Research of morphology evolution of precipitation during aging and the effects of precipitation on creep property of 617B superalloy

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Abstract: 617B alloy is one of the alternative materials for ultra-supercritical power generating units, its microstructure will change during service under extremely harsh conditions. The research of precipitation behavior of 617B superalloy and other similar nickel-based superalloy during aging is summarized. It is concluded that the main phases of 617B superalloy during aging include γ' phase, μ phase and M23C6 carbide. The precipitation behavior of the three phases is affected by aging temperature and aging time. The microstructure of materials has a direct influence on the properties of materials. Therefore, in the aging process of 617B superalloy, the creep property of the alloy will be affected by these phases. This paper summarizes the effect of these phases on the creep behavior of 617B superalloy. It is found that γ' phase has a positive effect on the creep behavior of 617B superalloy, while μ phase has a negative effect. M23C6 has two-sided effects depending on its size.

1. Introduction

Conventional coal fuel power generation has driven global economic and technological development in the past few decades. In the 21st century, traditional coal fuel power generation is still dominant. However, coal fuel contains a large number of trace elements such as S and N, which will produce SOx, NOx and other harmful gases after combustion. A large amount of CO2 gas will also be produced, causing the greenhouse effect at the same time. Therefore, in the 21st century, in order to protect the environment, and reduce CO2 emissions, advanced ultra-supercritical generator set came into being[1]. Compared with traditional coal-fired generating units, ultra-supercritical generator units have the advantages of higher power generation efficiency and lower pollution. Since this kind of generator set needs to work in the environment of high temperature and high pressure (about 600℃ and 30 MPa), the materials used to build the generator set should have great thermal corrosion resistance, creep performance and long-term stability[2]. Conventional materials such as austenitic and ferritic steel simply cannot work in such extreme conditions, while nickel-based superalloys can[3,4]. Inconel 617B superalloy is one of the ideal alternative materials. Inconel 617B is a nickel-based superalloy strengthened by solution and carbide, which is the best grade of commercial 617 alloy[5]. Creep deformation is the main failure mode of metal materials under high temperature and pressure. During the use of 617B superalloy, there will be many precipitates, such as γ’ phase, μ phase and M23C6 carbide. These phases will change the microstructure of materials and affect the mechanical properties of materials greatly. Thus, it is necessary to do the research which combine the microstructure changes with the macroscopic creep properties. Based on the researches in recent years, this paper summarized
the precipitation phase (include the types of precipitates and the changing of morphology of phase during aging) and the effects of creep property of superalloy 617B during aging at high temperature.

2. 617B superalloy

617B superalloy is a common nickel-based superalloy. As a nickel-based superalloy, the main element is Ni with a high proportion of Co, Cr and Mo. Trace elements include Fe, Ti, Al, Cu, B, etc. The element composition of alloy 617B is shown in Table 1. Co and Mo elements can strengthen the solution, while Al and Ti can form γ’ phase, which play the role of precipitation strengthening. Because 617B superalloy has great creep resistance, oxidation resistance and corrosion resistance, it has become one of the alternative materials for ultra-supercritical generating units[6-10]. The 617B alloy differs from the traditional 617 alloy in that it contains more B elements, so that the creep and corrosion resistance of 617B alloy are significantly improved[11]. 617B is normally in solid solution state and is used at around 700℃. So it is necessary to study the organizational evolution of 617B during its’ service. 617B superalloy used in experiments can be prepared by vacuum induction melting (VTM) and electroslag remelting (ESR)[12], and the as-received alloy was solution-treated at about 1200℃ and water-quenched or oil-quenched.

Table 1. Element composition of 617B superalloy (wt%)[2]

| C  | Cr  | Co  | Mo  | Al  | Ti  | Fe  | Nb  | B   | Ni  |
|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0.06 | 22.0 | 12.0 | 9.0 | 1.3 | 0.4 | 1.2 | 0.03 | 0.003 | Bal. |

3. Precipitated phase in aging process

3.1. γ’ phase

γ’ phase is the most important phase in the aging process of 617B alloy at high temperature. γ’ phase dispersed and precipitated not only in grains but at grain boundary with the shape of cube. γ’ phase is Ni₃Al with a Cu₃Au face-centered cubic ordered structure in nickel-based alloys.

