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The Influence of Thermal Oxidation on Hardness and Microstructure of Beta-Type Titanium Alloy Ti-29Nb-13Ta-4.6Zr (TNTZ)

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ABSTRACT

Thermal oxidation is one of the simple and low-cost methods that can improve tribological characteristics of titanium and its alloys by generating a protective layer on their surfaces. In this study, the experiment parameters were applied on thermal oxidation (TO) at 598, 673 and 723K for 40, 50 and 60s on TNTZ. The micro-Vickers hardness tests and microstructure analysis were performed for specimens before and after TO. The results exhibited that the hardness of TNTZ was increased by increasing TO temperature, but it was decreased by enlarging of TO time. Metallographic tests showed that oxidised TNTZ have equaxial β grains with a grain size approximately about 20-30μm. No significant change of microstructure (grain size) was detected after increasing TO temperature because the short time oxidation process was applied.

1. Introduction

Nowadays, the demand of biomaterials is continue increase due to the enlarge population of aged people. Biomaterials are widely used as artificial materials for any biomedical applications, such as: joint replacements in hips, shoulders and knees, bone cement, artificial ligaments and tendons, bone plates, blood vessel prostheses, contact lenses, stents in blood vessels, heart valves, artificial tissue, breast implants, and dental implants [1-3]. Among them, it is predicted that the number of hip replacements and knee arthroplasties will be risen significantly by the end of 2030 [4]. Biomaterials are employed for implant applications in purpose to enhance the quality and longevity of human life.

Titanium is assigned as one of the most favourable biomaterials in medical field due to its superior properties in strength, high corrosion resistance and high biocompatibilty [5-9]. The superior

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biocompatibility and excellent corrosion resistance of titanium and its alloys are caused by their spontaneous formation of passive layers. It is known that a natural oxide layer plays an important part in biocompatibility and it can minimize the penetration of ions of alloying elements to the human body. The commercially pure titanium (cp Ti, grade 2) and Ti-6Al-4V (grade 5) alloy are mostly applied materials in biomedical field especially for hard tissue replacements in artificial bones, joints and dental implants because they have low elastic modulus that can produce smaller stress shielding.

Recently, it has been introduced β-phase titanium alloys, such as Ti-29Nb-13Ta-4.6Zr (TNTZ) for implant biomaterials which have lower Young's modulus values (50 GPa) than Young's modulus for the α or (α+β)-phases titanium alloys (105–165 GPa) [10-12]. The value of Young's modulus of TNTZ is close to the human bone and it is expected to defeat the bone resorption problem because of stress shielding effect. Various β-phase titanium alloys have been designed for orthopedic applications [13,14]. However, because their natural passive layers on the surface are very thin about 3-10 nm which consist of metal oxides (ceramic films), they do not establish suitable level of resistance to tribological properties, which restrict the wider application of titanium in medicine [15-18]. The poor tribological properties of β-phase titanium produces a high and unstable coefficient of friction [19]. Therefore, the surface treatment are necessary applied to β-phase titanium alloys that purpose to improve their near-surface strength, hardness and tribological properties by fabricating. The composition structure and thickness of the film are signicant factors which determined the stability of the oxide [20].

Current research has been pointed on the formation of surface layer covering a base metal that exhibit good properties of physical, chemical dan mechanical [21]. Thermal oxidation is one of the facile ways which can improve the poor tribological properties of titanium and its alloys by generating a thick and hard protective layer on the surface [22-24]. Temperature and time are predominant parameters for thermal oxidation process to attain the excellent TiO_2 (titanium dioxide) layer. Thermal oxidation is performed at high temperature ranged from 400°C to 1100°C that affected by dry gases without an electrolyte usage [25-28]. Thermal oxidation applied at temperature above 800°C for long period will produce an adequate thickness layer, but they are brittle [29,30]. On the other hand, too thin oxide layer will be formed when apply the lower oxidation temperature for short oxidation period; thus it is unsufficient for tribological applications. So, medium temperature of thermal oxidation is recommended to provide a sufficient thickness layer.

There are several forms of created layers crystallographic constructed during oxidation process, such as: anatase, rutile and brucite [31]. The crystalline layers (mainly based on rutile) which produced during thermal oxidation of titanium alloys can enhance their hardness, corrosion and wear performance (tribological properties) and biocompatibilty [27].

