Enhancement Corrosion Behavior of Pure Titanium for Biomedical Applications

Mohsin Talib Mohammed[1], Nabeel Alawi Kadhim[2]
[1]Nanotechnology and Advanced Materials Research Unit, Faculty of Engineering, University of Kufa, Najaf, Iraq
[2]Materials Engineering Department, Faculty of Engineering, University of Kufa, Najaf, Iraq

***Abstract*-- Thermal oxidation (TO) is one of the most important techniques in the field of surface modification to enhance the required properties of engineering materials. In the present study, the influence of TO process on the corrosion behavior of a commercial pure titanium (CP-Ti) was investigated. The oxidation process was conducted at different temperatures, i.e., at 500 and 800 ºC for 8 h, in a muffle furnace with a controlled environment at atmospheric pressure. The characterization of modified surface layers was examined. It is found that TO process promotes the formation of adherent surface oxidized layers on the CP-Ti samples without spallation. The superior electrochemical performance is found in oxidized CP-Ti samples compared to untreated samples.**

***Index Term*-- Titanium, Thermal oxidation, Corrosion, Biomedical applications, Surface modification**

1. INTRODUCTION

The use of biomaterials is an imperative engineering field which found ever-increasing applications in medical area with increasing of an aging global population. The highest number of implants is presented for hard tissue replacements such as joints, artificial bones and dental structures. Hence, design of fitting material satisfying different requirements demanded by human body is an intricate task of engineers, scientists and researchers. Outstanding combination of high mechanical properties, superior wear and corrosion resistances, low elastic modulus and exceptional biocompatibility is very crucial [1]. Metals and alloys are widely employed as implantable materials such as stainless steels, Co-Cr alloys, and Ti-based alloys due to their excellent mechanical properties. However, these materials sometimes show instability in physiological media owing to their mechanical and electrochemical failure [2].

Nowadays, Ti materials are the most fitting materials for medical applications in comparing with other competing materials because of their excellent biocompatibility and corrosion properties [1, 3, 4]. Commercially pure titanium (CP-Ti) is considered as an important kind of Ti as it satisfies the requirements of biomaterials in some cases especially biocompatibility and corrosion resistance. Corrosion properties of Ti play a significant role for improving its long-term stability and biocompatibility in physiological fluids. The electrochemical reactions between Ti implants and human body's electrolytic environment affects directly on the integrity of the implants and causes release ion metallic debris. These results induce an inflammatory reactions, increasing cytotoxicity and failure of the implant. Consequently, development the corrosion behavior of Ti implants in physiological fluids is essentially required. As is well known, the spontaneous formation of an oxide layer on the surface of the material is the main motivation of its higher corrosion resistance and biocompatibility since it prevents the diffusion of the oxygen from the environment. In the case of Ti, this metal has high reactivity and affinity with oxygen to create spontaneously defensive oxide layer (TiO_2) over its surface. This surface layer has an immense ability to prepare itself immediately when disruption or damage is occurred with the presence of air or oxidizing media [5]. Various surface modification techniques are employed for improving the surface properties of Ti with the goal of increasing its corrosion resistance. TO is one of these methods to achieve this aim with increasing the thickness of the protecting oxide layer. This technique is a natural, conventional and cost-effective procedure used for growing thicker surface oxide layers by heating the material in an oxygen rich environment [6]. In the present work, an attempt is made to study and improve the corrosion behavior of CP-Ti using TO process at different temperatures for biomedical applications.

2. MATERIALS AND METHODS

CP-Ti grade-2 samples (1 x 1 x 0.3 cm^3) were used as the substrate of TO process. Prior to TO, the samples were grounded using different grades of SiC paper at a slow speed followed by polishing with 0.5 µm diamond paste to get mirror finishing. Afterword, the samples were cleaned ultrasonically in a solution of distilled water and acetone for 15 min and then dried.

