Microstructure stability of a ru-containing nickel based single crystal superalloy

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**Abstract.** The microstructure evolution and stress rupture properties at 1100°C/140MPa of a Ru-containing single crystal superalloy after long term aging at 1100°C for 200h-1000h were investigated. The results showed that the γ′ phase rafting and the γ matrix channel broadening appeared after long term aging. The rafting degree enhanced with increasing of aging time. A small amount of TCP phase began to appear after aging for 200h. The volume fraction of TCP phase after aging for 1000h was only 0.1%, which indicated the alloy had excellent microstructure stability. The stress rupture life of the alloy at 1100°C/140MPa represented the decrease tendency with increasing of aging time. The γ′ rafting and TCP phase precipitation were the main factor for this degradation.

**Keywords:** single crystal superalloy; long term aging; microstructure stability

1. **Introduction**

In recent years, nickel based single crystal superalloys are key materials for the production of turbine blades in modern aerospace engines [1, 2]. The temperature capability of the single crystal superalloys has greatly improved over the past few decades. Significant progress has been gained by raising the content of refractory elements [3-5]. These refractory elements, such as Re and W, can enhance the creep properties of single crystal superalloys. However, deleterious topologically close packed (TCP) phase are often appeared in the single crystal superalloys with high fraction refractory elements. The mechanical properties at high temperature can decrease because of TCP phase precipitation [6, 7]. So microstructure stability is a focus problem in the design process of next generation single crystal superalloy [8-10]. This paper examines the effect of long term aging on the microstructure and stress rupture properties of the new generation single crystal superalloy. The microstructure development and TCP phase formation during long term aging were investigated. The purpose of this study is to improve the application of a new generation single crystal superalloy.

2. **Experiment**

A Ni-Cr-Co-Mo-Ta-Nb-Re-Ru-Al-Hf system single crystal with [001] orientation were produced using spiral selected crystal method in a directional solidification furnace. The crystal orientation of the specimens deviated from [001] direction within 10 degrees. The specimens received a heat treatment according to following process system: 1345 °C/6 h, AC+1 120 °C/4 h, AC + 870 °C/32 h, AC . The alloy was long term aged at 1100°C for 200h, 400h, 600h, 800h and 1000h, respectively. Standard
tensile specimens for stress rupture tests were processed after heat treatment. The stress rupture properties of the alloy after aging for different time were tested at 1100 °C/140 MPa, respectively. Microstructures of the alloy at different condition were examined using a scanning electron microscope.

3. Experimental results

3.1. Evolution of γ′ phase morphologies

Figure 1(a) illustrates the microstructure of the alloy after full heat treatment. It can be seen that it contains greater than 60% volume fraction of γ′ precipitates in cubic shape with 0.43µm edge width and γ matrix channel through quantitative analysis. Figure 1(b) ~1(f) show the microstructures evolution of the alloy after long term aging at 1100°C for 200h, 400h, 600h, 800h and 1000h, respectively. The γ′ precipitates directional rafting appeared after long term aging. The γ′ precipitates after aging for 200h is no longer cubic shape. The lateral merging of γ′ phase had obviously developed along the cubic direction. The adjacent γ′ particles met and fused together to form rafts. The rafting degree of γ′ precipitates enhanced with increasing of aging time. The γ matrix appeared in the separation state and was thus entirely covered by the γ′ phase after aging for 1000h.

The γ′ precipitates rafting is ascribed the directional diffusion of alloying elements of γ′ phase and γ matrix in the long term aging. That resulted from the joint actions of thermodynamics and kinetics. The reduction of the surface energy and lattice mismatch stress between the γ′ phase and γ matrix would be driving force for γ′ precipitates rafting[11]. In the LSW theory, the γ′ precipitates rafting is the diffusion-controlled process, and the followed formula is valid [12].

\[
(r_t^3 - r_0^3) \frac{1}{3} = K t \frac{1}{3}
\]

where \( r_0 \) is initial particle radius, \( r_t \) the instantaneous particle radius, \( K \) the rate constant and \( t \) the aging time. When the γ′ particle has a cubic shape, \( r = a/2 \), where \( a \) is the cube edge width. For the rafted γ′ phase, \( r = (a_1 \times a_2)/2 \), where \( a_1 \) and \( a_2 \) are the length and width of rafted γ′ precipitate, respectively. In order to illustrate the γ′ rafting mechanism, plots of \( (r_t^3 - r_0^3) \) versus \( t \) are constructed and shown in figure 2(a).
Figure 2. Effect of long term aging on the size of the $\gamma'$ phase and $\gamma$ matrix of the alloy
(a) correlation between $(r^{0}_{x} - r^{0}_{y})$ and aging time; (b) correlation between $\gamma$ matrix channel width and aging time.

It can be seen from figure 2(a) that the rafting kinetics of the $\gamma'$ phase slightly deviated from the linear relationship, which was not in good agreement with the LSW theory. The $\gamma'$ precipitate rafting was mainly in the way of the adjacent $\gamma'$ particles meeting and fusing together along the [001], [010] and [100] direction during early stage of long term aging, so its growth rate was relatively fast. However, the complete rafting formed during later aging process, the growth rate of $\gamma'$ phase became relatively slow. The $\gamma'$ phase morphology tended to be constant as the $\gamma'$ phase growth was limited by the coherency stresses due to the lattice misfit between $\gamma$ and $\gamma'$ phases after long term aging for a certain time[13]. Figure 2(b) shows the correlation between the $\gamma$ matrix channel width and the aging time. It can be seen that the $\gamma$ matrix channel width increased with an increasing aging time, so the $\gamma'$ volume fraction of the alloy decreased after long term aging.

