Precipitation of $\gamma'$ Phase of DD6 at Unequal Service Temperatures

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Abstract. In this paper, the DD6 alloys after complete heat treatment were heat-treated at 900, 1000, 1100, 1200, 1300 °C for 1 h, then was air cooled. Microstructures treated by different temperatures were investigated by OM and FESEM. The microstructures evolution of alloys were estimated using JMatPro software and Image-Pro Plus. Conclusion illustrates the size of $\gamma'$ phase increases gradually after the DD6 alloy heat-treated at 900, 1000, 1100 and 1200 °C for 1 h, and the size reaches the maximum after heat-treated at 1200 °C. Most of the $\gamma'$ phase dissolves and then precipitate the irregular small $\gamma'$ phase, about 0.20 nm after preservation at 1300 °C. The size distribution of the $\gamma'$ phase turned into more and more uniform, and the best distribution state is achieved after preservation at 1100 °C; The matrix channel of the microstructure of DD6 widens gradually with temperatures increasing and reaches a maximum value at 1100 °C, about 65 nm. The matrix channel is narrowed gradually, and the most part of $\gamma'$ phase has serrated $\gamma'/\gamma$' phase surface after heat treatment at 1200 °C. After heat preservation at 900 °C, volume fraction of $\gamma'$ increases contrast that after complete heat-treatment; after heat-treatment at temperature degree of 1000-1200 °C, $\gamma'$ volume fraction decreases gradually; $\gamma'$ phase volume fraction increases again at 1300 °C. The different microstructure characteristics of DD6 after heat-treatment at unequal temperatures are obtained, indicating that the using temperature has a significant effect on the microstructure of DD6 alloy.

Keywords: DD6 alloy, single crystal superalloy, $\gamma'$ phase, microstructure evolution.

1. Introduction

Nickel-based single crystal superalloys are extensively expended on the manufacturing of turbine blades of gas turbines and jet engines, owing to their superior megathermal resistance, oxidation resistance saving good erosion rejection [1-3]. The future casting process of engine blades directly determines the performance of the engine and it is also a prominent symbol of the level of the national aviation industry. Therefore, further improving the service life of engine turbine blades under high degree of heat and high voltage have become the top priority of the current problem [4]. DD6 are independently studied by China. It has the advantages of high temperature strength, good comprehensive performance, stable structure and good casting process performance. Its tensile, long-lasting, anti-oxidation and heat-resistant corrosion properties have reached or exceeded the
performance of second-generation single-crystal superalloys PWA1484, René N5, CMSX-4, which are widely used abroad [5-6]. The γ' phase plays a major role in intensify the superalloys and it is completely coherent with the matrix γ phase, as indicated in figure 1. The size, shape, quantity and distribution of γ' phase has a great influence on the performance of DD6 superalloys [7-8]. The single crystal alloy is produced by directional solidification and spiral grain selection methods, and the solute is redistributed during the preparation process because crystallization rate is slow. The dendrites of the as-cast alloy are enriched with a large number of Al and Ta. They belong to γ' forming elements. The γ forming elements for instance W and Re are concentrated in the dendrites, which makes the single crystal superalloy during solidification. The dendritic morphology is intact and there is obvious dendrite segregation, which significantly effects the performance of DD6. Therefore, heat preservation of alloy is necessary [9]. The heat treatment can not only reduce the dendrite segregation, eliminating the eutectic segregation in the alloy, but also dissolve then re-precipitate γ' to obtain the finer, uniform and regular phase, and improve the performance of DD6. The heat treatment process of the single crystal superalloy is matched with the alloy composition design and other processes to make the single crystal alloy reach the optimum state. The heat treatment of single crystal superalloys is usually multi-stage heat treatment so as to eliminate segregation and eutectic structure towards the utmost extent, improving the initial melting temperature of the alloy, finally achieve a best collocation of the number, shape and composition of γ' phase. Thus, it is indispensable to conduct examination on the affect of high operating temperature on microstructure of superalloys. Standard heat-treated DD6 alloy was heat-treated at distinct temperatures to simulate alloy's service temperature. The microstructure evolution characteristics of the alloy at different temperatures were analyzed. The development mechanism of alloy structures were discussed by phase diagram calculation.