For each experiment, TO process was made in air at 500 and 800 ºC for 8 h (TO samples are designated as "500/8 and 800/8 hereafter) at 5 ºC /min as constant heating rate. As the temperature is an important factor for TO, it is changed to recognize the nature of oxide film created at each thermal condition. After completing TO process, all oxidized samples were left to cool in furnace to room temperature to ensure that all samples experienced the same cooling rate and also to prevent spallation.

The surface oxide layer of CP-Ti samples was examined by field emission scanning electron microscope (FESEM, TESCAN MIRA3). The micro-hardness of the investigated Ti samples has been measured with a Vickers pyramid indenter, using micro-hardness tester (Modele: HVS 1000, Spain). The parameters of micro-hardness test was chosen to be 200 gf and 10 seconds for load and dwell time respectively. The average of five indentations was made for each sample.

Three-electrode cell potentiostat was used to increase the corrosion resistance of the investigated CP-Ti samples. Open circuit potential (OCP), corrosion current density (I_{corr}), and

corrosion rate were used for estimating the corrosion characteristics. The samples were ultrasonically cleaned after standard grinding and polishing processes using waterproof SiC papers of up to #2500 grit and diamond paste of 0.5 µm respectively. For each experiment, 0.126 cm^2 surface area was exposed to fresh and naturally aerated solution of 0.9% NaCl at 7.4 pH and 37 ± 1 ^oC to simulate physiological environment. The OCP was determined as a function of time until the steady state was attained. Moreover, corrosion potential (E_{corr}) and I_{corr} of the investigated CP-Ti samples were estimated from the polarization curve of potential vs. current density via the extrapolation technique. A scan rate of 0.166 mV/s in the range from -750 to 2500 mV(Ag/AgCl) was used through the test.

3. RESULTS AND DISCUSSION

Visual inspection of oxidized CP-Ti samples showed the development of an extremely different coloration on their surfaces. The color of the surface of treated samples varies from light blue to dark brown with increasing temperature from 500 to 800 ◦C. This result is owing to the growing in the thickness of the surface oxide layer which changes the interference of the incident light radiation. In the present work, the duration of TO is selected to be 8 h in order to prevent spallation. It was reported that the OT at high temperature and long time causes debonding of the oxide layer formed on the surface of Ti [7]. Moreover, after completion the dwell time of TO, the oxidized samples were cooled by furnace cooling as the spallation of the oxide scale is observed from both air and water cooled samples [8]. It is expected that the spallation occurs on both air cooled and water cooled samples owing to fast cooling. The variation of thermal expansion coefficients between Ti and its oxide layer induces huge thermal stresses which later on cause the spallation [8].

Surface morphology assessment of the of oxidized samples at different temperatures is very essential to recognize the nature of the oxide layer. Fig. 1 shows the surface morphology of the oxidized CP-Ti samples at 500 and 800 ◦C for 8 h. This figure is obviously certifies the formation of surface oxide scales without spallation in both two oxidation temperatures. The development of a thin and smooth surface oxide scale along with a few nodular oxide particles was observed over the oxidized samples at 500 ◦C (Fig. 1a).In addition, entirely covered surface oxide scales were formed over the oxidized samples at 800 ◦C for 8 h (Fig. 1b).It is well known that the oxide layer nucleates instantaneously throughout the surface when it comes in contact with oxygen. After nucleation, growth and agglomeration of oxide particles occur and their extent depends strongly on the TO temperature. This result is clearly observed when the temperature increases from 500 to 800 ◦C. Increasing the temperature allows the enhancement in the oxide particles size which in turn increases the porosity of the oxide layer. Hence, in the present work, the porosity of CP-Ti samples oxidized at 800 ◦C is higher comparing with the samples oxidized at 500 ◦C.

