

OPEN ACCESS

Study of alpha-case depth in Ti-6Al-2Sn-4Zr-2Mo and Ti-6Al-4V

To cite this article: R Gaddam *et al* 2013 *IOP Conf. Ser.: Mater. Sci. Eng.* **48** 012002

View the [article online](#) for updates and enhancements.

You may also like

- [Statistical evaluation and performance analysis of electrical discharge machining \(EDM\) characteristics of hard Ti-6Al-2Sn-4Zr-2Mo alloy](#)
A Perumal, A Azhagurajan, S Baskaran et al.
- [Efficacy of - grade titanium alloy powder \(Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si\) in surface modification and corrosion mitigation in 3.5% NaCl on friction stir processed armour grade 7075-T651 aluminum alloys—insight in defence applications](#)
Omolayo M Ikumapayi and Esther T Akinlabi
- [CO₂ corrosion behavior of high-strength martensitic steel for marine riser exposed to CO₂-saturated salt solution](#)
Dazheng Zhang, Xiuhua Gao, Weijuan Li et al.



DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Study of alpha-case depth in Ti-6Al-2Sn-4Zr-2Mo and Ti-6Al-4V

R Gaddam¹, B Sefer¹, R Pederson^{1,2} and M-L Antti¹

¹Division of Materials Science, Luleå University of Technology, S-97187 Luleå, Sweden

²Research Centre, GKN Aerospace Engine Systems, S-46181 Trollhättan, Sweden

E-mail: raghuveer.gaddam@ltu.se

Abstract. At temperatures exceeding 480°C titanium alloys generally oxidises and forms a hard and brittle layer enriched with oxygen, which is called alpha case. This layer has negative effects on several mechanical properties and lowers the tensile ductility and the fatigue resistance. Therefore any alpha-case formed on titanium alloys during various manufacturing processes, such as heat treatment procedures, must be removed before the final part is mounted in an engine. In addition, long time exposure at elevated temperatures during operation of an engine could possibly also lead to formation of alpha-case on actual parts, therefore knowledge and understanding of the alpha-case formation and its effect on mechanical properties is important. Factors that contribute for growth of alpha-case are: presence of oxygen, exposure time, temperature and pressure. In the present study, isothermal oxidation experiments in air were performed on forged Ti-6Al-2Sn-4Zr-2Mo at 500°C and 593°C up to 500 hours. Similar studies were also performed on Ti-6Al-4V plate at 593°C and 700°C. Alpha-case depth for both alloys was quantified using metallography techniques and compared.

1. Introduction

The titanium alloys, Ti-6Al-2Sn-4Zr-2Mo (Ti-6242) and Ti-6Al-4V (Ti-64) are widely used for components in aeroengines because of their excellent combination of weight and strength [1-3]. The maximum service temperature for these alloys is limited to 450°C for Ti-6242 and 350°C for Ti-64 [2,3]. It is partly because of degradation of mechanical properties above these respective temperatures as at elevated temperatures (above 480°C), titanium alloys oxidises in oxygen containing environments; this results in simultaneous formation of an oxide (TiO₂) scale on the surface and an oxygen-rich layer beneath the scale, commonly referred to as alpha-case (α -case). Alpha-case is a continuous, hard, and brittle layer with higher oxygen content [1,2]. It forms because of higher solid solubility of oxygen in α -titanium (i.e. 14.5 wt.% [4]) and higher affinity of titanium to absorb oxygen, which instantaneously reacts and stabilise the α phase. This brittle alpha-case degrades the mechanical properties such as tensile ductility and fatigue strength [5-10]. Therefore it is necessary to remove any alpha-case formed on parts manufactured from titanium alloys if they are subjected to high loads and/or dynamic loading conditions.

Environmental and economical requirements on future aero engines set higher demands on the efficiency and thereby pressure ratio. The increased pressure leads to higher temperatures, which could make it necessary to replace titanium alloys with nickel based super alloys in the front end of the engine. Unfortunately this increases the weight of the engine and leads to an increase of fuel consumption and is therefore undesirable. However, there is a possibility to increase the maximum working temperature of the currently used Ti-6242 alloy in compressor parts by developing a better understanding on how different mechanical properties and physical phenomena such as oxidation mechanisms are affected in the high temperature regimes. And since some aeroengine parts consists of a combination of both Ti-64 and Ti-6242. Hence both of these alloys are investigated in the current study. The objective of present study was to investigate the effect of heat treatment conditions on the



depth of alpha-case in two common aerospace grade titanium alloys; Ti-6242 and Ti-64. The heat treatment conditions investigated include the temperatures and times in ambient air that are of interest for heat treatment during manufacturing and for application in an aeroengine for both of these alloys.