This work aims to evaluate the hardness and microstructural performance of TNTZ developed by thermal oxidation at 598, 673 and 723K in an air ambient atmosphere for 40-60s.

2. Methodology

Experimental methodologies are shown in a flowchart in Figure 1. Metkon manufactures the Manual Abrasive Cutting Machine type Metacut 250 and the Polishing & Grinding Machine type Forcipol 2V, both of which are utilized for preparing samples. Heating ovens and furnaces are used for the characterization of experimental samples. The hardness test is performed using a Microhardness Tester type FM-300 by Future Tech, and the surface microstructures are analyzed using a Metallurgical Microscope type M17100 by Meiji Techno.

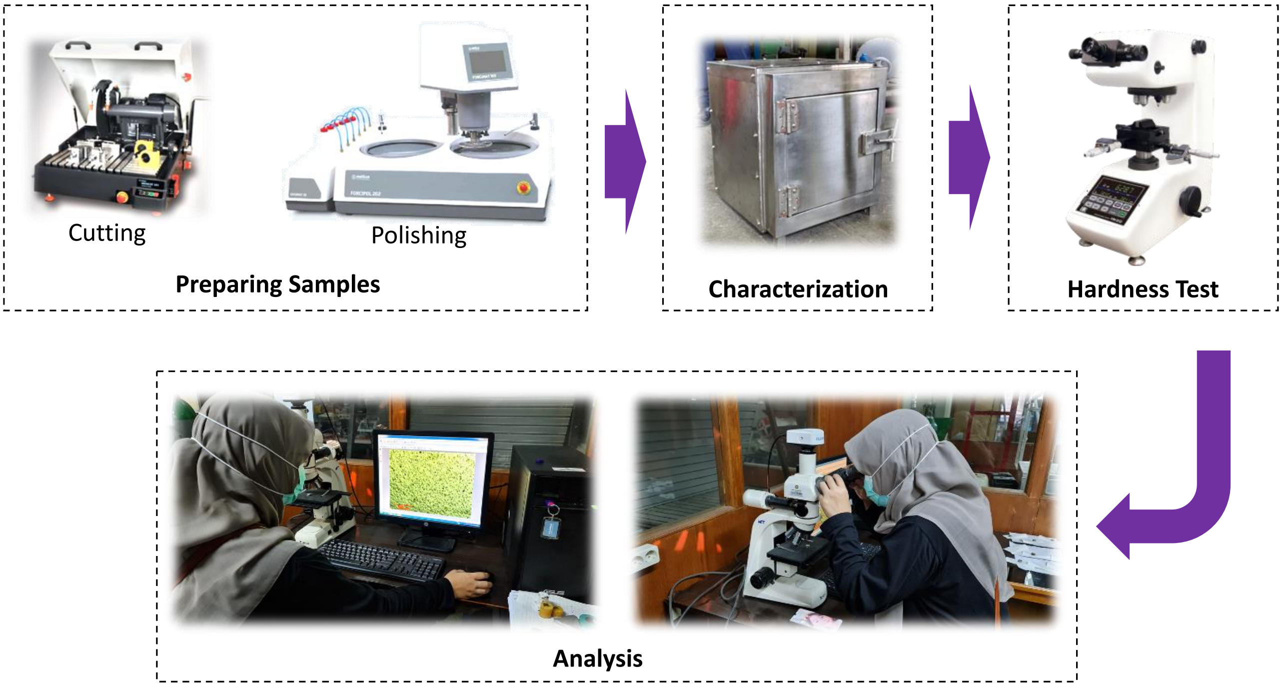


Fig. 1. Flowchart of experiments

Samples shapes made from Ti-29Nb-13Ta-4.6Zr are used to characterize the mechanical properties and evaluate the optical microstructures before and after thermal oxidation. Rods with dimension of 15 mm in diameter and a length of 5 mm were used for hardness measurement and observation of the optical microstructures. The chemical composition of TNTZ is shown in Table 1.

