Effect of long term aging on microstructure and stress rupture properties of a nickel based single crystal superalloy

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Abstract A nickel based single crystal superalloy with [001] orientation was prepared by the screw selecting method in the directionally solidified furnace. The long term aging (LTA) of the alloy after full heat treatment was performed at 1040 °C for 200–800 h. The microstructure and stress rupture properties at 980 °C/250 MPa and 1070 °C/140 MPa of the alloy long term aged (LTAed) for different time were investigated. The coarsening γ’ phase and the broadening γ matrix channel are observed in the samples LTAed at 1040 °C, but the γ’ morphology is still in cubic shape after LTA for 800 h. No TCP phase precipitates after LTA for 400 h, while needle shaped and granular TCP phase forms in dendritic core of the alloy after LTA for 600 h. With increasing aging time, the volume of the TCP phase increases and it grows from the dendritic core to the interdendritic region along a fixed direction. The composition of the TCP phase is mainly composed of Re and W. With increasing aging time the rupture life of the alloy at 980 °C/250 MPa and 1070 °C/140 MPa all turns shorter. Finally, the relationship between the microstructure and the stress rupture properties is discussed.

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1. Introduction

Single crystal superalloys have been widely used as major material for the blades in aerospace turbine engines. The temperature capability of the turbine blade has increased significantly for the past several decades. Some of the advances have been achieved through improving the content of refractory alloying elements [1–4]. These refractory alloying elements, such as Re, W and Mo, can improve the strength and creep performance of the single crystal superalloys.
For example, the mass fraction of refractory elements in the single crystal superalloys from the first generation to the third generation, i.e., CMSX-2, CMSX-4 and CMSX-10, is 14.6%, 15.4% and 20.7%, respectively [5]. The Re content in the third generation single crystal superalloys CMSX-10 [1] and ReneN6 [2] is 5.4% and 6%, respectively higher than 3% in the second generation single crystal superalloys CMSX-4 and ReneN5 [5], so the temperature capability of the CMSX-10 and ReneN6 alloys has been improved by about 30 °C. However, the superalloys with high fraction refractory elements are susceptible to the precipitation of deleterious topologically close packed (TCP) phases [6,7], and the stress rupture properties decrease as a result of the TCP formation [8,9]. Microstructure and phase instability at elevated temperatures, including coarsening of the γ′ phase and formation of the TCP phase, have been concerned for the second, third and even the fourth generation single crystal superalloys [10–12]. Long term aging, as a technology approach, can simulate the service conditions of the turbine blade and evaluate the phase stability at high temperatures. The present study examines the effect of the LTA on the microstructure and stress rupture properties of the single crystal superalloy.

2. Experimental procedures

Pure raw materials were used in this experimental study. A Ni–Cr–Co–Mo–W–Ta–Nb–Re–Al system single crystal with [001] orientation were cast by means of crystal selection method in the directionally solidified furnace with a temperature gradient of 80 °C/cm. The nominal chemical compositions of the alloy are shown in Table 1. The crystal orientations of the specimens were determined with Laue X-ray back reflection method, and the crystal orientation deviations were maintained within 10° from the [001] orientation. The single crystal specimens received a standard heat treatment comprising of a solution treatment (1340 °C/5 h, AC) and a two-step aging treatment (1 120 °C/4 h, AC+870 °C/24 h, AC). Then, the specimens were long term aged at 1040 °C for 200 h, 400 h, 600 h and 800 h, correspondingly. The standard cylindrical specimens for stress rupture tests were machined from the long term aged (LTAed) alloy, and the stress rupture tests were conducted at 980 °C/250 MPa and 1070 °C/140 MPa in air using a DST-5 testing machine with furnace attachment. For microstructure observations, the samples were electrolyzed in a solution of 2.5 g citric acid, 2.5 g ammonium sulfate and 300 ml water which dissolves the γ phase or etched with 5 g CuSO₄+25 ml HCl+20 ml H₂O+5 ml H₂SO₄ which dissolves the γ′ phase. Microstructures of the LTAed alloy, fracture surface of the stress ruptured samples were examined using a S4800 scanning electron microscope.

3. Results

3.1. Microstructure after LTA

Fig. 1(a) illustrates the typical microstructure of the alloy after the standard heat treatment. It can be seen that the primary γ′ and γ/γ′ eutectic dissolved completely. It contains more than 60% γ′ phase in cubic shape with 0.3–0.5 μm edge width and γ matrix channel. Fig. 1(b–e) shows the microstructures of the alloy LTAed at 1040 °C for 200 h, 400 h, 600 h and 800 h, respectively. With increase in the aging time, the size of the γ′

<table>
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<tr>
<th>Table 1</th>
<th>Nominal chemical compositions of experimental alloy (mass fraction, %).</th>
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<tbody>
<tr>
<td>Element</td>
<td>Cr</td>
</tr>
<tr>
<td>Content</td>
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</table>

Fig. 1 Microstructures of the alloy after LTA at 1040 °C for different time: (a) 0 h; (b) 200 h; (c) 400 h; (d) 600 h; and (e) 800 h.
precipitates gradually increase and their morphology is still in cubic shape even aged for 800 h (Fig. 1(e)). The γ matrix channel width increases with the aging time.