2. Materials and Methods

The materials investigated are Ti-6242 and Ti-64 with the chemical compositions shown in table 1. Ti-6242 is a near- α alloy that has been solution and precipitation heat treated; and was obtained in forged condition according to AMS 4976G [11]. It consists of a bi-modal microstructure with primary α and transformed β (see figure 1(a)). Ti-64 is a $\alpha+\beta$ titanium alloy that has been obtained in plate form according to AMS 4911L [12], which consists of a microstructure with equiaxed primary α and elongated α in transformed β (see figure 1(b)).

Table 1. Chemical composition (wt.%) of the materials investigated.

Material	Al	Sn	Zr	Mo	N	O	C	H	Fe	Si	V	Ti
Ti-6242	6.5	2.2	4.4	2.2	0.05	0.15	0.05	0.05	0.1	0.1	-	Bal.
Ti-64	6.75	-	-	-	0.05	0.20	0.08	0.015	0.3	-	4.5	Bal.

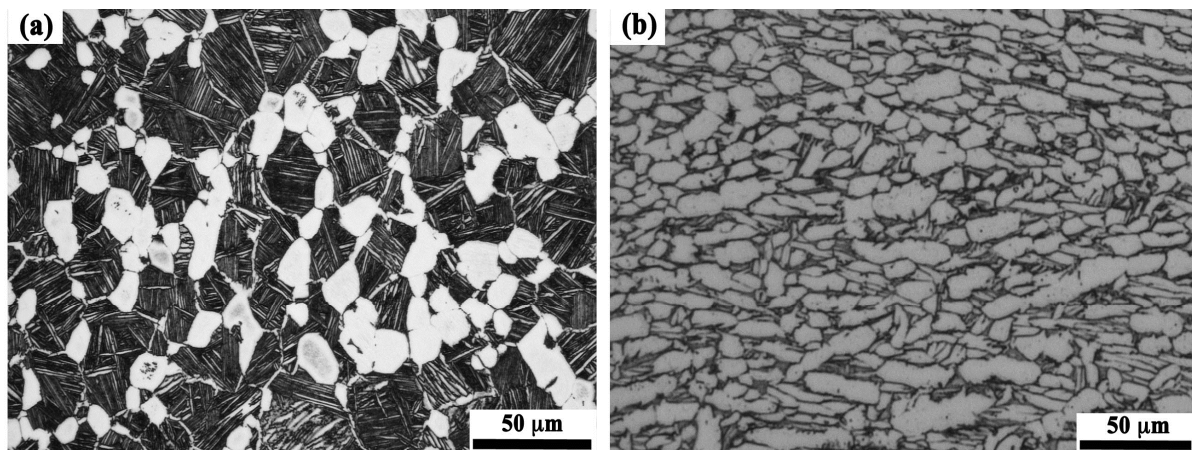


Figure 1. Optical micrographs showing the microstructure of as received materials, (a) forged Ti-6242 and (b) Ti-64 plate. In micrographs light or grey areas is α phase and dark areas is β .

2.1. Heat treatment

The samples for heat treatments were cut using electric discharged machining (EDM) from the as received material in dimensions of 10 x 5 x 10 mm. Totally 64 samples were cut out, where two samples were used for each exposure time and temperature. All the sample surfaces were metallographically polished to remove the recast layer. Thereafter, the polished samples were ultrasonically cleaned in technical acetone for approximately 15 min and rinsed with ethanol. The cleaned samples were heat treated in ambient air using a Nabertherm box furnace (N11/R) and a Nabertherm tube furnace (RHTC 80-450/15) at atmospheric pressure. The temperature inside the furnace is calibrated using a reference sample with a thermocouple welded to it and positioned at the locations inside the furnace where the samples are placed. The temperature inside the furnace was about $\pm 5^\circ\text{C}$ of the desired temperature. The samples were placed onto an Al_2O_3 plate or crucible and then introduced into the furnaces at the desired temperature and isothermally held for selected exposure times as shown in table 2. All samples were weighed using a microbalance with an accuracy of ± 0.0001 g before and after each heat treatment. In addition, heat treatments were also performed on Ti-6242 and Ti-64 samples, with a cross section of 17 x 2.5 x 10 mm, in dry air (i.e. technical air)

using a simultaneous thermal analysis instrument (STA 449C from Netschz Gmbh). The samples were isothermally held at 593°C for 200 hours.