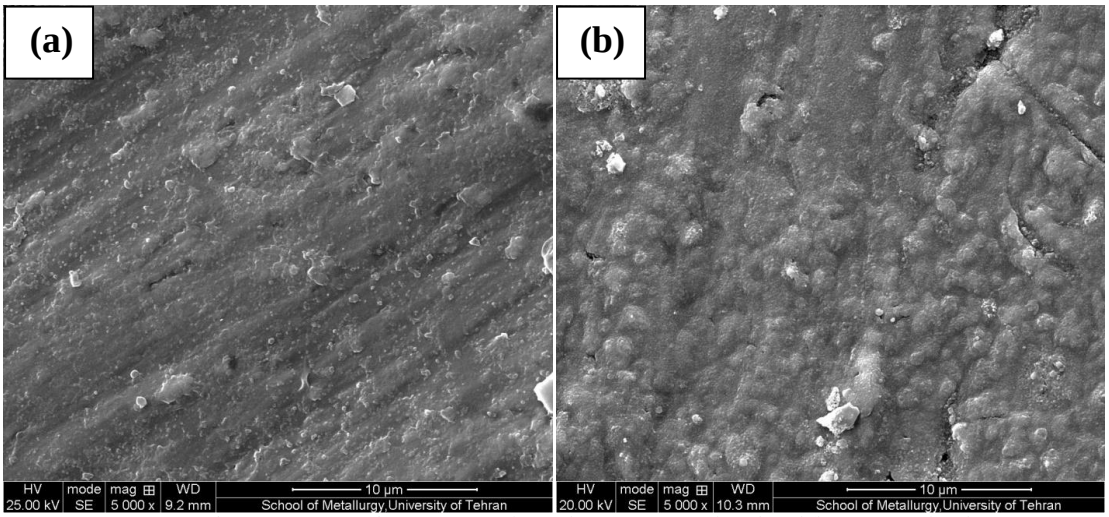

Fig. 1. Surface morphology of oxidized CP-Ti samples (a) at 500 ◦C for 8 h and (b) at 800 ◦C for 8h.

Depending on literature, it is expected that the predominant phases in the thin oxide layer consist of oxygen diffused Ti (Ti(O)) and rutile structure (TiO_2) when the TO is performed at 500 and 800 ◦C for 8 h respectively [9-11]. The incidence of rutile phase in CP-Ti samples oxidized at 800 ◦C suggests the development of a thick oxide layer, while the presence of Ti(O) phase on the samples oxidized at 500 ◦C signifies the creation of a thin oxide layer [7].

As well known, Ti oxide considers as a crucial factor that affects significantly the values of hardness and other properties of biomedical Ti alloys. Therefore, in the present work, the oxidation behavior of the CP-Ti was investigated over two temperatures (500 °C and 800 °C), for 8 h in air. The values of the micro-hardness of untreated and oxidized CP-Ti samples under different temperatures are illustrated in Fig. 2. It can be seen from the figure that the surface hardness after oxidation increases in all oxidized samples compared with untreated samples as result of the formation of oxide layer. It was reported that the improvement in micro-hardness of oxidized CP-Ti samples compared to untreated samples is

owing to the increase in c/a ratio (strains in matrix) as a result of the lattice distortion caused by the dissolved oxygen [12]. In this research, the values of surface hardness of CP-Ti samples are modified and improved by using thermal oxidation process. The effects of such process to hardness values can be concluded as the optimum value of hardness (HV= 524) is resulted from the thermal oxidation process at temperature 800 °C. It is well known that at higher temperature of the process, the more diffusion of oxygen atoms through the surface. Generally, oxidation rate is gotten to be more in high temperature condition than in low temperature one. Therefore, the rate of oxidation is increased at higher temperature (800 °C) comparing with lower temperature(500 °C). The development of a thick oxide layeris related to the increasing of temperature owing to the dissolution of oxygen beneath the oxide layer [13]. Thus, the superior hardness values were kept for samples which are treated at higher oxidation temperature. This shows that the deeper hardened layers were attained at high oxidation temperature. In other words, this confirms that this process is appropriate for improving the hardness of the surface.

