Microstructural Instability of an Experimental Nickel-Based Single-Crystal Superalloy

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Abstract

Microstructural instability with the precipitation of topologically close-packed (TCP) phases of an experimental nickel-based single-crystal superalloy has been investigated. A significant amount of σ phases are distinguished in the interdendritic region of the as-cast samples after thermal exposure at 900 °C for 1000 h. The σ phases are preferentially precipitated at the periphery of coarse γ/γ' eutectic, and their morphological evolution from needles to granules is observed. Microstructural analysis suggests that the local segregation of Cr and Ti at the periphery of coarse γ/γ' eutectic accounts for the formation of σ phases in the as-cast samples. After heat treatment with low solution temperature and short holding time, the dendritic segregation of alloying elements (i.e., W, Re, Ti and Ta) and the volume fraction of γ' phase in the interdendritic region are similar to that of the as-cast samples. However, no TCP phases are present in the interdendritic region of the heat-treated samples after thermal exposure, which is primarily ascribed to the elimination of local segregation of Cr and Ti near the coarse γ/γ' eutectic. Moreover, small quantities of μ phases are precipitated in the secondary dendrite arm near the interdendritic region after thermal exposure, due to the increased volume fraction of γ' phase and the concomitant enrichment of W and Re in the γ matrix.

Keywords Nickel-based single-crystal superalloy · Topologically close-packed (TCP) phases · Segregation · Eutectic

1 Introduction

Ni-based single-crystal (SX) superalloys are widely applied in industrial gas turbines, aircrafts and jet engines due to their excellent mechanical properties at elevated temperature. In order to improve high-temperature strength and creep resistance, high levels of refractory elements, such as Mo, W and Re, are added in SX superalloys, which strongly promote the precipitation of topologically close-packed (TCP) phases [1–3]. TCP phases, such as σ and μ phases, are detrimental to the mechanical properties of SX superalloys since they promote the depletion of refractory elements

in the γ matrix, and can initiate cracks or accelerate crack propagation [4–6].

Usually, TCP phases are preferentially distributed in the dendrite core due to the dendritic segregation of Re and W [7]. In order to avoid the formation of TCP phases, heat treatment with high solution temperature and long holding time was applied to reduce the dendritic segregation [8–10]. For example, the volume fraction of TCP phases in the CMSX-4 superalloy significantly decreased after thermal exposure by elevating temperature and prolonging holding time of the solution heat treatment to reduce the dendritic segregation of Re and W [8]. However, it seems that the TCP phases do not change monotonically with the variation of dendritic segregation [11–14]. In our previous study [11], the volume fraction of TCP phases in a heat-treated SX superalloy increased after thermal exposure by elevating solution temperature, although the dendritic segregations of W and Re were reduced. It has been reported that TCP phases were distinguished in the interdendritic region of an as-cast SX superalloy after thermal exposure, which was ascribed to the partitioning of Ta, leading to an increase in the volume fraction of γ' phase in the interdendritic region and a concomitant enrichment of Mo and

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particularly Cr in the γ matrix [12]. Long [14] has also found σ phases formed at the periphery of the eutectic in the interdendritic region even during solidification process in a polycrystalline superalloy. They suggested the local segregation of Cr, Mo, Co and W at the periphery of the eutectic accounts for the formation of σ phases. However, more evidences are required to clarify this mechanism. Therefore, it is suggested that the precipitation of TCP phases is not only determined by the dendritic segregation of refractory elements, such as W and Re.

In this study, a significant amount of TCP phases precipitated in the interdendritic region of an as-cast SX superalloy after thermal exposure at 900 °C. However, no TCP phases were distinguished in the interdendritic region of heat-treated (with low solution temperature and short holding time) samples after thermal exposure, although the strong dendritic segregation of W, Re, Ti and Ta could be found. This work aims to further investigate the relationship between the dendritic segregation and the precipitation of TCP phases. Moreover, important guidance for further reducing TCP phases in as-cast SX superalloys, especially for the superalloys which serviced in the as-cast condition, such as DD26 SX superalloy, could be summarized from the present study.

2 Experimental

The nominal chemical compositions of the experimental superalloy are listed in Table 1. Single-crystal bars were cast by directional solidification in a Bridgman furnace, and the crystallographic orientation of select samples was close to the $\langle 001 \rangle$ direction (deviation less than 10°). The samples were cut into slices with the size of 16 mm in diameter and 5 mm in thickness by electrical discharge machining. Some samples were subjected to heat treatment with low solution temperature and short holding time, as listed in Table 2. Both as-cast and heat-treated samples were thermally exposed at 900 °C for 1000 h.