Table 2. Heat treatment conditions.

Material	Temperature (°C)	Exposure times (hour)
Ti-6242 forged	500	5, 10, 50, 100, 200, 300, 400 and 500
	593	
Ti-64 plate	593	
	700	

2.2. Alpha-case evaluation

Heat treated samples were cut into half, parallel to the face that is placed on the crucible (10 x 5 mm²), thereafter ultrasonically cleaned in technical acetone for 15 min and rinsed with ethanol. Cleaned samples were mounted in bakelite using BUEHLER Simplimet model 1000 mounting machine and then metallographically prepared, which involves grinding and polishing the surface up to 0.05 µm with colloidal silica using a semiautomatic BUEHLER Phoenix 4000 polishing machine. The polished samples were etched in two steps to observe the alpha-case: first, swabbing the sample surface with Kroll's reagent (a mixture of 1-3 ml HF, 2-3 ml HNO₃ and distilled water) and second, immersing in Weck's reagent (1-3 g NH₄HF₂ and distilled water) for approximately 10 sec. Alpha-case layer was observed using a Nikon Eclipse optical microscope (model MA200) and the depth of alpha-case layer was quantitatively measured using NIS elements software. Totally 60 individual measurements of alpha-case depth on each sample were made along the entire perimeter at approximately 500 µm spacing on two samples of Ti-6242 and Ti-64 at each temperature and time combination, and the average values of alpha-case depth is then reported. The hardness measurements related to the alpha-case at the surface was obtained by applying a load of 100 g using MXT- α microhardness tester from Matsuzawa with a Vickers indenter (indent size is approximately 20 – 25 µm).

3. Results and Discussion

3.1. Weight gain

Figure 2(a) presents the amount of weight gain (ΔW) per surface area (A) for Ti-6242 and Ti-64 when isothermally held at 593°C for 200 hours in dry air. It is calculated by dividing the weight gain values of the samples, measured using STA 449C, with their total surface areas. The unit is (mg/cm²). From figure 2(a) it can be seen that the ($\Delta W/A$) increased with time and approximately followed a parabolic relationship for both the alloys. Similar behaviour for both the alloys was observed on samples that were isothermally held in a laboratory furnace at 593°C for up to 500 hours in ambient air, where the weight gain is calculated by weighing before and after the heat treatment. It was noted that in Ti-6242 samples held at 500°C for up to 500 hours the weight gain followed approximately a parabolic relationship, while deviating from parabolic below 100 hours. In contrast, Ti-64 samples held at 700°C showed deviation from parabolic relationship beyond 200 hours. The observation of weight gain in both the alloys is obtained by fitting and performing regression analysis of the weight gain data using the following equation [13]:

$$(\Delta W/A) = Kt^{1/n} \quad (1)$$

where K is the rate constant and n is the reaction index. At a constant temperature, the weight gain is assumed to be linear if $n=1$, parabolic if $n=2$. The weight gain in the Ti-6242 alloy at the tested temperatures is consistent with other investigators [8, 14]. On the other hand, the Ti-64 alloy that was

held at 700°C for up to 500 hours, indicated a transition from parabolic to linear weight gain at about 200 hours. This confirms with the results found by others [15-17]. In figure 2(a) it can be seen that weight gain is much higher in Ti-64 compared to Ti-6242 at the constant temperature and time. This could be due to the thicker oxide layer ($\approx 5 \mu\text{m}$) in Ti-64 than in Ti-6242 ($< 1 \mu\text{m}$), see figure 2(b) and figure 2(c).

