Study on the high temperature microstructure stability of the high Al content Ni-based single crystal superalloy

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Abstract. The high-temperature structure stability of high Al content Ni-based single crystal superalloy was studied, the microstructure was observed, and the micro-mechanism of the thermal stability of the material was analyzed. The results show that the exposure time and exposure temperature have significant effects on the stability of the alloy’s high-temperature structure. With the increase of exposure temperature and/or exposure time, the γ′ phase in the material becomes coarser, gradually connects and grows, and the stability of the material structure is obviously reduced. Compared with standard heat-treated alloys after high temperature exposure, The absolute value of the γ′ and γ phases misfit increases significantly. With the increase of exposure time, although the absolute value of the two-phase misfit continues to increase, the increase of its absolute value gradually slows down. The long-term structural stability of the alloy under continuous exposure to high temperature environment is good.

1. Introduction

Superalloys are metal materials that can maintain service stability even when serve in a complex environment above 600°C. Superalloys are commonly used in aerospace engines and various industrial gas turbines. With the continuous increase in the thrust and thrust-to-weight ratio of aero-engines in recent years, the temperature of the turbine inlets has gradually increased, and the requirements for mechanical properties of parts have gradually increased. Materials of aero-engine turbine blade are also being updated. Superalloys are slowly developed into casting alloys, then to directionally solidified alloys, and finally to the single crystal alloys used in recent years. Now single crystal superalloys have become the main materials used in aerospace engines. The γ′ phase of high volume fraction and regular arrangement, and the solid solution strengthening of refractory elements ensure the good mechanical properties of superalloys. Under long-term thermal exposure conditions, almost every superalloy will appear to a varying degree changes of the organization. Organizational stability characterizes the safety and reliability of a material during the long-term use. Since the properties of the material will change with the microstructure, it is very important to the reliability of aero-engine whether the superalloy can maintain good organizational stability during the long-term work.\textsuperscript{[1-5]} So it is necessary to study the stability of the material under high temperature conditions. In this paper, a high Al content Ni-based single crystal superalloy is selected to study the evolution and mechanism of its structure under high-temperature environments, providing a basis for engineering application of superalloy and further optimization of material structure.
2. Test materials and methods

The samples used in this experiment are synthesized from the raw materials provided by the Beijing Nonferrous Metals Research Institute: Ni (purity 99.98%), Al (purity 99.99%), Mo (purity 99.91%), Ta (purity 99.9%), Re (purity 99.8%). The raw materials used in this experiment have high purity to reduce the influence of impurity elements on the microstructure and properties. The composition of the single crystal superalloy used in this test is shown in Table 1.

|       | Al | Mo | Re | Ta | Ni |
|-------|----|----|----|----|----|
| (at.%)| 18 | 7  | 1  | 1  | bal.|

The raw materials of high purity prepared in advance were mechanically polished to remove the surface oxide scale. Then we cleaned with acetone for decontamination and degreasing. Finally we dried for later use. The dried raw materials were weighed according to the weight percentage. The master alloy was smelted in an ISO/III-S vacuum furnace. Casted. After being uniformly smelted, the polycrystalline alloy test bars were obtained. The master alloy obtained after vacuum induction smelting was cut into alloy ingots. Washed, dried after sandblasting and grinding to remove the oxide scale. The single crystal superalloy were prepared by the spiral crystal selection method in the directional solidification furnace. Finally a rod-shaped single crystal superalloy of Ø15×135 mm was prepared.

The prepared single crystal superalloy test rods were cut into two sections on average. Then we put them in a tube heat treatment furnace for standard heat treatment. The heat treatment system used in this experiment was: solid solution 1280°C/4h+1290°C/4h+1300°C/4h, aging 1100°C/4h+850°C/24h, the cooling method was air cooling. The temperature-control accuracy of this experiment in the heat treatment process was ±2°C. All heat treatments were carried out in air under normal pressure.

The standard heat-treated single crystal superalloy test rods were cut into semi-cylindrical specimens of Ø20×10mm. In order to reduce the influence of air oxidation on the experimental results and simulate the actual environment of the alloy to the greatest extent. The tube was vacuum sealed and filled with argon for protection. Then, a tube furnace was used to conduct long-term unloaded heat exposure experiments at 1220°C and 1250°C for 200h, 400h, 600h, and 800h, respectively. In order to further eliminate the influence of high-temperature oxidation on the change law of alloy microstructure, the sample after long-term heat exposure was sectioned from the middle along the axial direction. The obtained section was the observation surface of the sample. Scanning electron microscope and X-ray diffractometer were used to observe the microscopic appearance of the sample and detect the misfit between different phases. Analyze the changing rule of its structure and misfit. Study the influence of temperature and exposure time on the high-temperature structure stability of the material.