Standard metallographic techniques were employed for the preparation of samples. To reveal the γ - γ' microstructure, the samples were etched with a solution of 4 g CuSO₄, 10 mL HCl, and 20 mL H₂O. Another etchant consisting of 80 mL HCl, 20 mL H₂O, 2 mL HNO₃ and 16 g FeCl₃ was used to investigate the TCP phases. Microstructural observations were carried out using a field-emission Inspect F50 scanning electron microscope (SEM) operating at 20 kV. The volume fraction of γ' phases was determined using the SEM micrographs.

Compositional information and elemental mapping were obtained using a Cameca SX100 electron probe microanalyzer (EPMA, Shimadzu EPMA1610) operating at 20 kV.

The detailed methods of quantitatively measuring the compositions of dendrite core and interdendritic region have been reported elsewhere [11]. The degree of dendritic segregation was characterized using the segregation ratio K_i , which was defined as Eq. (1) [15]. By definition, K_i is taken to be the ratio of the dendrite core composition over the interdendritic composition level. The value of K_i greater or less than unity means that the element i segregates to the dendrite or the interdendritic region.

$$K_i = C_{\text{dendrite}}^i / C_{\text{interdendrite}}^i \quad (1)$$

About 500 μm disks in thickness were cut from the samples perpendicular to the $[001]$ direction for transmission electron microscopy (TEM) analysis. They were mechanically ground to 50 μm in thickness, and 3 mm disks in diameter were punched out from the pieces. Finally, they were electrochemically polished at -25 °C and 20 V in a solution of 10% perchloric acid in alcohol. An FEI Tecnai F20 transmission electron microscopy (TEM) was used to analyze the microstructure and composition of TCP phases.

3 Results

Scanning electron micrographs of the as-cast sample are presented in Fig. 1. Typical dendritic pattern with a few of γ/γ' eutectics in the interdendritic region is shown in Fig. 1a. The fine γ' phases in the dendrite core (Fig. 1b) and coarse γ' phases in the interdendritic region (Fig. 1c) were found. The γ/γ' eutectic can be morphologically characterized by fine γ/γ' network and coarse γ' phase as marked in Fig. 1d. Unlike the coarse γ' phase in the interdendritic region, a layer of fine γ' phase was observed at the periphery of coarse γ/γ' eutectic. After solution heat treatment, the fine γ' phases were dissolved, and the γ zone formed at the periphery of coarse γ/γ' eutectic, while the coarse γ' phases were not dissolved (Fig. 2a). Some fine precipitates were observed in the γ zone as marked by arrow in Fig. 2b. The microstructures of the heat-treated (with solution and aging heat treatment) samples are shown in Fig. 3. The regular and cuboidal γ' phases

Table 2 Heat treatment schedule for the experimental alloy

Experiment	Heat treatment schedule
Solution heat treatment	600 °C-1 h-1000 °C-1 h-1260 °C/AC
Aging heat treatment	1130 °C/4 h/AC + 870 °C/24 h/AC

Table 1 Nominal compositions of the experimental alloy (wt%)

Cr	Co	Al	Ti	W	Mo	Ta	Re	C	Ni
9	9	3.8	3.8	4.5	1	5.5	2	0.05	Bal.

Fig. 1 Scanning electron micrographs of **a** as-cast sample in **b** dendrite core, **c** and **d** interdendritic region

could be observed in the dendrite core (Fig. 3a). As compared with the coarse γ' phases in the interdendritic region (Fig. 3b), the γ' phases were obviously fine at the periphery of coarse γ/γ' eutectic (Fig. 3c). It is notable that the volume fraction of the fine γ' phases is much lower than that of the coarse γ' phases. In addition, the volume fractions of γ'

phases in the interdendritic region of as-cast and heat-treated samples were $55.6 \pm 1.1\%$ and $54.6 \pm 0.5\%$, respectively.

The segregation ratios are shown in Fig. 4. It was found that W, Mo, Cr, Co and Re segregated to the dendrite core, while Al, Ti and Ta partitioned to the interdendritic region in the as-cast sample. Moreover, it was obvious that

Fig. 2 Scanning electron micrographs of the sample after solution heat treatment **a**, **b** is magnified morphology of the white zone in **a**

Fig. 3 Scanning electron micrographs of the heat-treated sample: **a** dendrite core, **b, c** interdendritic region

Fig. 4 Segregation ratio of as-cast and heat-treated samples

the dendritic segregation of W, Re, Ti and Ta was notably strong. Compared with the as-cast sample, the dendritic segregation was only slightly reduced in the heat-treated sample. It was indicated that the heat treatment with low solution temperature and short holding time was far from eliminating dendritic segregation. EPMA element maps of γ/γ' eutectic of the as-cast and heat-treated samples are shown in Figs. 5 and 6, respectively. It was clearly observed that the coarse γ/γ' eutectic was enriched in Al, Ti and Ta. Moreover, the local segregation of Cr and Ti was visible at the periphery of coarse γ/γ' eutectic in the as-cast sample (Fig. 5). However, the local segregation of Cr and Ti was eliminated in the heat-treated sample (Fig. 6).