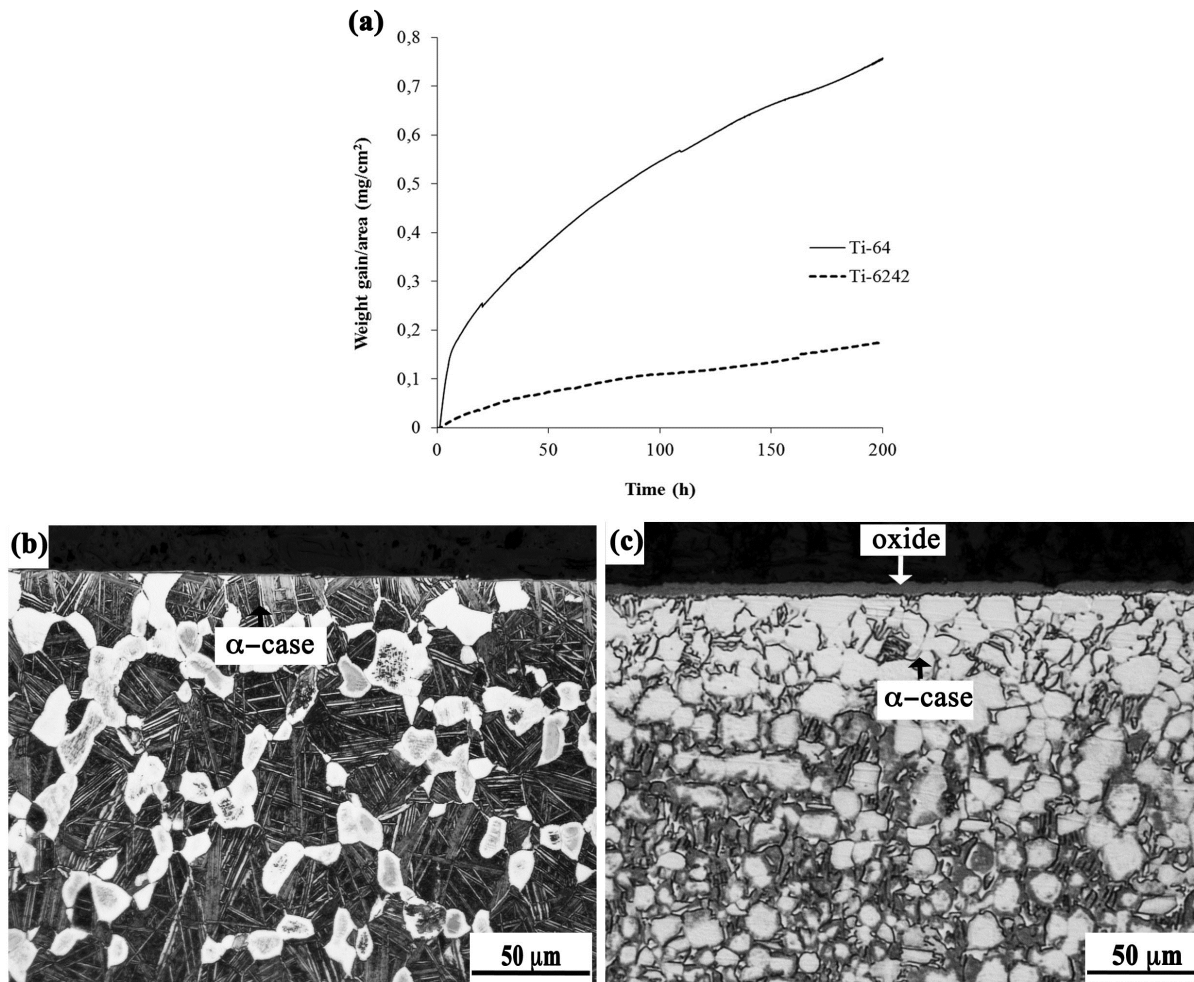


Figure. 2 (a) Plot showing the weight gain per unit area (mg/cm^2) in Ti-6242 and Ti-64 held at 593°C for 200 hours in dry air, (b,c) optical micrographs of Ti-6242 and Ti-64, showing the oxide layer and alpha case.

3.2. Alpha-case evaluation

Figure 3 shows the representative optical micrographs of alpha-case (white layer) in Ti-6242 and Ti-64 after long exposure time (500 hours) at 593°C. It can be seen that alpha-case is formed beneath the surface simultaneously with the oxide (see Figure 3(b)). Figure 4 shows the plot of alpha-case depth versus exposure time for Ti-6242 and Ti-64 at the tested temperatures. Here, alpha-case is measured quantitatively using the optical micrographs. From figure 4, it can be seen that depth of alpha-case is increased with temperature and time in both the alloys and mainly follows a parabolic relationship at the selected heat treatment conditions. The maximum depth of alpha-case formed in Ti-6242 is approximately 30 μm when exposed at 593°C for 500 hours, and 10 μm at 500°C after 500 hours (see figure 4). The depth of alpha-case in Ti-64 when exposed to 593°C for 500 hours was about 30 μm . In addition, it is observed that a thick alpha-case layer of approximately 200 μm is formed in Ti-64 when exposed at 700°C for 500 hours.

