Effect of $\gamma'$ formation and strengthening elements on microstructures and stress rupture property of single crystal super-alloys

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Abstract: An investigation was carried out to study the effects of $\gamma'$ formation and strengthening elements (Al, Ti and Ta) on the microstructure and stress rupture properties of nickel base single crystal super-alloys. The results show that with the increase of $\gamma'$ formation and strengthening elements, the percentage of $\gamma$-$\gamma'$ eutectic and the misfit degree of $\gamma$-$\gamma'$ increases. Detailed microstructural analysis revealed that with the increase of $\gamma'$ forming element content, the morphology of $\gamma'$ changed from spherical to cubic, then irregular shape; and the size of $\gamma'$ increases gradually. Excessive $\gamma'$ formation and strengthening elements will lead to the precipitation of $\mu$ phase during stress rupture tests. The alloy with 5wt.%Al, 1wt.%Ti and 6wt.%Ta has the best stress rupture property.

Key words: $\gamma'$ phase; microstructures; stress rupture property; single crystal super-alloy


Ni-base single crystal super-alloys have become the major material for turbine blades in aerospace engines$^{[1]}$. These alloys have a face-centered cubic $\gamma$ matrix strengthened by a high volume fraction (up to 70 vol.%) of the ordered Ni$_3$Al type $\gamma'$ precipitates; and their outstanding high-temperature mechanical strength benefits from the addition of a number of refractory alloying elements$^{[2]}$. The $\gamma'$ precipitate is the main strengthening phase in the Ni-base single crystal super-alloy, whose strength, morphology and the relationship with the matrix all influence the mechanical properties of the alloys. All the factors are determined by the composition of alloys and the solidification process. It was first reported by Harada$^{[3, 4]}$ that the creep rupture life was the longest in the vicinity of 65% $\gamma'$ under any creep condition in the polycrystalline Ni-base super-alloy Inconel 713C. This tendency was expected to be applicable to single-crystal super-alloys, and in fact, many studies at around 60% to 70% in $\gamma'$ fraction have been carried out in the last two decades to find the optimum chemical composition of Ni-base super-alloys with rhenium element.

Takao Murakumo$^{[4]}$ used the tie line method to study the optimum $\gamma'$ volume fractions with the same compositions of each phase. The composition and volume fraction of $\gamma'$ phase have direct relationships with the content of $\gamma'$ phase and strengthening elements (Al, Ti and Ta).

However, the optimum chemical composition and volume fraction of $\gamma'$ phase in single crystal super-alloy without rhenium have not been reported. In this study, the creep behavior and microstructural evolution during stress rupture tests of Ni-base single crystal super-alloys with various $\gamma'$ forming and strengthening elements are investigated.

1 Experimental materials and methods

A series of Ni-base super-alloy compositions were set in a controlled manner, so that the chemical effects of Al, Ti and Ta can be independently assessed. The nominal compositions of the alloys being tested are listed in Table 1.

Table 1: Nominal compositions of the five tested alloys (wt.%)
Each experimental alloy was produced by means of a crystal selection method in a vacuum directional solidification furnace under a high thermal gradient. Longitudinal orientation of all specimens was within 10 degree of deviation from the [001] direction. DTA was used to analyze the incipient melting temperature and other transformation temperatures. All specimens received a standard heat treatment comprising a solution treatment (1305 °C/4 h AC) and a two-step aging treatment (1,080 °C/4 h AC + 870 °C/24 h AC). The heat-treated bars were machined into stress rupture specimens with gauge length of 25 mm and gauge diameter of 5 mm. The stress rupture tests were carried out on a GWT304 constant load high temperature creep-testing machine, the loading condition being 248 MPa at 1,010 °C. The microstructures were examined using a JSM-6301F scanning electron microscope (SEM) equipped with energy dispersive spectrometers (EDS). The compositions of $\gamma$ and $\gamma'$ phases were measured using a Philip EM 420 transmission electron microscope with EDS. In order to determine the species of phases precipitated during stress rupture tests, X-ray diffraction (XRD) analyses were made on the longitudinal section.

2 Results and discussions

2.1 As-cast microstructure

Figure 1 shows the as-cast optical photographs of five test alloys, with different levels of Al, Ti and Ta, in the section normal to the solidification direction. It can be seen that the microstructures contain dendrites composed of the gamma ($\gamma$ solid solution) and the gamma prime phase ($\gamma'$ Ni,Al-based inter-metallic phase). These dendrites are the first part formed during solidification. The $\gamma$ phase forms first and the $\gamma'$ phase precipitates from the $\gamma$ solid solution during subsequent cooling. In addition, the structure containing pools of $\gamma/\gamma'$ eutectic, which appears light-grey in the OM images of the inter-dendritic region and it is the final part to solidify as shown in Fig. 1.