Table 1
Chemical composition of Ti-29Nb-13Ta-4.6Zr (TNTZ), mass %

Ti	Ta	Zr	Fe	C	N	O	Nb
Bal.	12.2	4.3	0.05	0.02	0.04	0.10	29.2

Pretreatment was performed on the specimen's surface before thermal oxidation, to make it appropriate for mechanical properties and metallography examinations. In the beginning, the specimen surface was abraded by emery paper from 300 to 2000 grits followed by acetone bath. Then, the surface of the specimen was continued mechanically polished using the diamond paste with grain size 2 and 1 micrometer until the mirror-like surface provided. A mirror-like surface is suitable for accurate hardness and microstructural measurements. By existing of atmospheric air, thermal oxidation was conducted in a chamber furnace at 598, 673 and 723K (325°, 400° and 450°C) for an oxidation period of 40-60s. After reached the specified temperature, specimens were taken out from the furnace and then cooled in air. The morphology of oxide layers was subjected to X-ray phase analysis by XRD and microhardness measurements. The diffractograms were obtained using the Bruker D8 Advance diffractometer with Cu-tube operated at 40 kV/35 mA, 250 mm goniometer radius, 2.5 deg Soller slit (primary and secondary) and 1-D LYNXEYE-XET detector without $K\beta$ filter. The data were acquired at a 2θ range of 30°–100°, with a step size of 0.02°, using an automatic Divergence slit to have a fixed area illumination of the sample. The Rietveld refinement was carried out with Bruker-Topas v.6 implemented with a convolution-based profile adjustment/fundamental parameters approach (FPA), which provides high accuracy and precision in determining lattices and structure parameters [32-34]. The micro-Vickers hardness was evaluated using a micro-Vickers tester with a load of 1.96N (200gf). An Optical Microscope analyzed the surface microstructures of the oxidized specimens on the specimens etched by HF 5% for 20 s.

3. Results

3.1 Surface Hardness Measurements

The oxidation temperature and duration (time) of the oxidation process are two important parameters that influence the value of surface hardness. Referring to previous research, by oxidizing at temperature above 800°C, the oxide layer produced on the titanium surface get more brittle and splint out from the surface [30]. Therefore, the hardness measurement in this study was carried out for a sample that at oxidation temperature of 300°-450°C. Oxidation time and temperature show their effects on surface hardness, as displayed in Figure 2. In the beginning, the value of surface hardness observed for non-oxidised titanium substrate is determined as 189.3 Hv. After thermal oxidation, the titanium surface is distinguished by larger hardness. As shown in Figure 2, the surface hardness of TNTZ increase with the increasing of the oxidation temperature. The highest hardness is detected at the highest oxidation temperature of 723 K for the 50s of oxidation time. The high hardness value for the oxidised surface is due mainly to the formation of an oxide phase layer. The homogeneous and uniform oxide layer can be provided at the high oxidation temperature.

The elavated oxidation temperature involves a low molecular density; due of the distance between atoms is quite distant. In this condition, the interaction between atoms or molecules becomes small because the attraction between molecules is very low, this causes the molecular bonds to break and become charged ions, namely free radicals. These charged molecules react easily due to the instability of their charge. These radical ions will form new bonds when they meet with other ions to form a new equilibrium [35]. This circumstance can be seen in the oxidation process of titanium.

