Morphology evolution of unstable $\gamma'$ in Ni–Co based superalloy

L. Xu¹, C. G. Tian¹, C. Y. Cui*¹, Y. F. Gu² and X. F. Sun¹

The evolution of $\gamma'$ morphology was investigated during cooling and isothermal aging in a newly developed Ni–Co based wrought superalloy. The results showed that unstable flowery $\gamma'$ precipitated at a cooling rate of 5°C min⁻¹ and became stable during isothermal aging, and its shape was either spherical or cuboidal depending on the aging temperatures. The evolution mechanism of $\gamma'$ morphology was discussed in terms of the diffusion effects, the elastic strain energy and the $\gamma'/\gamma$ interface energy.

Keywords: Ni–Co based superalloy, $\gamma'$ morphology, Aging temperature, Elastic strain energy, Interface energy

Introduction

Wrought superalloys have widespread applications in a number of critical technology areas, especially for those bearing complicated loadings such as turbine discs. Their superior mechanical properties are derived from solid solution hardening, grain boundary hardening and precipitation hardening caused by $\gamma'$ phase. Therefore, the microstructural characteristics of the $\gamma'$ phase, including morphology, size distribution and composition, play important roles in determining the mechanical properties.¹⁻⁴

It is found that the $\gamma'$ presents various morphologies depending on the alloys’ thermal processing conditions in wrought superalloys. Researchers have carried out much work on the evolution of $\gamma'$ morphology in some commercial turbine disc superalloys during heat treatments.⁵⁻⁸ The results show that the $\gamma'$ morphology transforms from spherical to flowery as the cooling rate decreases.⁹⁻¹² However, there are some controversies relating to the formation mechanism of the complicated flowery $\gamma'$. Some researchers believe that whenever a $\gamma'$ phase grows into a supersaturated matrix in a diffusion controlled manner, the point effect of diffusion dominates and the $\gamma'$ evolves into a flowery morphology in Ni based superalloys.¹³⁻¹⁵ while others firmly insist that the elastic strain energy caused by the $\gamma'/\gamma$ mismatch is the main reason for the formation of complicated $\gamma'$ morphology.¹⁶⁻¹⁸ Therefore, the mechanism for the $\gamma'$ morphology evolution from spherical to a complex flowery morphology during slow cooling is still unclear.

Besides the original microstructure that formed during cooling, the stability of $\gamma'$ morphology during aging is also essential for the service life of superalloys. Many studies have been performed on the evolution of $\gamma'$ morphology during isothermal aging in some commercial Ni based superalloys.¹⁹⁻²¹ Many researches focused on the evolution of spherical $\gamma'$, while little attention was paid to the evolution of the flowery $\gamma'$, which also contributed to the macroscopic mechanical properties. Past results of researches carried out on PWA1173 have shown that the complex flowery $\gamma'$ morphology was beneficial to improve the mechanical properties.²²⁻²³ Therefore, it is of great importance to study the flowery $\gamma'$ evolution during aging in wrought superalloys.

Ni–Co based superalloy is a newly developed wrought turbine disc superalloy, so the objective of this paper is to investigate the mechanism of the formation of the complex flowery $\gamma'$ during slow cooling and its evolution mechanism at different aging temperatures in this newly developed wrought superalloy. The influences of the diffusion effects, elastic strain and interface energies on the evolution mechanism were investigated.

Experimental

The chemical composition of the selected alloy was 49.89Ni–25.0Co–13.7Cr–5.5Ti–2.5Mo–2.2Al–1.0W–0.2Si–0.029Zr–0.015C–0.015B (wt%). The ingot was prepared by vacuum induction melting followed by hot extrusion. Specimens with dimensions of 5×5×8 mm were heat treated at 1200°C for 8 h to achieve a homogenised microstructure and to dissolve all the $\gamma'$ in the alloy. After that, some samples were cooled to 1060°C (5°C min⁻¹) and then aged at 1060°C at different times followed by water quenching to retain the microstructure, while others were cooled to 850°C (5°C min⁻¹) to gain fully developed flowery $\gamma'$, and then aged at 900 and 1100°C respectively at different times followed by water quenching. The samples for scanning electron microscopy (SEM) observation were polished and then electrolytically etched in 17 mL H₂O–1 mL glacial acetic acid–2 mL nitric acid solution at 1·5 V for 30 s. The area fraction of $\gamma'$, measured by SEM image with the Image Pro-Plus software, was used to stand for the volume fraction of $\gamma'$. The $\gamma'/\gamma$ misfit (δ) was determined by X-ray diffraction (XRD), recorded on a
Rigaku DMX-2500 diffractometer with Cu $K_a$ radiation operating at 50 kV and 300 mA. The concentration gradient across the $\gamma'/\gamma$ interface was obtained by the three-dimensional atomic probe (3DAP) technique.