The directional growth of the γ’ particles is a result of the combined actions of thermodynamics and kinetics. The driving force for coarsening of the γ’ particles is the decrease of the interfacial energy between the γ’ particles and γ matrix [13]. As the diffusion distance of the atoms for growth of the γ’ particles is short, the difference of coarsening rate in the various directions is small. Thus, the shape of the γ’ particles after aging for 800 h remains cubic and only the size increases evenly. The γ’ phase has excellent stability because there are some high-melting-point elements such as Re, W, Mo, Ta and Nb in it, which increases the activation energy of the γ’ phase growth. The larger γ’ particles grow while the smaller ones dissolve with the aging time. In the LSW theory [14], the coarsening of the γ’ phase is controlled by diffusion, and the followed formula is valid.

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

where \( r_0 \) is initial particle radius, \( r_t \) is the instantaneous particle radius, \( K \) is the rate constant and \( t \) is the aging time. Since the γ’ phase has a cubic shape, the average length of a cube edge, i.e. \( r = a/2 \), where \( a \) is the cube edge width. In order to characterize the mechanisms of the γ’ coarsening, plots of \( (r_t^3 - r_0^3) \) versus \( t \) are constructed and shown in Fig. 2(a). It is clear that the coarsening kinetics of the γ’ particles follows closely a linear line, which is in good agreement with the LSW theory, while the linear slope is related to the diffusion coefficient. Fig. 2(b) shows the correlation between the γ matrix channel width and the aging time. It can also be seen that the γ matrix channel width increases with an increasing aging time, on the other hand, the γ’ volume fraction shows a decreasing tendency with the aging time.

The phase stability at elevated temperatures is a key issue for the single crystal superalloys. The investigation indicates that no TCP phase is found in the alloy after LTA at 1040 °C for 400 h, while a small amount of needle shaped TCP phase is observed when LTAed for 600 h (Fig. 3(a)), and more form when LTAed for 800 h (Fig. 3(b)). The TCP phase initially precipitates locally within the dendrite core and gradually spreads into the interdendritic regions with increasing aging time at high temperature. This is caused by micro-segregation which exists even after homogenization due to the low diffusivity of refractory elements with high melting point. In addition, it is found that the TCP phase precipitates and grows along fixed direction. The EDX pattern and chemical composition of the TCP phase in the alloy LTAed for 800 h are shown in Fig. 4 and Table 2, respectively. It is displayed that Re and W are enriched in the TCP phase. The formation of the TCP phase in the Ni-base single crystal superalloys has generally been attributed to the super-saturation of the refractory elements (Re, W) within the disordered γ phase [15]. The crystal structure of the TCP phase is extremely complex and the size of the unit cell is much larger than the

Fig. 2 Effect of LTA on the size of the γ’ phase and γ matrix of the alloy: (a) correlation between \( (r_t^3 - r_0^3) \) and aging time; and (b) correlation between γ matrix channel width and aging time.

Fig. 3 TCP precipitates in the alloy after LTA at 1040 °C for (a) 600 h; and (b) 800 h.
lattices of the $\gamma$ and $\gamma'$ phases. So a large nucleation barrier serves to prevent the formation of the TCP phase in the microstructures [16]. When the TCP phase forms in the alloys, it nucleates preferentially on close-packed planes, forming a semi-coherent interface and exhibiting distinctive orientation relationships with the parent crystal [17].

3.2. Stress rupture properties

The stress rupture properties, stress rupture life and elongation, of the LTAed alloys at 980 °C/250 MPa and 1070 °C/140 MPa are shown in Fig. 5. It indicates that the stress rupture life under two conditions represents the same tendency and decreases in some extent with the aging time (see Fig. 5(a and c)). The stress rupture life of the alloy aged for 800 h is 353 h at 980 °C/250 MPa and 362 h at 1070 °C/140 MPa, which is much better than those of the second generation single crystal superalloys, CMSX-4, SC180, RenêN5 and DD6, without LTA. For example, the stress rupture life of the CMSX-4, SC180, RenêN5 and DD6 superalloys at 980 °C/250 MPa is 178 h, 197 h, 228 h and 275 h, respectively [18,19]. The elongation of the alloy at 980 °C/250 MPa and 1070 °C/140 MPa as shown in Fig. 5(b and d) decreases at first when aged for 200 h. Then it increases until the aged time of 600 h.

![Fig. 4](image_url) EDX analysis of TCP phase in the alloy after LTA for 800 h at 1040 °C.