3. Test results and analysis

3.1. The changing process and law of material structure

Figure 1 shows the microstructure of the alloy after standard heat treatment. The alloy consists of a high volume fraction of γ' phases and a small amount of γ phases. The γ' phases are cubic. The regularly arranged γ' phases are embedded in the γ matrix. Except for the two phases of γ' and γ, no other precipitated phases were observed in the tissue.
Figure 1. Microstructure of alloy after standard heat treatment.

Figure 2 shows the structure evolution of the alloy after 200h, 400h, and 600h non-stress high temperature heat exposure at 1220°C. Compared with the alloy microstructure after standard heat treatment, the size of the γ' phases become larger obviously. With the extension of the heat exposure time, the particle size of the γ' phases gradually become larger and the regularity becomes worse. The longer the high-temperature heat exposure time, the larger the size of the γ' phases. Parts of the γ' phases are connected to each other. After the standard heat-treatment sample is exposed to high temperature for 200h, the size of the γ' phases increase, parts of the γ' phases become round, and some of the γ' phases connect and grow. The shape of the γ' phases change, but some remain cubic and ordered. After exposure of 400h, the γ' phases connect and grow more obviously. The alloy structure is basically connected to the long-strip γ' phases. After exposure of 600h and 800h, the γ' phases connect to grow up seriously. Almost all γ' phases become long-strip structures. The width of the matrix γ phase channels are also significantly increased. The γ' phases even become a type of raft. During long-term exposure at high temperatures, the rafting process of single crystal superalloys is unavoidable.

Figure 2. Microstructure after long-term exposure at 1220°C. (a) 200h, (b) 400h, (c) 600h.

Figure 3 shows the microstructure evolution of the alloy after 200h, 400h, 600h, 800h non-stress high temperature heat exposure at 1250°C. According to the microstructure in the figure, the γ' phases of the alloy after heat exposure at 1250°C show the similar changing rule under the condition of 1220°C heat exposure. But the coarsening behavior of the γ' phases under the condition of 1250°C heat exposure is more obvious.
The high Al content Ni-based single crystal superalloy is exposed under non-stress conditions in high-temperature environments. The coarsening behavior is controlled by diffusion. According to the LSW theory, the γ' phases will coarsen after long-term exposure. The driving force is mainly the decrease of the interface free energy between the γ' phases and the γ matrix phases. The size of the γ' phases have a linear relationship with the cube root of time. The relationship can be summarized as:

$$r_t^3 - r_0^3 = kt$$  \hspace{1cm} (1)

In the above formula, $r_t$ is the average radius of the γ' phase when the exposure time is t, $r_0$ is the average radius of the γ' phase when the exposure time is 0, and k is the coarsening rate constant. Although the LSW theory was developed on the assumption that the precipitated particles are spherical and the volume fraction is zero. Combining with the results of computer simulations and many experimental measurements, in the non-spherical precipitated particles with elastic interfaces, the relationship between the average particle size and time also conforms to this cubic relationship.

In the alloy after standard heat treatment, the γ' phases are arranged in a regular and orderly cubic shape, and the γ' phases have good coherent relationship with the matrix γ phases. The Young's modulus along the [100] direction in the (001) crystal plane is relatively low. The elastic stress gradient along the [100] direction is larger. Therefore, the elastic strain energy of the γ'/γ interface on the (001) crystal plane in the [100] direction is higher than that of other crystal directions. The coarsening process of the γ' phases is controlled by the diffusion of alloying elements. When exposed to a high temperature of 1220 °C, under the action of the elastic strain energy and the interface energy, the γ' phases begin to grow along the [100] direction. With the continuous heat exposure time growing, a dislocation network will appear at the γ'/γ interfaces.[6,7] The interfacial dislocation network can coordinate the coherent misfit stress of the two phases, resulting in changes in the elastic stress field of the γ' phases that originally existed in a cubic shape. Coherent elastic strains only exist in some areas between the dislocation networks of the two-phase interfaces. The elastic strain gradient promotes the weakening of the directional diffusion of alloying elements. The growth of the γ' phases can only rely on the reduction of interface energy.[8] The reduction of the boundary area of the γ' and γ phases lead to a decrease in the interface energy, so the γ' phase continues to coarsen. Therefore, compared with the long-term exposure at 1220 °C, the alloying elements exposed at 1250 °C diffuse faster, the interface energy is reduced more, and the coarsening rate of the γ' phases is faster.[9]