**Results**

Figure 1 shows the evolution of $\gamma'$ morphology after direct aging at 1060 °C at different times. The $\gamma'$ had an irregular flowery morphology with protrusions after slow cooling from 1200 to 1060 °C, as shown in Fig. 1a. Apparently, when subjected to aging at 1060 °C, the $\gamma'$ morphology became regular and the protrusions started to dissolve as the aging time increased (Fig. 1b–d). To be specific, the average protrusion number of each $\gamma'$ decreased from eight in the non-aging samples to four after aging at 1060 °C for 0-25 h (Fig. 1b). With further aging at 1060 °C for 24 h, the protrusions dissolved completely and the $\gamma'$ morphology was transformed from unstable flowery to chamfered cuboidal, as shown in Fig. 1d. At the beginning of aging, the measured volume fraction of $\gamma'$ was 17.5%. After aging for 0-25 h, parts of the protrusions of the large flowery $\gamma'$ dissolved, so the volume fraction decreased to 15.4-4%. As aging continued, the $\gamma'$ protrusions further dissolved, and some $\gamma'$ after the protrusion dissolved began to grow, which contributed to an increased volume fraction (22.0%) after aging for 24 h.

To further study the effects of the aging temperature on the evolution of $\gamma'$ morphology, the samples were slowly cooled from 1200 to 850 °C to obtain unstable flowery $\gamma'$ with more protrusions and then the samples were aged at 1100 and 900 °C. Figure 2 shows the flowery $\gamma'$ development during aging at 1100 °C. The initial $\gamma'$ cooled to 850 °C displayed a thicker flowery morphology and a higher volume fraction of $\gamma'$ (52.2%) than the other $\gamma'$ cooled to 1060 °C, as shown in Fig. 2a. When these $\gamma'$ were aged at 1100 °C for 0-25 h, their protrusions dissolved dramatically and their size decreased quickly due to the highly raised solid solubility at the elevated temperature, so the volume fraction of $\gamma'$ greatly decreased to 11.5%, as revealed by Fig. 2b. After aging for 2 h, the $\gamma'$ thoroughly transformed from flowery to spherical ones with different particle sizes, and the volume fraction of $\gamma'$ slightly increased to 12.5% for the growing of $\gamma'$, as shown in Fig. 2c. Further evolution was driven by the minimisation of the total precipitate surface area as aging progressed: small particles dissolved and large ones grew larger. This was attributed to coarsening or the Ostwald ripening process, as shown in Fig. 2d. As $\gamma'$ continued growing, the volume fraction of $\gamma'$ increased to 15.4%. It is apparent that volume fraction of $\gamma'$ under this aging temperature was much lower than that under 1060 °C for the larger solid solubility at the higher temperature. Fine tiny particles in Fig. 2d precipitated during the water quenching step. During quenching, the temperature dropped rapidly so that the alloy was in a highly undercooled state, resulting in a high degree of supersaturation in the matrix. Therefore, the driving force for the nucleation of $\gamma'$ was very high, which led to a high nucleation rate that produced a high density of quenching $\gamma'$. Thus, the high density unstable flowery $\gamma'$ evolved into low density spherical ones during aging at 1100 °C.

The development of $\gamma'$ morphology aged at 900 °C is shown in Fig. 3. The $\gamma'$ morphology was still completely flowery even after aging for 4 h (Fig. 3a), which could be caused by the moderately raised solid solubility and low atom diffusion velocity. However, the volume fraction of $\gamma'$ still decreased from the initial value of 52.2-44.8%, which indicates that the protrusions also have started to dissolve. As the aging time increased, the protrusions continued dissolving and the volume fraction of $\gamma'$
decreased to 39.8% after 8 h (Fig. 3b). After aging for 200 h, γ' transformed to nearly cuboidal ones with rough faces, and the volume fraction started to rise (49.0%) as γ' grew, as shown in Fig. 3d. After aging for 2500 h, they finally grew into a steady state with a regular cuboidal shape and the volume fraction finally increased to 64.0%. Compared with the samples that were aged at 1100 °C, no γ' precipitated during the last water quenching process because the supersaturation was nearly exhausted by the high density cuboidal γ'. Thus, under low temperature aging (900 °C), the flowery γ' evolved into high density cuboidal ones.