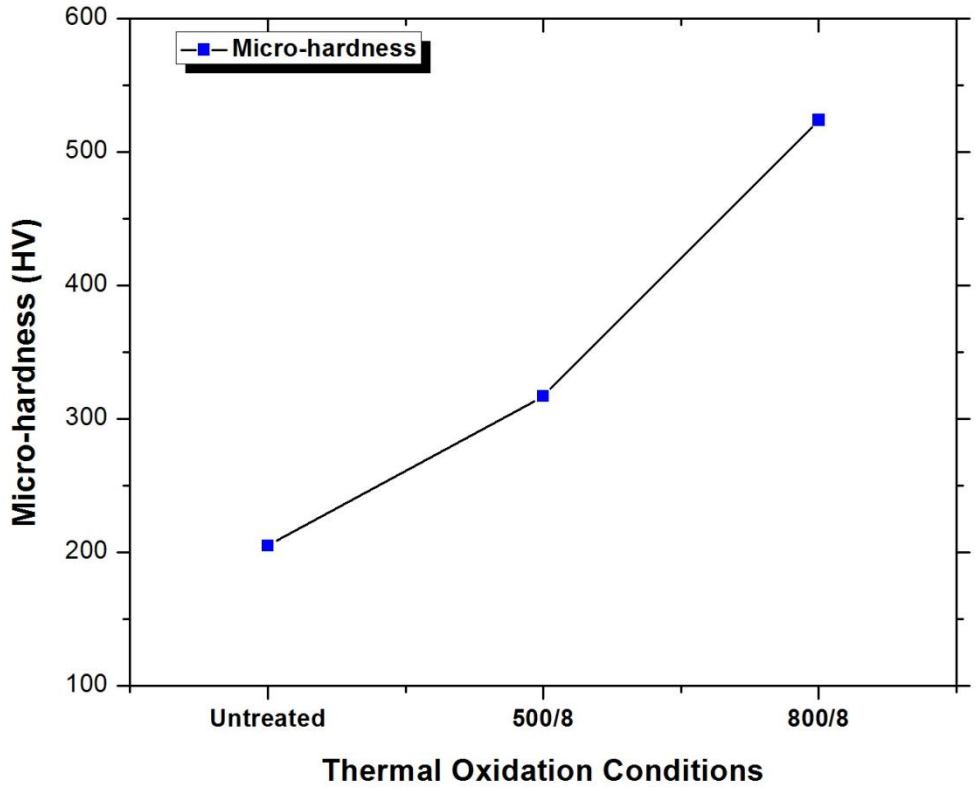

Fig. 2. Micro-hardness of untreated, oxidized at 500°C for 8 h (500/8) and at 800°C for 8 h (800/8) CP-Ti samples.

Fig. 3 shows the values of open-circuit potential (OCP) of the untreated and oxidized Cp-Ti samples as a function of time until the steady state was attained. The figure shows the effect of thermal oxidation process conditions on the steady state OCP of CP-Ti samples.