The microstructures of the as-cast sample subjected to thermal exposure at 900 °C are shown in Fig. 7. After exposure at 900 °C for 100 h, a small amount of granular and needle-like TCP phases could be clearly distinguished at the periphery of coarse γ/γ' eutectic (Fig. 7a). Subsequent annealing resulted in mass precipitation of TCP phases surrounding the coarse γ/γ' eutectic, extending throughout the interdendritic region (Fig. 7c). Moreover, the morphological evolution of TCP phases from needles to granules can be seen, as shown in Fig. 8. After exposure at 900 °C for

1000 h, the granular TCP phases were distributed around the eutectic with the needle-like TCP phases away from the eutectic. These TCP phases were identified as σ phase by selective area electron diffraction (SAED) (Fig. 9a, c). The compositions of σ phases were determined by TEM with energy-dispersive X-ray spectroscopy (EDS), as listed in Table 3. They were enriched in Re and Cr. However, in the heat-treated samples, no TCP phases could be observed in the dendrite core and interdendritic region up to 1000 h exposure at 900 °C (Fig. 10a, b). Only a small amount of TCP phases were detected in the secondary dendrite arm near the interdendritic region (Fig. 10c), which were identified as μ phase (Fig. 9b, d). They were enriched in Re and W, as listed in Table 3.

4 Discussion

As the main forming elements of TCP phases, W and Re significantly increase the propensity to TCP phase formation [16, 17]. The dendritic segregation of W and Re is prone to form, which strongly accelerates the precipitation of TCP phases [7, 10]. In the present paper, it is noted that the dendritic segregation of W, Re, Ti and Ta is particularly strong in both the as-cast and heat-treated samples. However, the behavior of TCP precipitations is quite different in the two samples (Figs. 7, 10).

In the as-cast sample, a significant amount of σ phases are observed in the interdendritic region (Fig. 7). Karunaratne et al. [12] attributed it to the increased volume fraction of γ' phase in the interdendritic region and a corresponding enrichment of Mo and Cr in the γ matrix. However, in the present study, σ phases are preferentially precipitated at the periphery of coarse γ/γ' eutectic, where the volume fraction of γ' phase is quite low (Figs. 1d, 7a).

It has been reported that the coarse γ/γ' eutectics with high content of Ta and Ti form at the last stage of solidification, and the excess Ti is enriched at the front of the coarse γ/γ' eutectic [18, 19]. Moreover, the formation of coarse γ/γ' eutectic would cause the accumulation of Cr

Fig. 5 EPMA element maps of γ/γ' eutectic in the as-cast sample

and Mo ahead of the eutectic due to the low solubility of these elements in the γ' phase [20–22]. The local segregation of Ti and Cr is visible near the coarse γ/γ' eutectic, as shown in Fig. 5. Ti is shown to cause a stronger partitioning of γ matrix forming elements, such as Re, W, Cr, Co and Mo, to the γ phase, which in turn promotes the precipitation of TCP phases [23, 24]. Moreover, as the main forming element of σ phases, Cr obviously increases the susceptibility of σ phases formation [25]. Therefore, σ phases in the form of granules and needles are preferentially

precipitated at the periphery of coarse γ/γ' eutectic after thermal exposure at 900 °C for 100 h (Fig. 7a). It is similar to the formation of σ phase at the eutectic in a polycrystalline Ni-based superalloy and α -Cr precipitation in the β phase observed in a Ni_3Al -based superalloy in the final stages of the solidification process, due to elemental segregation, especially Cr, in the residual liquid [14, 26]. It has previously been shown that the σ needles arranging very regularly have fully coherent interfaces with the surrounding matrix [27–29]. The morphological evolution of

Fig. 6 EPMA element maps of γ/γ' eutectic in the heat-treated sample

Fig. 7 Microstructures in the interdendritic region of the as-cast sample after thermal exposure at 900 °C for **a** 100 h, **b** 240 h, **c** 1000 h

