic areas.

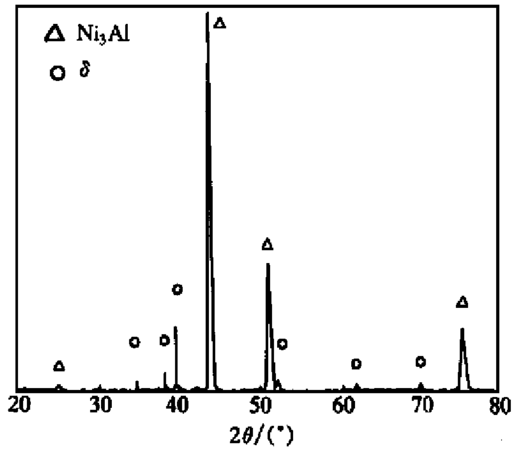

Fig.5 X-ray diffraction spectrum of specimen solidified at 1 280 ℃

Further studies of the relationship between average Al, Mo contents in interdendritic residual liquids of the alloy and the isothermal solidification temperature have also been shown in Fig.8. It shows that the average Mo content in the residual liquids increases with decreasing of the isothermal solidification temperature, while the average Al content of the residual liquids decreases with decreasing of thermal temperature. This confirms that the Mo, Al segregation extent of the alloy gradually increase with decreasing of temperature during the solidification process. When the heat treatment temperature is dropped down to about 1 300 ℃, the Mo, Al contents in residual liquids attain its summit and bottom respectively. As a result, the residual liquids at this temperature contain a large amounts of Mo, Ni, but contain less Al

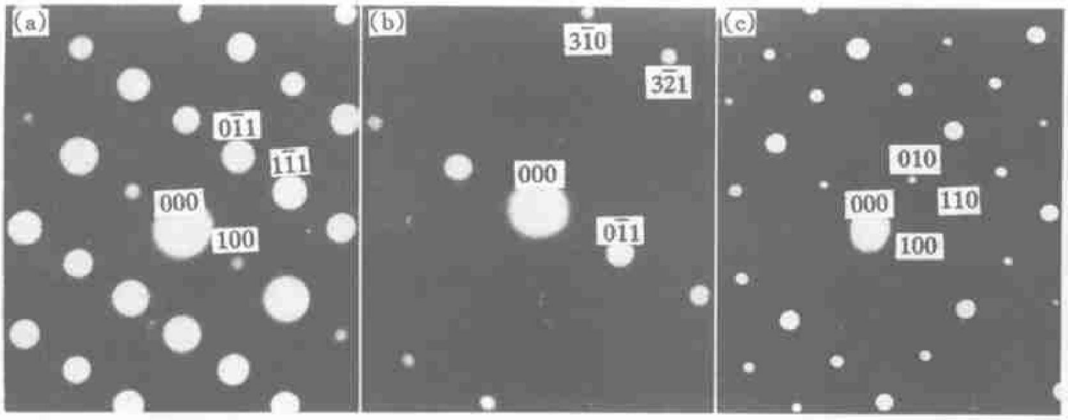

Fig.6 Selected-area electron diffraction patterns of δ $Ni_{0.76}Mo_{1.24}$ phase
(a) —$[0\bar{1}\bar{1}]$ zone axis; (b) —[133] zone axis; (c) —[001] zone axis