![Fig. 5](image_url) The stress rupture properties of the alloy at different conditions: (a,b) 980 °C/250 MPa; and (c,d) 1070 °C/140 MPa.

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>Re</th>
<th>Ta</th>
<th>W</th>
<th>Ni</th>
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<tbody>
<tr>
<td>Content</td>
<td>3.04</td>
<td>3.21</td>
<td>8.89</td>
<td>3.33</td>
<td>17.97</td>
<td>6.73</td>
<td>14.22</td>
<td>Bal.</td>
</tr>
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</table>

Table 2 Chemical composition of TCP phase in the alloy after LTA for 800 h (mass fraction, %).
Finally, it decreases again at the aged time of 800 h, but it is still larger than that before LTA. The elongation dependent on the aging time is different with that of the stress rupture life. Similar phenomenon is observed in the CMSX-10 [6]. Liu et al. pointed out that during LTA, the microhardness of the single crystal superalloy increases first and decreases afterward, but after LTA for some time the microhardness increases again [10]. This may be the reason why the elongation changes with the aging time in such a way, as shown in Fig. 5(b and d).

Fig. 6 illustrates the stress rupture fracture surface of the tested alloys aged at 1040 °C for 800 h. Under 980 °C/250 MPa and 1070 °C/140 MPa conditions the rupture surfaces are mainly characterized by square-shaped dimples, which reveal that the samples almost display a ductile fracture mode. Ductile fracture consists in square-like facets oriented <001> planes. On the fracture surfaces, the TCP phase can also be seen (see Fig. 6(b and c)). Although the TCP phase may affect the fracture process at some extent, it does not embrittle the alloy because the aged samples still have a tensile elongation larger than 20% and the dimple fracture characteristic is not changed by the TCP phase.

4. Discussion

The nickel-based single crystal superalloys are mainly strengthened by a high volume fraction of the γ’ phase embedded coherently in the γ matrix. The stress rupture properties depend on the morphology, size, volume fraction and distribution of the γ’ phase. It has been reported that the γ’ coarsening is responsible for the degradation of creep properties of single crystal superalloys [6,20]. At high temperatures, deformation is dominated by the dislocation climb. The width of the γ matrix channel is enlarged after LTA, resulting in the dislocations to easily move in the γ matrix. This leads to a decrease in strength. When the γ’ phase is coarsened during thermal exposure, the resistance to the dislocation movement by Orowan’s mechanism becomes weak owing to larger width of the γ channels [21]. Thus, the stress rupture life drops with a large magnitude. Moreover, the volume fraction of the γ’ phase reduces with the increasing aging time, which decreases the precipitation strengthening effect of the aged alloy as well.

It can be seen from Fig. 3 that the TCP phase precipitates in the alloy after LTA for 600 h. This is another reason for the decrease of the stress rupture life of the aged alloy. The TCP phase is detrimental to stress rupture properties of alloys [8,9]. There are three main reasons for the negative role of the TCP phase on the stress rupture properties. Firstly, the TCP phase is brittle; it is the site for crack initiation and the easy way for crack propagation. Secondly, the TCP precipitates destroy the continuity of the microstructure. Finally, the solid solution strengthening elements in the alloy, such as Re and W, are enriched in the TCP phase, as shown in Fig. 4 and Table 1, which results in poor Re and W in the γ matrix surrounding the TCP phase and decreases the solid-solution strengthening of the γ matrix. Therefore, these lead to an extensive envelope of the soften γ phase around the TCP phase which may potentially act as a channel for preferential deformation [8].

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Fig. 6 Fractographs of the stress ruptured alloys after LTA for 800 h: (a,b) 980 °C/250 MPa; and (c,d) 1070 °C/140 Mpa.
on the TCP phase, and the microcracks disrupt the rafted γ precipitates. High stress concentration at the TCP/γ matrix interfaces or at the locations where interlinking the TCP precipitates is thought to result in the microcracking. It can be concluded that the degeneration of the stress rupture life after LTA is dominated by the γ’ coarsening and TCP phase formation.

Based on the above investigation on the microstructure and phase stability of the LTAed alloy, it can adjust the content of Re and W element and the heat treatment regime to make the alloy be more resistant to the formation of the TCP phase.

5. Conclusions

(1). The γ’ coarsening and the γ matrix channel broadening are observed in the samples LTAed at 1040 °C, but γ’ morphology was still in cubic shape after LTA for 800 h. The coarsening kinetics of the γ’ particles closely follow a linear line.

(2). Needle shaped and granular TCP phase precipitated in the alloy when aged for 600 h. With further increasing of the aging time, the volume fraction of TCP phase increases. The TCP phase with high Re and W content precipitates and grows along a fixed direction.

(3). With increasing aging time, the rupture life of the alloy at 980 °C/250 MPa and 1070 °C/140 MPa all turns shorter. The degeneration of stress rupture life is dominated by the γ’ coarsening and TCP phase formation.

References