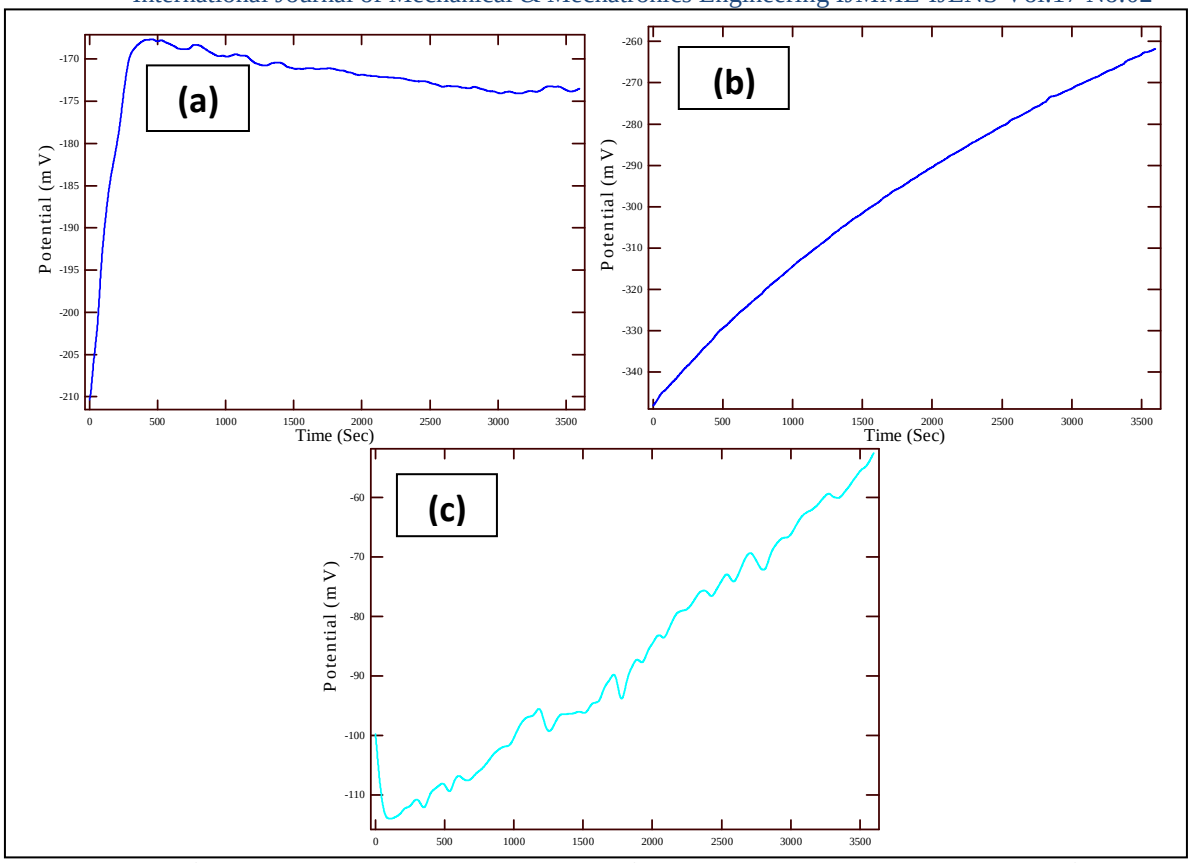

Fig. 3. OCP vs. time curves of the (a) untreated, (b) thermally oxidized at 500ºC for 8 h (500/8) and (c) thermally oxidized at 800ºC for 8 h (800/8) CP-Ti samples

It can be indicated from Fig. 3 that the 800/8 samples show the nobler behavior in contact with a 0.9% NaCl solution comparing with untreated and 500/8 samples . In the present work, the untreated samples revealed a substantial decrease in OCP with comparing to 800/8 and 500/8 samples. On the other hand, both 800/8 and 500/8 samples exhibited strong trend to shift toward noble direction as a result of formation strong and continuous oxide layers on their surface. However, 800/8 samples showed the larger trend to form spontaneous oxide layer in 0.9% NaCl solution.

Fig. 4 presents the potentiodynamic anodic polarization plots of the untreated, 500/8 and 800/8 CP-Ti samples in 0.9% NaCl solution in −750 mV to +2500 mV vs. saturated calomel electrode (SCE) with respect to OCP. This higher anodic potential (+2500 mV vs. SCE) was selected to detect the effect of oxidation process and accordingly the oxide film thickness and its effect on the passivity.

