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COARSENING KINETICS OF GRAIN BOUNDARY IN A CAST NICKEL BASE SUPERALLOY DURING LONG TERM AGING

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Abstract

A long term aging treatment at 900 ℃ for 3000 h was carried out on a heat treated conventional cast nickel base superalloy. The evolution of grain boundary (GB) morphologies was observed using OM and SEM respectively. It was found that the irregular serrated GBs, initially composed by discontinuously distributed MC carbide and γ' phases, were coarsening with aging time and the coarsening ratio of the MC was higher than that of γ' phase. MC carbides were gradually decomposed into M_6C carbide and η phase, while γ' particles were coalesced along the GB direction and formed γ' bands after 1000h. A Johnson-Mehl-Avrami-Kolmogorov (JMAK) type of function was employed to quantify the evolution of coarsening behaviors of the carbide and γ' phases part in serrated GBs respectively. The good agreement between calculated results and experimental data indicated that the serrated GBs were indeed evolved as a JMAK type of function.

Introduction

Grain boundary (GB) has long been a subject of research by metallurgists since it is one of the most vulnerable regions in polycrystalline alloys, where cracks often initiated during deformation or failure[1-3]. In order to explore the maximal application potentials of the material, many efforts were exerted to have a deep understanding on the characteristic evolution of grain boundaries in various practical processes.

Serrated grain boundaries (SGBs) have been frequently observed in kinds of alloys, such as austenitic stainless steels[4, 5], wrought Al alloys[6] and conventional cast and wrought nickel base superalloys[7-9]. Especially in cast nickel base superalloys, many widely used alloys, such as IN 738, René 95 and Astroloy et al., are of the characteristic of SGBs[10]. It is reported the grain boundary serrations can effectively enhance high temperature mechanical properties, especially stress-rupture properties of the alloy [11-13]. They are said to impede grain boundary sliding and increase the path for grain boundary diffusion, thereby considerably improving the resistance to crack growth.

Koul and co-workers pointed out that the formation of SGBs is due to the pinning effect of heterogeneously nucleated coarse γ' precipitates on the migration of grain boundaries during the last stage of solidification, while the unpinned boundary segments could continuously migrate, resulting in zigzag like boundary eventually[8, 10]. However, according to the investigation reported by Miyagawa et al, interactions between primary carbides and GBs can also lead to forming serration in GBs[5]. Though formation mechanisms of SGBs are still in controversy, an accordant viewpoint is that the formation of SGBs is contributed to the interaction between boundary precipitates and GBs.

During service or long term exposure at high temperatures, the coarsening of serrated grain boundaries was observed and the width of GBs increased with the time[14, 15]. It is reported that the occurrence of grain boundary coarsening is closely associated with the decomposition of primary carbides and the growth of primary γ' phase precipitated within the grain boundaries[15, 16]. When the alloy was exposed at elevated temperatures, On the one hand, the coarse blocky primary MC carbides were decomposed into fine $M_{23}C_6$ or M_6C carbides, which size increased with exposing time and eventually transformed to be carbide chains consecutively distributed along GBs[15, 17]; on the other hand, the size of primary γ' precipitates also increased with aging time. The coarsening of γ' precipitates can proceed by coalescence (merging of two or more smaller precipitates to be a larger one) or Ostwald ripening (growing of a larger precipitate at the expense of smaller ones)[18, 19]. The above research work indicated that the coarsening of SGBs is a diffusion controlled dynamic growing process occurred in precipitates. It is desirable to study the evolution of precipitates transformation during long term exposure at high temperatures, which helps to understand how these precipitates affect the SGBs coarsening. Previously, kinetics of coarsening of precipitates in alloy matrix have been modeled and calculated[19-21], but studies on coarsening behaviors of precipitates within SGBs were rarely reported.

In the present study, the coarsening kinetics of SGBs of a conventional cast nickel base superalloy during long term exposure for 3000 hours was investigated. The dynamic growth and transformation of precipitates within SGBs were examined using optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS). The coarsening evolution of was nicely quantified using modified Johnson-Mehl-Avrami-Kolmogorov (JMAK) type of equations.

