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ARTICLE

Dual Effects of Ruthenium on TCP Precipitation of a Single Crystal Superalloy at 980 and 1160 °C

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Abstract: In order to study the effect of Ru on the microstructure stability of high generation single-crystal superalloys, two single-crystal superalloys D1 and D2 containing 6wt% Ru and 4.5wt% Ru were prepared, respectively. After complete heat treatment, they were long-term aged at 980 and 1160 °C for 200 h. The alloy microstructure of different scales, compositions of topologically close-packed (TCP) phase and TCP crystal structures were investigated. Results show that after long-term aging at 980 °C for 200 h, the precipitation of TCP in D1 alloy containing more Ru is higher than that in D2 alloy; after long-term aging at 1160 °C for 200 h, no TCP phase is observed in D1 alloy, while a small amount of TCP phase is observed in D2 alloy; the TCP phases in both alloys are of the same type, and Ru is one of the main forming elements. The experimental results were analyzed combined with d-electrons concept and thermodynamic calculation. Results show that the influence of Ru on the TCP precipitation of single crystal superalloys has two sides. On the one hand, adding Ru can increase the d-electron energy level of single crystal superalloys, which can increase the TCP precipitation tendency. On the other hand, the increase of Ru content can reduce the segregation of refractory elements in γ phase, thus reducing the amount of TCP phase precipitation caused by the supersaturation of refractory elements. At different temperatures, the main influencing factors are different.

Key words: single crystal superalloy; ruthenium; microstructure stability; topologically close-packed phase; dual effects

Continuing demand for developing Ni-based superalloys with higher temperature capability has led to more and more refractory alloying additions, such as W, Mo, Ta, Re, Nb[1-7]. However, this not only increases the high temperature strength of the alloy, but also increases the precipitation tendency of the harmful topologically close-packed (TCP) phase in the alloy. In order to reduce the adverse effect on the microstructure stability caused by high content of refractory elements, the element ruthenium (Ru) is introduced into single crystal superalloys[8,9].

It is generally believed that the element Ru can inhibit TCP precipitation and improve the high temperature capability of single crystal superalloys[10-13]. Since it begins to appear in the fourth generation single crystal superalloys, increasing more Ru content has been tried. In some reports, the Ru content of the studied alloy is even as high as 7wt%[14]. However, in some later studies, it is found that Ru is also a TCP forming element, which can promote TCP precipitation[15,16]. Therefore, the influencing mechanism of Ru on the precipitation behavior of TCP phase in single crystal superalloys has seldom been determined[17].

In order to reveal the influence of Ru on the microstructure stability of single crystal superalloy, two single crystal superalloys containing different Ru amounts were investigated after long-term aging at 980 and 1160 °C. The beneficial and harmful effects of Ru on the microstructure stability of high generation single crystal superalloys were studied.

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1 Experiment

Two single crystal superalloys were designed according to the composition characteristics of single crystal superalloys containing Ru, whose Ru content is 6wt% (named as D1 alloy) and 4.5wt% (named as D2 alloy). Both D1 and D2 alloys contain 22.5wt% refractory elements including W, Mo, Ta, Re and Nb.

The single crystal bars of Φ15 mm×170 mm were cast with a crystal selection method in a directionally solidified furnace with high temperature gradient. After complete heat treatment, the two single crystal superalloys were long-term aged at 980 and 1160 °C for 200 h. The dendrite core region was selected for analysis to avoid the influence of element dendrite segregation. The microstructure in different scales was observed by DM4000M type optical microscope (OM) and Nava NanoSEM450 type field emission scanning electron microscope (FSEM). The micro-area compositions were tested by JXA-8100 type electron probe. The TCP compositions were detected by JEM2100F type field emission transmission electron microscope (FTEM), and the phase structures of TCP phase were analyzed by XRD.

After analyzing above results with the combination of d-electron energy level calculation and thermodynamic calculation, the beneficial and harmful effects of Ru on the microstructure stability of high-generation single crystal superalloy and the synergistic effect of Ru on the microstructure stability of high generation single crystal superalloys were discussed.

2 Results

Fig.1 shows the dendrite microstructures of D1 and D2 alloy after complete heat treatment. As can be seen, the eutectic phase has been completely eliminated in both alloys. Due to dendrite segregation, there is a slight color difference between the dendritic cores and interdendrites[18]. In order to avoid the influence of element dendrite segregation, the dendrite core region was selected for analysis.

