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An investigation into the effect of Triode Plasma Oxidation (TPO) on the tribological properties of Ti6Al4V

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ABSTRACT

Improving the tribological properties of titanium alloys has been the subject of extensive research for many years. A number of thermochemical processes have been developed for that purpose. In this study, surface hardening of Ti6Al4V is achieved by Triode Plasma Oxidation (TPO) which differs from conventional diode plasma treatments through the use of a third electrode; a negatively biased tungsten filament to enhance the ionisation levels in the plasma. The resultant surface generally consists of a top oxide layer with an oxygen diffusion zone lying immediately underneath it. The effects of process parameters such as substrate temperature, current density and oxygen partial pressure have been investigated. Surface hardness measurements at various indentation loads were carried out to assess the changes in hardness with depth across the diffusion layer. The hardness profiles obtained confirmed the gradual decrease in hardness with treatment depth and provided an indication of the thickness of the hardened layer produced. Ball-on-plate reciprocating sliding wear data and glancing angle XRD analyses of the oxidised samples are also presented. The results indicate that a harder and deeper case is achieved at both high substrate temperature and high oxygen partial pressure. Furthermore, XRD data show that the substrate temperature strongly affects the structure of the oxide layer produced. All TPO-treated samples exhibit significantly better wear performance compared to the untreated material.

1. Introduction

Titanium and its alloys are widely used in many industries as they possess a range of desirable properties such as high specific strength, low density, good corrosion resistance and excellent biocompatibility [1]. However their use in engineering applications has been severely restricted over the years due to poor tribological properties. To overcome this problem and improve the wear and friction characteristics of titanium alloys, a range of diffusion-based treatments has been extensively investigated [1,2]. Among them, oxidation processes in particular have attracted much interest due to the high solubility of oxygen in titanium. Processes such as thermal oxidation, plasma immersion ion implantation, plasma electrolytic oxidation and plasma oxidation [1–4] have been used to harden the surface of titanium alloys. Nitriding of titanium alloys has also been extensively investigated, although recent work demonstrated that thermal oxidation exhibits better wear performance [5]. The widely used thermal oxidation treatment, which generally takes place in air, or, in a mixture of argon and oxygen, is proven as a simple and effective way of improving the wear properties of titanium by generating a hardened oxygen-rich layer on its surface [3,5–7]. The oxidised surface actually consists of a thin, hard (but often poorly adhered) top oxide layer with an oxygen diffusion zone lying underneath it. Subsequent work in this field has attempted to increase the thickness of the diffusion layer by following the thermal oxidation process with a boost diffusion treatment in vacuum [8,9]. However, in order to generate a thick oxygen-rich layer on the surface of titanium alloys, components must be oxidised for several hours at high temperatures, typically in the range of 600–900 °C [5,6]. In recent years, plasma oxidation treatments of titanium alloys have been investigated with the aim to generate an oxide layer with much improved properties. Borgioli has shown that, for the same treatment time, the hardened layer produced during plasma oxidation of pure titanium [10] and Ti6Al4V [11] is thicker and possesses superior mechanical properties compared to the oxide layer generated by conventional thermal oxidation processes. The marked increase in surface hardness as a result of plasma oxidation leads a reduction in the wear rate of the titanium alloy [12,13], hence improving its tribological performance.

In the present study, Ti6Al4V alloys were subjected to Triode Plasma Oxidation (TPO) which differs from conventional plasma oxidation processes through the use of a heated tungsten filament as a third electrode which, when negatively biased, can enhance the degree of ionisation in the plasma through electron impact ionisation effect. The significant increase in ionised species in the glow discharge leads to an increase in the number of oxygen ions bombarding the substrate surface which

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Table 1
TPO process conditions. For each set of experiments, investigated process parameters are highlighted in bold.

	Temperature (°C)	Gas composition (% O_2)	Current density (mA/cm^2)
TPO experiment 1	**600**	35	1.5
	650	35	1.5
	700	35	1.5
TPO experiment 2	700	**26**	1.5
	700	**56**	1.5
	700	**69**	1.5
TPO experiment 3	700	30	**0.5**
	700	30	**1.5**

enables the formation of a dense, well-adhered compound layer at significantly reduced processing time. The effects of key process parameters, such as substrate temperature, oxygen partial pressure and current density, on the mechanical and structural properties of TPO-treated Ti6Al4V samples are described in this paper.

