IMPROVEMENT OF HARDNESS AND WEAR RESISTANCE OF T1- 6AL- 4V ALLOY BY THERMAL OXIDATION FOR BIOMEDICAL APPLICATION

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ABSTRACT– *Titanium and its alloys provide optimum metallurgical properties for implants. The formation of an oxide layer favours compatibility with the adjacent hard and soft tissues. This study is concerned with the improvement of hardness and wear resistance of Ti-6Al-4V surface by thermal oxidation. In this study, comparative investigation of thermal oxidation treatment for Ti–6Al–4V was carried out to appropriate the oxidation conditions for further evaluation of wear performance. Hardness examination conducted under four different indentation loads of 200 gf to 1000 gf with a Vickers pyramid indenter revealed that surface hardness increased from 450 for untreated samples to 1300 Hv upon oxidation at 900^{o}C for 45 h, which was accompanied by significant improvement in wear resistance. Characterization of modified surface layers was made by means of microscopic and X-ray diffraction analysis. This oxidation condition achieved 25 times higher wear resistance than the untreated alloy during reciprocating wear test conducted in a dry sliding.*

KEYWORDS: *Ti-6Al-4V alloy; Thermal oxidation; X-ray diffraction; Hardness; Wear*

1- INTRODUCTION

During the working of biomedical devices in the body, it is subjected to action of rubbing contact and sliding of articulating surfaces [1]. This condition of service leads to stresses at the contact areas and may cause damage on their surfaces. In addition, wear may occur on the implant surface very rapidly as a result of the combined effect of corrosion in the human body and wear resulting in severe surface damage.
Titanium and its alloys, particularly Ti-6Al-4V, have been frequently used for several kinds of industries which range from aerospace, motor sport and chemical engineering sectors through to a variety of medical applications like human joint replacements and dental implants due to its beneficial properties, such as low density, low modulus of

elasticity, excellent corrosion resistance and biocompatibility [2-4]. However, titanium and its alloys have poor tribological properties such as poor abrasive wear resistance, low hardness values and high coefficient of friction [5].

It has been reported that, excessive wear of titanium and its alloys is caused by their characteristics leading to mechanical and chemical instability of the surface layers. This problem can be avoided by changing the nature of the surface of titanium and its alloys using thermo-chemical treatments such as oxidation. A variety of surface modification processes have been proposed for titanium alloys. The surface is changed from elemental titanium to a hard compound of titanium. The methods used to improve wear resistance of titanium and its alloys include surface modification and heat treatment [6-10]. Oxidation technique, as a heat treatment method, is widely used to improve the wear resistance of titanium alloy components. When titanium alloy is exposed to air at a temperature above 200^{o}C, it is rapidly oxidized and a thick surface oxide scale on an inner hard diffusion layer is produced [10]. Increasing temperature induces the formation of a thicker oxide layer, which is accompanied by the dissolution of oxygen beneath it [11].

Ti-6Al-4V alloy is a widely used biomaterial and structural material among the titanium alloys due to its excellent mechanical properties and good corrosion resistance. However, a few studies have been reported on the wear of oxidised Ti-6Al-4V alloy. In this work, the influence of thermal oxidation at a temperature ranging from 600^{o}C to 900^{o}C and time ranging from 5 h to 45 h on the wear properties of Ti-6Al-4V alloy was studied using reciprocal pin-on-disc type wear tests. The aim is to appropriate the thermal oxidation condition of a Ti–6Al–4V alloy on the basis of wear response.

2- EXPERIMENTAL PROCEDURE

Ti–6Al–4V alloy used in the present investigation was received as 20mm diameter cold drawn rod. The cylindrical samples were machined to 10 mm diameter to be suitable for wear test. The samples cut from the rod with height 10mm were prepared with a standard surface-finishing route. Samples were ground with SiC abrasive papers up to 2000 mesh and polished using 1 micron alumina. Later the samples were cleaned in acetone and dried in hot air. Thermal oxidation treatments were conducted at 600^{o}C, 700^{o}C, 800^{o}C and 900^{o}C for 5 h, 15 h, 30 h, and 45 h in an air circulating furnace at normal atmospheric condition. The samples were kept in the furnace until reach to room temperature. Characterization of the surfaces was made by surface roughness and hardness measurements, X-ray diffraction (XRD) analysis and optical microscopic examinations. To accurately determine relevant properties, three samples were averaged at each characterization test. The surface roughness was performed on the surface of the samples before and after the treatments using a stylus surface tester. The effect of oxidation conditions on surface roughness was determined according to average roughness (Ra) values. Hardness tests were carried out with a Vickers pyramid indenter. Hardness measurements were performed on the surfaces of the samples under four different indentation loads, 200, 300, 500 and 1000 gf. At each load level, 10 successive measurements were made. A Rigaku X-ray diffractometer was used for the XRD analysis. The glancing incidence X-ray diffraction technique was used for surface