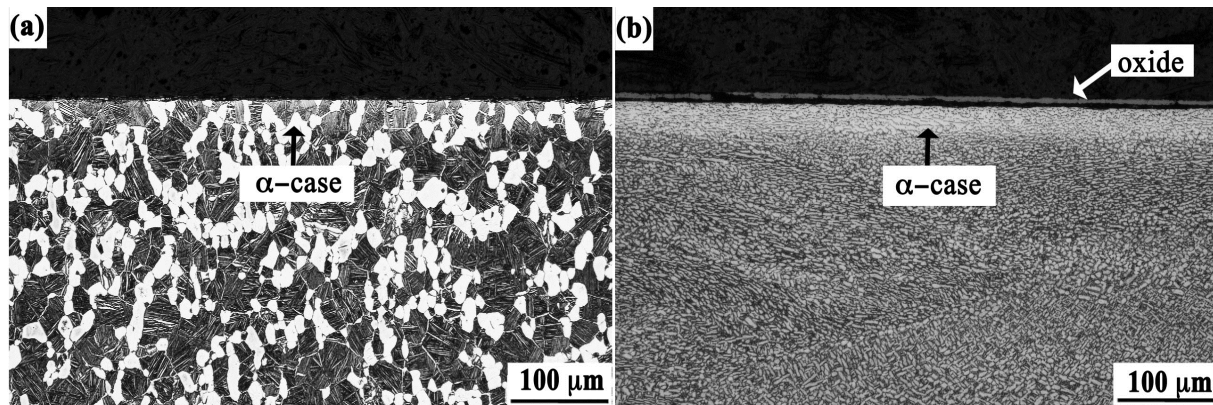


Figure 3. Optical micrographs showing alpha-case (white layer) in (a) Ti-6242 and (b) Ti-64 heated at 593°C up to 500 hours.

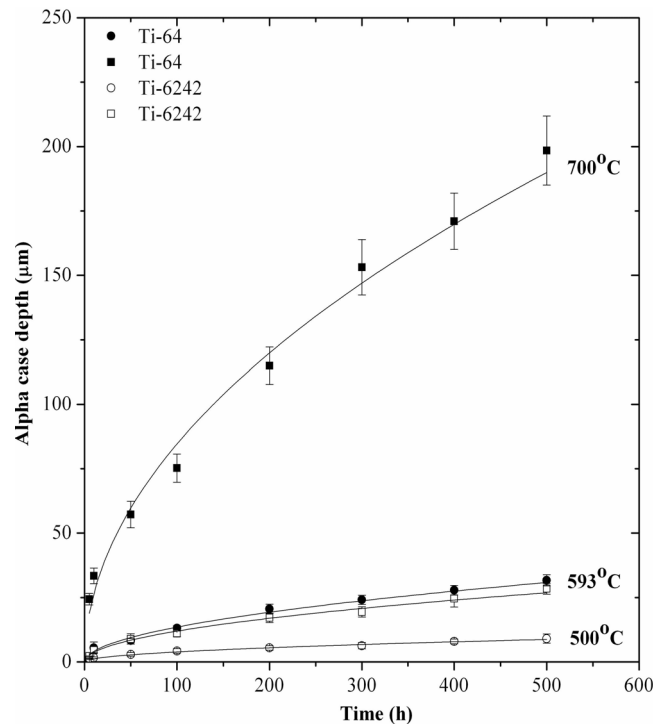


Figure 4. Variation of alpha-case depth in Ti-6242 and Ti-64 as a function of time at different temperatures. Empty data points correspond to Ti-6242 and filled data points are for Ti-64.

From figure 4, it can be seen that the growth of alpha-case in both Ti-6242 and Ti-64 alloys exposed at 593°C for 500 hours follows a parabolic relationship, which can be related to the bulk diffusion. The approximate solution that describe Fick's second law of diffusion is given by $x = \sqrt{Dt}$, where x is alpha-case depth, D is the diffusion coefficient (m^2/s), and t is exposure time. Figure 5 shows a log-log plot of alpha-case depth versus exposure time. It shows a linear relationship with R-values 0.995. The exponents from the linear fits are nearly equal to 0.5. Hence, the values for D are calculated from the slope obtained from the best-fit lines. The D calculated here is found to be in the order of $10^{-16} \text{ m}^2/\text{s}$ for Ti-6242 and Ti-64. From the present study, it can be seen that there is no significant change in the depth of alpha-case and the diffusion of oxygen in Ti-6242 and Ti-64 when

exposed at 593°C up to 500 hours. This shows that there might be no substantial influence of the difference in chemical composition and the microstructure between the two alloys on alpha-case depth. Similar observations were also noted for both the alloys when exposed at 704°C for 24 hours in air [18].

