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Thermal Oxidation Effects on Sub-Surface Microstructure and Mechanical Properties of Cast and Forged α/β Titanium Alloys

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Abstract

Ti-6Al-7Nb (Ti67) alloy has recently been developed to replace the commercial Ti6Al4V (Ti64) biometallic alloy because of the reported toxicity of the elemental vanadium. Thermal oxidation is an important processing method applied to improve the hardness and wear properties of such titanium alloys. Since the developed alloy, Ti67, contains Nb as beta phase stabilizing element instead of V in the case of Ti64, it is expected to behave differently upon processing by thermal oxidation. In addition, this behavior may be influenced by the processing method. Therefore, it is of interest to investigate the influence of thermal oxidation on the surface properties of Ti67 alloy in its forged and cast conditions and compare the results to the commonly used Ti64 alloy. It was observed that the thickness of alpha case formed in Ti64 after oxidation at (1173 K-1373 K) (900-1100 °C) was greater than in Ti67. In addition, the equiaxed microstructure of the forged samples showed a thicker alpha case than the widmanstätten microstructure of the cast samples for the two alloys. Both forged and cast Ti64 showed significant improvement in dry sliding wear resistance after thermal oxidation at (1173 K-1373 K) (900 °C and 1100 °C), while alloy Ti67 showed less improvement despite the improved surface hardness.

Keywords: Titanium alloys, Bio-implants, Corrosion, Phase stability, Microstructural analysis.

1. Introduction

Titanium has a desirable combination of properties in terms of high strength, good corrosion resistance, and excellent biocompatibility. Titanium alloys are therefore considered the horse of metallic biomaterials as described by Boyer [1] and Hin [2]. Ti6Al4V is α/β alloy and was the first titanium alloy registered as a metallic biomaterial in ASTM standard F 136-82 [3]. However, Scales and Black [4] reported this alloy to be toxic due to the release of vanadium ions and reaction with human tissue. The new alloy, Ti6Al7Nb, was developed to overcome this drawback and standardized as a biomaterial in the ASTM standard F 129-11 [5]. This alloy has been developed for use in the dental field, for example, dental implants, denture bases, crowns, clasps, etc., which are produced mainly by either forging or investment casting.

In medical devices, surface properties that are different from bulk properties are required. For example, blood compatibility in blood-containing devices, good bone formability in hard tissue replacement parts, good wear and corrosion of the joints and dental implants are also required. The proper surface modification is the one that improves specific surface properties without changing the bulk attributes of titanium alloys. Izman et al. [6] described some of the surface modification processes like thermal oxidation, chemical treatments, electrochemical treatments, sol-gel coatings, chemical vapor deposition,

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physical vapor deposition, ion implantation, and plasma spray.

During the service of titanium implants in the human body, they are subjected to rubbing contact and sliding of other surfaces that cause stresses at the contact areas, and may cause severe damage to their surface. Wear may occur on the implant surface very rapidly, resulting in severe damage. According to Molinari et al [7], the poor tribological properties due to crystal structure and electron configuration characteristics of titanium alloys limited their widespread use in many industrial fields. The wear resistance and surface hardness of titanium alloys can be improved by surface treatment. Guleryuz and Cimenoglu [8] showed that with the reactivity of titanium with nitrogen and oxygen, it is possible to improve the surface characteristics of titanium alloys by means of diffusion-based treatments as anodization, nitriding and oxidation treatments.

Thermal oxidation technique (TO) is a simple and cost-effective way to change the nature of the surface and to improve the wear resistance and the surface hardness of Ti6Al4V alloy. Titanium has a higher chemical affinity to oxygen than to hydrogen. at room temperature, titanium reacts with oxygen, forming TiO_2 when exposed to air. This oxide layer has a tetragonal crystal structure and is often called scale; it is n-type anion defect as studied by Kim et al [9]. This allows oxygen to diffuse through it and provide protection for the metal surface from further oxidation. also, titanium has a high solid solubility of oxygen about (14.5 wt.%) as indicated in Ti-O phase diagram shown in Fig. 1 [1].