Experimental Materials and Methods

The material used in present work was the polycrystalline René80 nickel base superalloy, which nominal chemical composition in weight percentage was: C = 0.17, Cr = 14.0, Mo = 4.0, W = 4.0, Al = 3.0, Ti = 5.0, Co = 9.5, B = 0.015, Zr = 0.06, and Ni = balance. Cylinder bars, which dimensions were 10 mm in diameter and 100 mm in length, were produced by the vacuum precision casting. The alloys bars were homogenization heat treated at 1210 ^{o}C for 2 hours followed by an air cooling. A two step high temperature aging, at 1090 ^{o}C for 4 hours and at 1050 ^{o}C for 4 hours respectively, was carried out followed by an air cooling. The former aging treatment was used to precipitate γ' phase in the alloy matrix sufficiently and the later was used to stabilize microstructure after coating. After cooling, the samples were aged at 840 ^{o}C for 16 hours followed by an air cooling. In order to examine the microstructure stabilization, a further long term exposure at 900 ^{o}C for 3000 hours was carried out on heat treated samples. During this process, samples with different aging times were taken out from furnace and cut into small pieces for microstructure examination.

The initial observation of microstructure was performed using an optical microscope and a scanning election microscope equipped with a field emission gun was used to examine the evolution of phase transformation of the alloy upon long term exposure. The composition of precipitates within GBs was measured using an energy dispersion spectroscopy.

Results and Discussion

Microstructure of the Alloy after Solution and Aging heat treatment

Figure 1 shows the microstructure of the René 80 alloy after solution and aging heat treatment. It can be seen that a serrated grain boundary structure was formed in the heat treated alloy (Figure 1(a)), which is significantly different from the common observed straight or slightly curved grain boundaries. In a higher magnification as shown in Figure 1(b), some coarse blocky carbides were observed both in the GBs and alloy matrix. Since carbides were discontinuously distributed in the peaks or valleys of SGBs, the resulting width of SGBs is varied with the distribution of carbides. EDS analysis indicated that these carbides were Ti rich MC type carbides, which is consistent with the microstructure analysis of the same alloy reported by reference [7]. The chemical composition of precipitates within SGBs is given in Table 1.

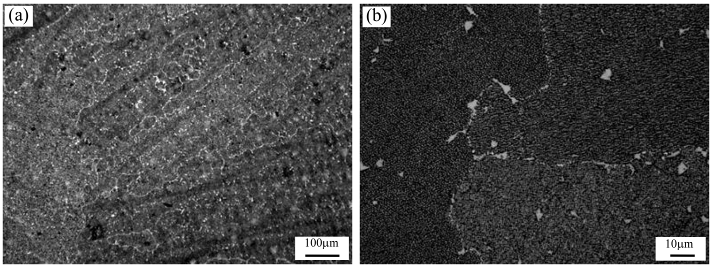


Figure 1. Micrograph of the alloy after solution and aging treatment
(a) morphology of GBs and (b) carbides within GBs and matrix

Table.1 Chemical composition of precipitates in the serrated grain boundaries of the René 80 alloy measured by EDS（atomic fraction,%）

Precipitate	Aging time	Cr	Mo	W	Al	Ti	Co	Ni
MC	0h	2.57	11.54	11.53	0.27	67.6	0.93	5.56
γ'	1000h	10.33	1.1	0.17	10.88	9.37	4.29	63.86
M_6C	1000h	18.25	20.4	12.86	2.41	6.35	10.77	29.32
η	1000h	3.03	0.51	1.89	4.17	18.58	4.50	67.33

Coarsening of SGBs during long term aging

Figure 2 presents the OM micrographs of the width evolution of SGBs of heat treated René 80 superalloy aged at 900 ^{o}C for 100h, 500h, 1000h and 3000h respectively. By comparing the grain boundary width of the alloy with different aging time, it is found that the width of SGBs coarsened with the increase in aging time. After aging for 100h, the morphology of carbides on SGBs (Figure 2(a)) was very similar to that of carbides before aging (Figure 1(b)), which appeared to be regularly blocky shape. When the alloy was aged for 500h, the carbides shape became irregular and the contrast of image in the edge region was different from that in the center region, indicating that the edge of carbides was being transformed (Figure 2(b)). After aging for 1000h, the width of SGBs was significantly coarsened and the shape and image contrast in the previous carbides region were almost completely changed (Figure 2(c)). The boundary width had a further small increase after aging for 3000h (Figure 2(d)).