![Figure 1. Two phase structure of DD6 alloy](image)

2. Experimental procedures
Nominal composition of Nickel-based single crystal superalloy was employed as shown in Table 1. [001] oriented DD6 single crystal superalloy test bars were prepared by spiral grain selection methods and directional solidification. The preferred <001> direction was within 10° from the direction of the principal stress axis for investigation from the as-cast specimen bar. The specimens was completely heat treated first and specimens were kept at 900, 1000, 1100, 1200, and 1300°C for 1 h individually, and then air-cooled specifically. Figure 2 demonstrates the heat-treated system. Heat treatment structures and microstructures of the alloy treated with different temperatures were inspect by OM and FESEM. The volume fractional number of γ' was survey and evaluate by Image-Pro Plus. The thermodynamic calculation of the alloy was carried out by JMatPro software.

| Co  | W  | Ta | Al | Cr | Mo | Re | Nb | Hf | C   | Ni  |
|-----|----|----|----|----|----|----|----|----|-----|-----|
| 9   | 8  | 7.5| 5.6| 4.3| 2  | 2  | 0.5| 0.1| 0.006| Bal. |
3. Results and analysis

3.1. Standard heat-treated organization of alloy

Figure 3 shows the standard heat treatment conformation of DD6 after solution heat treatments and subsequent aging heat treatment. Since the micro structure of the as-cast superalloy contains more γ and γ′ eutectic, dendritic segregation and rough γ′ phase, these structures influence mechanical performance of alloys at high temperature, therefore the alloys must be solution heat treatments to dissove γ/γ′ eutectic and minimize chemical heterogeneities. The aging treatment is then carried out to adjust the γ′ phase structure to a suitable shape, quantity and size. It can be seen from the macroscopic structure shown in figure 3a that the morphology of the as-cast dendrite is not obvious. The dendritic and interdendritic are homogenized while the γ/γ′ eutectic is also eliminated substantially when completely heat treated. Presented in table 2, the γ′ phase is well-formed to a degree of 0.44 μm, the volume fraction of which is approximately 61%, and the average matrix channel width of the γ phase is 57 nm after standard heat treatment. The calculation results are the same as those of Shi Zhenxue et al. [10].

3.2. Microstructures of DD6 after heat treatments at different temperatures

Figure 4 shows that γ′ phase structure of DD6 at distinct temperatures for 1h. Figure 4 illustrates that after alloy is kept at 900 °C for 1 h, the γ′ phase still maintains cubic form, and the degree of cubicization and size are basically unchanged; the matrix channel is more straight than before, and volume fractional number of γ′ also show no significant change contrast the complete heat treatment. After 1000 °C heat treatment, the γ′ phase in DD6 superalloy still maintains cubic shape, and the degree of cubicization increases slightly. The size of the γ′ phase begins to increase slightly about 0.52 nm; the matrix channel becomes straight and significantly wider than complete heat treatment. The γ′ phase is still cubic, but the phase becomes larger, about 0.57 nm and its size and homogenization reach the best state after heat-treated at 1100 °C; the matrix channel is more straight, the volume fractional number of γ′ further grows. The size of γ′ continues to increase to 0.6 nm and the degree of cubication increases but the degree of homogenization decreases; the interface of γ′/γ phase is serrated after heat preservation at 1200 °C for 1 h. The most part of γ′ phase incomplete solution then reprecipitate into irregular small γ′ phase after heat-treated at 1300 °C.
3.3. Quantitative analysis of different organization of DD6
The quantitative analysis of the fine structure of the DD6 at distinct degree of heat treatment was carried out and compared with the standard heat-treated microstructure of figure 3, the results are shown in Table 2. The size of γ′ phase grows with increasing temperature, the volume fractional number of γ′ decreases gradually within the range of 900 °C to 1200 °C. The magnitude and volume percentage of γ′ improve when the temperature is 1200 °C-1300 °C. The volume fractional number of γ′ phase grows to distinct extents after heat treatments at distinct temperatures. The morphology of γ′ was not effected much after being kept at 900-1100 °C for 1h respectively, but it changed greatly after being kept at 1200 and 1300 °C for 1h.