phase identification of untreated and oxidized samples. Cu Ka radiation source was used and the incidence beam angle was 2^o. Diffraction angle range was between 20^o and 80^o, with a step increment of 0.05^o and a count time of 1 s.

The wear test was performed using a pin-on-disk wear testing machine. The tested samples were in the form of a cylindrical pin of 10 mm diameter, and 10 mm in length. These pins were rubbed against a hardened steel disk (AISI 5190) of surface hardness of 62 HRc, finished to better than RMS 0.3 μm. The wear tests were carried out at three different applied load (50, 100 and 150 N), and three linear sliding speeds at the friction surface (0.5, 1.0, and 1.5 m/s), for a maximum sliding distance of 3000 m for each test which provide to be sufficient for highlighting reliable differences among the specimens. These conditions were chosen to change wear mechanism from oxidative to delamination. Each specimen was weighed before and after each wear test and the volume loss was calculated. Tests were conducted at room temperature without lubricant. The wear resistance was measured in terms of weight loss of the tested materials using a precision balance with a resolution of 0.1 mg. Finally, the morphology and constitution of the worn samples and debris were examined by a JEOL JSM 5900 Oxford scanning electron microscope (SEM).

3- RESULTS AND DISCUSSION

The surface of all samples was covered with a brown colored oxide layer. At high temperatures (800^oC and 900^oC) and for all oxidation time, poorly adherent layers of oxide scale were removed from the samples. The thickness of these layers increased drastically with increasing oxidation time as shown in **Figure 1**. As can be seen from this figure, increasing oxidation temperature or oxidation time accelerates the oxidation rate, allowing the formation of thicker oxide layer. On the other hand, at low temperature 600^oC and 700^oC and at any oxidation time these layers were not removed. The temperature of oxidation and oxidation time affect not only the thickness of the oxide layers but also the surface roughness. The average roughness of samples before treatment was 0.114 μm. Roughness of oxidized surfaces increased drastically with increasing oxidation time and oxidation temperature as presented in **Figure 2**. Dong et al [12] reported that the rougher surface of the oxidized samples can be ascribed to the growth mechanism of oxide layer. As the time of oxidation increases, this layer becomes porous and develops an arranged structure with an increase of the surface roughness.

Figure 3 shows the XRD pattern of the untreated alloy. Corresponding to different crystallographic planes of untreated alloy α-Ti and β-Ti peaks were obtained at different angles. XRD patterns of surface layers of thermally oxidised samples at 600^oC for 30 h and 800^oC for 30 h are shown in **Figure 4**. As evidenced from **Figure 4** a, the surface of the Ti-6Al-4V alloy was covered by anatase and rutile modification of TiO_2. Peaks of α-Ti phase also appeared on the pattern after oxidation. The X-ray diffraction analysis of samples oxidized at 800 ^{o}C for 30 h (**Figure 4b**) shows that, after the removal of the poorly adherent part of oxide scale, the compound diffusion layer consists mainly of rutile TiO_2. Also the diffusion layer consists of α-Ti phase, small amount of Ti_3Al was detected.

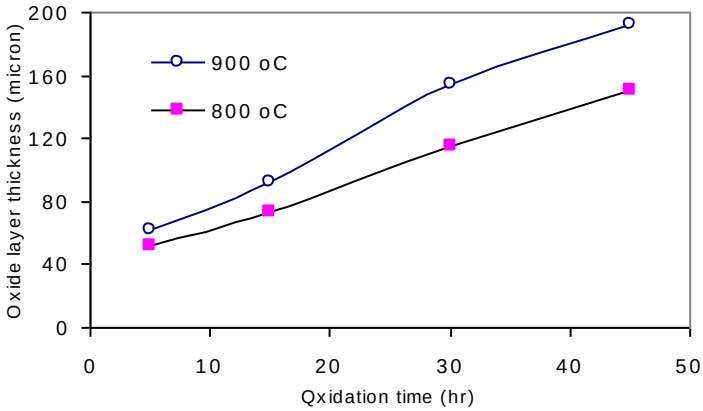

Figure 1. Effect of oxidation time on the thickness of oxide layer at high temperature.

