Journal of Alloys and Compounds 651 (2015) 255–258

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Letter

In-situ environmental TEM study of γ′-γ phase transformation induced by oxidation in a nickel-based single crystal superalloy

Keywords:
Phase transition
In-situ TEM
Electron energy loss spectroscopy
Nickel-based superalloy
Oxygen diffusion path

A B S T R A C T

Oxidation induced phase transformation from γ′ to γ phase can severely degrade creep properties of superalloys and has been studied by in-situ environmental transmission electron microscopy, energy dispersive spectrometer and electron energy loss spectroscopy in detail. The in-situ observation showed that, during oxidization, the ordered γ′ phase ($L1_2$) gradually transformed to disordered γ phase (face-centered cubic (fcc)) with the appearance of oxidation product consisted of γ-Al_2O_3 crystallites with a strong crystallographic texture. This directly proves that γ′-γ phase transformation are induced by aluminum oxidation with aluminum depleted in γ′ phase. Furthermore, the oxygen was demonstrated to diffuse preferentially through γ′-γ phase interface which is different from previously thought (γ matrix).

1. Introduction

Nickel-based single crystal superalloys have been widely used as aeronautical engine blades due to their excellent mechanical and creep properties at high temperature. These unique properties are related to their specific microstructure—high volume fraction of ordered second strengthening phase γ′ ($L1_2$) precipitating inside the disordered γ phase (fcc) [1–10] matrix. Due to the fact that the thinned blades (<1 mm) cannot only reduce the weight, but also increase the cooling efficiency [11–13]. However, creep tests performed on thin wall specimens made of M247LC SX [12], René N5 [13], PWA 1484 [14], and MC2 [15] generally showed result that a reduction in wall thickness would decrease the creep rupture life and reduce the creep strength. This inferior creep performance of thin wall superalloys is suggested to be attributed to the oxidation induced γ/γ′ microstructure modification in the near-surface area, namely γ′-free and γ′-reduced layers [11,15–17]. In these two layers, γ′ phase is completely or partially transformed to γ phase, thus volume fraction of the second strengthening phase reduced. Therefore, the thickness of optimal microstructure of the load-bearing cross-section is decreased, and this will cause performance degradation [11,16–20]. Hence for better understanding failure of those thinned components, clearly unveiling the whole process of how the γ′ phase transforms to γ phase is of great importance.

The γ′-free and γ′-reduced layers have been found in many superalloys after oxidation. EDS studies show that generally, the inner of surface oxide layer is rich in Al and the content of Al in γ′-free layer significantly decreased. Therefore, the cause of γ′-γ phase transition is considered to be the intake of specific elements, especially Al, in the oxide scale [16,21]. However, so far, the γ′-γ phase transformation mechanism is not clear, due to lacking of in-situ observation of oxidation process.

In addition, the oxygen diffusion path (ODP), which greatly influences the way of phase transition, has not been well understood yet, due to both of the difficulty of specimen preparation and low oxygen sensitivity in most elemental composition analysis. In the oxidation process, oxygen is considered to diffuse into bulk alloy through porous oxide of γ phase. By employing the wavelength dispersive spectrometer, Edmond et al. [22,23] observed that oxidation was confined to the γ′ particles while γ channels remained unoxidized. Based on this observation, they suspected that γ′ phase was preferentially oxidized because of low critical partial pressure of γ′ phase for oxidation and the ODP was the γ channels. However, these assumptions have not yet been discussed, and the oxidation process has not yet been directly observed. Therefore, a detailed study is needed to clarify which is the ODP in superalloys, the γ channels, γ′ phase or the phase boundary.

In present work, the γ′-γ phase transformation is demonstrated in a direct way. The in-situ process have been investigated at 850 °C under an oxygen pressure of $5*10^{-2}$ Pa and the underlying cause of this transformation has been determined. In addition, the ODP which can significantly influence the transition process has been explored as well.

2. Experimental details

The material tested was a second-generation single crystal superalloy and the nominal composition in wt.% is: 6.2Al, 7.1Cr, 7.8Co, 1.7Mo, 6.8Ta, 6.3 W, 3.7Re and balance Ni. The heat treatments were performed according to the following regime:

http://dx.doi.org/10.1016/j.jallcom.2015.07.017
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1310 °C/2 h + 1313 °C/2 h + 1130 °C/4 h + 900 °C/16 h. This alloy was directionally solidified along <001>-direction and the TEM samples were prepared by a twin jet electro-polisher (Model MTP-1A) in a solution containing 5 vol.% perchloric acid in ethanol at −25 °C.

In-situ observation of the transition and selected-area electron diffraction (SAED) during the observation were carried out in an environmental transmission electron microscopy (ETEM) (Hitachi, H-9500). A probe Cs-corrected Chemi-STEM (FEI Titan 80-200) equipped with Super-X detectors [24] was employed to characterize the oxide of γ′ precipitates after in-situ experiment. Bright field (BF) scanning transmission electron microscopy (STEM) image and energy dispersive spectrometer (EDS) analysis were carried out. In addition, electron energy loss spectroscopy (EELS) was employed to explore the ODP due to its higher sensitivity of oxygen than other analysis methods.