| Standard heat-treatment | Primary γ′ phase size/μm | Volume fraction of Primary γ′ phase/% | Morphology of primary γ′ phase | Space of γ matrix channel/nm |
|-------------------------|--------------------------|-------------------------------------|--------------------------------|--------------------------------|
| 900                     | 0.44                     | 61                                  | Cubic                          | 57                            |
| 1000                    | 0.45                     | 65                                  | Cubic                          | 54                            |
| 1100                    | 0.52                     | 64                                  | Cubic                          | 59                            |
| 1200                    | 0.57                     | 62                                  | Cubic, most with serrated γ/γ′ interface | 56                            |
| 1300                    | 0.20                     | 59                                  | Irregular cubic                | 31                            |

4. Discussion

4.1 Thermodynamic calculation and phase equilibria
The differences in microstructure between DD6 alloys at different temperatures are due to the fact that the alloys are heat treated at different temperatures, resulting in differences in the growth, dissolution and form sediment of γ′ phase. Calculation software JMatPro and its corresponding nickel-based alloy database are used to calculate the equilibrium phase of the DD6 alloy, presented in figure 5. As can be seen from the figure, in the temperature extent of 900 to 1300 °C, DD6 alloy is mainly composed of γ matrix, γ′ phase and a bit of carbide. The γ′ content in the equilibrium state of the alloy is substantially zero at 1315 °C; and the γ′ content in the equilibrium state in DD6 is 72% below 600 °C. Therefore, when the DD6 single crystal superalloy is cooled to room temperature after solution treatment at 1315 °C, the γ′ phase forming element in the γ matrix is highly supersaturated, which causes a large amount of γ′ phase precipitation during cooling. The content of C is extremely small in the alloy, so the content of C changes slightly with temperature increasing. Figure 5 shows that the content of the γ′ phase is re-dissolved to the γ matrix gradually as the temperature increasing, and the complete re-dissolving temperature of the γ′ phase is about 1300 °C.

4.2. Microstructure evolution of DD6 alloy
The DD6 alloy is heat-treated at 900-1200 °C respectively. Since heat treatment temperature below the large re-dissolving temperature of γ′ phase of 1270.1 °C[10], there are two processes are carried out simultaneously. One is the growth of γ′ phase, the other is the re-dissolution of γ′ phase. γ′ phase will
grow according to the Ostward method, the large $\gamma'$ phase relatively will grow, and the small $\gamma'$ phase will dissolve. $\gamma'$ phase growing up follows the LSW roughening theory [11]:

$$\frac{a}{(r_t^3 - r_0^3)} = K\sqrt{t}$$  \hspace{1cm} (1)

where $r_t$ is the average radius of the precipitated particles after aging, $r_0$ is the average radius of the precipitated particles before aging, $k$ is the coefficient related to the aging temperature, and $t$ is aging time.

According to the Arrhenius law [12]:

$$D = D_0 \exp\left[-\frac{Q}{RT}\right]$$  \hspace{1cm} (2)

where $D$ is diffusion coefficient, $D_0$ is solute diffusion constant, $R$ is molar gas constant, $Q$ is diffusion activation energy and $T$ is thermodynamic temperature.

Equation (2) illustrates temperature is the most important factor effecting the diffusion of elements in the alloy. The higher the temperature, larger the diffusion coefficient is, the diffusion rate of the elements is faster, $\gamma'$ phase grows faster. Therefore, in the case where the heat treatment time is the same, the higher the temperature of the heat treatment, the size of $\gamma'$ is larger. While growth rate of $\gamma'$ phase is significantly greater than dissolving ratio of $\gamma'$ phase. It can also be seen from Table 2 that when the temperature is 900 -1100 °C, the size of the $\gamma'$ phase increases gradually. Part of the $\gamma'$ phase begins to dissolve, the width of matrix channel increases during heat preservation process. When the temperature is raised from 900-1100 °C, the number of $\gamma'$ re-dissolved grows, and the matrix channel becomes wider. When the heat treatment temperature achieves 1200 °C, which near the large amount of re-dissolving temperature of the $\gamma'$ phase. Therefore, when DD6 is kept at 1200 °C for 1 h, the amount of re-dissolving is also large, and most of the $\gamma'$ phase begins to dissolve. During the cooling process, the precipitation way of the $\gamma'$ is different from which is at the lower temperature. $\gamma'$ phase at 1200 °C is dependent on the $\gamma'$ phase which has been precipitated by aging. Since the growth mode has a heterogeneous nucleation, this kind of growth is easier to carry out. MIYAZAKI et al. [13] pointed out the $\gamma'$ phase has high elastic strain energy locally, re-precipitated $\gamma'$ will precipitate along the (011) plane to reduce the energy that considering the interfacial energy and elastic strain energy of $\gamma'$ phase anisotropy. Therefore, the precipitation is directionality, and the precipitation along the (011) plane grows faster, which causes the $\gamma'/\gamma'$ phase interface to appear serrated, as shown in figure4 d2 and d3. 1300 °C is higher than the complete re-dissolving temperature of the $\gamma'$ phase and less than the junior melting temperature of DD6, the $\gamma'$ phase will dissolve into $\gamma$ matrix completely at 1300 °C for 1 h. Fine and irregular $\gamma'$ phase is then re-precipitated during the cooling process.