Besides the above characterisation on the microstructural evolutions, the values of lattice mismatches of the γ'/γ interfaces close to the equilibrium states were measured by XRD for both 1100 and 900 °C aging treatment. The values were 0.14 and 0.36% for spherical γ' (1100 °C aging for 200 h) and cuboidal ones (900 °C aging for 2500 h) respectively. This reveals that the equilibrium γ'/γ' misfit decreases with the increase in aging temperature, which is consistent with the conjecture of Ricks et al. They claimed that the thermal expansion coefficient of the γ' phase was less than that of the γ matrix. According to their claim, all alloys with a
positive misfit should be reduced as the temperature increases. So the alloy we used in the present study had a positive misfit and it was reduced as the temperature increased.

The concentration gradient across the $\gamma'/\gamma$ interface for the $\gamma'$ formed at 1100 and 900°C during slow cooling was obtained from the 3DAP technique, as shown in Fig. 4. The nucleation rate was low at high temperature for the low undercooling degree, and the volume fraction of $\gamma'$ was low, which left a high concentration of the $\gamma'$ forming element in the matrix, such as Ti and Al shown in Fig. 4a. With the growth of $\gamma'$, the $\gamma'$ forming elements diffused from $\gamma$ matrix to $\gamma'$ phase. As a result, the concentration of Ti and Al elements in the matrix decreased as observed from Fig. 4b. In addition, at high temperature, the solid solubility of the matrix was large, which also led to a high content of Ti and Al in the matrix (Fig. 4a). For the small solid solubility of the matrix at low temperature, the Ti and Al content in the matrix was low at low temperature (Fig. 4b). Therefore, the supersaturation in the matrix increases as the temperature decreases.

Discussion

Formation mechanism of flowery $\gamma'$ during cooling

According to classical thermodynamics, the microstructural evolution of $\gamma'$ should be driven by the minimum of global free energy. During the growth process of $\gamma'$ phase, the energy primarily includes the chemical free energy $G_c$, the elastic strain energy $E_s$, and the interface energy $\gamma$, which correlates to supersaturation, elastic distortion and the newly formed $\gamma'/\gamma$ interfaces respectively. Among these three factors, both $G_c$ and $E_s$ may be the causes for the unstable flowery morphology during slow cooling, as supported by previous studies. However, as for $E_s$, which increased as the temperature decreased in the alloy with the positive misfit, if it was really the dominant factor, the flowery $\gamma'$ that nucleated during slow cooling should have grown into a more complicated flower, or at least it should have remained flowery, during the following isothermal aging process for the high value of $E_s$. Apparently, this does not accord with the experimental results that flowery $\gamma'$ transformed into spherical $\gamma'$ during the aging process

where $G_c$ reaches a minimum value, as illustrated by Fig. 1. Therefore, $G_c$, which increases continuously as the temperature decreases because of the increased supersaturation in the matrix, should be responsible for the formation of flowery $\gamma'$ during slow cooling. However, to produce flowery crystals, $G_c$ alone is not enough because it can only produce dendritic ones, so $\gamma$ is supposed to play a relevant role in smoothing the branch tips into petals.

As discussed above, the role of $E_s$ in the flowery $\gamma'$ evolution can be ignored during cooling, and then the parameter and the growth rate of the spherical harmonic amplitude ($\delta = \delta / \delta t$), proposed by Mullins and Sekerka, can be used to evaluate the stability of $\gamma'$. The decrease in $\delta$ will increase the stability of the spherical morphology and facilitate spherical particles, while its increase tends to generate other shaped particles, such as flowery. The $\delta$ can be described by following equation proposed Mullins and Sekerka

$$ \delta = \frac{c_0 D (l-1)}{(C - c_R) R^2} \left( \frac{c_0 - c_0}{c_0} - \frac{\Gamma D}{R} \right) $$

where $D$ is the diffusion coefficient, $l$ is the number of protrusions along the longitude, $C$ is the concentration of solute in the precipitate, $c_R$ is the concentration on the undistorted sphere, $\gamma$ is the capillary constant and $R$ is the radius of the undistorted sphere. $c_0$ is the equilibrium concentration at a flat interface, and $c_e$ is the initial solute concentration in the supersaturation matrix. Therefore, $(c_e - c_0)/c_0$ represents the relative supersaturation $S$.