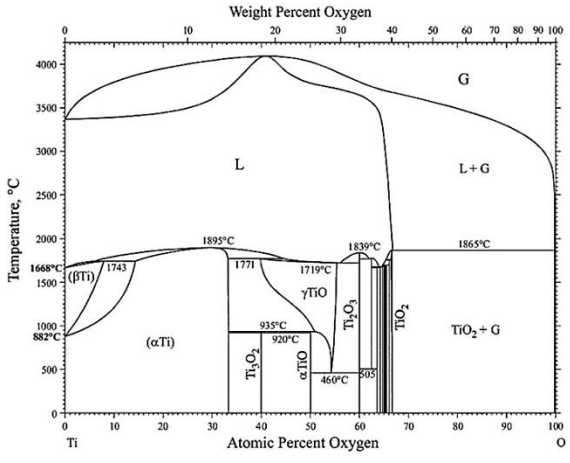

Fig. 1 Ti-O phase diagram [1].

Therefore, the oxidation process of titanium has two principal effects; formation of oxide scale and dissolution of oxygen in the subsurface zone of the base metal. This oxygen diffusion layer has high O concentration, and thus the wear resistance of titanium alloys increases.

Since thermal oxidation alters the subsurface microstructure of titanium alloys as described, it is important to deeply understand the effect of this surface treatment on any developed biometallic alloy. In the current study, the influence of thermal oxidation on the surface properties of Ti67 alloy in its forged and cast conditions was investigated. The results were then compared to those of the commercial Ti6Al4V alloy, considering the same processing and testing for the two alloys. , prosthetic knee and hip joints, orthopedic and dental implants, and screws for fixing fractures [7, 8].

2. Experimental Procedures

Forged and cast samples of Ti-6Al-4V (Ti64) and Ti-6Al-7Nb (Ti67) alloys were used. The forged samples were processed as described in [10] and were received as 10 mm diameter bars. The cast samples were prepared using the centrifugal casting machine illustrated in Fig. 2. At first, wax patterns shaped as bars were prepared and used to make the mold cavity. The mold was prepared using a silicon former and investment powder specially made for casting titanium and its alloys. The slurry was mixed under vacuum to decrease the titanium chemical reactivity. In addition, the melting crucibles were made of zirconia-bonded ceramic material to avoid reaction with titanium. The standard steps for mixing, de-waxing, and sintering were followed as in Sopcak [11]. The investment mold was preheated to 1123 K (850 °C) before casting and positioned as shown in Fig. 2. The titanium alloy pieces were placed in the melting crucible and the melting chamber washed several times by argon. When the melt reaches the desired temperature 1943 K (1670 °C), the rotation starts and the molten metal fill in the mold cavity under centrifugal force. The samples were then taken out of the mold, cleaned, cut and polished for isothermal oxidation.

Samples of forged and cast Ti-6Al-4V and Ti-6Al-7Nb alloys were thermally oxidized (TO) in air circulating furnace. Taking into consideration the phase diagram shown in [1], the thermal oxidation treatments were conducted for 5 h at (973 K, 1173 K and 1373 K) (700 °C, 900 °C and 1100 °C), under the normal atmospheric pressure. The samples were then cooled in air until reaching the room temperature. The cross-sections of the TO samples were gently grinded with SiC abrasive paper up to 1200 mesh, then polished using 1 μ alumina, and etched with 2% HF solution.

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Microstructure characterization was done by optical and field emission (FEM) microscopy. To identify the type of surface oxides, the poorly adhering oxide scales were removed, and the surface was characterized using thin film X-ray diffraction (XRD), with Cu Kα radiation source. A Vickers microhardness tester (HV0.5) was used to determine the hardness of the newly developed alpha case. Wear resistance of different samples, after removal of the oxide case, was evaluated using a pin-on-disc wear test. The samples were fixed against a rotating stainless-steel ring (63 HRC), under a constant load of 180 N, at a speed of 1.0 m/s, for a 1800 m sliding distance. Dry sliding was used. The wear resistance was measured in terms of the weight loss of the tested materials.

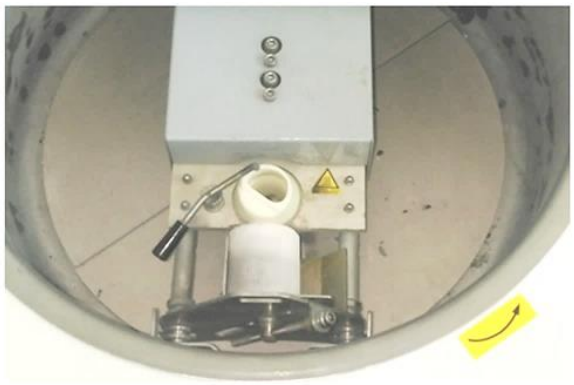

Fig. 2 Casting setup using a vacuum centrifugal casting machine.