3. Results and discussion

Fig. 1A shows the morphology of oxidized γ′ phase and Fig. 1B the zoom-in BF STEM image of the oxide (corresponding region is indicated by white rectangle in Fig. 1A). It can be clearly observed that the original Ni_3Al is no longer single crystalline after oxidation. However, clusters or nanoparticles with diameter 1–3 nm are presented. SAED of the oxide (inset of Fig. 1B) shows twelvefold pattern and all diffraction spots are elongated. These observation imply that the oxide may consist of highly orientational ordered crystallites. Fast fourier transformation (FFT) was performed on selected areas of BF STEM image (Fig. 1B), as shown in Fig. 1C(a–c). The FFT results show that crystallites in the marked areas are γ-Al_2O_3. It is interesting to note that, the γ-Al_2O_3 crystallites have two main orientations with about thirty degree difference (Fig. 1C(d)) according to the SAED pattern. Comparing FFT diffraction patterns of crystallites in the similar orientation, an angle deviation between them can be clearly visible, as shown by the white dotted arrows which is at the same place in Fig. 1C(a) and Fig. 1C(c). This angle deviation is considered to be responsible for the elongation in SAED.

Furthermore, EDS quantitative analysis of the oxide shows that the composition of the γ′ phase in at.% is 17.7Al, 3.8Ta, 0.8Cr, 0.3Mo, 0.7Ni, 76.7O (the abnormal oxygen content may be ascribed to absorbed oxygen). Thus the oxide is mainly composed of alumina, which agrees well with the diffraction results. It should be mentioned that the oxide barely contains nickel which is the domain element of γ′ phase. Most nickel in original Ni_3Al phase seems vaporized even though the test temperature is not high enough for Ni vaporization. Additionally, the existence of Al_2O_3 can suppress elemental vaporization [25]. The whereabouts of nickel in γ′ phase during oxidation need a further study.

Direct observation of the whole in-situ oxidation process has been recorded (supplementary movie M1). Series BF images (Fig. 2a–d) and corresponding SAED of the specific γ′ precipitate (Fig. 2f–h) at different oxidation stages are shown in Fig. 2. Fig. 2a shows the morphology of the chosen γ′ precipitate before heating. The margin is relatively thinner due to the specimen preparation. At the early stage, the interface of the oxide and unoxidized crystal (IOC) is smooth and almost parallel to the edge of specimen, as shown in Fig. 2b. However, after specimen oxidized for 264s, IOC become zigzag and is gradually inclined to be {110} planes, which is indicated by white arrows in Fig. 2c. When oxidation time reach 566s, it seems that oxidization stagnates for seconds and then continues from the intersections of two mutually orthogonal {110} planes, indicated by white dotted arrows in Fig. 2c. Fig. 2d shows the microstructure of the γ′ precipitate oxidized for 1909s and it should be noted that the edges of remained crystals are {110} planes, reasonably.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.jallcom.2015.07.017.

During the whole in-situ process, {110} planes seem difficult to be oxidized while {100} planes are readily oxidized. However, this phenomenon contradicts earlier first-principle calculation [26] which suggests that oxidation resistance of Ni_3Al(001) is better than Ni_3Al(011) for stronger affinity of O and Al on (001) surface which means more stable Al_2O_3. This inconsistent result may arises from the different ingredients, since that addition of easy oxidized elements, such as tantalum and chromium, will complicate the oxidation process. However, in the early stage of oxidation, the phenomenon that IOC is not {110} planes but parallel to the sample edge may ascribe to that the edge is thinner and more likely a steep slope rather than a plate.

Before oxygen was introduced, SAED of original γ and γ′ phase have been captured, as shown in Fig. 2e and f respectively. Due to the fact that γ′ phase is an ordered $L1_2$ structure while γ phase is a disordered fcc structure, the SAEDs of these two coherent phases can be distinguished by extra points, such as (100)and (010), which are peculiar to γ′ phase and labeled with smaller font in Fig. 2f. After oxidation begins, the extra spots of γ′ precipitate are weaken and gradually disperse (Fig. 2f–h). After oxidation for 1909s, all of the specific diffraction spots disappear except for two faint spots (120) and (−1–20) which are marked out in Fig. 2h. Based on this phenomena, we believe that if the oxidation last long enough, the specific spots would all disappear ultimately, which means that the γ′ phase totally transforms to γ phase. Similar as the coherency relationship which has been found in

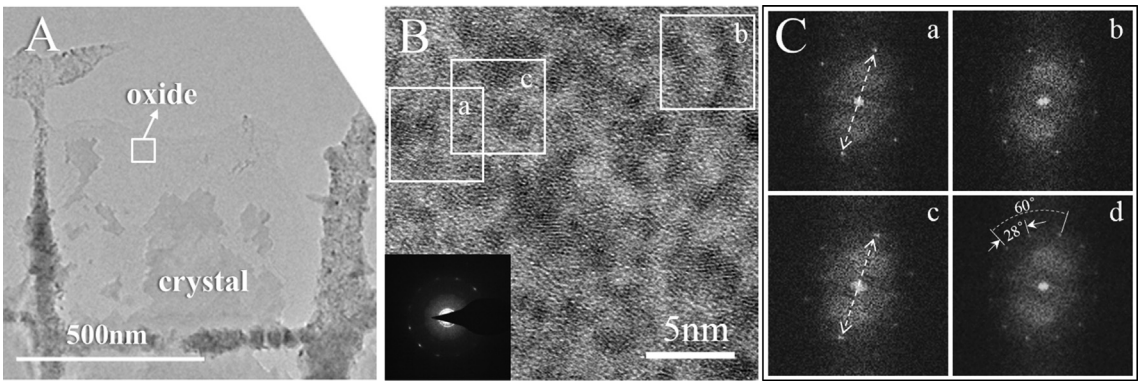

Fig. 1. Characterization of the oxide of γ′ phase. A is a TEM image of the oxidized γ′ phase and B a BF STEM image of oxide in the white rectangle in A. Inset of B is SAED of the oxide. C(a–c) are the corresponding FFT diffraction patterns of the selected areas a-c in B, and C(d) is a superimposed image of C(a) and C(b).