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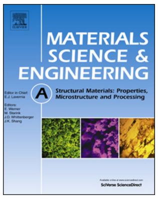

Effect of long-term aging on the microstructure, stress rupture properties and deformation mechanisms of a new cast nickel base superalloy

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ABSTRACT

The microstructure, stress rupture properties and deformation mechanisms of a new alloy during long-term aging were investigated. The microstructure evolution mainly included the coarsening of γ′ phase and the precipitation of η phase. During aging at 700 °C, 750 °C and 800 °C, the coarsening rate k of γ′ phase was about 7.818 nm^3/h, 42.927 nm^3/h and 178.226 nm^3/h, respectively. The activation energy Q for γ′ coarsening was about 279.98 kJ/mol, which meant that element diffusion controlled the coarsening of γ′ phase. After aging at 750 °C for 3000 h and 800 °C for 2000 h, a new needle-like η phase was precipitated near GBs and around MC carbides, then grew into the grain interiors. The quantity of η phase increased with the increase of aging time. With the growth of η phase, γ′ depleted zones were found around η phase. This was principally because both γ′ phase and η phase were enriched in Ni and Ti, and the growing up of η phase absorbed γ′ phase. After aging at 700 °C for 300–3000 h and 750 °C for 300–2000 h, the stress rupture life at 750 °C/430 MPa remained at a high level and most of them were higher than 100 h. That was because the slightly grown-up γ′ phase acted as strong obstacles to the dislocation motion, Orowan bypassing combing stacking fault shearing acted as the dominant mechanism during stress rupture deformation. After aging at 750 °C and 800 °C for 3000 h, the stress rupture life decreased to 45.7 h and 7.68 h, respectively. One reason was that the seriously grown-up γ′ phase was very hard to impede the dislocation motion, almost all γ′ phases were cut by dislocations with leaving stacking faults inside them during stress rupture deformation. The other reason was that needle-like η phase promoted dislocation pile-up and contributed to the nucleation of micro-cracks, meanwhile the γ′ depleted zones could be conductive to the propagation of micro-cracks.

1. Introduction

Nickel base superalloys are the most important materials for many high temperature applications because of their excellent mechanical properties, corrosion and oxidation resistance at high temperatures [1–3]. The microstructure of nickel base superalloys mainly consists of the disordered face-centered cubic γ matrix and the coherently precipitated $L1_2$-structure γ′ phase. The unique properties of these alloys are strongly linked to the ordered γ′ phase because the dislocation movement can be hindered by γ′ phase during plastic deformation [4–7]. Recently, a new cast nickel base superalloy primarily strengthened by γ′ phase [8] is developed for the aero-engines applications owing to its excellent mechanical properties at temperatures up to 750 °C.

The microstructural stability of nickel base superalloys is important for keeping the excellent mechanical properties during long-term service [9–11]. Owing to many alloying elements such as Al, Ti, Nb Cr, W, Mo and Co etc. are added into nickel base superalloys, some undesirable phases are possible to be precipitated during long-term aging at high temperature [12–14]. The formation of undesirable phases such as σ, η, and δ phases always cause the change of local composition and lead to the degradation of mechanical properties [15–17]. Besides the possible formation of undesirable phases, long-term aging also influences the size, shape and volume fraction of γ′ phase. The γ′ size has a significant effect on the deformation mechanism of nickel base superalloys. Fu et al. [18] have reported that the deformation mechanism changes from anti-phase boundary (APB) shearing to stacking fault shearing to Orowan bypassing in a Co-rich nickel base superalloy as the increase of γ′ size. The transition of deformation mechanism is also found in Nimonic alloy [19] and TMW alloy [20]. The γ' size of nickel base superalloys

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generally increases with long-term aging time [21–23]. Therefore, experiments are desired to systematically investigate the influence of γ′ size on the deformation mechanism of new alloy during long-term aging. Besides the evolution of γ′ phase, η phase was found in the new alloy after long-term aging [8]. Until now, there is little literature presenting the distribution characteristic of alloying elements in η phase through the experimental observation and characterization. In this paper, the main alloying elements of η phase and γ′ phase would be identified clearly by using TEM/EDS. In addition, the influence of microstructure evolution during long-term aging on the stress rupture properties of new alloy was studied. After stress rupture deformation, the dislocation configurations were observed, and the correlation between the microstructure evolution and the stress rupture properties was explained.

2. Materials and methods

The cast ingot of new alloy was prepared via vacuum induction melting, and then the mechanical bars were casted. According to the results of Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES), the chemical composition of new alloy was (wt%) 19.44Cr, 5.06Fe, 4.35(W + Mo), 4.39(Ti + Al), 1.58Nb, 0.12C, 0.006B, and the balance Ni. In this study, thirty bars were prepared for stress rupture tests, and sixteen specimens taken from other bars were prepared for microstructure observation. All bars and specimens were solution annealed at 1120 °C for 4 h in air and air cooling, and then were aged at 800 °C for 20 h following by air cooling. One specimen was firstly used for microstructure observation. After that, two bars and one specimen were acted as a group, each group were carried out long-term aging treatments at 700 °C, 750 °C or 800 °C for 300 h, 500 h, 1000 h, 2000 h or 3000 h. After different long-term aging treatments, all bars were machined into stress rupture samples with a gauge diameter of 5 mm and a gauge length of 25 mm. Two stress rupture samples were tested at 750 °C and 430 MPa, the average value was used to determine the stress rupture life and elongation.