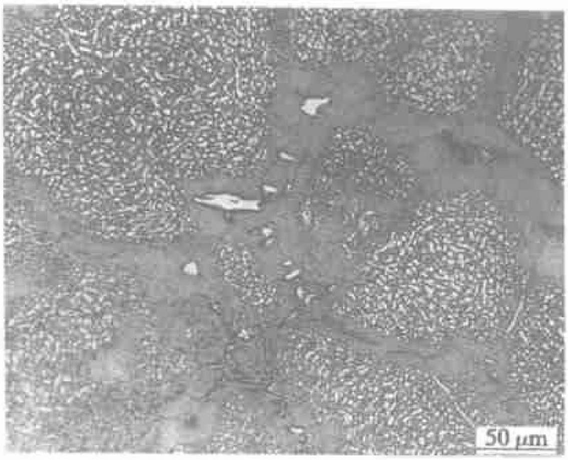

Fig.7 Morphology of Mo_2NiB_2 phases precipitated at 1 260 ℃

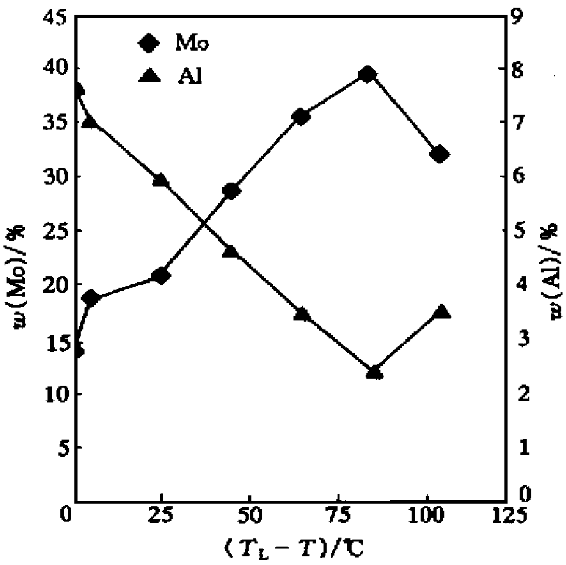

Fig.8 Composition variations of liquid pools with temperature

(about 2.4%, mass fraction), thus the primary δ $Ni_{0.76}Mo_{1.24}$ phases precipitated with the eutectic reaction of $L' \rightarrow \delta + \gamma + L''$. However, when the reaction is over, the Mo contents in the residual liquids begin to drop down whereas the Al contents begin to grow up, as shown in Fig.8.

3.4 Discussion

Unlike the as-cast microstructure of the alloy, there is no eutectic γ' precipitation during the solidification process, while there is a kind of eutectic δ $Ni_{0.76}Mo_{1.24}$ phase precipitated during the isothermal solidification process. This may be attributed to the relatively lower cooling rate of the liquids during the isothermal solidification process.

The cooling rate of liquids during isothermal solidification is about 10 ℃/min, whereas the practical cooling rate of liquids during unidirectionally solidified casting of the IC6 alloy is estimated to be about 60 ℃/min, therefore, the cooling rate of liquids during isothermal solidification is much slower than that of unidirectionally solidified casting process. In addition, the element segregation extent in nickel superalloys are believed to be related closely to the cooling rate of liquids in former studies[3~5], that is, the lower the solidification cooling rate is, the more severe the element segregation extent is.

Therefore, during the isothermal solidification process of the IC6 alloy, Mo element segregated sharply in the residual liquids of the interdendrites, while the residual liquids contain less amount of Al element, as shown in both Table 1 and Fig.7. As a result, δ $Ni_{0.76}Mo_{1.24}$ phases instead of eutectic γ' are precipitated during the isothermal solidification process.

4 CONCLUSIONS

1) The liquidus, solidus, boride (Mo_2NiB_2 phase) melting point and secondary γ' precipitation temperature of the IC6 alloy are about 1 390 ℃, 1 310 ℃, 1 270 ℃ and 1 280 ℃ respectively, which

Table 1 Micro-segregation of IC6 alloy (mass fraction, %)

Element	as-cast		1 380 ℃		1 320 ℃	
	Dendrites	Interdendrites	Dendrites	Interdendrites	Dendrites	Interdendrites
Ni	80.2	75.4	80.3	74.2	79.4	61.0
Al	8.7	7.3	8.9	7.1	9.3	3.5
Mo	11.1	17.3	10.8	18.7	11.3	35.5

are notably higher than those of most conventional nickel base superalloys due to its higher Mo content.

2) The element segregation behavior during the isothermal solidification process is that Mo strongly segregates in the interdendrites, while Al element segregates at the dendrites.

3) A kind of primary δ-$Ni_{0.76}Mo_{1.24}$ phase precipitates at a temperature range from 1 300 ℃ to 1 280 ℃ by the eutectic reaction $L' \rightarrow \delta + \gamma + L''$.

4) Secondary γ' phase of the IC6 alloy precipitates at dendrites in advance of interdendrites, which is opposite to the normal precipitation sequence of γ' phase in nickel base superalloy, and its precipitation temperature is also significantly higher than that of traditional nickel base superalloys.

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(Edited by YANG Bing)