OXIDATION BEHAVIOR OF Ti6Al4V ALLOY EXPOSED TO ISOTHERMAL AND CYCLIC THERMAL TREATMENTS

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Abstract

One of the most common titanium alloys for aerospace industry is Ti6Al4V (usually designed as Ti64) which is used for manufacturing aero-engine components, such as fan discs, compressor discs, blades and stators. The maximum service temperature for this alloy is limited partly because of degradation of mechanical properties at elevated temperatures (above 480 °C). During the first stage of oxidation the oxide scale is protective, whereas after prolonged oxidation time it loses its protective nature and favours higher diffusion of oxygen through the oxide. In the present study, cyclic thermal treatments were performed in air at 500 and 700 °C, up to 500 hours, and compared with similar studies carried out on isothermal oxidation conditions. The evolution of the surface oxidation was analyzed by metallographic techniques and X-ray diffraction, together with a detailed advanced characterization of the microstructure by Scanning Electron Microscopy and Focus Ions Beam. The results point out that the cyclic thermal treatments induced a strong increase of the weight gain compared to isothermal treatments. The analysis of the oxide scale revealed not only the presence of rutile, at 700 °C, but also anatase and TiO_x at 500 °C for both isothermal and cyclic thermal treatments. At 700 °C, thermal stress caused by cyclic thermal treatments promoted the fracture of the oxide after the first 20 hours.

Keywords: Titanium, oxidation, isothermal treatments, cyclic thermal treatments

1. INTRODUCTION

Ti64 is one of the most popular and most used titanium alloy. Its production comprises over 50 % of the total production of titanium alloys worldwide [1]. Ti64 has an excellent combination of properties, such as specific strength and corrosion resistance, and therefore it finds broad application in different engineering fields; namely aerospace, automotive, marine and biomedicine [2, 3]. In aerospace applications, Ti64 is mainly used for manufacturing aero-engine components, such as fan discs, compressor discs, blades and stators, where the maximum service temperature does not exceed 300-350 °C [4, 5].The maximum service temperature limitation is closely related to pronounced oxidation when titanium alloys are exposed at elevated temperature in oxygen containing environments. Oxidation proceeds as two simultaneous reactions which involve: 1) formation of a thin (5-10 nm) n-type oxide scale (TiO_2) on the surface, and 2) inward diffusion of oxygen into the bulk metal [1, 6]. During the first stage of oxidation the oxide scale is protective, whereas after prolonged oxidation time it loses its protective nature and favours higher diffusion of oxygen [1, 7]. Additionally, it is known that oxygen has high solid solubility in α-titanium (about 14.5 wt.%) [8]. Therefore, exposure of Ti64 to temperatures above 480 °C in an oxygen containing environment results in simultaneous formation of an oxide scale, which consists of a multilayered structure of TiO_2 and Al_2O_3 [9], and an oxygen enriched layer beneath this scale. The oxygen enriched layer is commonly referred to as alpha-case. The name alpha-case originates from the fact that oxygen is a strong α-stabilizing element and its elevated content in titanium and its alloys promotes increase of the β-transus temperature and triggers phase transformation of the retained β-phase to

α-phase. Thus, this result in increase of the α/β phase ratio in two phase titanium alloys [10]. In addition, it also increases the strength of titanium via solid solution hardening [11].

Most of the results that can be found in the literature were achieved by isothermal treatments. Thus, the main goal of the present work is to compare the oxidation behavior of Ti64 alloy under isothermal and cyclic thermal treatments within the same range of temperatures and time of exposure.

2. EXPERIMENTAL PROCEDURE

The studied material was a Ti6Al4V alloy obtained in plate form according to AMS 4911L [12]. The chemical composition of the as-received material in wt. % is given in **Table 1**.