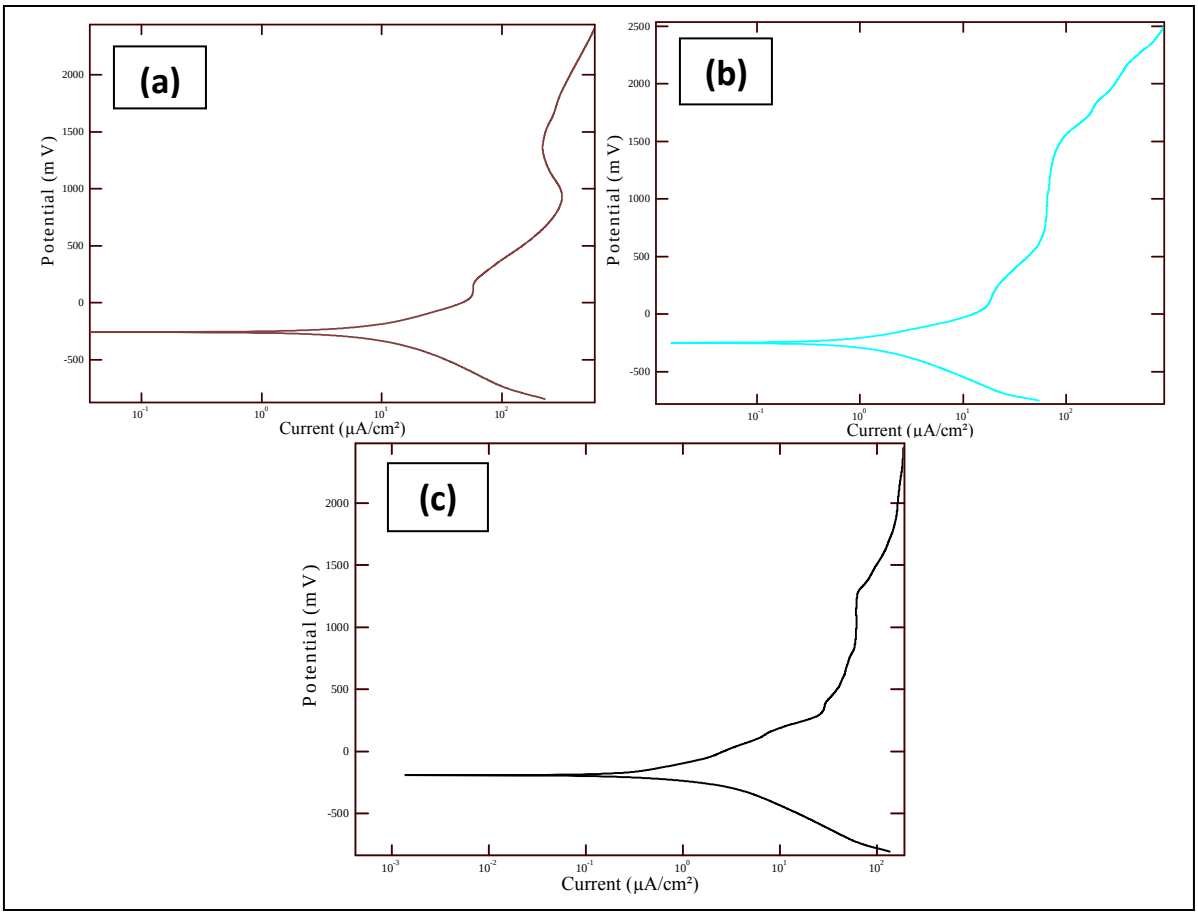

Fig. 4. Potentiodynamic anodic polarization plots of the (a) untreated, (b) thermally oxidized at 500 ºC for 8 h (500/8) and (c) oxidized at 800 ºC for 8 h (800/8) CP-Ti samples

Tafel curves in Fig. 4 reveals the typical active–passive characterization in all investigated CP-Ti samples. The electrochemical behavior transforms directly into the passive region after continuous increase of the anodic current with the potential. The passive current densities for investigated CP-Ti samples remained constant with increasing potential as a result of the thickening of their passive layers [14, 15]. However, polarization plots of thermally oxidized samples showed transferring of the active plot towards lower current density region. This obviously indicates the effect of the thermally formed oxide film to enhance the corrosion behavior.

