Effect of Ru on the concentration distribution of elements and creep properties of nickel-based superalloy

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Abstract. The effects of Ru on creep properties, microstructure and elemental concentration distribution of nickel-based single crystal superalloy containing without Ru and 2% Ru are studied by means of creep tests under high temperature, morphology observation after heat treatment and determination of elemental concentration distribution by atomic probe. The results show that Ru can inhibit the precipitation of TCP phase and improve the solid solubility of W element in the alloy and the creep life of the alloy at high temperature. At the same time, the addition of element Ru can make the alloy to produce "reverse distribution" effect, improve the alloying degree of \( \gamma' \) phase and the effect of solution strength, which finally significantly improve the high temperature creep rupture properties of the alloy containing Ru.

1. Introduction

Nickel-based single crystal alloy is a kind of superalloy with nickel as the matrix, which is composed of Al, Co, Cr, W and other elements. It is prepared by directional solidification technology, which has been used in aerospace, warships, power generation, chemical industry and other important industrial fields due to good high temperature strength, oxidation resistance, corrosion resistance and fatigue resistance [1,2].

The addition of Ru is one of the important signs of the fourth generation of nickel-based single crystal superalloy. It was found that Ru is slightly segregated in the dendrite regions during solidification, and Ru had not obviously effect on the segregation behavior of other elements in the inter-dendrite/dendrite regions [3,4]. Other studies showed that no obvious the Ru is segregated in the inter-dendrite/dendrite regions [4,5], but can reduce the segregation of W, Mo and other refractory elements. The morphology of the alloy containing Ru showed that Ru can reduce the size of \( \gamma' \) phase and increase the cubic degree of \( \gamma' \) phase, which it can make the mismatch degree of \( \gamma /\gamma' \) two phases more negative[6,7]. However, it has been reported that Ru has no significant effect on the mismatch of \( \gamma /\gamma' \) two phases [8]. O'Hara et al.[9] found that Ru can change the distribution ratio of elements in the two phases of \( \gamma /\gamma' \), and propose the "reverse distribution" effect. The so-called "reverse distribution" effect refers to the diffusion of element that was mainly segregated in \( \gamma' \) phase to \( \gamma \) phase by adding Ru, thus reducing the concentration of the element in \( \gamma' \) phase and increasing the concentration in \( \gamma \) phase.
The element which was mainly segregated in $\gamma$ phase diffused into the $\gamma'$ phase, which reduced the concentration of the element in the gamma phase and increased the concentration in the gamma phase.

Ofori et al. [10] showed that Ru can indeed change the distribution ratio of elements in two phases of $\gamma'/\gamma$, especially Ru can significantly reduce the distribution ratio of Re, at the same time, the addition of Ru can reduce the possibility of TCP phase precipitation. However, some studies have different conclusions, for example, Cui et al. believed that Ru had no effect on the distribution behavior of elements Cr, Mo and Co, and that Ru should not inhibit the precipitation of TCP phase.

In this paper, 2%Ru alloy was designed and prepared. By means of observation of microstructure, determination of element concentration and creep properties test, the effects of Ru on element concentration distribution, high temperature creep properties and morphology of nickel-based single crystal alloys were studied, and which is tried to find a way to prepare high performance Re-free nickel-based single crystal alloys containing Ru for providing theoretical basis and data support in future alloy composition design.

2. Experimental materials and methods

Three nickel-based single crystal alloys have been designed and prepared, which their mass fraction and atomic fraction are shown in Table 1. The main difference between the three alloys lies in the presence or absence of Ru elements. Ru-free alloys containing 4%W is defined as alloy 1 and Ru-free alloys containing 6%W as alloy 2, and 2%Ru alloys containing 6%W is defined as alloy 3.

| Table 1. True chemical composition of the alloys. |
|-----------------------------------------------|
| Al | Ta | Cr | Co | Mo | W | Ru |
| wt.% | at.% | wt.% | at.% | wt.% | at.% | wt.% | at.% | wt.% | at.% |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Alloy 1 | 5.98 | 13.35 | 7.62 | 2.54 | 5.82 | 6.74 | 5.97 | 6.10 | 6.25 | 3.92 | 4.07 | 1.33 | 0 | 0 |
| Alloy 2 | 6.00 | 13.46 | 7.65 | 2.55 | 5.80 | 6.58 | 5.90 | 6.12 | 6.25 | 3.92 | 5.99 | 2.04 | 0 | 0 |
| Alloy 3 | 5.99 | 13.69 | 7.55 | 2.53 | 5.80 | 6.58 | 5.89 | 6.12 | 6.07 | 3.81 | 5.96 | 2.02 | 1.98 | 1.20 |

DSC curves of the three alloys show that the initial melting temperatures are about 1323°C. Thereby, the heat treatment process of the alloy is determined as follows: 1280°C × 2 h, A. C + 1315°C × 4 h, A. C + 1070°C × 4 h, A. C + 870°C × 24 h, A. C (A.C is air cooling). After completely heat treatment, the sheet creep specimens with cross section of 4.5mm × 2.5mm and gauge length of 20mm were prepared. After mechanical grinding and polishing, the creep samples were putted into the creep testing machine named GTW504 to test the creep properties under different conditions.