### 3.2. Analysis of the misfit between the γ' and γ phases

As mentioned above, the microstructure change of the alloy during the heat exposure process is controlled by the diffusion process of the elements, and the misfit between the γ' and γ phases will have a huge impact on the diffusion process of the elements. Therefore, in-depth study on the changes...
of the misfit during the exposure process plays a vital role in proving the mechanism of the structure change of the alloy during high temperature service. [10] According to the characteristics of the Ni-based single crystal superalloy, the diffraction peaks of the γ' and γ phases obtained in the X-ray diffraction spectrum are superimposed on each other. The volume fractions of the γ' and γ phases are different, so the synthetic diffraction peaks are asymmetric. In this experiment, Origin software was used to split the synthesized diffraction peaks of the γ' and γ phases, and the Gaussian function was used for fitting, so that the fitting degree of the separated peaks reached more than 99% to ensure the accuracy of peak separation. Then use the following formula to calculate the lattice misfit of the alloy. [11]

\[
\delta = \frac{2}{\lambda} \left( \frac{a_{\gamma'} - a_\gamma}{a_{\gamma'} + a_\gamma} \right)
\]

Figure 4 shows the separated X-ray diffraction peaks of the high Al content Ni-based single crystal superalloy sample exposed for 0h, 400h and 800h at 1220°C. The γ' phases have a higher volume fraction, so the diffraction peak intensity is higher. The γ phases have a lower volume fraction, so the diffraction peak intensity is weaker.

Table 2 lists the calculated misfits between the γ' and γ phases of the alloy in each state. The fitting degrees of diffraction peaks are all above 99%. The accuracy of the peak splitting results is high enough. It can be concluded from Table 2 that the absolute value of the misfit increases significantly after exposure for 400 hours. With the extension of the exposure time, the absolute value of the misfit continues to increase. But the growth rate of the absolute value of the misfit slowed down.

Table 2. The degree of misfit between the γ' and γ phases.

| 2theta | Misfit (%) | Goodness of fit (%) |
|--------|------------|---------------------|
| original | γ phase 50.88272 | -0.0606 | 0.99442 |
|          | γ' phase 50.88514 |         |        |
| 400 h   | γ phase 50.03072 | -0.1512 | 0.99933 |
|          | γ' phase 50.11201 |         |        |
| 800 h   | γ phase 50.03712 | -0.1893 | 0.99521 |
|          | γ' phase 50.13712 |         |        |

In Ni-based single crystal superalloys, the lattice constants of the γ' and γ phases are different, so there is misfit between the two phases. The misfit is the driving force for the coarsening and aggregation of the γ' phase particles. The bigger the misfit, the bigger the interface strain energy. At the beginning of the high-temperature heat exposure, the coarsening of the γ' phases is mainly due to the reduction of the interface energy, which is controlled by diffusion. The initial diffusion speed is fast, and the misfit between the γ and γ' phases changes greatly. As the exposure process continues, the elastic coherent stress caused by the misfit between the γ and γ' phases gradually increases, the coherent stress also begins to affect the coarsening process of the γ' phases.

According to the Ostwald principle, with the extension of the high-temperature exposure time, the γ' phases gradually grow up during the high temperature exposure process. The dislocation networks appear at the interface between the γ' and γ phases. The interfaces between the γ' and γ phases in the
alloy appear in the semi-coherent state, the misfit stress is released and the \( \gamma' \) phases are promoted to grow further, so the misfit between the \( \gamma' \) and \( \gamma \) phases in the alloy increases.

Under normal circumstances, if the lattice misfit of the alloy is lower, the interface strain will be correspondingly smaller, and the alloy’s structural stability will be better. In this experiment, with the increase of the misfit, the interfacial strain energy of the alloy increases, and the structural stability decreases, but the long-term stability is good.

4. Conclusion
1) The high Al content Ni-based single crystal superalloy is exposed in the high-temperature environment. As the exposure time increases, the \( \gamma' \) phases in the material gradually become coarser and communicate with each other. The coarsening of the \( \gamma' \) phases is controlled by the diffusion of the elements. At higher temperature, the elements diffuse faster, the interface energy reduces more, and the coarsening speed of the \( \gamma' \) phases is faster.

2) Compared with the misfit of the standard heat-treated alloys, the absolute value of misfit is obviously increased after the material is exposed to high temperature. With the prolonged exposure time, the absolute value of the misfit continues to increase, but the increasing rate of its absolute value gradually slows down. The long-term structural stability of the alloy continuously exposed to high temperature environment is good.

3) In the early stage, diffusion promotes the coarsening of the \( \gamma' \) phases in the high Al content Ni-based single crystal superalloy. Causing dislocation networks to appear at the interface between the \( \gamma' \) and \( \gamma \) phases, thereby releasing the misfit stress. With the misfit between the two phases increasing, the increase of the misfit further promotes the coarsening of the \( \gamma' \) phases, which promotes the decrease of the high-temperature structure stability of the material.

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