3. Results and Discussions

3.1 X-ray pattern for the oxide layer

The XRD- thin film patterns of the untreated and the thermally oxidized Ti64 and Ti67 samples are shown in Fig. 3 [12]. The untreated samples of the two alloys have an alpha phase with a small amount of beta. After thermal oxidation at 973 K (700 °C), the oxide layer was developed on the surface; the XRD pattern confirmed that this oxide layer consists mainly of rutile TiO_2. Upon increasing the oxidation temperature to (1100 K and 1373 K) (900 and 1100 °C), the peaks of TiO_2 nearly disappeared and the oxygen dissolved inward the titanium surface stabilizing the α phase as confirmed by the broadened alpha peaks at the low theta side. These results are in accordance with the results of Dong and Li (2000) on the thermal oxidation of Ti64 alloy. Moreover, a small amount of NbO was observed in Ti67 alloy at 1373 K (1100 °C).

Here, it is worth noting that Al_2O_3 also formed during the oxidation; however, it was like a brittle layer that was not adherent to the surface and fell just after the samples were taken from the furnace. It was reported by Perkins et al [13] that the oxide scale in Ti6Al4V consists of a layer of TiO_2 and Al_2O_3. The number of TiO_2 and Al_2O_3 increases with increasing temperature and exposure time, TiO_2 is formed at metal surface separating the alloy from its environment making the oxygen partial pressure at the gas/oxide interface relatively high which allows the formation of Al_2O_3 layer on the top of the formed TiO_2 layer, then oxygen diffuses inward to oxide/metal interface.

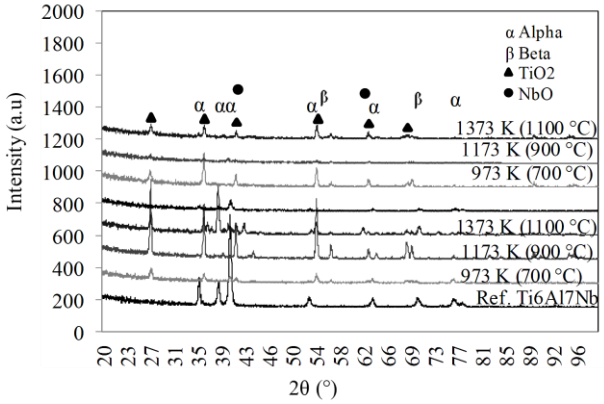

Fig. 3 XRD patterns of the as-received and oxidized Ti64 and Ti67 samples, License from [12].

3.2 Microstructure investigation

The microstructures of as-forged and as-cast Ti64 and Ti67 samples before oxidation are shown in Fig. 4. As can be seen, the microstructure of the forged samples, Fig. 4 (a, b), consists of fine equiaxed grains of α and some β phase, while the cast microstructure, Fig. 4 (c, d), shows typical widmanstätten colonies of α with prior β grains. After oxidation at high temperature, some changes in the subsurface microstructure were expected. Titanium was reported to react with oxygen to form TiO_2, and as the temperature increases above 823 K (550°C), the transport of oxygen through the titanium oxide scale becomes high enough to allow excess oxygen to dissolve in the alloy and form alpha case.

It was also reported that the solubility of oxygen in α-titanium is about 30 at. %, whereas in ß–titanium it reaches a maximum of 8 at. % at 1973 K (1700 °C). In addition to the stabilizing effect of the oxygen for the HCP structure of α-phase [14].