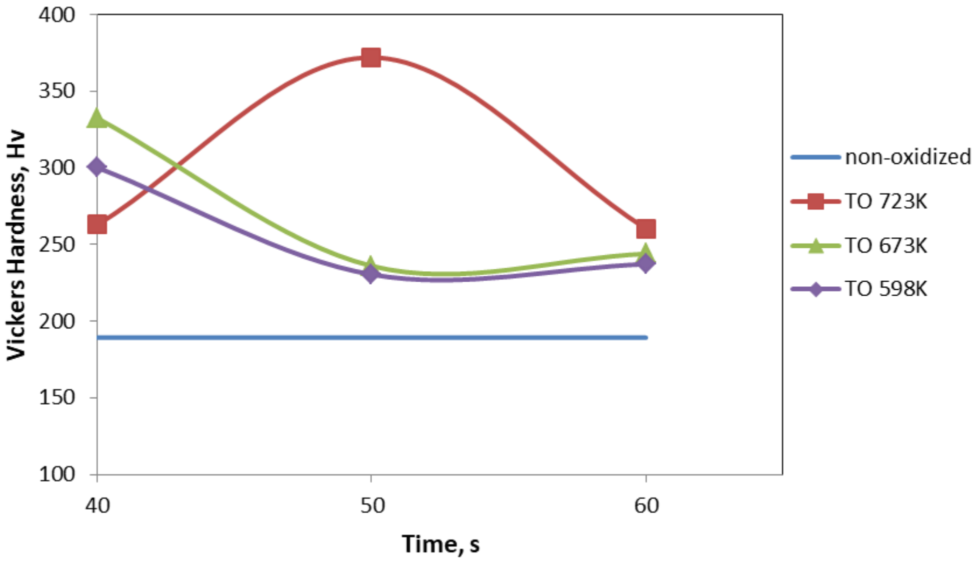


Fig. 2. Difference in surface hardness with oxidation variables (temperature and time) before and after oxidation process of TNTZ

High temperature oxidation of microstructured surfaces also affects the thermal radiation characteristics. During the heat transfer state, the temperature boundary layer thickness increase with large values of thermal radiation and temperature ratio [36,37]. Therefore, the mass of oxygen become enlarge and it reacts with the titanium surface to promote the formation of a titanium oxide

(TiO_2) layer. The surface thermal radiation properties of high-temperature metal oxides are also important in high temperature applications.

Figure 2 also displays a different trend of hardness during the time of thermal oxidation. The hardness of oxidised samples tends to be decreased for 598K and 673K, except for 723K of oxidation temperature when the time of oxidation increased. Differed to the both temperatures, at 723K, the hardness becomes larger when the time of oxidation is prolonged to 50s, but it reduces again after that time. This result is not similar with the previous study, which detected that the surface hardness is enlarged when the oxidation time is increased [38]. The short-time period of the oxidation process might lead to the reduction of hardness value because the oxide layers obtained at lower temperatures and shorter times are not sufficiently thick (too thin) for use in specific tribological applications. Therefore, the value of hardness is not distinguished correctly. The drop in hardness line is also probably due to the significant measurement errors are appeared as a result of small indent size for small loads [38]. From above results, it confirms that temperature plays a more critical role than oxidation time in the growth of oxide layers and thereby has a more significant influence on the thickness of the layers formed [39]. A similar conclusion is also stated by Wang *et al.,* [40].

Figure 3 shows the diffraction pattern of beta (β)-Ti with an impurity phase of KCl and a tiny rutile peak that can only be seen in the inset figure. The β-Ti is identified and refined with ICDD PDF No. #04-003-7272 (cubic crystal system and space group of Im-3m), while the rutile phase is refined with #04-002-2667 (tetragonal crystal system and space group of P42/mnm), and KCl is refined with #04-015-4079 (cubic crystal system and space group of Pm-3m). The intensity of the rutile (101) peak looks with the increase of oxidation time, which is also confirmed by the Rietveld refinement result as shown in Table 2. The rutile phase's weight percentage (wt%) is 0.87, 1.32 and 1.68, respectively, corresponding to 40, 50 and 60-sec of oxidation time. From this evidence, it can be said that the cause of the highest hardness on the surface of oxidised samples at the temperature of 723K is due to the higher rutile peak revealed. In addition, any previous research noticed that more intensive growth of the oxide phase occurred at a higher temperature using analysis of kinetic curves [41]. The oxidation kinetics influence the properties of oxide layer [42,43].

Table 2
Quantitative phase analysis result

	ICCD PDF card no.	Quantitative (wt%)		
		40 Sec	50 Sec	60 Sec
β-Ti	04-003-7272	98.92(2)	98.51(1)	98.01(2)
Rutile	04-002-2667	0.87(3)	1.32(5)	1.68(4)
KCl	04-015-4079	0.21(2)	0.17(2)	0.31(3)