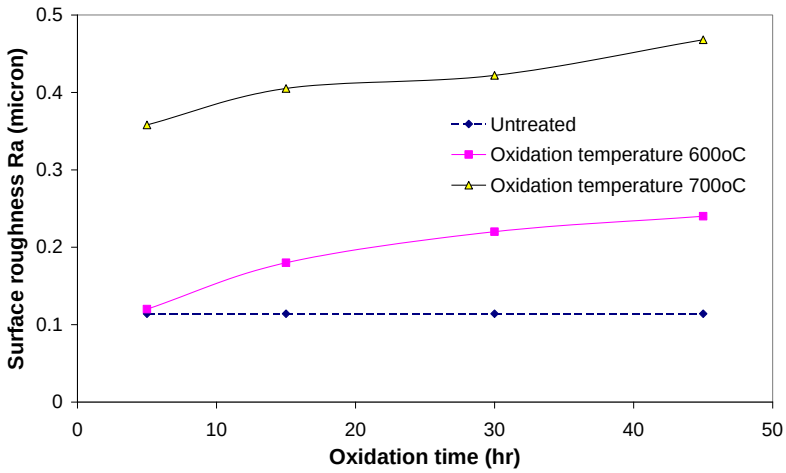

Figure 2. Effect of oxidation temperature and oxidation time on the roughness of oxidation surface.

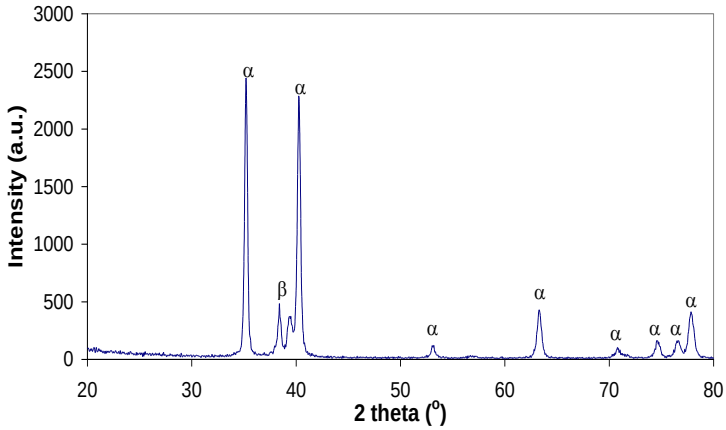

Figure 3. XRD pattern of untreated sample (α: hcp titanium, β: bcc titanium).

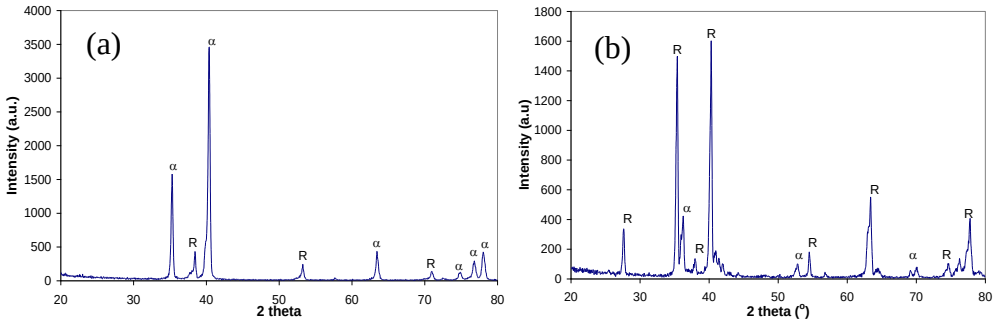

Figure 4. XRD patterns fore oxidised samples a) after oxidation at 600°C for 30 h, and b) after oxidation at 800°C for 30 h.