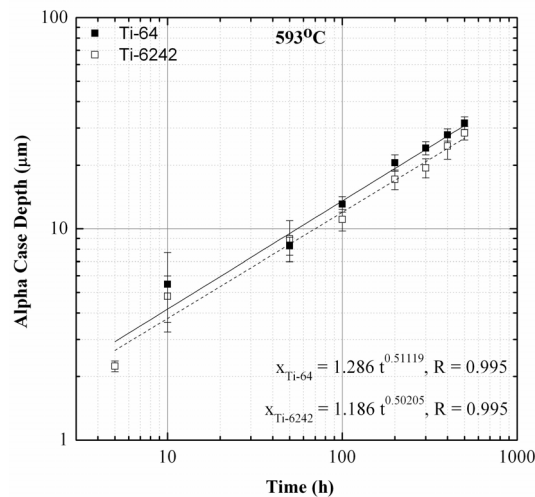


Figure 5. Plot showing the alpha-case depth vs exposure time for Ti-6242 (empty boxes) and Ti-64 (filled boxes) at 593°C up to 500 hours (log- log scale).

Alpha-case is commonly referred to a region enriched with oxygen. It is known that oxygen stabilizes the α phase and increases the strength of titanium by solid solution strengthening [2-3]. Therefore the alpha-case layer is harder than the bulk. Table 3 shows the results obtained from the microhardness measurements on Ti-6242 that are isothermally treated at 593°C; Ti-64 at 593 and 700°C for up to 500 hours. It was found that the hardness values in the alpha-case are higher in magnitude than in the bulk. Figure 6 shows the variation of hardness on the sample held at 700°C for 500 hours from the surface to the bulk. It can be seen that hardness values are gradually decreasing from the surface into the material to approximately 250 μm . From optical measurements on the samples held at 700°C for 500 hours, the depth of alpha-case is approximately measured to be 200 μm (see figure 4 and figure 6). The hardness values decrease with decreasing oxygen content. The difference in depth of alpha-case measured in optical microscope (OM) and indicated by the plateau in the hardness measurements suggests that there are uncertainties in identifying the border between the alpha-case layer and the bulk material in optical microscope after etching.

Table 3. Average hardness values (HV) for Ti-6242 and Ti-64 exposed at different temperatures.

	Ti-6242	Ti-64	
	593°C	593°C	700°C
Alpha case	511 $\pm$ 40	412 $\pm$ 37	630 $\pm$ 34
Bulk	362 $\pm$ 23	332 $\pm$ 10	300 $\pm$ 2.88

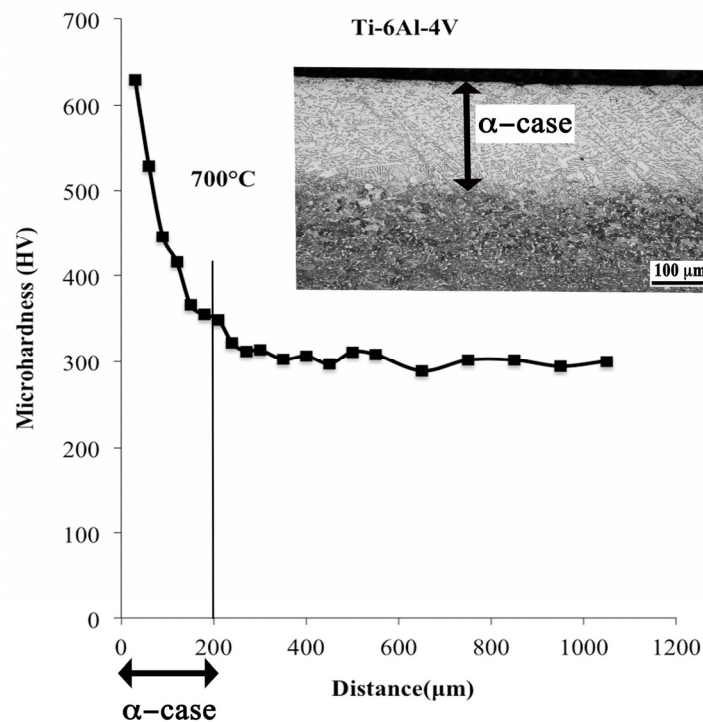


Figure 6. Variation of hardness from the surface to the bulk of the Ti-64 sample exposed to 700°C for 500 hours. An optical micrograph of the corresponding sample showing the alpha-case is also included (the white layer in the micrograph).