2. Experimental

Ti6Al4V test discs (Ø30 mm × 3 mm) were subjected to Triode Plasma Oxidation treatments in a Tecvac IP70 PVD machine. The test discs, polished to a mirror finish ($R_a = 0.04 \pm 0.01$ μm), were received in the annealed condition with a bulk hardness of 3.43 ± 0.1 GPa. Prior to diffusion treatment, a sputter cleaning step was performed in an argon diode plasma at 2 Pa pressure and −1000 V substrate negative bias, to remove all impurities from the surface of the samples. During TPO, a D.C. glow discharge was generated by negatively biasing the workpiece (Ti6Al4V test discs and holding fixtures) at −200 V with respect to the chamber walls. A hot tungsten filament (also biased at −200 V) was used to provide plasma enhancement by thermionic electron emission. A constant cathode current density was maintained throughout the diffusion process by adjusting the A.C. heating current passing through the tungsten filament. All TPO treatments were carried out for 4 h in a gas mixture of argon and oxygen to a total pressure of 0.4–0.5 Pa. As detailed in Table 1, three sets of experiments were performed varying a number of process parameters:

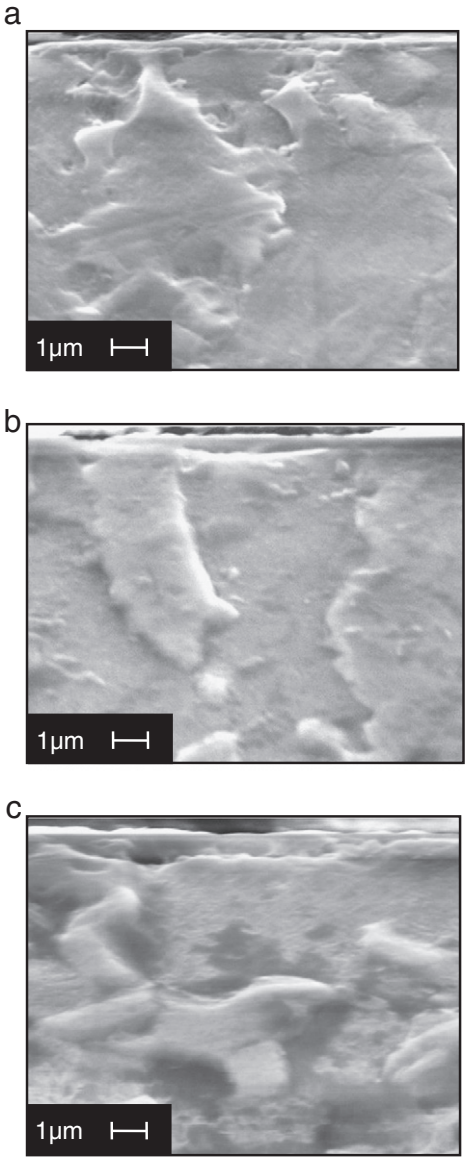

Fig. 1. SEM photomicrographs (×10,000) of polished and etched (in H_2O_2 + KOH) cross-sections of TPO-treated samples showing the oxide layer formed after TPO at a) 600 °C, b) 650 °C and c) 700 °C.

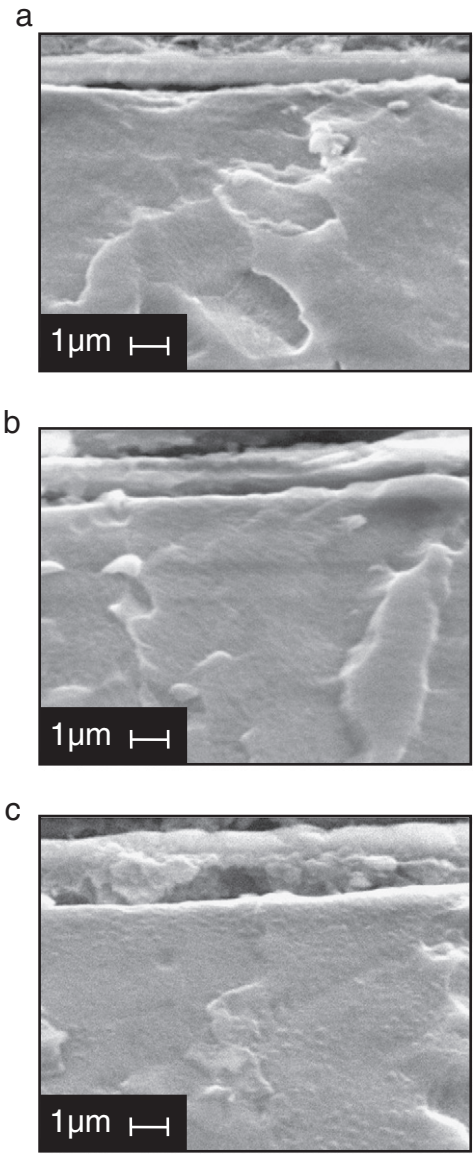

Fig. 2. SEM photomicrographs (×10,000) of polished and etched (in H_2O_2 + KOH) cross-sections of TPO-treated samples showing the oxide layer formed after TPO using a) 26% O_2, b) 56% O_2 and c) 69% O_2.

substrate temperature, oxygen content in the gas mixture and current density.