The results of microhardness measurements of untreated and oxidized samples under varying indentation loads are shown in **Figure 5**. The surface hardness of untreated samples for indentation loads of 200, 300, 500, and 1000 gf is almost constant at about 360. The hardness values for untreated samples show a small amount of scatter. In contrast, the hardness values of oxidized samples show a large amount of scatter. In general, increasing the temperature and/or time of oxidation leads to an increase in surface hardness of the samples. As can be noticed from **figure 5** the surface hardness of all samples treated at 600 °C, and 700 °C, at which the oxide layers not removed from the samples, was increased approximately by the same values. However, a dramatic increment of surface hardness was happened for the samples treated at 800 °C, and 900 °C, at which the measurements were carried out not on the oxide layers as for samples treated at 600 °C, and 700 °C but on the diffusion layers of the treated samples. The modified surface of the samples treated at 900°C for 45 h shows a maximum value of hardness (1300 Hv). Also, as can be seen from this figure, the hardness was decreased with increasing indentation load. This decrease can be attributed to involvement of softer regions at high penetration depths of the indenter. With increasing oxidation temperature and time, higher hardness values were maintained for a wide indentation load range. This shows that, deeper hardened layers were accomplished at high oxidation temperature and/or time. Increasing of surface hardness after oxidation can be attributed to the hard oxide layer covering the surface and donation of strains in the matrix due to dissolution of oxygen [10].

Figure 6 shows cross-sectional optical micrographs of the oxidized samples. As can be seen, increasing temperature promoted formation of the thick oxygen diffusion zone. Beneath the oxide layer an oxygen diffusion zone appeared as dark colored region after etching. The microhardness profiles across the diffusion zone were measured. **Figure 7** shows the hardness depth profiles after oxidation treatment at 600 °C, and 900 °C for 45 h. It can be seen that the hardness measurements conducted on the cross-section depicted the gradual decrease of surface hardness through the core. The significant solid solution hardening had taken place beneath the TiO_2 layers. The treatment produced a total hardened layer of about 40 μm in depth for the samples treated at 900 °C for 45 h and 20 μm for the samples treated at 600 °C for 45 h.

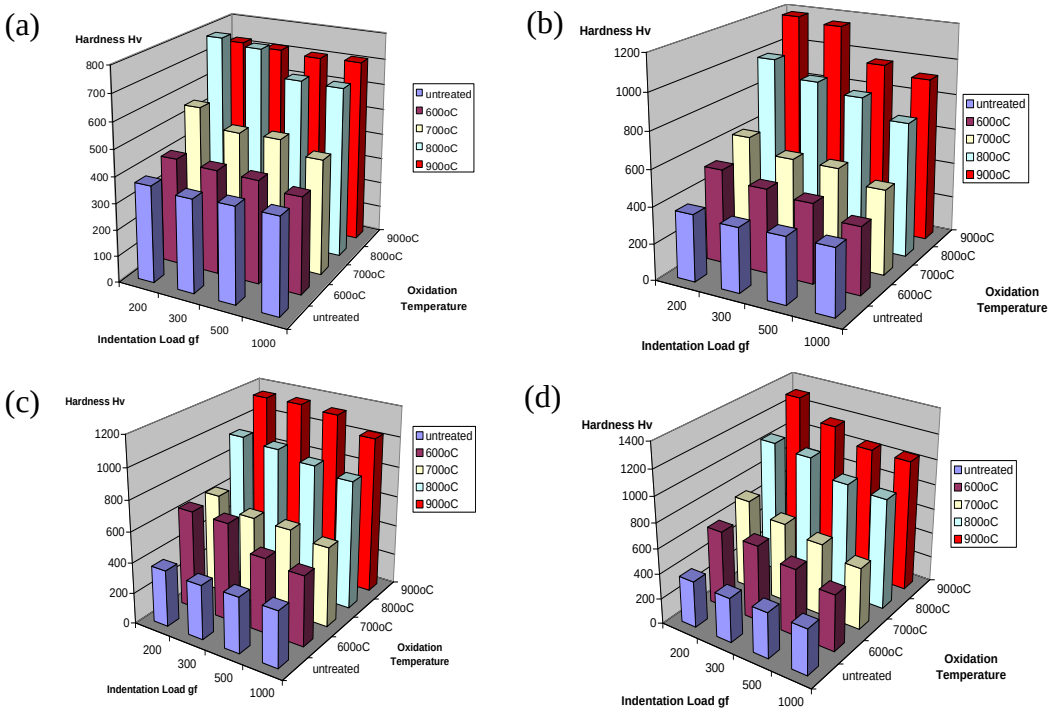

Figure 5. Effect of oxidation time on the hardness of samples a) 5 hr, b) 15 hr, c) 30 hr, and d) 45 hr.