After different long-term aging treatments, the microstructures of new alloy were analyzed by scanning electron microscope (SEM). SEM specimens were prepared via mechanical polishing and chemically etching in a solution with 20 g $CuSO_4$, 150 ml HCl and 80 ml H_2O for general SEM observation. Deep electrochemically-etching method with a solution of 13 ml H_3PO_4, 42 ml H_2SO_4 and 45 ml HNO_3, which stripped away γ matrix, was employed for the observation of γ′ phase. To minimize error, two hundred particles were chosen to measure the size of γ′ phase by Image-Pro Plus software.

After stress rupture tests, all samples were cut into discs along the vertical direction of the stress axial line and thinned down to 50 μm mechanically. After grinding, TEM foils were electrochemically thinned in a solution of 10 vol% $HClO_4$ and 90 vol% C_2H_5OH at − 20 °C and at a voltage of 24 V. Structural and chemical composition analyses were undertaken on a Tecnai G^2 F30 transmission electron microscope (TEM) equipped with a high angle annular dark field (HAADF) detector and an X-ray energy dispersive spectrometer (EDS) system. Dislocation configurations resulting from stress rupture deformation were investigated by a Tecnai G^2 F20 TEM.

3. Results and discussion

3.1. Initial microstructure

After standard heat treatment, the constituent phases of new alloy include γ matrix, blocky MC carbides, granular $M_{23}C_6$ carbides and fine spherical γ′ phase, as shown in Fig. 1. Blocky MC carbides were distributed randomly in the grain interiors or at grain boundaries (GBs), granular $M_{23}C_6$ carbides were only precipitated at GBs, and fine spherical γ′ phase were distributed uniformly in γ matrix with the mean radius of 13.5 nm.

3.2. The coarsening of γ′ phase

During long-term aging, the coarsening of γ′ phase was observed in the new alloy. Fig. 2 shows the representative evolution of γ′ phase after long-term aging at 700 °C, 750 °C and 800 °C for 500 h, 1000 h and 3000 h. It was clear that γ′ phases basically kept the spherical morphology and were distributed uniformly in γ matrix, but the γ′ size increased obviously with increasing the aging temperature and time. After different long-term aging treatments, the average radius of γ′ phase for all specimens was measured by Image-Pro Plus software. After aging at 700 °C, 750 °C and 800 °C for 300 h, the average radius of γ′ phase was about 21.6 nm, 27.8 nm and 34.1 nm, respectively. With aging time increasing to 3000 h, the average radius of γ′ phase increased to 31.5 nm, 51.6 nm and 80.5 nm, respectively.

It is well known that the coarsening of γ′ phase in nickel base superalloys occurs via Ostwald ripening process, which is a diffusion-controlled process [24,25]. The diffusion nature of Ostwald ripening is the LSW theory presented by Lifshitz and Slyozov [26], and Wagner [27]. The LSW theory can be written by the following Eq. (1).

$$r_t^3 - r_0^3 = kt \tag{1}$$

where r_0 and r_t are the average particle radius of γ′ phase before aging and after aging at the time *t*, respectively. The coarsening rate *k* is a constant and depends on several parameters as expressed in Eq. (2).

$$k = \frac{8\gamma V_m D C_m}{9RT} \tag{2}$$

Where γ is the interfacial energy between precipitate and matrix, V_m is the molar volume of the precipitates, *D* is the diffusion coefficient of solute in matrix, C_m is the atomic fraction of solute in equilibrium with the precipitate of infinite size, *R* (8.314 J mol^{-1} K^{-1}) is the gas constant and *T* is the absolute temperature. *D* in the Eq. (3) is defined as

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \tag{3}$$

where D_0 is a constant factor and *Q* is the activation energy for precipitates coarsening. Assuming that the interfacial energy γ, the volume fraction V_m and the atomic fraction of solute C_m do not change in the given alloy [28,29], the formula can be attained based on Eqs. (2) and (3) as

$$\ln(kT) = \text{constant} - \frac{Q}{RT} \tag{4}$$

Eq. (1) is applied to the γ′ coarsening behavior of the new alloy at 700 °C, 750 °C and 800 °C. The cube of average radius of γ′ phase after various aging times at three temperatures is plotted as a function of the aging time in Fig. 3(a). The linear relationship between the cube of γ′ average radius and aging time demonstrates that the coarsening of γ′ phase follows the LSW theory. According to the slope of each line in Fig. 3(a), the values of the coarsening rate *k* at 700 °C, 750 °C and 800 °C are about 7.818 nm^3/h, 42.927 nm^3/h and 178.226 nm^3/h. The higher aging temperature, the greater the coarsening rate of γ′ phase. The values of coarsening rate constant *k* suggest that γ′ phase coarsen more rapidly with the increase of aging temperature. This is mainly because the high temperature is better for the diffusion of elements.

According to Eq. (4), the relationship between temperature T and the coarsening rate *k* is plotted in Fig. 3(b). The activation energy *Q* for γ′ coarsening is determined as 279.98 kJ/mol from the slope of the plot of ln(KT) versus 1/T. The calculated *Q* in new alloy was consistent well with that in other nickel base superalloys (in the range of 250–290 kJ/mol), and compared favorably with the diffusion activation energy of Ni (287.0 kJ/mol), Al (270.0 kJ/mol) and Ti (256.9 kJ/mol) in γ matrix [29–32]. The activation energy 279.98 kJ/mol, together with the cubic growth kinetics of γ′ phase, indicated that the coarsening of γ′ phase in new alloy was mainly controlled by the diffusion of Ni, Al and Ti in γ matrix.