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The development of the subsurface layer after thermal oxidation at (973 K, 1173 K, and 1373 K) (700 °C, 900 °C, and 1100 °C) was observed in the compositional images of Figs. 5 and 6 for the forged and cast alloys. As can be seen, a continuous white layer was developed along the surface of the two alloys beneath the oxidized layer (OL), which is known as alpha case or oxygen diffusion layer (ODL). Increasing the oxidation temperature increases the thickness of α in the two alloys. The increase in the thickness of this oxygen diffusion layer was more pronounced in the optical micrographs presented in Figs. 7 & 8 for forged and cast samples, respectively. Inside this α layer, there was less intergranular beta phase observed at (973 K and 1100 K) (700 and 900 ºC), Fig. 6. With increasing oxidation temperature up to 1373 K (1100 ºC), this diffusion layer in Ti64, Fig.7 (top), has almost no β while some inter-granular beta remained inside α case in Ti67, Fig. 7 (bottom). Since the current alloys were oxidized at 1373 K (1100 ºC) for 5 h in the range of the beta phase, a significant change in microstructure was observed. It was remarkable that the microstructure of the base metal in the forged samples changed from the equiaxed to the widmanstätten microstructure, Fig. 7. Moreover, the case in the Ti64 was thicker and more homogeneous than in Ti67.

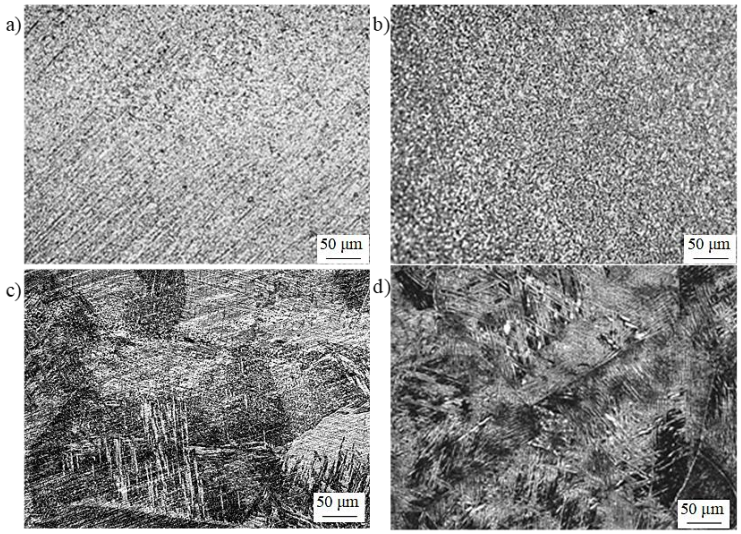

Fig. 4 OM of the as-forged (a,b) and as-cast (c,d); Ti64 and Ti67 alloy samples, respectively, from the left side. License from [12].

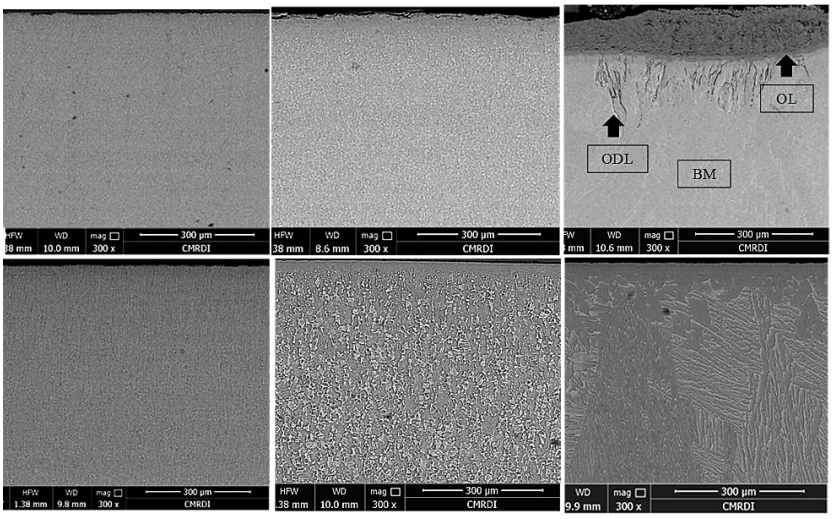

Fig. 5 FEM compositional image of the oxidized –forged samples, Ti64 (top) and Ti67 (bottom) at 973 K (700 ºC), 1173 K (900 ºC) and 1373 K (1100 ºC) respectively from the left side. The oxide layer, oxygen diffusion layer, and base metal were denoted as OL, ODL, and BM, respectively.