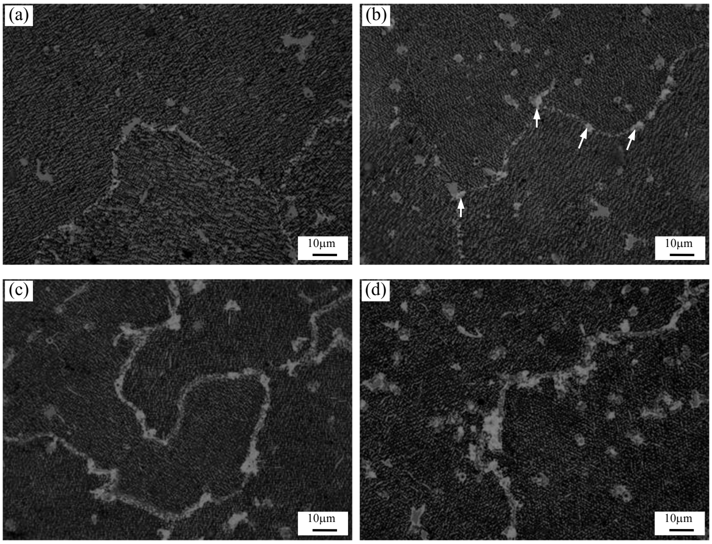


Figure 2 Optical images showing that evolution of serrated grain boundaries as a function time of the heat treated alloy aged at 900 °C (a)100h, (b)500h, (c)1000h and (d)3000h

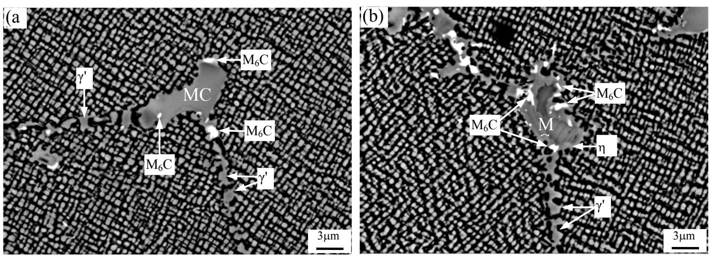
As shown in Figure 2, MC carbides within SGBs were decomposed gradually with aging time (Figure 2(a) – (d)), which is a obvious reason for SGBs coarsening. However, it is found that the width of SGBs parts without MC carbides was coarsened with the aging time as well. To elucidate the cause for this phenomenon, it needs to examine the microstructure of SGBs in a higher magnification with the aid of SEM observation.

Development of Grain boundary structure during Coarsening

Figure 3 exhibits SEM micrographs of the microstructure evolution of SGBs with aging time, which corresponds to the OM micrographs shown in Figure 2. As shown in Figure 3(a), it can be observed that coarse γ' precipitates with a size of 1.0-1.5 μm, significantly higher the size of γ' precipitates in the matrix (0.35-0.45 μm), were discontinuously distributed within SGBs. With the aging time to 500h, γ' precipitates within SGBs were still discontinuously distributed, but one can observe that parts of γ' precipitates were joined together, as shown in Figure 3(b). Compared to boundary width of 100h, the width of 1000h was not only coarsened dramatically, but previously separated γ' precipitates was sintered tightly to be a continuous distributed γ' band (Figure 3(c)), which is agreement with the optical observation shown in Figure 2(c). A completely continuous γ' band was formed with the aging time to 3000h and compared to boundary width of 1000h, the boundary width of 3000h had a further increment, as shown in Figure 3(d).