Table 1 Chemical composition of the as-received Ti6Al4V (wt.%)

Element	Al	V	Fe	O	C	N	H	Y	Ti
Concentration	6.75	4.50	0.30	0.20	0.08	0.05	0.015	0.005	Balance

Figure 1 shows the microstructure of the Ti64 alloy in as-received condition. The material presents equiaxed microstructure consisting of primary alpha grains and elongated alpha needles in transformed beta matrix. The volume fraction of α-Ti phase is 93-94 %, and accordingly the proportion of β-Ti phase is 6-7 %. β-Ti phase is dispersed between the primary alpha grains and the grain boundary triple points.
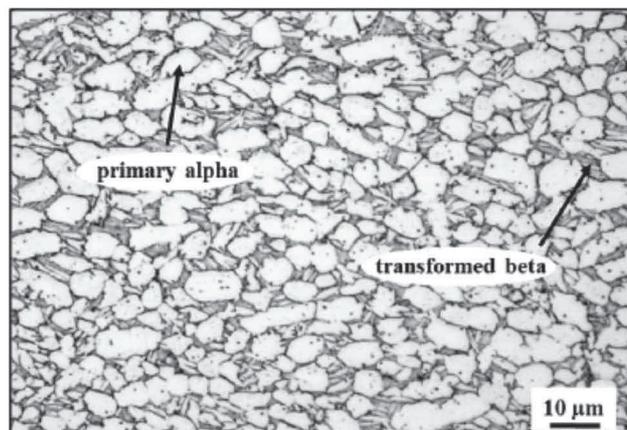

Figure 1 Microstructure of the studied Ti64 alloy [1]

The as-received material was cut by diamond disc in samples with dimensions 1.0 x 1.0 x 0.5 cm. All surfaces of the samples were polished with SiC grinding paper up to 2500 grid size in order to remove the recast layer. Thereafter, the polished samples were cleaned in acetone for 15 min in an ultrasonic bath, rinsed with ethanol and dried in air. The cleaned samples were then placed into Al_2O_3 crucibles and subjected to the thermal treatments. All samples were weighted using a microbalance with an accuracy of ±0.0001g before and after each heat treatment. The temperature inside the furnace was calibrated and controlled using thermocouples positioned at the locations inside the furnace where the samples were placed. The standard deviation of the temperature inside the furnace was ± 5 °C. Thermal treatments were carried out in air and at atmospheric pressure.

For isothermal treatments eight samples were inserted in the furnace for each studied temperature, i.e. 500 and 700 °C and cooled in air down to room temperature after 5, 10, 50, 100, 200, 300, 400 and 500 hours of exposure.

Regarding cyclic thermal treatments, one cycle is defined as 1 h at high temperature and 15 min at room temperature (**Figure 2**). The studied number of cycles was 5, 10, 50, 100, 200, 300, 400 and 500.
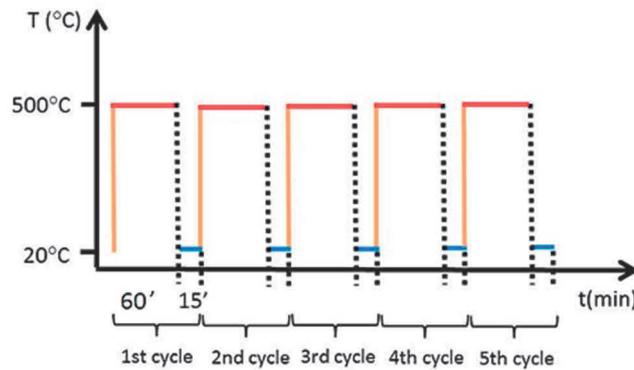

Figure 2 Schematic representation of cyclic thermal treatments

The observation of the surface after heat treatments was performed by means of Field Emission Scanning Electron Microscopy (FESEM). A detailed characterization of the subsurface was achieved by a dual beam Focused Ion Beam/FESEM (FIB/FESEM). A thin platinum layer was deposited on the sample prior to FIB machining in order to minimize ion-beam damage. A Ga+ ion source was used to mill the surface at a voltage of 30 kV. The final polishing of the cross-sections was made at 500 pA. The analysis of the oxide scale was carried out by X-Ray diffraction (XRD) and Energy-Dispersive X-ray Spectroscopy (EDS).