At the same temperature, γ’ phase has a tendency to grow larger and coarser with the extension of aging time. With the increasing of aging temperature, the time for precipitation of γ’ phase become less, and the change of morphology of γ’ phase can be affected by aging time and aging temperature. The precipitation of γ’ phase was found at the initial stage of aging at the temperature of 725℃, and the additional stress would not affect the precipitation of γ’ phase. However, in the later stage of aging process, additional stress would affect the precipitation of γ’ phase because of lattice instability[13]. SEM images of alloy 617B aged at 750℃ for 300h, 1000h, 3000h and 5000h are shown in figure 1. It was found that the diameters of γ’ phase particles were 20-70nm, 40-80nm, 70-130nm and 60-170nm, showing an obvious growing trend[14]. The growth of γ’ phase can be explained by Ostwald maturation theory. Ostwald maturation theory points out that in the later stage of precipitation phase of supersaturated solid solution, due to the effect of interface energy, smaller particles will melt and larger particles will grow, which will reduce the overall free energy of the system. Thus, γ’ phase’s growth is a spontaneous growth process. Meanwhile, during the aging of 600℃, the precipitation of phase could only be found after 500h. With the aging process, there was also a growing trend, and the morphology of gamma’ phase was spherical in the whole process.
During aging at 704℃ and 720℃, the precipitation and growth process of phase were similar to that at 750℃, and the morphology of the precipitated phase was observed to change from spherical to rectangular during aging. During aging at 800℃, coarsening of γ’ phase was observed at the initial stage (30h), and the precipitation amount of γ’ phase was significantly reduced in the whole aging process with uneven distribution. After 500h, the morphology of γ’ phase became extremely uneven, and the overall stability of the alloy was poor. This result suggests that temperature affects the precipitation and coarsening of the phase, which is caused by the diffusion and redivision of elements. And when aging experiments were carried out at the same temperature with alloys containing different Al and Ti proportion, γ’ phase particle size remained between 20-40nm within 5000 hours, which indicated that trace alloying elements could affect the precipitation phase during aging\textsuperscript{[12]}. Morphology evolution during aging of γ’ phase at different temperatures are shown in figure 2. This result further proves that the diffusion and redistribution of elements play an important role in the precipitation and coarsening of γ’ phase.
3.2. $M_{23}C_6$

During the aging process, 617B alloy is not only accompanied by the precipitation of standard phase such as $\gamma'$ phase and $\mu$ phase, but also the precipitation of carbides. There are four kinds of carbides precipitated from superalloy in the aging process: MC, $M_{23}C_6$, $M_6C$ and $M_7C_3$\cite{15}. $M_{23}C_6$ is the main carbide precipitated from 617B alloy during aging. In 617B superalloy, Cr and Mo elements are mainly contained in $M_{23}C_6$. During the aging of 617B alloy at 725°C, $M_{23}C_6$ carbide particles were found to precipitate at grain boundary at the initial stage, and the precipitation time was the same as that of $\gamma'$ phase\cite{14}.\[14\] Change of morphology of grain boundary carbides was observed during aging at 600°C. At the beginning of aging, the morphology of carbides was similar to that of carbides after solution treatment. After 300h, the morphology of carbide began to appear irregular thin film. After 500h to 1000h, the thin film carbides begin to thickened, and are converted into cellular carbides after 3000h. At the late aging stage, about 5000h, a large number of porous carbides gathered in the grain boundary\cite{16}.

\[12\] 

Figure 2. Morphology evolution during aging of $\gamma'$ phase at different temperature.
All these results can be seen in figure 3. Since 617B alloy has to undergo solid solution treatment before being put into use or carried out experiments, after solid solution treatment, supersaturated solid solution is formed. Due to the high free energy of atoms in grain boundary, the surface energy increased by forming new phase is the minimum, so carbides will be formed and grow up at grain boundaries\textsuperscript{[17]}.

Figure 3. Morphology evolution of M23C6 carbide during aging time\textsuperscript{[16]}. 
3.3. $\mu$ phase
During the aging process of nickel-based superalloy, except for $\gamma'$ phase and carbides that would precipitate out, $\mu$ phase will also precipitate out under certain conditions. $\mu$ phase is a kind of A7B6 compound formed by transition elements and VI group elements, which can be found after 7000h during 704℃ aging, composed of Cr, Co, Ni, Mo and other elements. The number of $\mu$ phase increased with the aging time and only distributed in grain boundary\cite{12}. $\mu$ phase and precipitated $\text{M}_{23}\text{C}_6$ carbide both contain Cr and Mo elements, $\mu$ phase competes with carbide for Cr and Mo elements, thus affecting the precipitation and growth of carbides. In addition, the time of $\mu$ phase precipitation varies at different temperatures, the higher the temperature is, the earlier the phase precipitate, but the evolution trend of microstructure with aging time is similar. Compared with the result of $\gamma'$ phase, the precipitation and growth of $\mu$ phase are also the diffusion and redistribution of elements.

4. Effect of Phase Precipitation on Creep Property
The precipitation of many phases has great influence on microstructure of 617B, which would influence the mechanical properties of 617B. Therefore, creep property of 617B alloy must be affected during aging.