The average E_{corr} can be obtained from the polarization curves as -258.98, -249.81 and -191.31 mV (vs. SCE) for untreated, 500/8 and 800/8 samples, respectively. It can be seen that the oxidized samples show a shift in E_{corr} towards the noble direction (from -258.98 to -191.31 mV vs. SCE). Also, Fig. 4 clearly indicates that the 500/8 samples have further decrease in E_{corr} comparing with that of the 800/8 samples. Moreover, the mean I_{corr} and corrosion rates were obtained using Tafel extrapolation analysis technique. The equivalent corrosion data of untreated, 500/8 and 800/8 CP-Ti samples are summarized in Table 2. A considerable decrease in I_{corr} (from 4.145 to 1.4105 μA/cm^2) and corrosion rate (from 3.2441 to 1.103 mils/yr) was obtained in oxidized samples compared to that of untreated samples. In other words, the degree of decrease in I_{corr} and corrosion rate enlarges with increasing the oxidation temperature from 500 to 800 °C (Fig. 4 and Table 2). This indicates that the surface layer formed on the 800/8 samples is more compact and protective owing to increasing in the thickness of oxide layer. The oxide film acts as a barrier or obstruct to pass higher current for additional chemical reactions of CP-Ti samples in the biofluid. Therefore, the I_{corr} of 800/8 samples is about 3 times lower comparing with that of untreated samples.

Table II
Electrochemical parameters of the untreated and thermally oxidized CP-Ti samples.

Sample No.	E_{corr} (mV)	I_{corr} (μA/cm^2)	Corrosion rate (mils/yr)
Untreated	-258.98	4.145	3.2441
500/8	-249.81	3.2	2.6053
800/8	-191.31	1.4105	1.103

The better corrosion behavior of various thermally oxidized biomedical Ti materials in simulated body fluid is confirmed by several investigations [7, 8, 16-20]. Further confirmation is achieved through this research about the truth of improvement the corrosion characteristics of CP-Ti samples due to the effect of TO process. Based on the present study, the electrochemical enhancements of the untreated and oxidized CP-Ti samples can be ranked as follows: CP Ti (800 °C) > CP-Ti (500 °C) > untreated CP-Ti.

4. CONCLUSIONS

On the basis of the study conducted, followings are the main conclusions:

1. The surface morphology of the oxidized samples at 500 ºC and 800 ºC for 8 h reveals surface oxide scales without spallation.
2. The development in the surface morphology varies from a thin and smooth surface oxide scale along with a few nodular oxide particles at 500 ◦C to entirely covered surface oxide scales at 800 ◦C.
4. TO process at 800 ºC for 8 h introduces a considerable enhancement in micro-hardness compared to that of samples oxidized at 500 ºC. Approximately a three-fold increase in micro-hardness is achieved for samples oxidized at 800 °C compared to that of untreated samples.
5. The E_{corr}, I_{corr}, and corrosion rate of the oxidized samples show a strong dependence on the nature and thickness of the surface oxide film. The above corrosion values of the samples oxidized at 800 °C are more nobler compared to that of untreated samples and oxidized samples at 500 °C. This suggests that the oxide layer formed on 800/8 samples is more compact and protective than in untreated and 500/8 samples.
6. The present study clearly shows that the thermally oxidized CP-Ti at 800 °C for 8 h offered superior corrosion behavior and hence, it is a potential candidate for biomedical applications. However, additional studies for addressing many aspects of the mechanical/tribological characteristics and biocompatibility as well, are an imperative to identify its overall potential for this application.