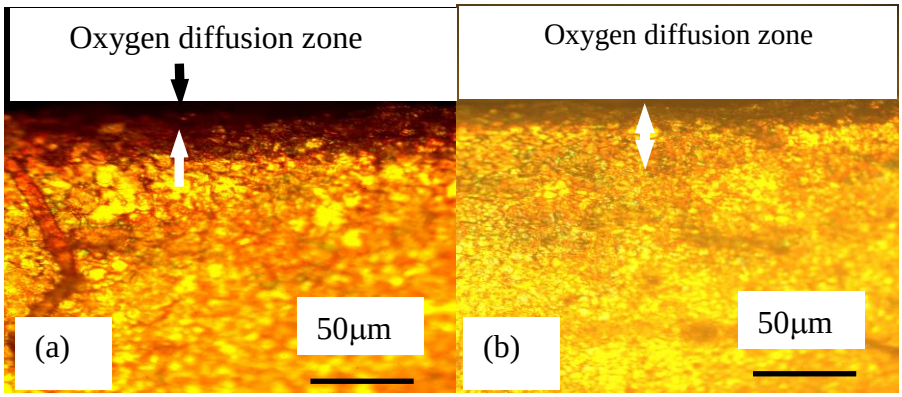

Figure 6. Cross-sectional optical micrographs of a sample oxidized at a) 600 ^{o}C for 45 h, and b) 900 ^{o}C for 45 h.

The wear loss of untreated and treated samples measured after 3000 m sliding distance at a constant sliding velocity (1 m/s) and constant load (100 N) is shown in **Figure 8**. As can be seen, on the untreated surface the wear was occurred with the creation of a large amount of wear loss. It is clearly seen that the wear loss decrease gradually for the samples treated at 600^{o}C for different times. It was interesting to note that the wear

loss of samples treated at 600°C for different times was found to be close to untreated samples. This is may be due to the layer of TiO_2 which created by oxidation at 600°C for time up to 45 h was thin and the thickness of the inner diffusion layer was small as well. On the other hand, increasing temperature to 700°C and oxidation time 30 and 45 h leads to a decrease in wear loss more rapidly. However, increasing temperature to 800°C or 900°C leads to dramatic decreasing in wear loss. Thus, thermal oxidation at 800°C or 900°C for 5, 15, 30 and 45 h provided excellent protection against wear. Generally, the weight loss of oxidised samples at 800 °C and 900 °C is lower than that of untreated and oxidised samples at 600 °C and 700 °C, so that a substantial improvement of the wear resistance is obtained.

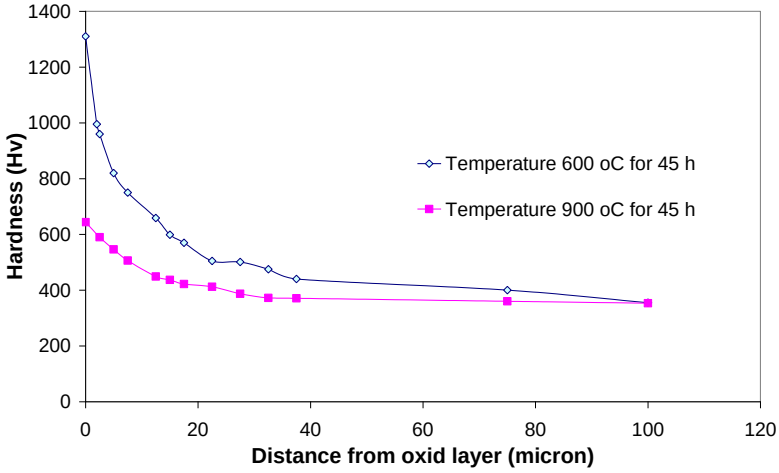

Figure 7. Microhardness-depth profiles for oxidised Ti-6Al-4V samples treated at 600°C and 900°C for 45 h.