Equation (1) shows that $\delta$ is composed of two terms: a positive term proportional to concentration gradient (i.e. supersaturation) favouring the increase in the harmonic by the point effect of diffusion, which opposes the spherical shape, and a negative term representing the capillary effect supporting the spherical particles. According to this model, the precipitation and evolution mechanisms are illustrated in Fig. 5a. During the process of slow cooling, the supersaturation located near the nucleated $\gamma'$ is increasing continuously as the temperature is decreasing as shown in Fig. 4. Therefore, the growth of protruberances is led by the point effect of diffusion together with the effect of $\gamma$ yields an unstable flowery morphology. However, as the cooling temperature further decreases, the flowery $\gamma'$ ceases to grow.
because of the low diffusion velocity, then secondary spherical $\gamma'$ begins to precipitate in the untouched areas where the supersaturation has been highly reduced for the growth of the primary $\gamma'$. The $\gamma'$ precipitation process has been reported in detail in another paper. Consequently, during the cooling process where $G_v$ dominates and the point effect of diffusion is realised, the flowery $\gamma'$ first appears, then grows up, and finally gives birth to secondary tiny spherical $\gamma'$, as reflected by Fig. 5a.

**Flowery $\gamma'$ evolution during isothermal aging**

During isothermal aging, the supersaturation in the matrix has been greatly consumed by $\gamma'$ nucleation and growth so that the supersaturation steadily decreases to a certain value with the $\gamma'$ growth. Therefore, there is no supersaturation in the matrix during isothermal aging after $\gamma'$ has fully grown, and the pure capillary effect becomes effective. Owing to the Gibbs–Thomson effect, the solute concentration in the matrix beside the $\gamma'$ will increase as the radius of curvature decreases. Therefore, the relatively higher concentrated elements in the protrusion part will impel materials to flow to the depression part by capillary effect, reducing the perturbation. As a result, the protrusions of $\gamma'$ dissolve and the $\gamma'$ morphology changes into a stable state during isothermal aging as shown in Figs. 2 and 3.

However, the stable morphology of $\gamma'$ exists in more than one state depending on the aging temperatures. During isothermal aging, the $\gamma'$ morphology evolution is controlled by both the interface energy $\gamma$ and the elastic strain energy $E_s$. For these two factors, previous research shows that $\gamma$ almost remains constant with temperature changes, whereas $E_s$ increases as temperature decreases. Combining this with the change of $\gamma'$ volume fraction, it is reasonable to infer that $\gamma$ and $E_s$ control the $\gamma'$ morphology evolution at the high and low temperatures respectively, as described by the two schematic lines in Fig. 5b. Aging at high temperature, with low $\gamma'$ volume fraction and low $E_s$, $\gamma$ plays an important role in determining the $\gamma'$ morphology, resulting in a spherical shape, while aging at low temperature, with high $\gamma'$ volume fraction and high $E_s$, $E_s$ dominates and causes a stable cuboidal morphology. In between the high and low temperatures, both factors control the growth of $\gamma'$, which leads to a stable chamfered cuboidal one, as summarised in Fig. 5b.

**Conclusions**

In summary, the $\gamma'$ morphology evolution after various heat treatments in a Ni-Co based superalloy was investigated. It was found that the $\gamma'$ grew into an unstable flowery morphology during slow cooling via the point effect of diffusion, which was facilitated by the increasing chemical driving force, $G_v$. However, during isothermal aging where the supersaturation no longer existed, all unstable $\gamma'$ evolved into stable ones by the capillary effect of diffusion, with either spherical or cuboidal morphologies depending on the competition between the elastic strain energy $E_s$ and the interface energy $\gamma$. At high temperature, $\gamma'$ evolved into a
spherical shape so that it would reduce the interface energy. In addition, at low temperature, γ’ transformed into a cuboidal shape so that it would diminish the elastic energy.

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