3. RESULTS AND DISCUSSION

Figures 3a and **3b** compare the amount of weight gain per surface area for samples subjected to isothermal and cyclic thermal treatments at 500 and 700 °C, respectively. The different scale of both Figures must be remarked, because at 500 °C the maximum weight gain per area is less than 0.5 mg/cm2, whereas at 700 °C it reaches almost 80 mg/cm2. As it can be observed, for both temperatures cyclic treatments lead to a higher increase of weight gain than isothermal ones. Differences between heat treatment conditions are more marked for samples subjected to 700 °C, where after 500 h / 500 cycles, the weight gain becomes one order of magnitude higher for cyclic thermal treatments.
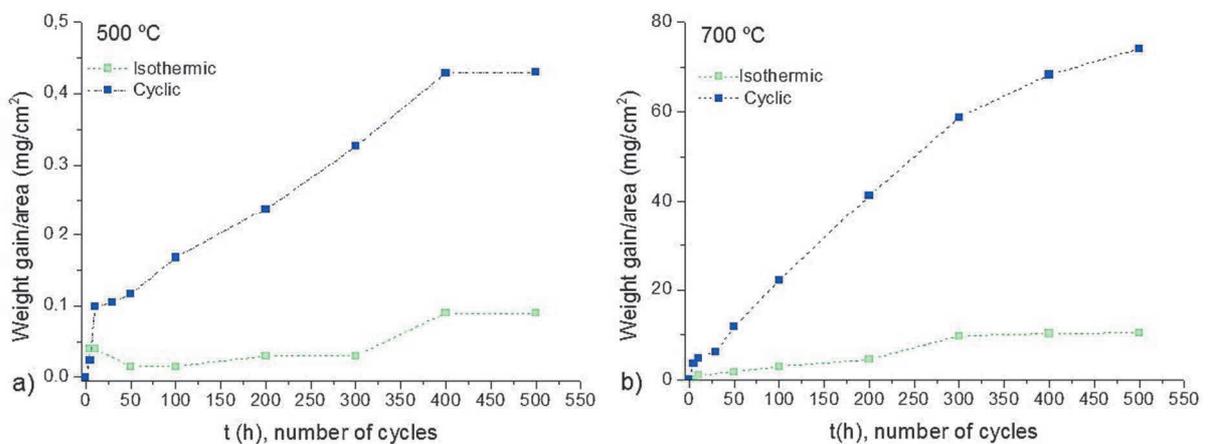

Figure 3 Weight gain per surface area as a function of time for isothermal *t* (hours) and cyclic heat treatments (number of cycles) at: a) 500 °C; b) 700 °C

It is known that an increase in weight after oxidation in titanium alloys is due to the simultaneous formation of oxide scale and diffusion of oxygen into the bulk [13]. In order to identify the phases present in the oxide, XRD was carried out on the top of the scales (i.e. plane view). There are important differences between XRD patterns obtained at 500 and 700 °C for both isothermal and cyclic thermal treatments. At 500 °C,it was possible to identify picks of rutile, anatase, TiOx, α-Ti and β-Ti after 500 cycles (**Figure 4a**). Anatase and rutile are tetragonal, and both have crystal structures consisting of TiO_6 octahedron, sharing four edges in anatase and two in rutile [14]. The presence of α and β-Ti phases is due to penetration of X-ray through the oxide scale (< 5 μm) into the alloy substrate. At 700 °C, mainly rutile was present after 500 hours of exposure (**Figure 4b**). Rutile has tetragonal crystal structure with an n-type oxide exhibiting significant non-stoichiometry TiO_{2-x}, where x could vary up to ~0.008 depending on temperature and oxygen partial pressure. For Ti oxidation at temperatures below 1000 °C and at near-atmospheric pressures, only TiO_2 rutile type has been detected in oxide scales [15].
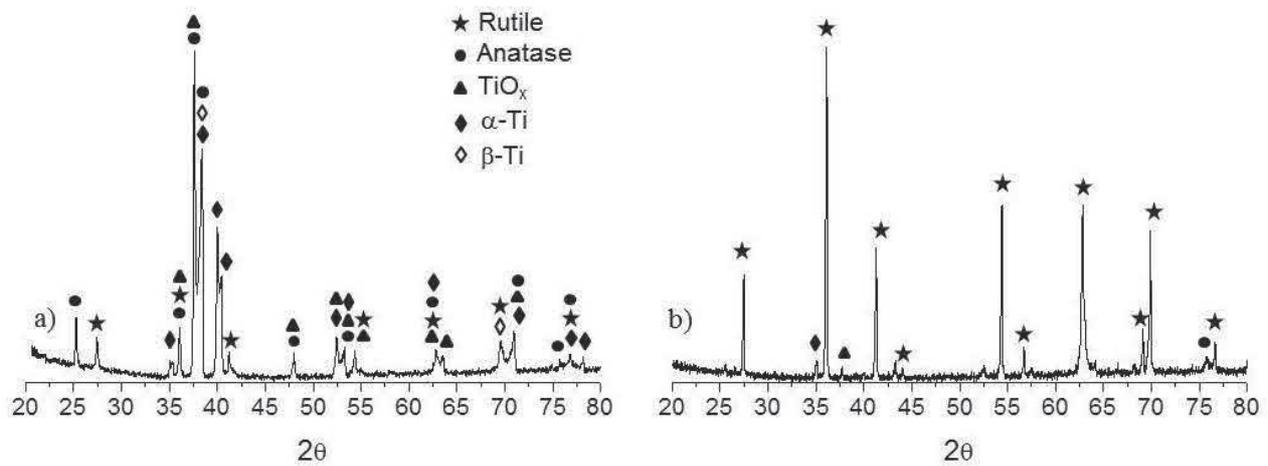