Fig. 8 Morphological evolution of TCPs near the eutectic after thermal exposure at 900 °C for **a** 240 h, **b** 1000 h

Fig. 9 TEM micrograph and diffraction pattern associated with **a, c** σ phase in the as-cast sample and **b, d** μ phase in the heat-treated sample

σ phases from needle-like to granular leads to a reduction in the coherency of the σ -matrix interface. Moreover, the granular precipitates transformed to spheroidization would minimize the interfacial energy [29]. It is possible that

the interdiffusion between the coarse γ/γ' eutectic and the interdendritic region significantly promotes this morphological evolution after further thermal exposure. Therefore, the morphological evolution from needle-like to granular is observed especially at the periphery of eutectics (Fig. 8). In addition, no TCP phases are present in the dendrite core after thermal exposure, owing to the high volume fraction of γ matrix and low supersaturation of Re and W in γ matrix, as reported in the previous study [11].

In the heat-treated sample, no TCP phases are distinguished in the interdendritic region after thermal exposure at 900 °C for 1000 h (Fig. 10). The dendritic segregation of W, Re, Ti and Ta has changed slightly, due to the low solution temperature and short holding time (Fig. 4). In addition, the volume fraction of γ' phase in the interdendritic region of heat-treated sample is similar to that of the as-cast sample. In that case, the quite different behavior of TCP precipitation in the two types of samples cannot be rationalized well. It is suggested that the eliminating segregation of Ti and Cr at the periphery of coarse γ/γ' eutectic primarily accounts for the quite different behavior of TCP precipitation of the heat-treated sample in comparison with that of the as-cast sample.

The fine γ' phases were dissolved, and the γ zone formed at the periphery of coarse γ/γ' eutectic after low-temperature solution heat treatment. It is noted that the γ zone is prone to TCP phase formation due to the segregation of Ti and Cr. The fine precipitates in the γ zone are

Table 3 Compositions (wt%) of σ in the interdendritic region of the as-cast sample and μ in the secondary dendrite arm of the heat-treated sample determined by TEM with EDS

Phase	Cr	Co	W	Mo	Al	Ti	Ta	Re	Ni
σ	25.5	11.2	11.5	6.4	1.1	2.1	2.6	13.1	26.6
μ	11.9	9.4	21.8	3.8	1.3	1.5	2.9	17.7	30.3

Fig. 10 Microstructures of the heat-treated sample after thermal exposure at 900 °C for 1000 h in **a** dendrite core, **b** interdendritic region, **c** secondary dendrite arm

considered to be σ phases, which are precipitated during the air cooling of solution heat treatment (Fig. 2b). These σ phases are absolutely dissolved in the subsequent aging heat treatment.

After solution and aging heat treatment, the segregation of Ti and Cr at the periphery of coarse γ/γ' eutectic is eliminated (Fig. 6). Therefore, there is no preferential nucleation position of TCP phases in the interdendritic region. However, Al, Ti and Ta diffuse from the interdendritic region to the dendrite core, leading to increased volume fraction of γ' phase in the secondary dendrite arm and resulting high enrichment of W and Re in γ matrix. The diffusion distance of Al, Ti and Ta is limited, due to the low temperature and short holding time of heat treatment. Therefore, small quantities of W, Re-rich μ phases are precipitated in the secondary dendrite arm near the interdendritic region rather than in the dendrite core.

5 Conclusions

Microstructural instability of the as-cast and heat-treated (with low solution temperature and short holding time) SX superalloys associated with the precipitation of topologically close-packed (TCP) phases was investigated. The following conclusions can be drawn:

1. Strong dendritic segregation of W, Re, Ti and Ta was found both in the as-cast and heat-treated samples. However, local segregation of Ti and Cr was present at the periphery of coarse γ/γ' eutectic in the as-cast samples, and their local segregations were eliminated in the heat-treated samples.
2. A significant amount of σ phases were distinguished in the interdendritic region of the as-cast sample after thermal exposure at 900 °C for 1000 h. The σ phases were preferentially precipitated at the periphery of coarse γ/γ' eutectic, and the morphological evolution of σ phases from needles to granules was observed. No TCP phases were present in the interdendritic region, and small

quantities of μ phases were detected in the secondary dendrite arm of the heat-treated samples after thermal exposure at 900 °C for 1000 h.

3. It is believed that the local segregation of Ti and Cr at the periphery of coarse γ/γ' eutectic accounts for the mass σ phases precipitation in the interdendritic region of the as-cast samples. The increased volume fraction of γ' phase in the secondary dendrite arm leads to high enrichment of W and Re in the γ matrix, then μ phases precipitate in the heat-treated samples.

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