![Optical micrographs of the as-cast samples for the five alloys: alloy A (a); alloy B (b); alloy C (c); alloy D (d) and alloy E (e)](image)

From Fig. 1, it can be seen that the main difference is the amount of $\gamma/\gamma'$ eutectic and the area of inter-dendritic region in the five pictures. For the alloy A, with the lowest content of Al, Ti and Ta, the amount of $\gamma/\gamma'$ eutectic and the area of inter-dendritic region are minimal. The alloy E has the opposite tendency, i.e., the amount of eutectic $\gamma/\gamma'$ structure increases as the sum of Al, Ti and Ta increases in the alloys. Because alloys B, C and D have the same content of $\gamma'$ phase forming and strengthening elements, the three alloys have similar dendritic structures.

Under the same solidification conditions, Al, Ti and Ta elements enrich the alloy melt in the inter-dendritic region. Therefore, the greater the overall content of Al, Ti and Ta, the larger the area of inter-dendritic region and the greater the amount of $\gamma/\gamma'$ eutectic in the inter-dendritic region.

2.2 DTA curves

Figure 2 shows the DTA heating traces with various endothermic peaks for the five alloys. The peaks in the DTA curves can be matched to their specific reactions and phase transformation at the approximate temperatures. Three sets of peaks are highlighted in Fig. 2. A small initial peak (1) at about 1,350 °C corresponds to the melting point of $\gamma/\gamma'$ eutectic, since the $\gamma/\gamma'$ eutectic was formed at the final stage during solidification.

When the alloy does not contain other phases with low
melting point, the incipient melting temperature is the melting temperature of $\gamma' \gamma \gamma'$ eutectic, which is lower than that of the $\gamma$ matrix. Peak (2) indicates the temperature at which the matrix starts to melt. The small peak (3) at approximately 1,200 °C corresponds to the dissolution of the $\gamma'$ phase.

The DTA tests indicate that the content of $\gamma'$ forming element has no evident influence on the melting temperature of $\gamma' \gamma' \gamma'$ eutectic. However, in the non-equilibrium solidification range, the area of the peak in the DSC curves represents the latent heat of crystallization during solidification or the latent heat of fusion during melting. Therefore, from the area of the peak, the amount of transformation product can be deduced. Although similar features are observed for the five alloys, the height and the area of peaks (1) are different for the five alloys; the peak (1) height for Alloy E is the maximum; that for alloy A is the lowest; while the peaks for alloy B, C and D have similar peak heights. The results show that the amount of $\gamma' \gamma' \gamma'$ eutectic transformed during heating are different for these five alloys. The results are consistent with those obtained from the as-cast microstructure. From the positions of peak (2) for the five alloys, it can be concluded that with the increase of the amount of Al, Ti and Ta, the melting temperature of $\gamma$ matrix decreases gradually.

2.3 Microstructure after heat treatment

Figure 3 shows the $\gamma'$ morphology on the dendrite arm of the five alloys. For alloy A, the $\gamma'$ phase is cubic shape with round corners and the size of $\gamma'$ is about 300 nm (Fig. 3(a)). For the alloy B with more Al content, the morphology of $\gamma'$ precipitate is cubic with the size about 450 nm (Fig. 3(b)). The $\gamma'$ particles in alloys C and D are all cubic shape but the size is about 400 nm (Fig. 3(c), d)). In alloy E with more Ti and Ta, the $\gamma'$ precipitate is irregular and has the largest size (Fig. 3(e)).

After heat treatment of 8 h/1,305 °C AC + 4 h/1,080 °C AC +24 h/870°C AC the alloys, except for alloy E, were almost fully solid solution. In alloy E there still exist large amounts of remaining eutectic as shown in Fig. 3(f). In this alloy with the most $\gamma'$ formation and strengthening elements (Al, Ti and Ta), it is probable that the eutectic $\gamma' \gamma'$, which is formed in the inter-dendritic region during solidification, transforms to the single $\gamma'$ phase during heat treatment and subsequent cooling. This single phase $\gamma'$ is sometime called eutectic $\gamma'$[3]. The existence of a large amount of eutectic $\gamma'$ indicates that this alloy cannot be solution-treated completely under the conditions applied in this study.