The oxide layer formed was examined under the scanning electron microscope (SEM) for selected TPO-treated Ti6Al4V samples. Glancing angle X-ray diffraction (GAXRD) analysis was performed on untreated and TPO-treated Ti6Al4V test discs, using a Siemens D5000 diffractometer with CuKα radiation (λ = 0.154056 nm, tube voltage = 40 kV, current = 30 mA). The diffraction angle (2θ) was in the range of 20 to 60° with a step size of 0.02° and grazing incidence angles of 2° and 6°. The surface hardness of treated test discs was measured at various indentation loads (ranging from 0.245 N to 9.81 N) and Knoop microhardness measurements were carried out on polished cross-sections under a load of 0.245 N to evaluate the changes in hardness with depth of the diffusion layer. Ball-on-plate reciprocating sliding wear tests were carried out to assess the tribological properties of treated samples. The wear tests were performed without lubrication, using a 10 mm diameter WC–Co ball, run at a frequency of 5 Hz, speed of 0.1 ms^{-1} and a stroke length of 10 mm. An applied test load of 4 N was used throughout. For each TPO-treated sample, the average volume loss was measured as a function of the sliding distance travelled using a Veeco Dektak 3^{ST}stylus profilometer. The average wear volume loss was obtained from at least 3 wear tests performed at a given sliding distance. Scratch tests were performed using a CSM Revetest scratch tester on a selected TPO-treated sample to evaluate the adhesion of the oxide layer to the titanium alloy substrate. The tests were carried out at a loading rate of 10 N mm^{-1}, using a diamond indenter of radius 0.2 mm. The average critical load at which the oxide layer is completely removed from the scratch channel was recorded from a set of 3 scratches made on the TPO-treated sample. The scratch tracks were subsequently examined under a Carl Zeiss SEM (EVO MA25) with LaB6 source.

3. Results

3.1. SEM analysis of TPO-treated samples

SEM photomicrographs of the oxide layer were obtained for each TPO treatment performed in experiments 1 and 2 (Table 1). It is clear from the images that a dense, thin oxide layer was generated in all cases. As shown in Fig. 1, increasing the substrate temperature caused an increase in the thickness of the oxide layer generated. Thicknesses in the range of 0.1–0.2 μm at 600 °C, 0.2–0.3 μm at 650 °C and 0.7–0.8 μm at 700 °C were measured. A similar effect was observed when the oxygen content was progressively increased during experiment 2. The oxide layer thickness was found to be around 0.8 μm when the oxygen concentration was set at 26% by partial pressure, increasing to 1.2 and 1.7 μm when 56 and 69% oxygen were respectively used (Fig. 2).

3.2. XRD results

Glancing angle XRD analysis of the TPO-treated samples revealed that, at a given oxygen concentration (35% O_2 in this case), the structure of the oxide layer changed with increasing substrate temperature (Fig. 3). The oxide layer generated at 600 °C consisted of a mixture of the Anatase and Rutile TiO_{2-x} polymorphs. Although these two phases were still present at 650 °C, there was a noticeable increase in the intensity of Rutile peaks which suggested that this phase was more abundant than at 600 °C. At 700 °C, the oxide layer was characterised by the absence of Anatase peaks with only the Rutile phase remaining. A slight shift in the α-Ti peaks was observed for TPO-treated samples compared to the untreated material. The distorted Ti peaks formed due to the lattice expansion occurring as a result of oxygen dissolution during TPO treatment.

XRD data obtained for samples treated at different oxygen concentrations (Fig. 4) indicated that for TPO carried out with 26% oxygen, the oxide structure consisted mainly of the Rutile phase with a small Anatase peak present. As the oxygen content was increased to 56%, more intense Anatase peaks were observed. Further increasing the oxygen content (69%) during TPO brought about negligible changes to the phase structure of the oxide layer which consisted of a mixture of Anatase and Rutile; the latter present in abundance.