After mechanical grinding and polishing of alloys with different compositions and states, chemical corrosion was carried out. The composition of corrosion solution was HCl (38%, 100ml) + CuSO₄ · 5H₂O (20g) + H₂O (80ml) + H₂SO₄ (98%, 5ml). The corroded specimens were cleaned by ultrasonic and observed by SEM. The element concentration distribution of $\gamma'/\gamma$ two-phase in Ru-free alloy and 2%Ru alloy under different states were measured by atomic probe. The needle-like sample of 0.3 mm × 0.3 mm × 14 mm were prepared along the orientation of [001], and that were inserted into the three-dimensional atomic probe (3DAP) of LEAP4000XHR, which can determination element concentration distribution after electro polishing.
3. Results and Analysis

3.1 Effect of W on microstructure
After complete heat treatment, the microstructures of three alloys with different compositions are observed as shown in Figure 1, in which Figure 1(a) is the morphology of free-Ru/4% W alloy, Figure 1(b) is the morphology of free-Ru/6% W alloy and Figure 1(c) is the morphology of 2% Ru/6% W alloy.

It can be seen from the Figure 1 that the structure of three alloys is basically the same, all cubic γ’ phases are embedded in the matrix of γ phase with a coherent manner, and the cubic γ’ phases are arranged regularly in the direction of <100>. Among them, the size of γ’ phase in alloy 1 and alloy 2 is about 0.46μm, the size of matrix channel is about 0.1μm, and the volume fraction of γ’ phase is about 62%. The size of γ’ phase in alloy 3 is about 0.42μm, the size of matrix channel is about 0.05μm, and the volume fraction of γ’ phase is about 67%. TCP phase taken on short rod can be seen in alloy 2 as shown in the white arrow of Figure 1 (b). It is concluded that the difference of three alloys lies in the different contents of Ru and W. Compared with alloy 1, the W content of alloy 2 increased can led to. Compared with alloy 2, alloy 3 adding 2% Ru has not precipitation of TCP phase. Therefore, it can be inferred that the increase of W content is the main cause of precipitation of TCP phase, while the addition of Ru inhibits the precipitation of TCP phase.

![Figure 1. Morphology of (a) free-Ru/4%W alloy, (b) free-Ru/6%W alloy and (c) 2%Ru/6%W alloy after full heat treatment.](image)

3.2 Creep Property of alloy
The creep properties of three alloys after fully heat treatment were tested under high temperature. The experimental conditions were 1100℃/137MPa. The creep curves were drawn as shown in Figure 2, in which curves 1, 2 and 3 represented alloy 1, alloy 2 and alloy 3 respectively. It can be illustrated that the creep characteristics of the three alloys are obviously different. The creep life of alloy 3 is the longest of 182 hours, and creep can be divided distinctly into three stages, that is, initial stage, steady stage and acceleration stage, in which the steady stage lasts the longest time of 125 hours, and the strain rate is smaller of 0.0063%/h. Compared with alloy 3, alloy 2 has a longer creep life of 98h, and the three creep stages are not obvious, especially the strain rate value is bigger of 0.0527%/h in steady creep stage. The creep life of alloy 1 is the shortest of 42h, and the creep curve tends to be linear, and which is impossible to distinguish three stages of creep by creep curve.
The results show that the three alloys have different creep life. It can be inferred that the presence/absence of Ru and the different content of W are the main factors affecting the creep properties of the alloys under high temperature. It is considered that W of refractory element is the main solid solution strengthening element in nickel-based single crystal alloy, which the increase of W content can improve the high temperature properties, but W is also one of the main forming elements of TCP phase. The increase of W content can promote the precipitation of TCP phase and lead to the rigidly decrease of creep properties. The addition of Ru inhibits the precipitation of TCP phase. Therefore, the interaction between Ru and W is the main reason for the significant improvement of creep properties of the alloy.

![Image](image.png)

**Figure 2.** Creep curves of different alloys at 1100°C/137MPa.

3.3 **Effect of Ru on element concentration distribution**

Three-dimensional atomic probe (3DAP) was used to determine the concentration distribution of each element in the \( \gamma / \gamma' \) two phases of the two alloys. The concentration distribution of elements Ta and Mo was used to explain the test area and the distribution of element concentration, as shown in Figure 3. Figure 3 (a) and Figure 3 (b) are the concentration distributions of Ta and Mo in Ru-free alloys, which the dark region in the figure represents the higher concentration of the element and the light region represents the lower concentration of the element. According to the concentration distribution characteristics of Ta and Mo in single crystal nickel-based alloys, that is, Ta mainly distributes in \( \gamma' \) phase and Mo mainly distributes in \( \gamma \) phase, and thus it can be judged that area A is \( \gamma' \) phase and area B is \( \gamma' \) phase. Figure 3 (c) and Figure 3 (d) are the concentration distributions of Ta and Mo in 2%Ru alloys. Using the same method to judge the \( \gamma / \gamma' \) two-phase region, and it can be seen that the A region is \( \gamma' \) phase and the B region is \( \gamma \) phase. Take Figure 3 (c) as an example to illustrate the measure selection of concentration of atomic, and cubes of 25 nm x 30 nm are selected as the measurement areas of phase concentration in different phase regions. As shown by the square in the figure, only one phase area is shown in the figure, while the other phase area is the same, but not shown in the figure. In order to measure the concentration gradient at the interface of two phases, a cylinder measuring area of 10nm x 50nm is taken at the interface of two phases, as shown by the cylinder in the figure.