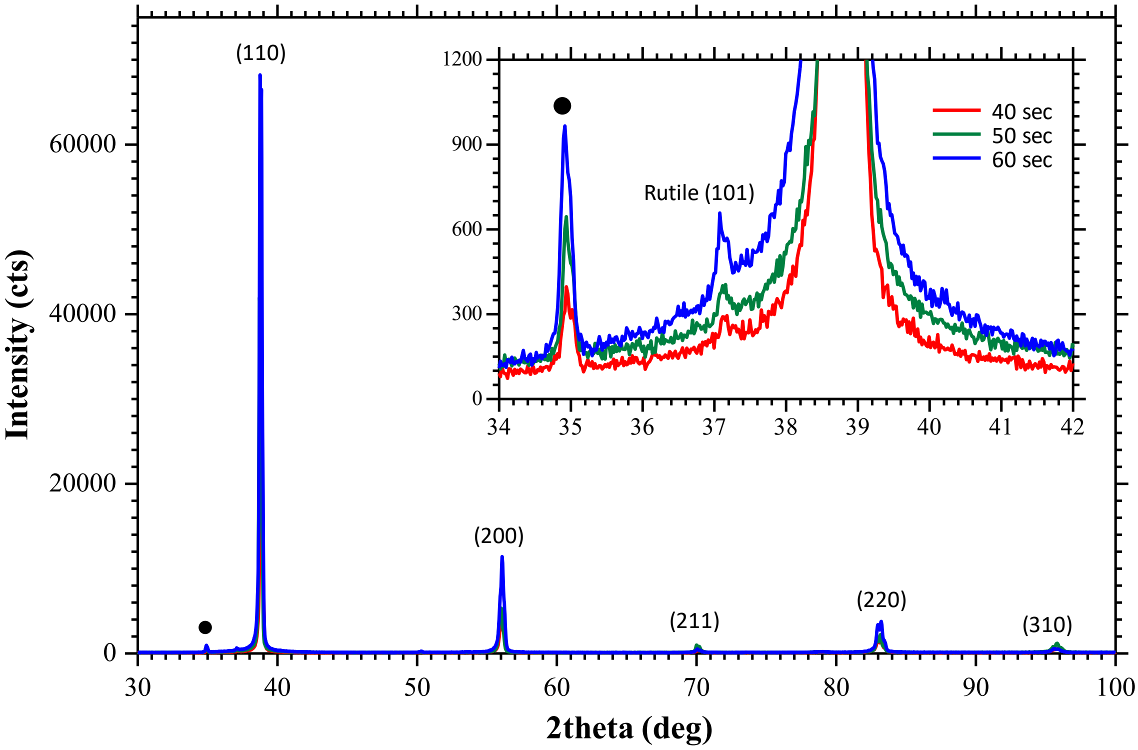


Fig. 3. XRD patterns were obtained for an oxidized 40, 50, and 60-second at temperature 723K. Inset is the region where the Rutile (101) peak is prominent. (Black dot – KCl)

3.2 Microstructure Observations

Figure 4 and Figure 5 show the morphology of TNTZ samples before (Figure 4) and after (Figure 5) oxidation at various temperatures and times. Microscopic metallographic examinations showed that the as-delivered TNTZ was characterised by a β grain structure (Figure 4).