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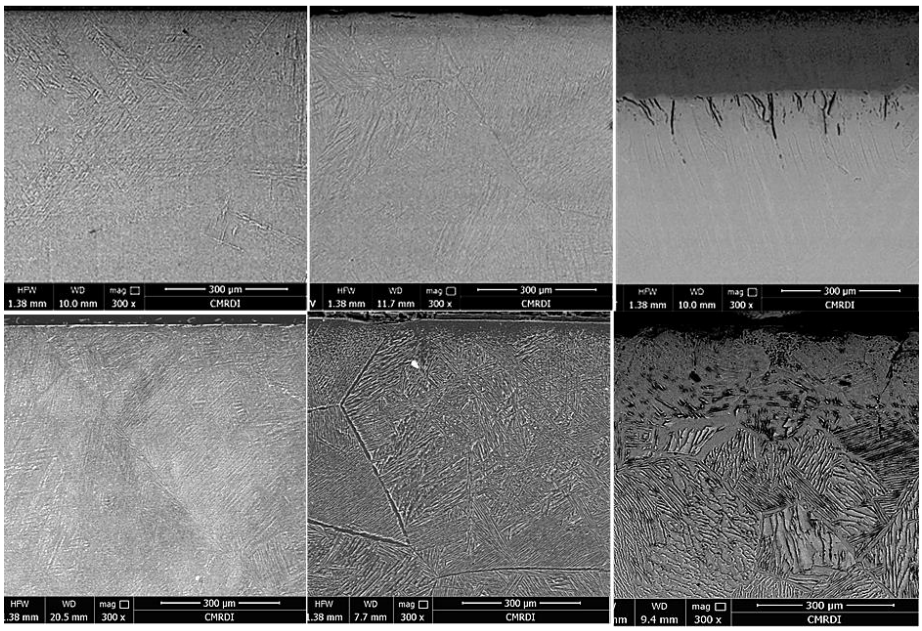

Fig. 6 FEM compositional image of the oxidized –cast samples Ti64 (top) and Ti67 (bottom) at 973 K (700 °C), 1173 K (900 °C) and 1373 K (1100 °C) respectively from the left side. The oxide layer, oxygen diffusion layer, and base metal were denoted as OL, ODL, and BM, respectively

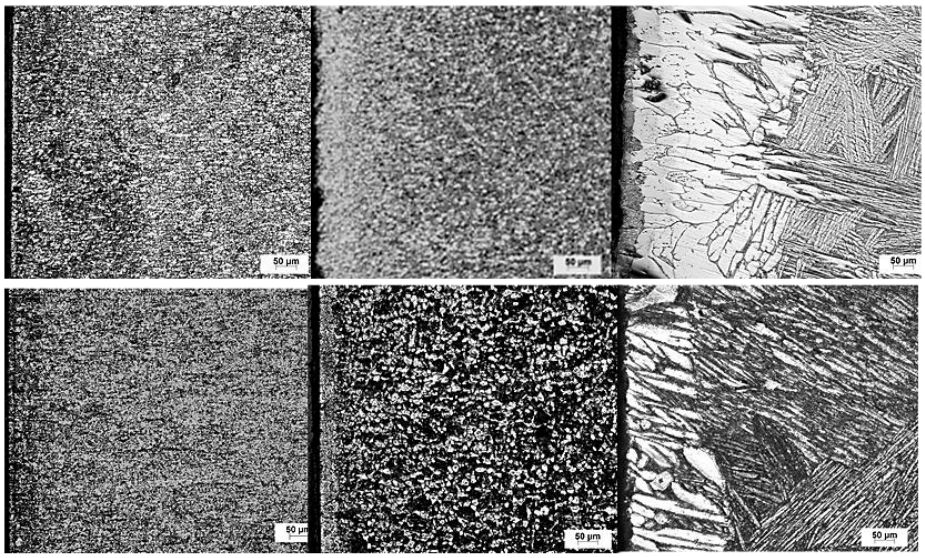

Fig. 7 Optical micrographs of the cross section of the forged samples Ti64 (top) and Ti67 (bottom), after oxidation at different temperatures, License from [12].

