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# Oxidation and alpha-case formation in Ti–6Al–2Sn–4Zr–2Mo alloy

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ABSTRACT

Isothermal heat treatments in ambient air were performed on wrought Ti–6Al–2Sn–4Zr–2Mo (Ti-6242) material at 500, 593 and 700°C for times up to 500 h. In the presence of oxygen at elevated temperatures simultaneous reactions occurred in Ti-6242 alloy, which resulted in the formation of an oxide scale and a layer with higher oxygen concentration (termed as alpha-case). Total weight gain analysis showed that there was a transition in the oxidation kinetics. At 500°C, the oxidation kinetics obeyed a cubic relationship up to 200 h and thereafter changed to parabolic at prolonged exposure times. At 593°C, it followed a parabolic relationship. After heat treatment at 700°C, the oxidation obeyed a parabolic relationship up to 200 h and thereafter changed to linear at prolonged exposure times. The observed transition is believed to be due to the differences observed in the oxide scale. The activation energy for parabolic oxidation was estimated to be 157 kJ/mol. In addition, alpha-case layer was evaluated using optical microscope, electron probe micro-analyser and microhardness tester. The thickness of the alpha-case layer was found to be a function of temperature and time, increasing proportionally, and following a parabolic relationship. The activation energy for the formation of alpha-case layer was estimated to be 153 kJ/mol.



## 1. Introduction

Oxidation of titanium and its alloys 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 [1,2]. 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 [2,3]. Additionally, it is known that oxygen has high solid solubility in α-titanium (about 14.5 wt.%) [4]. Therefore, exposure of titanium and its alloys to elevated temperatures above 480°C to any oxygen containing environment results in simultaneous formation of an oxide ($TiO_2$) scale and an oxygen enriched layer beneath the scale. The oxygen enriched layer is commonly referred to as alpha-case (α-case), as oxygen being an α-stabilising element it increases the amount of alpha phase within this layer [4]. In addition, it also increases the strength of titanium via solid solution hardening [5]. Alpha-case is defined as a continuous, hard and brittle layer formed because of the inward diffusion of oxygen [1,2]. It is formed during elevated temperature processing such as: casting, heat treatments, and thermo-mechanical treatments [6–8]. Additionally, prolonged exposure of titanium and its alloys at elevated temperatures, i.e. during service could also lead to the formation of alpha-case [1,2]. It is well known that the presence of alpha-case results in the reduction of important mechanical properties such as ductility, fracture toughness and fatigue life of titanium alloys [7,9–18]. Therefore, in aerospace applications alpha-case is often removed by machining and chemical milling processes [1,2,19], or avoided by using high temperature coatings [1,2,19–24]. The necessity of using these additional processes is one of the reasons for higher manufacturing cost of titanium and its alloys.

In addition to the higher manufacturing cost, titanium has restrictions in the operating temperature. Currently, the environmental restrictions and economic requirements of future aero-engines are setting higher demands on fuel efficiency. One way of improving the efficiency is to increase the pressure in the engines. However, by increasing the pressure, the temperature in the engine also increases. Today, the components in jet engines that are made of titanium are already being exposed to their maximum allowed temperatures (especially if close to the temperatures where alpha-case formation starts). Thereby an additional increase in temperature could become a serious issue with regard to the formation of brittle alpha-case layer during service. The time that a jet engine spends at maximum temperature during a normal flight is relatively short, but if each such short time is added over the period of time, then the time at the maximum temperature becomes significant, considering the fact that the jet engines run many thousands of flight hours during their total life. If a small amount of oxygen diffuses a short distance into the titanium alloy component during each such maximum envelope, the accumulative effect of this could eventually lead to the formation of critical amount of oxygen to form alpha-case. In order to be able to increase the maximum working temperature of the titanium alloys in jet engines it is important to increase

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the understanding of the physical phenomena such as oxidation mechanisms, alpha-case formation and its effect on mechanical properties. Many studies have been performed on evaluating the detrimental effect of alpha-case layer on the mechanical properties of titanium alloys [9–18]. However, there is scarcity in the understanding of oxidation mechanisms and the formation of alpha-case in high temperature titanium alloys especially for prolonged exposure times that are relevant for service. The most notable studies were by Shamblen and Redden [9], Shenoy et al. [12] and McReynolds and Tamirisakandala [25] on Ti-6242 alloy; Leyens et al. [13] on Ti–6Al–2.75Sn–4Zr–0.4Mo–0.45Si (Timetal 1100); Evans et al. [14] and Gurrappa [26] on Ti–5.8Al–4Sn–3.5Zr–0.5Mo–0.7Nb–0.35Si–0.06C (Timetal 834); and Jia et al. [27] on Ti–5.8Al–4Sn–3.5Zr–0.4Mo–0.4Nb–1Ta–0.4Si–0.06C (Ti60). In these studies, the thickness of alpha-case layer was either measured directly using optical microscope (OM) or indirectly by estimating the change in microhardness values from the surface to the bulk, which are standardised methods in the aerospace industry for evaluation of oxygen contamination in titanium alloys [28]. In addition to these methods, electron probe microanalyser (EPMA) is an advanced instrumental technique, which could be used as a complementary method to the more conventional methods in the evaluation of alpha-case thickness. EPMA could probe the gradient of oxygen in very thin layers. It is shown in [15,17,25,29] that EPMA is a reliable method, with capabilities of identifying light elements including oxygen, and simultaneously providing the distribution of other alloying elements within the alpha-case layer.