4.1. $\gamma'$ phase
$\gamma'$ phase is the main precipitation phase of 617B alloy, and has the most obvious effect on the creep properties of the 617B superalloy. By comparing different superalloys, the more phase, the better the creep performance of the alloy. By comparing the amount of $\gamma'$ phase in 740 alloy and CCA617 alloy (CCA617 alloy is a variant of 617 alloy), it was found that the amount of $\gamma'$ phase in 740 alloy was three times as much as that in CCA617 alloy, and the strength and creep properties of 740 alloy were significantly stronger than that of CCA617 alloy\cite{18}. As the grain boundary sliding and diffusion of superalloy are very sufficient in the creep process, it is easy to form cracks and other defects in the grain boundary, so intergranular creep fracture is the main creep fracture mode of superalloy. In the aging process, the $\gamma'$ phase at the grain boundary and the supersaturated elements in matrix will greatly hinder the occurrence of grain boundary dislocation, so the creep property of the alloy materials will be improved\cite{19}.

In addition, the structure of $\gamma'$ phase was similar to that of the matrix, so $\gamma'$ phase has the characteristics of dispersive uniform nucleation, coherent, particles are thin and the spacing is small, low interfacial energy and good stability during precipitation. Besides, $\gamma'$ phase itself is face-centered cubic orderly arrangement and geometric dense arrangement phase so that it has higher intensity. During the aging process, $\text{M}_{23}\text{C}_6$ carbide will grow into cells, which will affect the creep property of the alloy. But $\gamma'$ phase competes elements with the $\text{M}_{23}\text{C}_6$ carbides in the alloy so that it can slow down the coarsening of carbides to maintain stable coherent particle networks and increase the creep property of 617B superalloy\cite{20}. Therefore, $\gamma'$ phase was precipitated during aging of 617B alloy as a strengthened phase.

4.2. $\text{M}_{23}\text{C}_6$
The effect of carbide precipitation on 617B alloy is two-sided. In the aging process of many nickel-based alloys, fine carbide grains are precipitated at grain boundary. These fine grains will improve the creep properties of the alloy. However, with the extension of aging time, the carbide coarsening is obviously, which reduces the creep property of the material. This mainly because creep fracture of superalloy is intergranular creep fracture, and the coarse $\text{M}_{23}\text{C}_6$ carbide may induce brittle fracture along grain boundary\cite{21}. To sum up, during the aging process, the size of carbides should be controlled as much as possible so as to effectively improve the creep property of the alloy at the later aging stage.

4.3. $\mu$ phase
$\mu$ phase exhales as topological dense phase, and it usually precipitates in the grain boundary with the shape of rod or needle, which can affect the ductility of metal. The main elements contained in $\mu$ phase
are basically the same as those in carbides, so the μ phase can affect the precipitation of carbides. On the other hand, muons inhibit the growth of carbides. From these two aspects, the precipitation of μ phase has two effects on the creep properties of materials. Due to the solid solution strengthening mode of 617B alloy, when muon phase precipitates out, Cr, Mo and other elements would be absorbed from the matrix, so the solid solution strengthening effect will be weakened and the creep property of the alloy will be affected[23]. In addition, μ phases are generally in the shape of rod or needle. Just like how M₂₃C₆ affects 617B superalloy’s creep property, this kind of phase could cause brittle fracture between crystals. In general, the effect of μ phase precipitation on creep properties of alloys is more harmful than beneficial. So μ phase is generally regarded as harmful precipitated phase of alloy.

5. Summary
During the aging process of 617B alloy, the main precipitated phases includes γ’ phase, μ phase and M₂₃C₆ carbide. γ’ phase gradually coarsened in the aging process and the precipitation process was affected by aging temperature, aging time and trace elements, so it can be seen that the diffusion and redissolution of elements played a major role in the precipitation and growth process of γ’ phase. At the beginning of aging, granular M₂₃C₆ carbides will precipitate, and the carbides will be coarsened with the extension of time. In the later stage of aging, μ phase would precipitated under certain conditions, which would grow with aging.

Due to the morphology of γ’ phase, γ’ phase has high strength. The precipitation and growth of γ’ phase could enhance the creep property of the alloy. Whether M₂₃C₆ can enhance the creep property of 617B mainly depending on the size of M₂₃C₆ carbide. Granular carbides can enhance the creep properties of materials, while cellular carbides appeared in the later aging period are harmful to the creep properties of 617B. The element composition of μ phase is similar to that of M₂₃C₆ carbide in 617B. μ phase will compete with carbides for elements and slow down the precipitation and growth of carbides. Since the effect of carbides on the creep property of 617B is two-sided, it seems that the effect of μ phase precipitation on creep properties of 617B is also two-sided. However, μ phase is generally regarded as harmful phase because its morphology and precipitation mechanism are harmful to the creep properties of alloys.

γ’ phase is an important strengthening phase during aging of 617B alloy. The size of M₂₃C₆ carbide should be controlled to have a positive effect on the creep properties of materials. μ phase is always regarded as harmful phase and should be avoided as far as possible.

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