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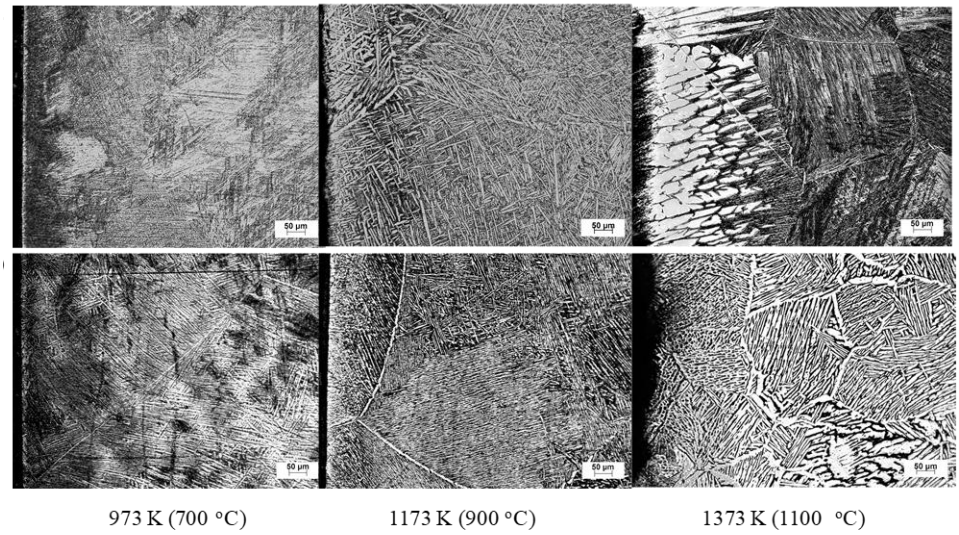

Fig. 8 Optical micrographs of the cross section of the cast samples Ti64 (top) and Ti67 (bottom) after oxidation at different temperatures. License from [12].

Figure 9 shows the maximum thickness of the alpha case obtained with oxidation temperature of the forged and cast Ti64 and Ti67 alloys. The difference in the maximum thickness of the α case between Ti64 and Ti67 is due to the rate of oxygen diffusion in the two alloys, which differs mainly in the β stabilizing element.

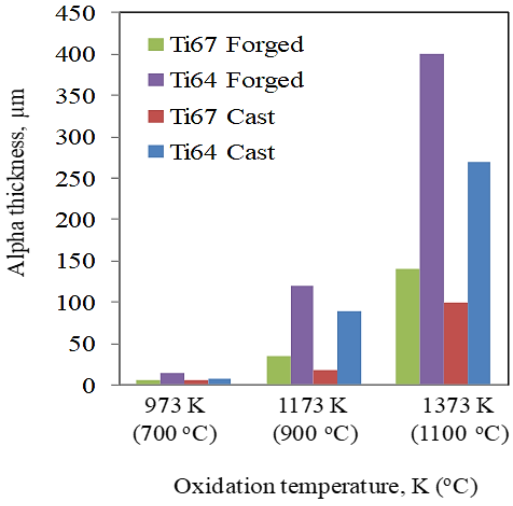

Fig. 9 Maximum thickness of alpha case in the oxidized samples from the micrographs of Figs. 7 &8

According to Jiang et al [15], the addition of Nb improves the oxidation resistance of the titanium alloys. Niobium can reduce the solubility and diffusivity of oxygen in the oxide scale and the base metal as well. Since titanium forms rutile (TiO_2) when it reacts with oxygen, forming a scale, this rutile scale has anion defects (oxygen vacancies) through which oxygen ions diffuse and react with titanium metal. The mass transport in TiO_2 can be changed by doping, when $Ti4^+$ ions are replaced by higher valency ions like $Nb^{5+,}$ according to eq.1adapted from Hui-ren et al (2008). In this case, oxygen vacancy concentrations are reduced in rutile, while ions with lower valencies increase oxygen vacancy concentration by occupying the titanium sites in the oxide lattice.

In order to confirm this phenomenon in the oxidized microstructure of the two alloys, EDX point analysis was performed on the diffusion layer of two forged Ti64and Ti67 samples after oxidation at 1373 K (1100 ºC), Fig. 10.

$$Nb_2O_5 + V^{**}O \xrightarrow{\text{Rutile}} 2Nb^{*}Ti + 2TiO_2 \qquad \text{eq.1}$$

Comparing the forged samples shown in Fig. 7 to the cast specimens presented in Fig. 8, the case developed in forged Ti64 and Ti67 alloys was thicker than in their cast condition. The alpha case thickness in forged Ti64 at (973 K, 1173 K, and 1373 K) (700 °C, 900 °C, and 1100 °C) was 15 µm, 120 µm and 400 µm, while in cast Ti64 it was decreased to 8 µm, 90 µm and 270 µm, respectively. A similar observation was found for Ti 64 in the forged and cast states. The difference in the thickness of the oxygen diffusion zone (α case) between the forged and cast conditions can be owed to the differences in their microstructure before oxidation.