XRD analysis of samples treated in experiment 3 (Fig. 5) revealed that the structure of the oxide layer formed was affected by changing the current density during TPO treatment. The results indicated that at low current density, Rutile peaks and a small Anatase peak were present, suggesting that the oxide structure was mainly Rutile, with a small trace of Anatase. However, as the current density increased

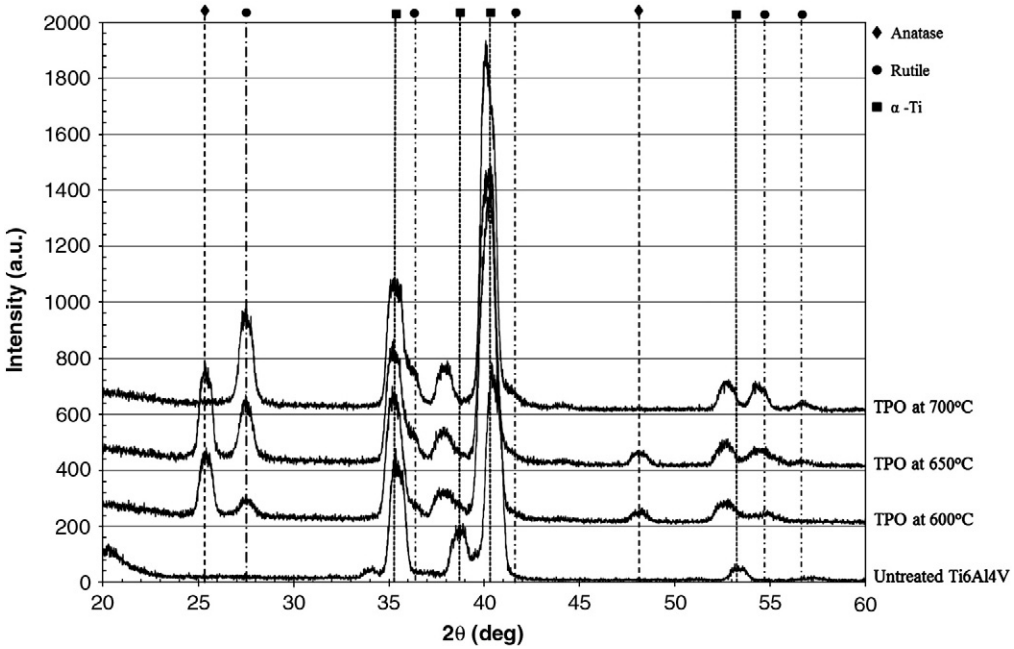

Fig. 3. GAXRD results of samples TPO-treated at different temperatures: 600 °C, 650 °C and 700 °C. A 6 degree glancing incidence angle was used. Peak intensity was shifted by + 200 for clarity purpose.