5. REFERENCES

[1] Long, M. & Rack. H.J. Titanium alloys in total joint replacement – A materials science perspective. Biomaterials 1998;19 1621-1639.
[2] Hanawa, T. Recent development of new alloys for biomedical use. Mater. Sci. Forum 2006, 512, 243–248.
[3] Lütjering, G.; Williams, J.C. Titanium, 2nd ed.; Springer: Berlin, Germany, 2003; pp. 20–22.
[4] Mohsin T.M., Zahid A.K., Arshad N.S. (2014) 'Beta titanium alloys: the lowest elastic modulus for biomedical applications: a review', International Journal of Chemical, Nuclear, Metallurgical and Materials Engineering, 8(8), pp. 726-731.
[5] Donachie M.J. Titanium: A technical guide. ASM International 2000.
[6] López M.F., Gutiérrez A., García-Alonso M.C., Escudero M.L., J. Mater. Res. 13 (1998) 3411.
[7] Kumar Satendra, Sankara Narayanana T.S.N., Ganesh Sundara Ramanb S., Seshadri S.K. (2010) 'Thermal oxidation of Ti6Al4V alloy: Microstructural and electrochemical characterization', Materials Chemistry and Physics 119, pp. 337–346.
[8] Jamesh M., Sankara Narayanan. T.S.N. and Paul Chu K. (2013) 'Thermal oxidation of titanium: Evaluation of corrosion resistance as a function of cooling rate', Materials Chemistry and Physics, 138, pp. 565-572.
[9] Guleryuz H., and Cimenoglu H. (2005) 'Surface modification of a Ti-6Al-4V alloy by thermal oxidation' Surf. Coat. Technol. 192(2-3), pp. 164-170.
[10] Siva Rama Krishna D., Brama Y.L. and Sun Y. (2007) 'Thick rutile layer on titanium for tribological applications', Tribol. Int., 40, pp. 329-334
[11] Jamesh M., Kumar S. and Sankara Narayanan T.S.N. (2012) 'Effect of thermal oxidation on corrosion resistance of commercially pure titanium in acid medium', J. Mater. Eng. Perform. 21(6), pp. 900-906.
[12] Yan W. and Wang X.X. (2004) , J. Mater. Sci. Lett. 39 5583.
[13] Borgioli, F., Galvanetto, E., Galliano, F.P. and Bacci, T. (2001) 'Air treatment of pure titanium by furnace and glow-discharge processes', Surface and Coatings Technology, 141(1), pp. 103–107.
[14] Ikeda M., Komatsu S.Y., Sowa I., et al., Aging behavior of the Ti–29Nb–13Ta– 4.6Zr new beta alloy for medical implants, Metall. Mater. Trans. A 33 (2002) 487–493.
[15] Mohsin Talib Mohammed, Zahid A. Khan, Geetha M., Arshad N. Siddiquee, Microstructure, mechanical properties and electrochemical behavior of a novel biomedical titanium alloy subjected to thermo-mechanical processing including aging, Journal of Alloys and Compounds 634 (2015) 272–280.
[16] Garcia-Alonso MC, Saldana L, Valles G, Gonzalez-Carrasco JL, Gonzalez-Cabrero J, Martinez ME, et al. In vitro corrosion behaviour and osteoblast response of thermally oxidised Ti6Al4V alloy. Biomats 2003;24:19–26.
[17] Guleryuz H, Cimenoglu H. Effect of thermal oxidation on corrosion and corrosion–wear behaviour of a Ti–6Al–4V alloy. Biomats 2004;25:3325–33.
[18] Satendra Kumara, T.S.N. Sankara Narayanana, S. Ganesh Sundara Ramanb, S.K. Seshadri , Thermal oxidation of CP Ti — An electrochemical and structural characterization, Materials Characterization 61 (2010) 589–597.
[19] E. Arslan, Y. Totik, E. Demirci, and A. Alsaran, Influence of Surface Roughness on Corrosion and Tribological Behavior of CP-Ti After Thermal Oxidation Treatment, JMEPEG (2010) 19:428–433 DOI: 10.1007/s11665-009-9504-9.
[20] Ming Wen, CuieWen, PeterHodgsona, YuncangLi, Improvement of the biomedical properties of titanium using SMAT and thermal oxidation, Colloids and Surfaces B: Biointerfaces 116 (2014) 658–665.