3.2. Precipitation of TCP phase

Figure 3 illustrates the TCP precipitates in the alloy with different long term aging time at 1100$^{\circ}\text{C}$. (a) 200h; (b) 400h; (c) 600h; (d) 800h; (e) 1000h.

Figure 3. TCP phase precipitates in the alloy with different long term aging time at 1100$^{\circ}\text{C}$. It can be seen that a small amount of needle shaped TCP phase began to appear after aging for 200h. It is found that the TCP phase precipitated and grew along a certain direction. The TCP phase initially appeared within the dendrite core and gradually grew into the interdendritic region with increasing of aging time. This is caused by dendrite segregation which still existed even after homogenization due to the low
diffusivity of refractory elements with high melting point. The volume fraction of TCP phase increased with increasing of aging time. However, the volume fraction of TCP phase of the alloy after aging for 1000h was only 0.1%, which indicated the alloy had excellent microstructure stability.

The EDX pattern and chemical composition of the TCP phase after aging for 1000 h is shown in figure 4 and table 1, respectively. It is shown that Re, W and Co were enriched in the TCP phase. The TCP phase formation in single crystal superalloys had generally been ascribed the super-saturation of the refractory elements in $\gamma$ matrix [14]. It was believed that Ru can decrease the precipitation and growth of TCP phase in single crystal superalloys. So the fourth generation single crystal superalloys such as MC-NG[2], EPM-102[3] and TMS-138[15] all contain Ru element. The addition of Ru can reduce the saturation degree of refractory elements in the $\gamma$ matrix, so the Ru-containing alloy can be more resistant to the formation of TCP phase[16]. So the alloy also contains 2~4% Ru element in this experiment. The crystal structure of TCP phase is fairly complex and the size of unit cell is much larger than the lattice of the $\gamma$ and $\gamma'$ phases. So there is much nucleation barrier to hinder the formation of the TCP phase in the alloy [17]. If they precipitated in the microstructure, they would nucleate preferentially on close-packed planes and exhibit distinct orientation relationships with the parent crystal [18]. Therefore, it can be seen from figure 3 that the TCP phase precipitated and grew along fixed direction.

![Figure 4. EDX analysis of TCP phase in the alloy after aging for 1000h at 1100°C.](image)

### Table 1. Chemical composition of TCP phase in the alloy after aging for 1000h (mass fraction, %).

| Element | Al  | Cr  | Co  | Ru  | W   | Re  | Ni   |
|---------|-----|-----|-----|-----|-----|-----|------|
| Content | 2.08| 2.61| 8.55| 2.53| 9.44| 18.35| Bal. |

3.3. Stress rupture properties

The stress rupture properties of the alloy after aging for different time at 1100 °C/140 MPa are shown in figure 5. It indicates that the stress rupture life represented the decrease tendency with increasing of aging time. The variation trend of elongation dependent on the aging time was different with that of the stress rupture life. This phenomenon was also observed in the CMSX-10 single crystal superalloy [4]. L.R. Liu pointed out that the microhardness of the single crystal superalloy increased first and decreased afterward during long term aging, but after aging for some time the microhardness increased again [10]. This might be the reason of the elongation changes with increasing of aging time.

The stress rupture properties of the alloy were influenced by the size, morphology, volume fraction and distribution of the $\gamma'$ phase. It has been reported that the $\gamma'$ coarsening leads to decrease of stress rupture properties of single crystal superalloys [4, 5]. The deformation is dominated by dislocation climb at high temperatures. The width of the $\gamma$ matrix channel is enlarged after long term aging, resulting into the dislocations to easily move into the $\gamma$ matrix. This will make strength of the alloy decrease. The $\gamma'$ phase rafting also brings about the resistance of the dislocation movement by Orowan’s mechanism to decrease[19]. Moreover, the volume fraction of $\gamma'$ phase which had strengthening effect reduced with increasing of aging time. So the stress rupture life of the alloy after long term aging was greatly reduced.
The TCP phase appeared in the alloy after aging for 200h. This was another reason for decrease of the stress rupture life. The TCP phase was brittle and destroyed the continuity of the microstructure. The TCP phase contained high content of solution strengthening elements. Their formation made the strengthening elements in the matrix surrounding the TCP phase decrease and was detrimental to stress rupture properties of the alloy [6, 7]. Figure 6 illustrates the microstructure near fracture surface of the ruptured specimen after aging for 1000h. It can be seen that the secondary crack formed and propagated along the TCP phase. So the degeneration of stress rupture life after long term aging is attributed to the γ' rafting and TCP phase precipitation.

4. Summary
The γ' phase rafting and the γ matrix channel broadening appeared in the alloy after long term aging at 1100℃. The rafting degree enhanced with increasing of aging time.

A small amount of TCP phase began to appear after aging for 200h. The volume fraction of TCP phase after aging for 1000h was only 0.1%, which indicated the alloy had excellent microstructure stability.

The stress rupture life of the alloy at 1100℃/140MPa represented the decrease tendency with increasing of aging time. The γ' rafting and TCP phase precipitation were the main factor for this degradation.

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