With aging time, the dynamical coarsening of SGBs was not only exhibited in the evolution of γ' phase, but also presented in the transformation of MC carbides. It can be observed that some fine white particles were formed at the edge of MC carbides after aging for 100h, as shown in Figure 3(a). It is reported that primary MC carbides can be decomposed into $M_{23}C_6$ or M_6C carbides in terms of the composition of alloys[17, 22]. According to the investigation reported by Choi et al[22], for the alloy with a relatively low contents of W and Mo elements (the sum of W and Mo less than 2 in atomic percentage), the decomposition of MC carbides is prone to form $M_{23}C_6$, while for a alloy with a W and Mo contents higher than 3.3%, the newly formed carbides are highly possible to be M_6C rather than $M_{23}C_6$. In present study, the sum of W and Mo element of René 80 alloy is 3.6%, indicating that M_6C carbides are very likely to be formed as the results of MC decomposition. After composition measurement with EDS, the white particles are identified as M_6C. When the aging time goes to 500h, M_6C appears to be dramatically lager and MC carbides were covered by a thin film of η phase, as shown in Figure 3(b). After 1000h, MC carbides were completely decomposed into M_6C and irregular η phase (Figure 3(c)), which composition is given in Table 1. As can be seen form optical micrograph shown in Figure 2(c), the considerable change in shape and contrast of the pervious MC region dose also indicate the degeneration of MC. This can be mutually evidenced with the SEM observation. It is noted from Table 2 that the sum of Ti and Al elements in η phase (22.8 at.%) is very close to that in γ' precipitates (20.8 at%), but the ratio of Ti to Al in the former (4.46) is much higher than that in the later (0.86). The high content of Ti element in η phase is very likely released from MC carbide, since MC contains Ti element as high as 67.6 at.% at the beginning of aging. With the aging time to 3000h, Figure 3(d) shows that η phase had grown into the inside of grain at the expense of fine secondary γ' phase and enveloped M_6C, which was initially formed at the edge of MC. Therefore, it can be concluded reasonably that the degeneration of MC carbides of René 80 alloy during long term aging at 900 °C can be proposed as:

$$MC + \gamma \rightarrow M_6C + \eta$$



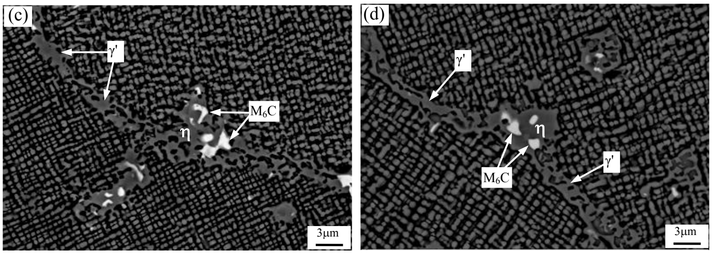


Figure 3 Back scattering SEM micrographs showing evolution of grain boundary structures of the alloy aged at 900°C for (a)100h, (b)500h, (c) 1000h and (d) 3000h respectively

Quantification of SGBs coarsening with aging time

As discussed above, the grain boundaries of René 80 alloy can be categorized into two groups: carbides parts and γ' phase parts respectively, both sizes of which were coarsened with aging time. In order to understand their effects on the coarsening of SGBs quantitatively, the width evolution of carbides part and γ' precipitates part was measured under SEM observation. For each aging time, twenty boundary images of GBs were taken and the width of carbides and γ' precipitates normal to the boundary direction was measured. The widest width was selected to represent the width of carbides part and γ' precipitates part in each single SGB respectively and the average width values measured in twenty SEM images were being the width of two boundary segments for each aging time. The development of boundary width for carbides part and γ' precipitates part with aging time is listed in Table 2.

Table.2 the development of the width of carbides part (CGB) and γ' phase part (γ'GB) in SGBs of René 80 alloy with time during long term aging at 900 °C

Aging Time (h)	0	100	200	500	700	1000	1250	1500	2000	2500	3000
γ' GB (μm)	1.44	1.42	1.44	1.71	1.94	2.58	2.65	3.10	3.24	3.25	3.29
CGB (μm)	2.71	2.63	3.37	3.89	4.65	6.58	7.34	6.97	8.51	8.37	8.70

Since the development of SGBs coarsening during long term isothermal exposure can be regard as a gradually transforming process, which is comprised of the influence of many factors, such as coalescence, Ostwald ripening, degeneration and the generation of a new phase, on the width of SGBs, it can be described quantitatively using a Johnson-Mehl-Avrami-Kolmogorov (JMAK) type function, similar to a phase transformation or recrystallization process quantified using JMAK equations[21, 23, 24]. In present study, similar empirical equations were used in order to quantify the evolution of coarsening kinetics of SGBs with aging time during long term exposure at 900 °C.