Figure 4 XRD patterns of the oxide scales for samples submitted to cyclic thermal treatments: a) 500 °C; b) 700 °C
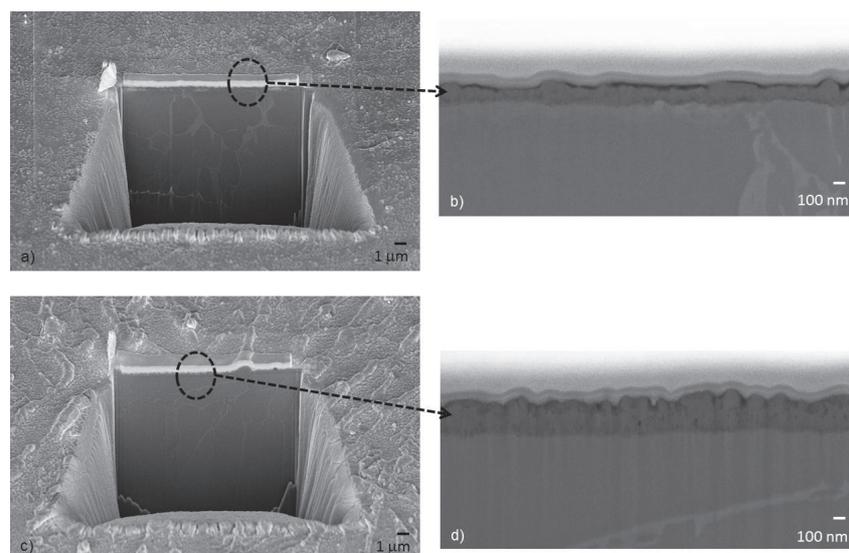
Figure 5 FIB trench on the top of the oxide scale after cyclic thermal treatment at 500 °C for: a) 5 cycles and c) 500 cycles; b) and d) higher magnification micrographs achieved in the marked zone of images a) and c), respectively