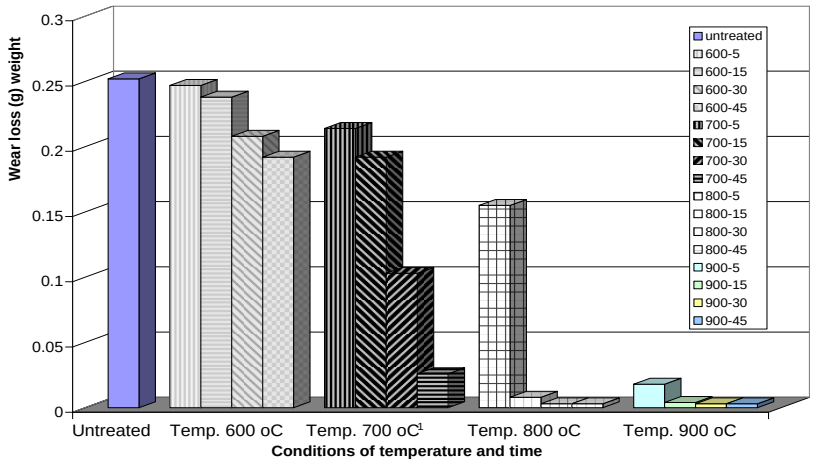

Figure 8. Wear loss vs. treatment conditions of untreated and thermally oxidised samples tested with 100 N coupling load, 1 m/s sliding velocity and 3000 m sliding distance.

The wear loss of treated samples at 600 ^{o}C for 30 h and 700 ^{o}C for 30 h measured after 3000 m sliding distance as a function of coupling load and sliding velocity are shown in **Figure 9**. As can be seen, the weight loss of the samples increased linearly with increasing loads and sliding velocity. The results show that, a significant decrease in weight loss was achieved upon increasing the temperature of oxidation from 600 ^{o}C to 700 ^{o}C for the similar time.

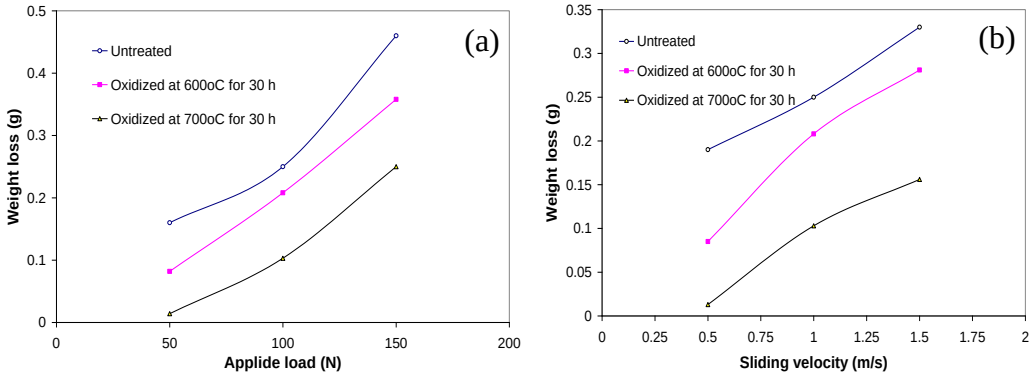

Figure 9. Wear weight loss of untreated and treated samples at 600 ^{o}C and 700 ^{o}C for 30 h at constant sliding distance (3000 m) versus a) applied load, and b) sliding velocity.

Figure 10. Shows a SEM micrographs of oxidised surface of a sample treated at 800 ^{o}C for 45 h and wear tracks that formed on oxidised samples treated at different temperature and constant time. As can be seen from **Figure 10a**, the diffusion layer consists of small grain size of rutile TiO_2 after oxidation. The wear tracks produced on oxidised samples exhibited different topography (as can be seen in **Figure 10b**, **c**, **d**, and **e**). A typical feature of rough wear tracks produced on surface of the samples treated at 600 ^{o}C and 700 ^{o}C for 45 h (**Figure 10b**, and **c**) were extensive shear deformation due to ploughing action of the samples on the disk. Thus, on oxidized surface at 600 ^{o}C and 700 ^{o}C for 45 h was initiated by disruption of oxide layers and followed by the wear of oxygen diffusion zone, which were removed at extended testing time. The wear tracks on oxidised surface of samples treated at 800 ^{o}C and 900 ^{o}C for 45 h (**Figure 10 d**, and **e**) were smooth without any significant change of the surface of the samples. The oxygen diffusion zone successfully restrained a very good progress of wear.

The wear debris of thermally oxidised samples treated at different temperature and the same treated time tested at 1 m/s sliding velocity, 100 N applied load, and 3000 m sliding distance are shown in **Figure 11**. Increasing the oxidation temperature leads to decrease the size of wear debris.