The compositions of $\gamma$ and $\gamma'$ precipitates were measured using TEM with EDS. According to the multivariable regression equation obtained from the large amount of experimental data from phase composition and the lattice constant of $\gamma$ and $\gamma'$ precipitates for super-alloys by Watanabe [5], the misfit of $\gamma$ and $\gamma'$ phases are calculated and listed in Table 2. It shows that the morphology of $\gamma'$ phase is correlated with misfit degree. At low
misfit degree, the strain energy is lower, the interfacial energy is dominant, and the quasi-spherical shape precipitates are observed. When the misfit degree increases, the coherent strain energy enlarges and becomes dominant; therefore the cubic shape is favored. When the misfit degree reaches a higher value, the two phases will lose the coherency, relaxing the elastic strain by interfacial dislocation. When the coherency is lost, the precipitates will give up their cubic shape for a more rounded and irregular one.

### 2.4 Stress rupture properties

Table 3 lists the stress rupture property data of the five alloys under conditions of 1010 °C and 248 MPa. It can be concluded that the amount of γ' phase forming and strengthening elements intensively influences the mechanical properties. Compared with alloy A, the stress rupture properties of alloys B, C and D were improved by adding more Al, Ti or Ta. Although these three alloys have approximately the same content of γ' phase forming and strengthening elements, their stress rupture data are obviously different, which shows that the strengthening effects of Al, Ti and Ta on γ' phase are different.

### 2.5 Microstructure after stress rupture tests

It was found that directional coarsening of γ' precipitates occurred and γ' rafts perpendicular to the tensile load axis formed during the prolonged exposure at 1,010 °C and 248 MPa in all the specimens, which is similar to the alloys investigated by Liu et al. and Guo et al. In alloy E, a large amount of needle-like and blocky phase precipitate was observed during the stress rupture tests. EDS analysis shows that the two phases are both enriched in Mo and W elements as shown in Fig. 4. An X-ray diffraction of the longitudinal section of the stress ruptured specimen indicates that the needle-like phase and blocky phase are both μ phase as shown in Fig. 5. As all known, μ phase is a brittle phase with W and Mo. Its precipitation not only damages the continuity of rafts but also spends the solid solution strengthening element severely, which is detrimental to the stress rupture properties.

The alloy A has the shortest stress rupture life and the highest elongation, which indicate that the strengthening effect of its matrix is not enough. When the γ' phase forming and strengthening elements are added, the volume fraction of γ' phase precipitation will be increased. At the same time, the volume fraction of γ matrix is decreased; the concentration of W and Mo element in matrix will thus be elevated, which improves the strengthening effect for the γ matrix. On the other hand, the increase of γ' phase volume fraction improves the strengthening effect by the second phase. Therefore, the stress rupture lives of alloys B, C and D, which are added 0.6wt.% Al, 1wt.% Ti and 2wt.% Ta more, respectively on the base of alloy A, are increased and the elongations are decreased (no change for D). Due to the different solution strengthening effects of the three alloy elements (Al, Ti and Ta) in γ' phase and γ matrix, the improvement of stress rupture property for three alloys is different as mentioned above. A large amount of retained eutectic with Ta and Ti elements exists in alloy E, which makes the Ta and Ti not able to exert
its strengthening effect fully. At the same time, in alloy E, there exists an obvious difference in the size of γ′ particle in the inter-dendritic region and dendrite core and the γ′ particle morphology is larger in size and irregular in shape. Moreover, the μ phase precipitation breaks the continuity of the rafting microstructure and deprives part of solution strengthening element, such as W and Mo. All these factors are detrimental to the mechanical properties of alloy E.

The coherency between the matrix and the precipitates has a significant influence on the stress rupture behavior. Generally, the stress rupture strength of Ni-base super-alloys decreases when the γ/γ′ interfaces in the as-heat-treated microstructure are semi-coherent. The coarse two-phase region observed in the alloy E is considered to be in a semi-coherent state because the interfaces are rounded and wavy. This can be attributed to the increase in the creep rate because the semi-coherent interfaces act as dislocation sources.

3 Conclusions

Stress rupture tests at 1,010 °C and 248 MPa were performed on the five experimental Ni-base single-crystal super-alloys and the microstructures of these alloys were observed by SEM. The summary is as follows:

1) With the increase of γ′ formation and strengthening elements, the amount of γ-γ′ eutectic and the misfit degree of γ′/γ increase.

2) With the same heat treatment, the alloy with excessive γ′ phase forming and strengthening elements cannot be fully solution treated and a large amount of remaining eutectic γ′ was left after heat treatment.

3) With the increase of γ′ forming elements, the morphology of γ′ changes from spherical to cubic and irregular shape and the size of γ′ increases gradually.

4) Excessive γ′ formation and strengthening elements lead to the precipitation of μ phase during stress rupture tests.

5) The alloy with 5wt.%Al, 1wt.%Ti and 8wt.%Ta has the best stress rupture property.

References