The typical microstructure of the dendrite core region after complete heat treatment is analyzed by a field emission scanning electron microscope (FSEM), as shown in Fig.2. Regular γ/γ' structures form in both alloys, and no TCP precipitation is observed.

The dendrite compositions were analyzed using electron probe microanalysis with the beam spot diagram diameter of 20 μm, as shown in Table 1. Except for Ru content, there is no much difference in composition between the two alloys.

The γ and γ' phase components of the D1 and D2 alloy after heat treatments are analyzed with TEM, and Eq.(1) is used to calculate the phase segregation coefficient k_i, as shown in Fig.3. Since the Nb contents are very low in both alloys, the Nb element is ignored here.

$$k_i = C_{\gamma,i}/C_{\gamma',i} \quad (1)$$

where $C_{\gamma,i}$ and $C_{\gamma',i}$ are the atomic concentration of the element i in γ phase and γ' phase, respectively.

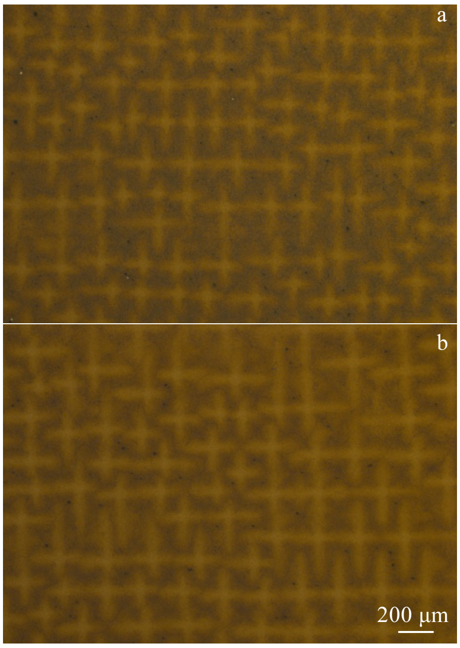

Fig.1 OM images of dendrite structure in D1 (a) and D2 (b) alloys

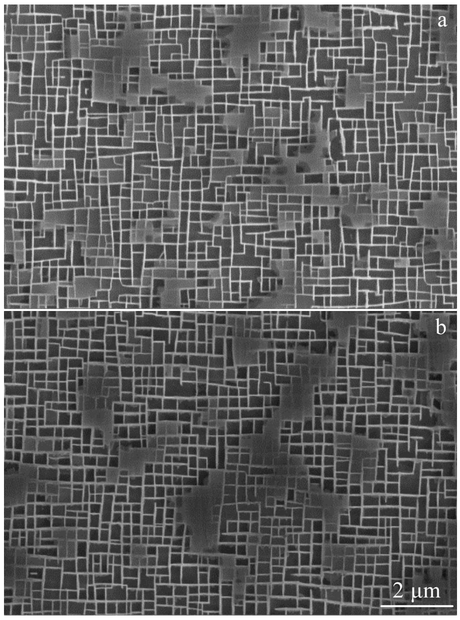

Fig.2 FSEM images of dendrite regions of D1 (a) and D2 (b) alloys

Table 1 Dendrite compositions of the two experimental alloys after heat treatment (wt%)

Alloy	Al	Ta	Ru	Co	W	Mo	Cr	Re	Nb	Ni
D1	5.4	7.2	6.1	6.3	7.7	1.7	2.0	8.5	0.4	Bal.
D2	5.3	7.4	4.7	6.5	7.4	1.8	2.1	8.7	0.4	Bal.

As can be seen from Fig.3, the D2 alloy with lower Ru content has larger phase segregation coefficients than D1 alloy. The segregation coefficient of Re is 6 in D1 alloy while it increases to 20 in D2 alloy.

The microstructures of the dendrite region after long-term aging at 980 and 1160 °C for 200 h are shown in Fig.4 and Fig.5. After aging at 980 °C for 200 h, D1 alloy with higher Ru content precipitates more TCP phase than D2 alloy with lower Ru content. However, after aging at 1160 °C for 200 h, TCP phase is precipitated in D2 alloy while no TCP phase is observed in D1 alloy.