Figure 5 demonstrates that the content of the $\gamma'$ phase in equilibrium state of the alloy is almost zero above 1300 °C; when it is below 600 °C, $\gamma'$ content is about 70%. After the alloy was preserved at 1315 °C for two hours then air cooled, the $\gamma'$ forming elements are supersaturated, causing $\gamma'$ precipitation in a large amount during cooling. The content of $\gamma'$ reached 61% after secondary aging. The volume fractional number of $\gamma'$ increases at the beginning then decreases final increases as temperature increasing. The magnitude and shape of new $\gamma'$ phase with original $\gamma'$ phase growing, dissolved and then re-precipitated grows are different when the alloy is preserved at distinct temperatures. Therefore, volume fractional diversification of $\gamma'$ phase needs further research. Large re-dissolving temperature of $\gamma'$ phase is 1270.1 °C. Growth of $\gamma'$ phase is main factor at 900 °C, the matrix channel becomes smaller, so the volume fractional number of $\gamma'$ increases. While temperature is carried out at 1000 °C and 1100 °C which near the large amount of $\gamma'$ phase, dissolution of $\gamma'$ becomes the major factor, and the matrix channel becomes larger. Therefore, volume fractional number of $\gamma'$ phase is reduced. When DD6 preserves at 1200 °C, the heat treatment temperature is higher, and the $\gamma'$ phase re-dissolved amount continues to increase, but new $\gamma'$ phase re-precipitates by original $\gamma'$ phase during subsequent air cooling. In this occasion, volume fractional number of the $\gamma'$ phase increases gradually. At 1300 °C, $\gamma'$ phase is completely dissolved, and $\gamma'$ phase which re-precipitates during subsequent air cooling is also relatively increased, so volume fractional number of $\gamma'$ phase is increased.

5. Conclusions
Figure 4. Microstructure of DD6 after different heat-treatment.
After standard heat treatment, the \( \gamma' \) phase is well formed. The size of the \( \gamma' \) gradually increases at 900-1100 °C. When alloy preserves at 1200 °C, the size of the \( \gamma' \) increases significantly, the most of \( \gamma'/\gamma \) surface is serrated. The \( \gamma' \) phase is completely dissolved, and then in to a fine, irregular \( \gamma' \) phase in the process of subsequent cooling after heat-treated at 1300 °C.

The volume fraction of \( \gamma' \) phase first increases and decreases and then increases, during the heat treatment from 900 °C to 1300 °C. When heat-treated at 900 °C, the growth of the \( \gamma' \) phase is the main factor, the matrix channel is narrow, and volume of the \( \gamma' \) phase grows. When the degree of heat maintains at 1000-1100 °C, the amount of \( \gamma' \) phase re-dissolved increases gradually and the matrix channel becomes wider and volume fractional number of \( \gamma' \) phase declines. \( \gamma' \) phase is further dissolved back after heat-treatment at 1200 °C, however during cooling, new \( \gamma' \) is re-precipitated by the original \( \gamma' \) phase, the matrix becomes wider, and volume fractional number of \( \gamma' \) phase decreases again. The \( \gamma' \) dissolves completely, a new fine and irregular \( \gamma' \) phase re-precipitates during cooling process after heat-treatment at 1300 °C. The matrix channel is narrowed and the \( \gamma' \) phase volume fraction increases.

The micro structure of DD6 heat treated at distinct temperatures is significantly different, indicating that the operating temperature has a great affect on the microstructure of the alloy.

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