4. Conclusions

In the present work, isothermal heat treatments were performed on the Ti-6242 and Ti-64 titanium alloys in ambient air and at atmospheric pressure in order to study the depth of alpha-case. The conclusions are as follows:

1. Alpha-case depth in both alloys increases with temperature and time. Alpha-case growth mainly follows a parabolic relationship at 500 and 593°C in Ti-6242, and at 593°C and 700°C in Ti-64.
2. At 593°C after 500 hours Ti-6242 and Ti-64 have similar values of alpha-case depth ($\approx 30 \mu\text{m}$).
3. The alpha-case depth in Ti-6242 is $10 \mu\text{m}$ after 500 hours at 500°C.
4. The alpha-case depth in Ti-64 is $200 \mu\text{m}$ after 500 hours at 700°C.
5. The microhardness is higher in the alpha-case and decreases into the bulk.
6. A thicker oxide layer forms on Ti-64 then on Ti-6242 when isothermally held at 593°C for 200 hours. This results in a higher weight gain/area for the Ti-64 alloy. The weight gain followed a parabolic relationship.

5. References

- [1] Lutjering G and Williams J C 2007 *Titanium* 2nd ed (Berlin, Springer-Verlag)
- [2] Leyens C and Peters M 2003 *Titanium and titanium alloys* (Wiley VCH Verlag GmbH, Weinheim) 187
- [3] Boyer R R 1996 *Mater. Sci. Eng. A* **213(1-2)** 103
- [4] Murray J L and Wriedt H A 1990 Binary alloy phase diagrams Massalski T B ed. (ASM International, Materials Park, Ohio) 2924
- [5] Shamblen C E and Redden T K 1968 *Proc. of The Science, Technology, and Application of Titanium*, Jaffee R I and Promisel N E eds, (Pergamon Press, Oxford, United Kingdom) 199
- [6] Ruppen J A and McEvily A J 1979 *Fatigue Engg. Mater. Struct.* **2** 63
- [7] Bendersky L and Rosen A 1980 *Engg. Fract. Mech.* **13** 111
- [8] Shenoy R N, Unnam J and Clark R K 1986 *Oxid. Met.* **26** 105
- [9] Fukai H, Iizumi H, Minakawa K-N and Ouchi C 2005 *ISIJ Inter.* **45(1)** 133
- [10] Chan K S, Koike M, Johnson B W and Okabe T 2008 *Metall. Mater. Trans.* **39A** 171
- [11] AMS 4976 G 2008 Titanium alloy, forgings 6.0Al-2.0Sn-4.0Zr-2.0Mo solution and precipitation heat treated (SAE-AMS/MAM)
- [12] AMS 4911 L 2008 Titanium alloy, sheet, strip, and plate 6Al-4V annealed (SAE-AMS/MAM)
- [13] Kofstad P 1988 *High temperature corrosion* (Elsevier Applied Science, Essex)
- [14] McReynolds K S and Tamirisakandala S 2011 *Metall. Mater. Trans. A* **42A** 1732
- [15] Guleryuz H and Cimenoglu H 2009 *J. Alloys Compd.* **472** 241
- [16] Frangini S, Mignone A and De Riccardis F 1994 *J. Mater. Sci.* **29** 714
- [17] Du H L, Datta P K, Lewis D B and Burnell Gray J S 1994 *Corros. Sci.* **36(4)** 631
- [18] Unnam J, Shenoy R N and Clark R K 1984 Effect of alloy chemistry and exposure conditions on the oxidation of titanium Report No. NASA TM-86295 (NASA Technical Memorandum)

Acknowledgments

The authors kindly acknowledge Graduate School of Space Technology and National Aviation Engineering Research Programme (NFFP) for funding the present work through research collaboration with GKN Aerospace Engine Systems, Sweden. We would also like to acknowledge Francois Mattera for assisting in the experiments.