The TCP phases of the samples in Fig.4 and Fig.5b are separated by extraction method, and the phase structures of TCP phase are analyzed by XRD. According to the XRD analysis results, all TCP phases in the above samples are the same phase, whose structure is hexagonal and the space group is $P6_3/mmc$. The XRD pattern of the TCP phase extracted from D1 alloy after aging at 980 °C is shown in Fig.6.

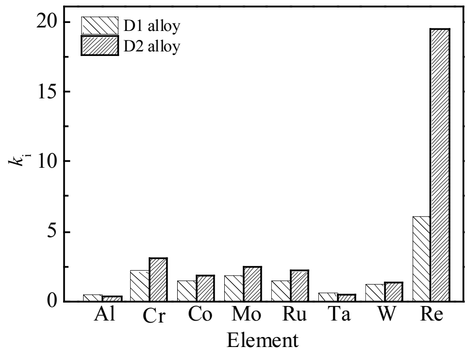

Fig.3 Phase segregation coefficient k_i of alloying elements after complete heat treatment

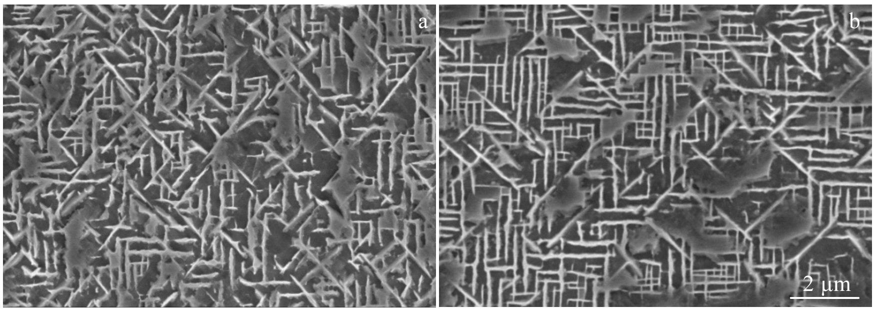

Fig.4 FSEM images of dendrite regions of D1 (a) and D2 (b) alloy after aging at 980 °C for 200 h

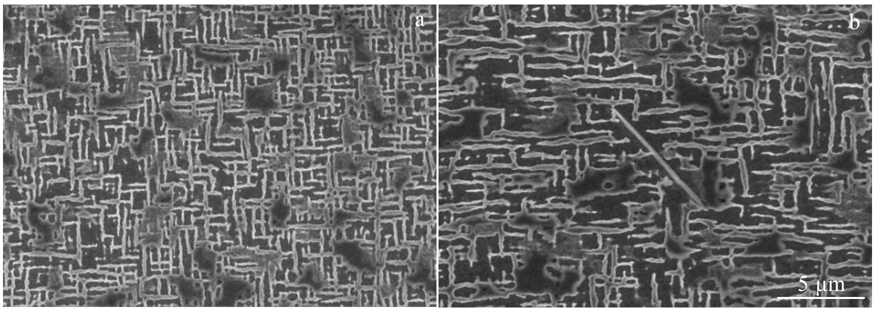

Fig.5 FSEM images of dendrite regions of D1 (a) and D2 (b) alloy after aging at 1160 °C for 200 h

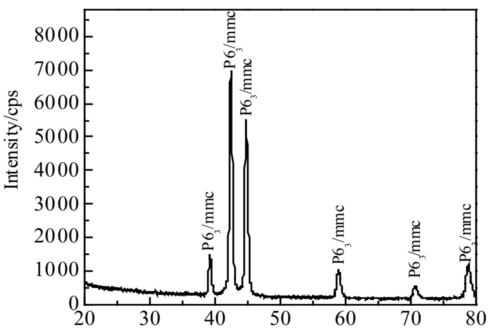

Fig.6 XRD pattern of extracted TCP phases

The components of TCP phases are analyzed by FTEM, as shown in Table 2. As can be seen, in addition to the most important TCP forming element Re, Ru also has a high content in the TCP phase of both alloys. This indicates that Ru is also the main forming element of TCP phase in this study.