The variation in the width of SGBs $f(t)$ with aging time can be expressed:

$$f(t) = \frac{W_t - W_0}{W_f - W_0} \qquad (1)$$

Where W_0, W_t and W_f are the width of grain boundaries at the beginning, at a given aging time t and at the end of aging process respectively. The relationship between $f(t)$ and aging time t takes the form of JMAK equation:

$$f(t) = 1 - \exp(-kt^n) \qquad (2)$$

Where k and n are constants, which can be determined by fitting a linear relationship in a $\ln[-\ln(1-f(t))]$ versus $\ln(t)$ plot, as shown in Figure 4. According to Equation (2), n is the slope of the linear line and ln$k$ is the intercept of the line on the vertical axis. The linear correlation coefficients for the two fitted curves are very close 1 (0.995 and 0.983 respectively), indicating that the fitted curves are good agreement in the width evolution of carbides part and γ' phase part within SGBs with aging time. The ln$k$ value of carbides part is greater than that of γ' phase part, which implies that the coarsening rates of the former is higher than the latter.

The final calculated grain boundary width vs. aging time curves of carbides part and γ' phase part are given in Figure 5. The good agreement between calculated curves and experimental date indicates that the coarsening behaviors of grain boundary width are evolved as JMAK function of aging time in the René 80 alloy during long term exposure at 900 °C. After parameters k and n were determined experimentally, the development coarsening behaviors of serrated grain boundaries can be predicted quantitatively during the long term exposure process. This method to predict coarsening behaviors of grain boundaries quantitatively in conventional cast superalloys is of particular value for practical application of cast superalloys, since it will help to evaluate realistic service life for polycrystalline components made of cast superalloy during service. This is especially important in the case of land based turbines that operate for very long time.

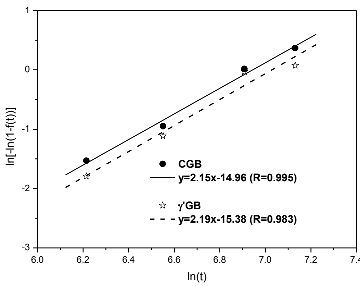


Figure 4 $\ln[-\ln(1-f(t))]$ versus $\ln(t)$ for the René alloy aged at 900 °C

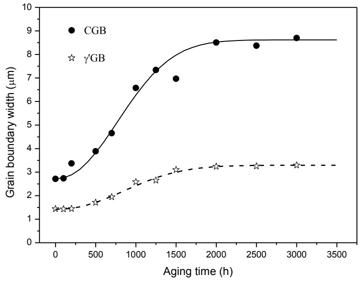


Figure 5 Evolution of the width of carbide part and γ' phase part within SGBs as a function of time for René 80 alloy aged at 900 °C. Points with different symbols are experimental data and the solid and dashed lines are fitted values.

Conclusions

1. The serrated grain boundaries, which were composed of blocky MC carbides and coarse γ' precipitates, were observed in the as-cast polycrystalline René 80 alloy. The width of the grain boundaries were coarsened significantly with time during long term aged at 900 °C.
2. Upon aging, the M_6C and η phase were initially formed at the edge region of MC carbide within in SGBs at the expense of fine secondary γ' phase. Therefore, the degeneration of MC carbide can be described as: $MC + \gamma \rightarrow M_6C + \eta$. On the other hand, the coarse γ' precipitates were mutually coalesced with aging time and formed γ' bands after aging time over 1000 hours.
3. The coarsening kinetics of SGBs was quantified using JMAK type equations. The good agreement between experimental data and simulated results indicates that the development of SGBs in René 80 alloy during long term aging at 900 °C could be predicted accurately.

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