The average concentration of elements in the \( \gamma / \gamma' \) phase in the Ru-free and 2%Ru alloy is
determined as showed in Table 2. In order to compare the concentration distribution of elements in the two phases, the distribution ratio is introduced, that is, the average concentration of an element in the $\gamma'$ phase divided by the average concentration of the element in the $\gamma$ phase. The smaller concentration value is defined as 1, whereas the relatively larger part is defined as the multiple of 1. From Table 2, it can be seen that the distribution trend of elements in $\gamma/\gamma'$ phase is the same, in which Al and Ta as the forming elements of $\gamma'$ phase are mainly distributed in $\gamma'$ phase, while Mo and W are mainly distributed in $\gamma$ phase, and Ru is mainly distributed in $\gamma$ phase. However, the distribution ratios of elements in $\gamma/\gamma'$ phases are significantly different, and the distribution ratios of Al elements in alloy 2 are significantly lower than alloy 1, while the distribution ratios of W and Mo elements are significantly higher. This is attributed to the "reverse distribution" effect, that is, the diffusion of elements mainly segregated in $\gamma'$ phase to the $\gamma$ phase results in the decrease of the concentration of the element in the $\gamma'$ phase and the concentration in $\gamma$ phase. The concentration of the element mainly segregated in $\gamma$ phase diffused to the $\gamma'$ phase, which can reduce the concentration of the element in the $\gamma$ phase and increase the concentration in $\gamma'$ phase.

![Figure 3](image-url)

**Figure 3.** Schematic maps of Ta and Mo concentration distributions and the ROI positions in (a) Ta—Ru-free alloy, (b) Ru-free alloy, (c) Ta-2%Ru alloy and (d) Mo-2%Ru alloy after fully heat treated.
Table 2. Concentration distribution of elements in $\gamma'/\gamma'$ phases of various alloys.

| Alloy   | Region | Al | Ta  | Cr  | Co  | Mo | W   | Ru | Total |
|---------|--------|----|-----|-----|-----|----|-----|-----|-------|
|         | $\gamma$ phase | 2.72 | 0.45 | 16.4 | 11.78 | 8.32 | 2.32 | 0 | 41.99 |
| Alloy 1 | $\gamma'$ phase | 18.91 | 3.72 | 1.68 | 3.00 | 1.53 | 0.81 | 0 | 29.65 |
|         | Ratio   | 6.95/1 | 8.28/1 | 1/9.74 | 1/3.92 | 1/5.44 | 1/2.85 | - | 1/1.42 |
|         | $\gamma$ phase | 4.69 | 0.49 | 15.12 | 10.75 | 7.13 | 2.27 | 3.13 | 43.58 |
| Alloy 3 | $\gamma'$ phase | 18.20 | 3.52 | 1.98 | 4.03 | 2.21 | 1.73 | 1.41 | 33.08 |
|         | Ratio   | 3.88/1 | 7.18/1 | 1/7.64 | 1/2.67 | 1/3.22 | 1/1.31 | 1/2.21 | 1/1.32 |

The results show that Ru can improve the solubility of elements and decrease the distribution ratio in $\gamma$ and $\gamma'$ phases. It is concluded that the main difference between the two alloys lies in the presence or absence of Ru element. It can be inferred that the addition of Ru element is the main reason for the "reverse distribution" effect. At the same time, adding Ru can increase the total atomic fraction of elements in $\gamma$ phase from 41.99% to 53.58%, and in $\gamma'$ phase from 29.65% to 33.08%. This indicates that Ru can improve the alloying degree of $\gamma'$ phase of alloy, which is also the main reason that alloy containing Ru has better creep properties under high temperature.

4. Conclusions

(1) The creep life of Ru/4%W alloy, Ru/6%W alloy and 2%Ru/6%W alloy is 42h, 98h and 182h respectively under 1100 C/137 MPa.

(2) W is one of the main forming elements of TCP phase. The increase of W content can promote the precipitation of TCP phase and lead to a sharp decrease in creep properties of the alloy.

(3) During high temperature creep, W in $\gamma'$ phase can migrate to $\gamma$ matrix of free-Ru alloy, meanwhile, W has a larger concentration gradient in $\gamma'/\gamma'$ phases transition region. The distribution of W in $\gamma'/\gamma'$ phase is relatively smaller, and the concentration gradient in $\gamma'/\gamma'$ phase transition region is also small in 2%Ru alloy.

(4) The addition of Ru can make the alloy produce "reverse distribution" effect, which can improve the alloying of $\gamma'$ phase, and make the alloy containing Ru have better high temperature creep properties.

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