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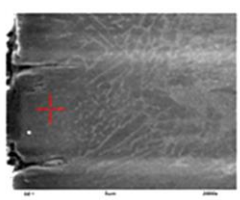
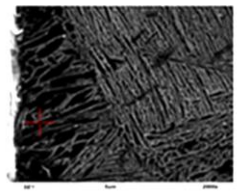
Sugahara et al [16] studied the effect of widmanstätten and equiaxed microstructures of Ti-6Al-4V on the oxidation rate and creep behavior, they observed that the widmanstätten structure is more resistant to oxidation than the equiaxed structure. This is because of the globular structure of the forged samples, which has more dislocation density and more vacancies, which facilitate the inward diffusion of oxygen.



Element	Wt.%	At %
O	13.05	29.91
Al	6.09	8.28
Ti	78.95	60.44
V	1.91	1.37



Element	Wt. %	At %
O	7.03	18.04
Al	6.12	9.31
Ti	82.40	70.67
Nb	4.46	1.97

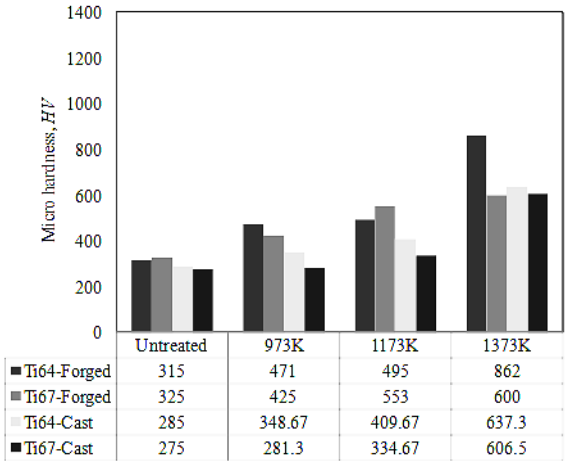
Fig. 10 EDX point analysis in the oxygen diffusion layer of the forged Ti64 (top) and Ti67 (bottom) samples oxidized at 1373 K (1100 ºC) [License from 12].

3.3 Mechanical properties evaluation

Oxygen is α-phase stabilizer in titanium alloys, and it increases the hardness of titanium alloys by solid solution strengthening. Since the oxygen diffusion layer formed as a result of surface oxidation, it is expected to affect the surface properties, microhardness, and wear behavior of the oxidized samples as explained by Liu and Welsch [14].

Figure 11 shows the microhardness measurements on the oxygen diffusion layer (α case) as a function of the oxidation temperature in forged and cast Ti64 and Ti67 after thermal oxidation. It is obvious that the hardness of the α case increases with increasing oxidation temperature in the two alloys. This is due to the acceleration of oxygen diffusion at higher oxidation temperatures. The hardness of the as-forged samples was around 320 HV for both Ti64 and Ti67 alloys. After oxidation, the maximum hardness achieved was 850 HV in Ti64 alloy at 1373 K (1100 °C), which means that a well-hardened case was obtained. In forged Ti67, the maximum hardness was 600 HV, which is lower than that of Ti64 at 1373 K (1100 °C). This can be explained by the higher oxygen concentration obtained in the Ti67 sample, Fig. 10. This emphasizes that Niobium decreases oxygen diffusion in the alloy, unlike Vanadium.

The maximum hardness achieved in cast Ti64 and Ti 67 samples treated at 1373 K (1100 °C) was 736 HV and 550 HV, respectively, as shown in Fig. 10. This shows that lower microhardness was observed in the cast samples than in the forged samples. This is due to the lower oxygen concentration in cast Ti64, which resulted from the reported resistance of the cast structure to oxygen diffusion [16] as previously described.



	Untreated	973K	1173K	1373K
Ti64-Forged	315	471	495	862
Ti67-Forged	325	425	553	600
Ti64-Cast	285	348.67	409.67	637.3
Ti67-Cast	275	281.3	334.67	606.5

Fig. 11 Microhardness of the untreated and oxidized samples just below the oxide layer.