The variation of TCP precipitation amount with Re and Ru content was calculated using the material calculation software JMatPro, taking the content of alloying elements other than Ru and Ru in Table 1 as the reference composition. The results are shown in Fig.7. It can be seen that the increase of Re and Ru content promotes TCP precipitation at both 980 and 1160 °C. At the higher temperature of 1160 °C,

Table 2 Element contents in TCP phase (wt%)

Alloy	Re	Ru	Co	Al	W	Cr	Ta	Mo	Nb	Ni
D1	25.0	9.8	4.8	1.7	8.7	2.0	6.2	2.5	0.4	Bal.
D2	35.0	9.9	5.2	1.2	8.0	2.8	4.2	2.5	0.3	Bal.

precipitation of TCP is less than that at 980 °C. The slopes of TCP equivalent line are calculated, which are −5.3 in Fig.7a and −4.2 in Fig.7b. This indicates that although Ru is also a TCP forming element, its promoting effect on the precipitation of TCP is weaker than the element Re.

3 Discussion

When designing the compositions of single crystal superalloys, the d-electrons concept is often used to judge the TCP precipitation tendency of the alloy[19,20]. The $\overline{\mathrm{Md}}$ level of the alloy is calculated by

$$\overline{\mathrm{Md}} = \sum_i x_i \mathrm{Md}_i \qquad (2)$$

where x_i represents the mole fraction of element i. Values of the Md_i parameters for each element can be taken from Table 3. When the $\overline{\mathrm{Md}}$ level is larger than 0.915, the alloy is considered to prone to TCP precipitation, and higher Md values indicate higher probability of TCP formation.

It can be seen from Table 3 that other than refractory elements such as Re, W, Mo, Ta, Nb, the Md value of Ru is also higher than 0.915. In other words, the increase of Ru content will also increase the TCP precipitation tendency. In fact, some studies in recent years have also reported that Ru is a TCP forming element[15,16], which is consistent with the

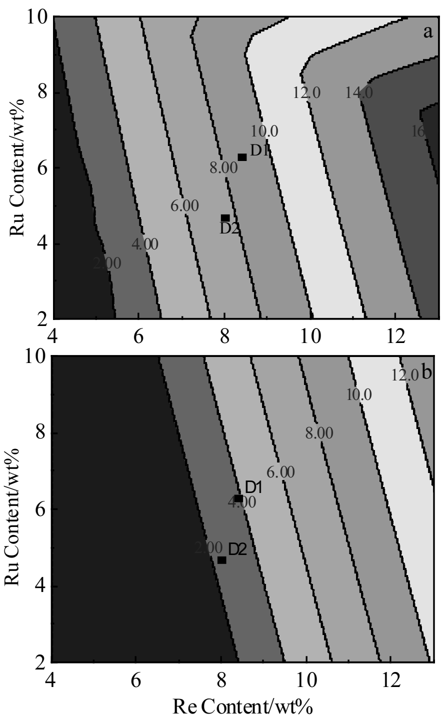

Fig.7 Variation of TCP precipitation with Re and Ru content at 980 °C (a) and 1160 °C (b)

Table 3 Md value of alloying elements in single crystal superalloys (eV)[20,21]

Ni	Co	Ru	Cr	Re	Mo	W	Al	Nb	Ta
0.717	0.777	1.006	1.142	1.267	1.55	1.655	1.9	2.117	2.224

phenomenon at 980 °C in this study. Then why has Ru always been regarded as an alloying element that inhibits TCP precipitation?

It is generally believed that refractory elements such as Re, W, Mo, Ta, Nb are the main reason for TCP precipitation, especially Re [16,22], while the element Ru can reduce the amount of TCP phase[12,13]. However, in this study, Ru is another TCP forming element next to Re.

Another question is, if Ru is the TCP forming element, why is it always regarded as an alloying element that improves the microstructure stability of single crystal superalloys? Accordingly, in this study, TCP is observed in D2 alloy at 1160 °C, while no TCP is observed in D1 alloy, which is contrary to the phenomenon at 980 °C.

As can be seen from Fig.7, the content of refractory elements in the γ phase of D2 alloy is much higher than that in the γ phase of D1 alloy. Since TCP phases tend to precipitate from γ phase due to the supersaturation of refractory elements in γ phase, their greater segregation in γ phase will increase the tendency of TCP precipitation in the alloy to some extent. The research of Yin et al suggests that the increase of supersaturation of matrix phase will increase the precipitation tendency of TCP in the alloy[23], which also supports the above viewpoint.