The objective of this study was to investigate the effect of temperature and time on the oxidation kinetics and alpha-case formation in wrought Ti-6242 alloy. The selected heat treatment conditions were of interest from manufacturing and application point of view. In addition, EPMA was used on selected samples to characterise the alpha-case layer, estimate the oxygen concentration profiles and compare the thickness of alpha-case layer with those measured by metallographic studies.

## 2. Experimental methods

The investigated alloy was a commercially available Ti-6242 forging, received in solution and aged condition according to the standard AMS 4976G [30]. Table 1 shows the chemical composition in weight percent. The as-received material had a bimodal microstructure consisting of 65 vol.% transformed β with grain size of about 25 μm and 35 vol.% primary α, with grain size about 18 μm (see Fig. 1(a)). Additionally, the transformed β had a microstructure with α and β lamellas (see Fig. 1(b)).

In total 48 samples with the dimension 10 × 5 × 10 mm were cut using electric discharge machining (EDM) followed by grinding and polishing to remove the recast layer derived from the EDM process. The samples were ultrasonically cleaned in acetone, rinsed with ethanol, and dried in hot air. After cleaning, the samples were isothermally heat-treated at 500, 593 and 700°C up to 500 h in ambient air. The heat treatments were performed using Nabertherm box furnace (N11/R), where two samples were placed on an alumina crucible at a desired temperature for each exposure time. The time intervals that have been tested were 0, 5, 50, 100, 200, 300, 400 and 500 h. After heat treatments the samples were cooled in air. All samples were weighed before and after each heat treatment using analytical microbalance Sartorius Analytic with an accuracy of ±0.0001 g.

The heat-treated samples were cross-sectioned at the mid-height, which was parallel to the base of the crucible. It was followed by cleaning in acetone, rinsing with ethanol and drying in hot air. Further, the samples were grinded and polished with colloidal silica using a semiautomatic BUEHLER Phoenix 4000 to achieve a surface roughness of ~0.05 μm. The polished sample surfaces were chemically treated by using two-step etching procedure that reveals the alpha-case layer. The first step involves swabbing the sample surface with Kroll's reagent (1–3 ml HF, 2–3 ml $HNO_3$ in 94–97 ml distilled water) and the second immersing in Weck's reagent (1–3 g $NH_4HF_2$ in 100 ml distilled water). The thickness of the alpha-case layer was estimated using a Nikon Eclipse OM (model MA200). In total 40 measurements of the alpha-case thickness were conducted on each sample, and the measurements were done along the entire perimeter with approximately 500 μm spacing. In addition, the alpha-case layer was characterised using Jeol JXA-8500F electron probe microanalyser (EPMA), with an accelerating voltage of 10 keV and beam current of 20 nA probe. The EPMA measurements were performed using 100–300 points from the edge to the bulk with a step width of approximately 0.5–2 μm.

**Table 1**
Chemical composition of the Ti-6242 (wt.%) in as received condition.

| Al | Sn | Zr | Mo | N | O | C | H | Fe | Si | Y | Ti |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 6.14 | 2.02 | 4.06 | 1.97 | 0.003 | 0.14 | 0.008 | 0.0049 | 0.02 | 0.08 | <0.0004 | Bal. |

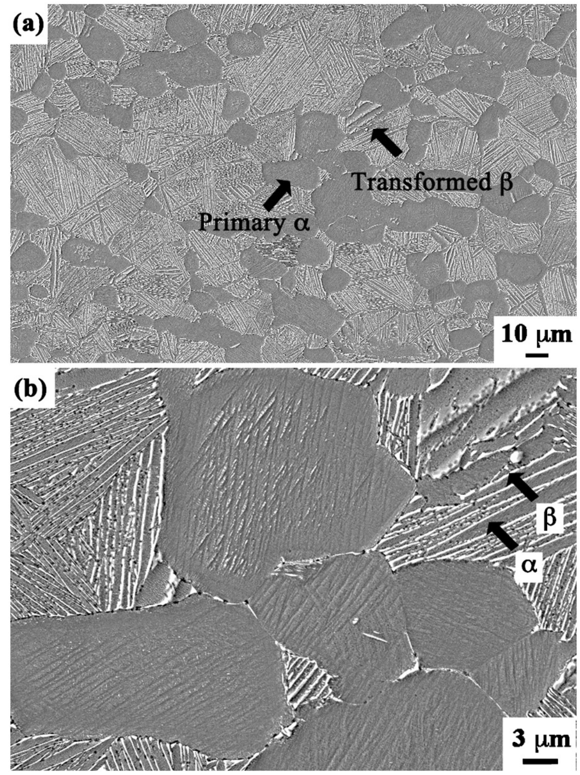

**Fig. 1.** Microstructure of as-received Ti-6242 alloy.

Scanning electron microscope (FEG-SEM, Merlin© from Zeiss) was used to characterise the oxide scale on the samples. Accelerating voltage of 3 kV, probe current of 1 nA and secondary/back-scattered electrons were used. The hardness measurements were performed using MXT-α Vickers microhardness tester from Matsuzawa with a load of 100 g during 15 s. The hardness values reported are the average of two measurements on one sample, which were recorded starting at 10 μm from the outer surface of the sample and continued until constant hardness values were obtained along the thickness.

## 3. Results and discussion

### 3.1. Weight gain analysis

Fig. 2 shows the weight gain per surface area (Δ*W*/*A*) for samples heat-treated at 500, 593 and 700°C in ambient air up to 500 h. The weight gain per surface area ($mg/cm^2$) was estimated by dividing the weight difference of the samples (Δ*W*) (weight measured before and