The oxidation at 500 °C resulted in very thin (<1 μm), dense, adherent and uniform oxide scales for both thermal treatments (**Figure 5**). At 700 °C, the behavior of the studied titanium alloy was completely different: for isothermal condition specimens oxidized until 100 hours show dense, well adherent and uniform scales, whereas these scales became porous for longer times [16]. For cyclic treatments, spallation was more severe. The oxide scale spalled off from the metal substrate as thin and brittle flakes after 25 cycles. As it can be seen in **Figure 6**, Back-Scatter Electrons (BSE) allows identifying differences in chemical composition on the surface of samples subjected at 700 °C after 500 cycles. The local semi-quantitative percentages of each element at points 1, 2 and 3 of **Figure 6** were determined by EDS analysis **Table 2**). In this sense, at the top of the oxide scales (points 2 and 3) the amount of oxygen was higher, together with aluminum and slightly increases of iron compare to the lower level (point 1), where the oxide scale had partially spalled off. These results are in agreement with previous studies [9] which have demonstrated that a compact Al_2O_3 layer is always formed on top of the TiO_2 during air oxidation of Ti64 at elevated temperatures. The main role of this dense Al_2O_3 layer is to inhibit oxygen diffusion to the alloy substrate. However, as pointed out by the authors in a previous work [16], although Al_2O_3 was present in oxide scales, it did not completely inhibit the oxygen diffusion into the substrate. Regarding Fe, it is classified as a neutral element that does not significantly affect the oxidation resistance of Ti-Al alloys [17]. However, Shannon *et al.* [18] has proved that since the effective ionic radii of six coordinated Fe^{3+} (78 pm) and Fe^{2+} (64 pm) are slightly lower than the six coordinated Ti^{2+} (86 pm) and similar to Ti^{3+} (67 pm) and Ti^{4+} (61 pm), Fe ions are preferably located in the substitutional sites of the rutile TiO_2 matrix. Thus, it is considered that the doping of the rutile structure would result in lowering the oxygen diffusion through the oxide structure.
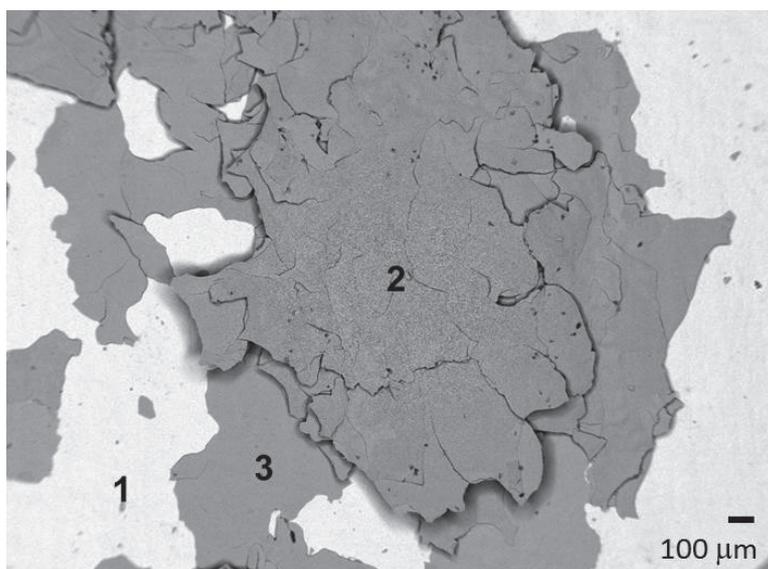
Figure 6 Topography of the surface for a sample subjected to 500 cycles at 700 °C obtained by back-scattered electrons in a FESEM

Table 2 Normalized chemical composition of the oxide scales achieved by EDS for positions 1, 2 and 3 of **Figure 6** in at.% formed after 500 cycles at 700 °C

		O	Al	Ti	V	Fe
Position	1	26.73	3.60	66.40	2.63	0.62
	2	43.37	10.50	42.43	2.44	1.16
	3	43.67	5.85	47.93	2.54	0.80

4. CONCLUSIONS

In this work, the oxidation behaviors of Ti6Al4V alloy exposed to isothermal and cyclic thermal treatments at 500 and 700 °C were compared. The main conclusions can be summarized as follows:

- Cyclic thermal treatments induced a clearly higher increase of weight gain per area compared to isothermal treatments, being more pronounced at 700 °C.
- Isothermal and cyclic thermal treatments performed at 500 °C led to the formation of rutile, anatase, TiOx, α-Ti and β-Ti while at 700 °C, rutile was the main crystal structure identified by XRD.
- A thin (<1 μm), dense, adherent and uniform oxide was formed at 500 °C for both thermal treatments.
- At 700 °C, spallation of the oxide scales was observed after 200 h for isothermal treatments, whereas for cyclic thermal treatments it started after only 25 cycles.

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