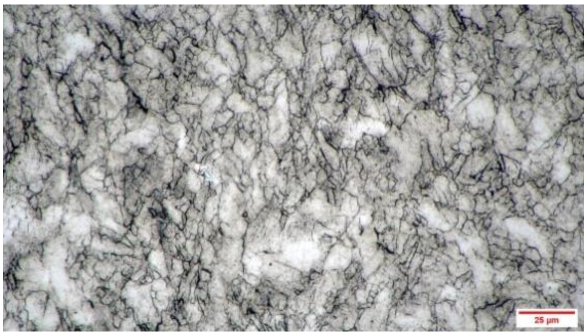
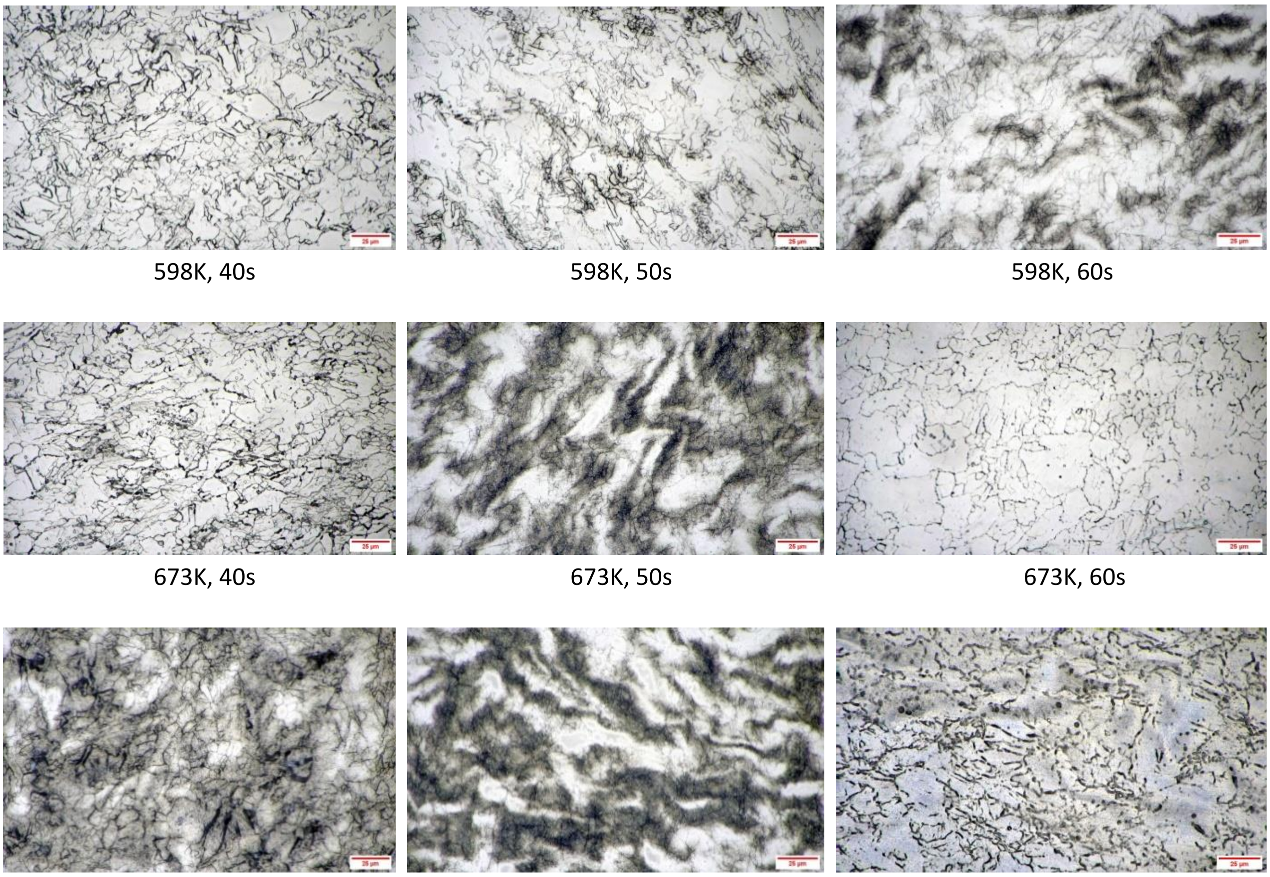


Fig. 4. Microstructure of TNTZ sample before the oxidation process



598K, 40s

598K, 50s

598K, 60s

673K, 40s

673K, 50s

673K, 60s

723K, 40s

723K, 50s

723K, 60s

Fig. 5. Variation in microstructure with oxidation parameters (temperature and time) for oxidised TNTZ

The microstructural characteristics of the alloy are significantly affected by the cooling environment. Figure 5 shows the oxidized specimens cooled in air mainly comprise equaxial β grains with an average diameter range of approximately 20-30µm. No apparent microstructural change can be seen near the surfaces for each oxidation temperature. One of the reasons is that the oxidation process in this research was applied in the short-time period.

4. Conclusions

In this reserach, thermal oxidation of pure titanium was performed at temperatures of 598K, 673K and 723K for oxidation time of 40s, 50s and 60s at each temperature. The hardness of TNTZ is improved by thermal oxidation temperature. The highest hardness is noticed at an oxidation temperature of 723K for the 50s. It is probably because the thickest oxide layer is detected at oxidation time of the 50s, which is proved by the highest peak of rutile. The microstructures of oxidised TNTZ samples for varying temperatures are contained by the equaxial β phase with grain size approximately about 20-30 µm.

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