According to the above analysis, Ru has dual effects on the microstructure stability of single crystal superalloys.

(1) The negative effect. Ru is a TCP forming element, and the increase of Ru tends to increase the TCP precipitation tendency of single crystal superalloys.

(2) The positive effect. The increase of Ru content can reduce the segregation of refractory elements in γ phase, which reduces TCP precipitation tendency of γ phase. As a result, the amount of TCP precipitation is reduced accordingly.

For all high generation single crystal superalloys containing Ru, the positive and negative effects of Ru on microstructure stability work simultaneously, but the determinants depend on the circumstances. For this study, the above negative effect of Ru on microstructure stability plays the major role at 980 °C, so more TCP phases are precipitated from D1 alloy. At 1160 °C, the positive effect of Ru plays the major role, resulting in a small amount of TCP precipitation in the D2 alloy while no TCP is observed in the D1 alloy.

Based on the above analysis, the design of high generation single crystal superalloy containing Ru should be considered from the following three aspects to obtain better microstructure stability.

(1) Macrocomposition of alloy. The increase of Ru content will increase the overall TCP precipitation tendency of the alloy. Therefore, the upper limit of Ru amount should be controlled, not more is better.

(2) Microcomposition of γ phase. Ru has a significant effect on the segregation behavior of refractory elements in γ phase, which affects the precipitation tendency of TCP phase. As a result, the influence of Ru on the microcomposition of γ and γ' phase should also be considered.

(3) Thermodynamic factor. For high generation single crystal superalloys containing Ru, temperature selected for the performance study may be higher than that for the study of microstructure stability, based on the reason that TCP precipitation may not be obvious at higher temperatures. Therefore, it is necessary to study the microstructure stability in a larger temperature range.

4 Conclusions

1) After long-term aging at 980 °C for 200 h, the TCP precipitation of D1 alloy containing 6wt% Ru is significantly higher than that of D2 alloy containing 4.5wt% Ru. After aging at 1160 °C for 200 h, no TCP phase is observed in D1 alloy, while a small amount of TCP phase is observed in D2 alloy.

2) The TCP phases precipitated in D1 and D2 alloy at 980 and 1160 °C are the same phase, whose structure is hexagonal and the space group is $P6_3/mmc$, and Ru and Re are the main forming elements.

3) For single crystal superalloys containing Ru, on the one hand, adding Ru can increase the d-electron energy level, thereby increasing the TCP precipitation tendency; on the other hand, the increase of Ru content can reduce refractory element segregation in γ phase, thus decreasing TCP phase precipitation caused by the supersaturation of refractory elements.

4) Ru has dual effects on the microstructure stability of single crystal superalloys. For the alloys in this study, Ru mainly plays the role of increasing TCP precipitation at 980 °C, while reducing the supersaturation of refractory elements in γ phase and reducing TCP precipitation at 1160 °C.

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钌对一种单晶高温合金 980 和 1160 ℃下 TCP 相析出影响的两面性

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摘 要：为研究 Ru 对高代单晶高温合金组织稳定性的影响，制备分别含有 6%和 4.5% Ru（质量分数）的 2 种单晶高温合金 D1 和 D2，完全热处理后置于 980 和 1160 ℃下进行 200 h 的长期时效，分析合金长期时效后的显微组织、不稳定拓扑密排相(TCP)成分及晶体结构。结果表明：980 ℃时效 200 h 后，含 Ru 较多的 D1 合金中 TCP 析出量显著多于 D2 合金；1160 ℃时效 200 h 后，D1 合金中未观察到 TCP 相，而 D2 合金中观察到少量 TCP 相；2 种合金析出的 TCP 相为同一种 TCP 相，Ru 为其主要形成元素之一。结合 d 电子能级计算和热力学计算分析表明：Ru 对单晶高温合金 TCP 析出的影响具有两面性。一方面 Ru 含量提高会使合金 d 电子能级增大，增加合金 TCP 析出倾向；另一方面 Ru 含量增加可降低高熔点元素在 γ 相中的偏析程度，进而减小因高熔点元素在 γ 相中过饱和而导致的 TCP 相析出量；在不同温度下，起主要作用的因素会有所不同。

关键词：单晶高温合金；钌；组织稳定性；TCP；两面性

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