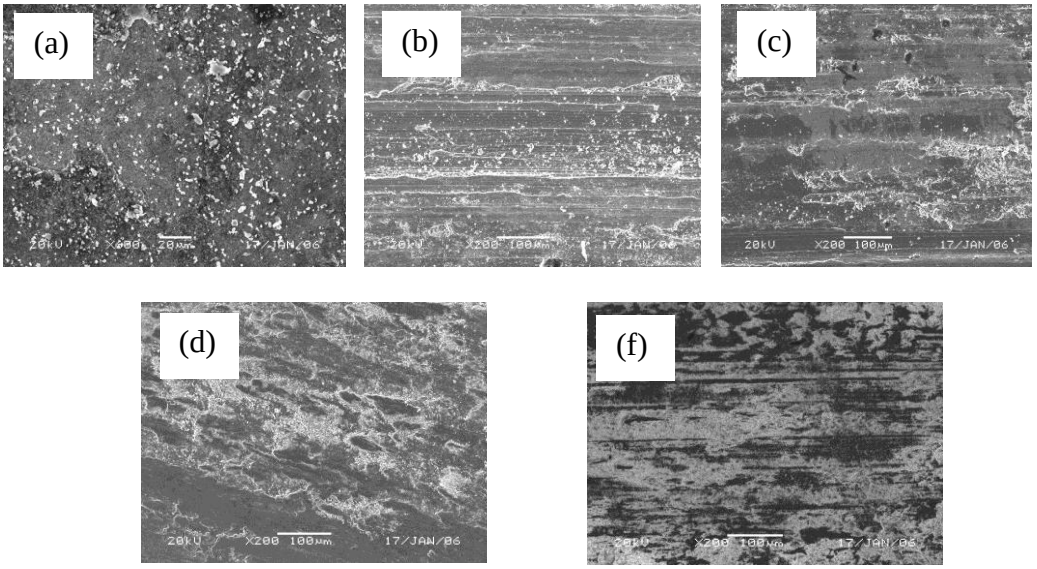

Figure 10. SEM micrographs of a) surface of oxidised sample at 800 ^{o}C for 45 h. b) wear tracks of sample treated at 600 ^{o}C for 45 h, c) wear tracks of sample treated at 700 ^{o}C for 45 h, d) wear tracks of sample treated at 800 ^{o}C for 45 h, and e) wear tracks of sample treated at 900 ^{o}C for 45 h.

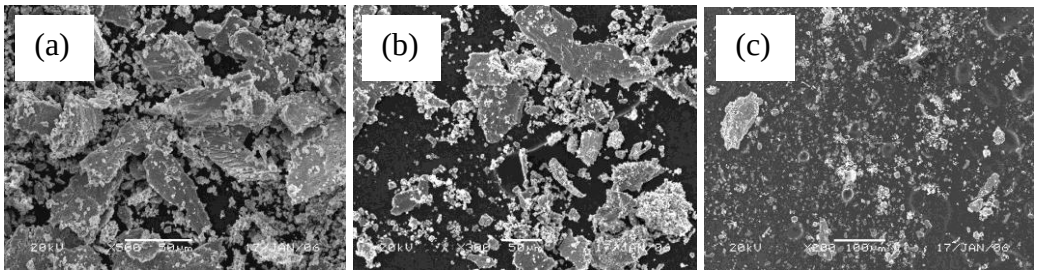

Figure 11. Wear debris of thermally oxidised samples tested at 1 m/s sliding velocity, 100 N applied load, and 3000 m sliding distance a) treated at 600 ^{o}C for 45 h, b) treated at 700 ^{o}C for 45 h, and c) treated at 900 ^{o}C for 45 h.

4. CONCLUSIONS

The Ti-6Al-4V alloy was thermally oxidized at 600 ^{o}C, 700 ^{o}C, 800 ^{o}C, and 900 ^{o}C to produce wear resistance surface layers. The work clearly demonstrates the beneficial effect of surface hardening due to the oxygen diffusion layer. Surface roughness increased with increasing oxidation temperature and time. Oxidation treatment of Ti–6Al–4V greatly improves its wear resistance, due to the formation of a hard, oxide layer on the surface of the alloy. Due to formation of a hard oxide layer and oxygen diffusion zoon beneath, a significant increment in surface hardness was achieved. There is roughly a threefold increase in hardness near the oxide surface compared to untreated samples and below this top layer hardness values decrease gradually to

nearly the same values for the untreated samples. Oxygen diffusion zoon, which generated at high temperature (800 ^{o}C, and 900 ^{o}C) produced the most wear and hardness resistance surface on Ti–6Al–4V alloy.