The wear resistance of the oxidized samples was expected to behave similar to hardness; however, some differences were observed. Figure 12 represents the wear resistance explained in terms of the weight loss of the forged samples. In the as forged state, the weight loss was 0.28 gm for Ti64 and 0.26 gm for Ti67, which means that the two alloys have almost the same resistance to wear in the as forged condition. After thermal oxidation, the wear resistance of Ti64 and Ti67 was significantly increased.

The weight loss in forged Ti64 and Ti 67 decreased with increasing oxidation temperature. In case of Ti64, the weight loss after thermal oxidation at 973 K (700 °C) was 0.25 gm, which is slightly less than the untreated condition since the alpha case was not thick enough to withstand wear loading. Increasing the oxidation temperature up to (1100 K and 1373 K) (900 °C and 1100 ºC) decreased dramatically the weight loss to 0.0018 gm. On the other hand, the weight losses in forged Ti67 decreased from 0.26 gm to 0.22 gm and 0.158 gm after thermal oxidation at (1100 K and 1373 K) (900 °C and 1100 ºC) respectively. This means that less improvement in the wear resistance was observed in forged Ti67 alloy than in forged Ti64 alloy after

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thermal oxidation. From the worn surface morphology, it was observed that the depth of the wear grooves was decreased in the two alloys after thermal treatment at 1373 K (1100 °C).

Considering the hardness data shown in Fig. 11, the wear resistance increased with increasing hardness in the surface of both forged Ti64 and Ti67 alloys. The difference in wear resistance between the two alloys after thermal oxidation can be owed to the case thickness shown in the micrographs of Fig. 7 and its quantitative analysis of Fig. 9. Based on these figures, forged Ti67 specimens have less alpha case depth than Ti64. Therefore, the thin layer in the case of Ti67 was not able to withstand for a long time under loading, so it fell, leaving the base metal with its lower hardness in direct contact with the test ring.

In the as-cast samples, the weight loss in Ti64 decreased from 0.3 gm down to 0.0015 gm with increasing oxidation temperature, while in Ti67 the weight loss was nearly unaffected by thermal oxidation treatment, even at 1373 K (1100 ºC). This is due to the relatively thinner α case and the lower hardness obtained in cast T67. The presence of Nb, which resists oxidation, decreased the oxygen concentration in the diffusion layer, similar to the case of forged Ti67 shown in Fig. 10. Concluding, the enhancement of surface hardness in both Ti64 and Ti67 with thermal oxidation depends on the concentration of oxygen in the oxygen diffusion zone. In addition to hardness, wear resistance also depends on the thickness of the hardened layer and how long it can withstand the loading conditions.

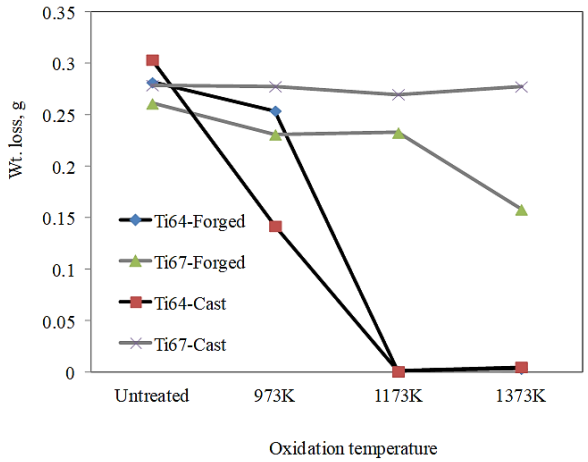

Fig. 12 Wear resistance of the untreated and oxidized forged samples.

Conclusions

In the current investigation, the effect of thermal oxidation on the tribological properties of forged and cast Ti6Al4V and Ti6Al7Nb alloys was investigated and the following conclusions were obtained;

- The oxygen diffusion zone, which was generated at high temperature, showed the best wear resistance in the case of Ti6Al4V alloy. On the other side, no remarkable enhancement of the wear property in Ti6Al7Nb alloy was observed in spite of the improved surface hardness.
- The development of alpha case in the cast samples was different from the forged ones. The widmanstätten microstructure of the cast samples showed thinner alpha case compared to the equiaxed structure of the forged samples in both alloys.

Acknowledgements

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