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5. REFERENCES

[1] D. M. Brunette, P. Tengvall, M. Textor, P. Thomsen, Heidelberg: Springer; (2001).

[2] M. M. Dewidar, H-C Yoon, and J. K. Lim, Mechanical properties of metals for biomedical applications using powder metallurgy process: A review, Journal of Metals and Materials, 193- 206, (2006).

[3] 3- M. Long, and H. J. Rack Titanium alloys in total joint replacement-a materials science perspective, Biomaterials 19, 1621-1639, (1998)

[4] H-S Kim, W-Y Kim, and S-H Lim, Microstructure and elastic modulus of Ti–Nb–Si ternary alloys for biomedical applications, Scripta Materialia, 54, 887–891, (2006).

[5] R. Boyer, G. Welsh, E.W. Collings, Titanium Alloys, ASM International, Materials Park, OH, (1994).

[6] F. Galliano, E. Galvanetto, S. Mischler and D. Landolt, Tribocorrosion behavior of plasma nitrided Ti–6Al–4V alloy in neutral NaCl solution , Surface and Coatings Technology, Vol. 145, 121-131, (2001).

[7] T. Novoselova , S. Malinov , W. Sha and A. Zhecheva, High-temperature synchrotron X-ray diffraction study of phases in a gamma TiAl alloy, Materials Science and Engineering A, Volume 371, 103-112, (2004).

[8] M. C. Garcia-Alonso, L. Saldana, G. Valles, J. L. Gonzalez-Garrasco, J. Gonzalez-Cabrero, M. E. Martinez, E. Gil-Garay, and L. Munuera, In vitro corrosion behaviour and osteoblast response of thermally oxidised Ti6Al4V alloy Biomaterials, 24,19–26, (2003).

[9] M. F. Lopez, J. A. Jimenez, A. Gutierrez, Corrosion study of surface-modified vanadium-free titanium alloys Electrochim Acta; 48:1395–1401, (2003).

[10] H. Guleryuz, H. Cimenoglu, Effect of thermal oxidation on corrosion and corrosion–wear behaviour of a Ti–6Al–4V alloy, Biomaterials 25, 3325–3333, (2004)

[11] P. A. Dearnley , K. L. Dahm and H. Ccedilimenolu, The corrosion–wear behaviour of thermally oxidised CP-Ti and Ti–6Al–4V Wear, Volume 256, 469-479, (2004).

[12] H. Dong, A. Bloyce, P. H. Morton, and T. Bell, Surface engineering to improve the tribological performance of Ti-6Al-4V, Surface Engineering, Vol. 13, 402-406, (1997).

تحسين خاصيتي الصلادة ومقاومة البري لسبيكة التيتانيوم- الومنيوم- فاناديوم باستخدام طريقة الأكسدة الحرارية وذلك لاستخدامها في التطبيقات الطبية

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يستخدم التيتايوم وسبائكه كبديل عن العظام الطبيعية للإنسان وذلك لخواصه الميتالورجية المثلي, وللتوافق بين هذه الأجزاء المغروسة في الجسم والأنسجة الطرية المتاخمة فإنه يفضل عمل غشاء مأكسد علي سطح الجزء المستخدم من التيتانيوم أو سبائكه.

هذه الدراسة تهتم بتحسين خاصيتي الصلادة ومقاومة البري لسطح سبيكة التيتانيوم وذلك عن طريق أكسدة السطح الخارجي عند درجات حرارة مرتفعه, وقد تم تغيير درجات الحرارة وكذلك زمن تعرض العينات لها بغرض تحديد العوامل المناسبة للحصول علي أفضل الخواص, وقد تمت قياسات الصلادة باستخدام أحمال مختلفة باستخدام طريقة فيكرز ووجد أن الصلادة قد ذادت من 450 للعينة غير المعالجة إلي 1300 للعينات التي تم أكسدتها عن 900 درجة مئوية ولمدة خمس وأربعون ساعة مقرونة بزيادة كبيرة في مقاومة البري. وقد تم تعيين وفحص طبقة السطح المؤكسد باستخدام الميكروسكوب وكذلك أشعة اكس, وفي النهاية وجد أن استخدام هذه الطريقة قد زادت من مقاومة البري للسبيكة بنسبة عالية تقدر بحوالي خمسة وعشرون مرة عن العينات الغير معالجة.