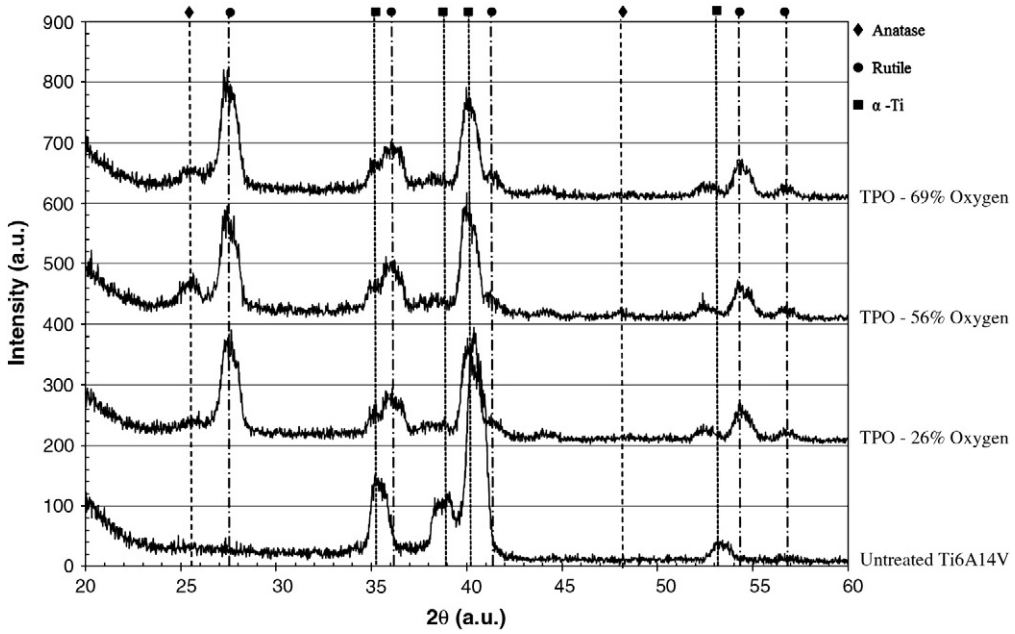

Fig. 4. GAXRD results of samples TPO-treated using different oxygen concentrations: 26% O_2, 56% O_2 and 69% O_2. A 2 degree glancing incidence angle was used. Peak intensity was shifted by +200 for clarity purpose.

more Anatase peaks with higher intensities formed and the structure of the oxide layer changed to a mixture of Rutile and Anatase.

3.3. Hardness measurements

A significant increase in surface hardness was recorded for all TPO-treated Ti6Al4V test discs compared to the untreated material. For samples treated at different substrate temperatures, the results showed that the surface hardness increased with increasing substrate temperature. Hardness measurements carried out at various indentation loads indicated that the highest surface hardness (~16 GPa) was measured on TPO samples treated at 700 °C (Fig. 6a), dropping to below 14 GPa for samples TPO-treated at 600 and 650 °C. Although the measured hardness progressively decreased as the indentation load increased, the samples treated at 700 °C appeared to be much harder than all other TPO samples even when 9.81 N load was applied. This indicates that a much deeper diffusion layer was formed at that temperature. This was confirmed by the hardness profiles obtained (Fig. 6b), which showed that a harder and thicker diffusion layer was generated at 700 °C compared to the ones achieved at 600 and 650 °C.

Increasing the oxygen content during TPO also affected the hardness of the oxide layer formed. As shown in Fig. 7a, the higher the oxygen content during the oxidation process, the harder the diffusion zone produced. However, from the hardness profiles obtained (Fig. 7b), it was clear that varying the oxygen content had very little effect on the thickness of the hardened layer, which was measured to be around 60 μm in all cases.

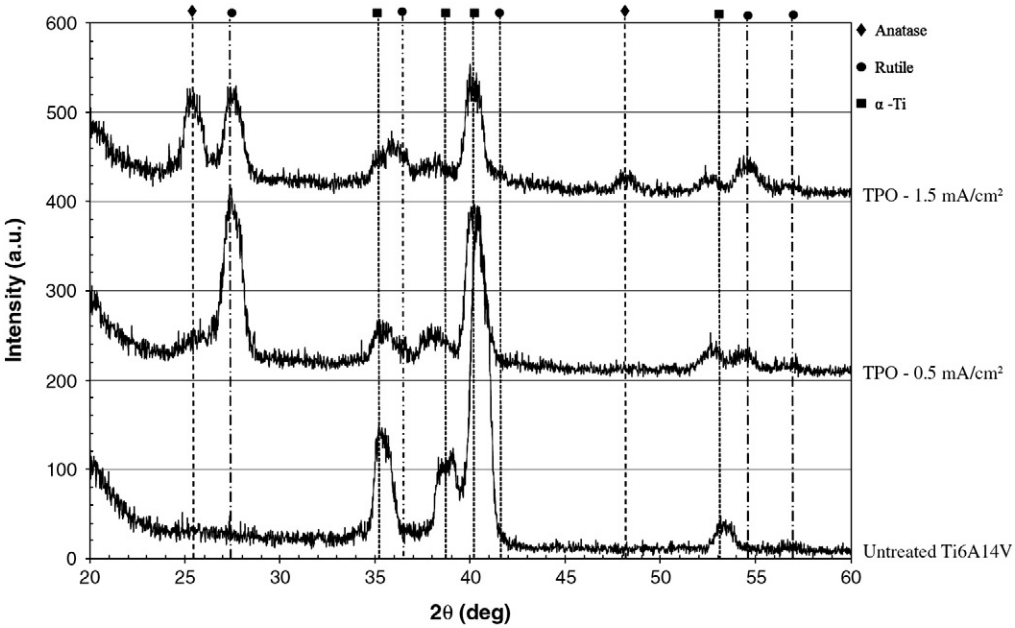

Fig. 5. GAXRD results of samples TPO-treated at different plasma densities: 0.5 mA/cm^2 and 1.5 mA/cm^2. A 2 degree glancing incidence angle was used. Peak intensity was shifted by +200 for clarity purpose.

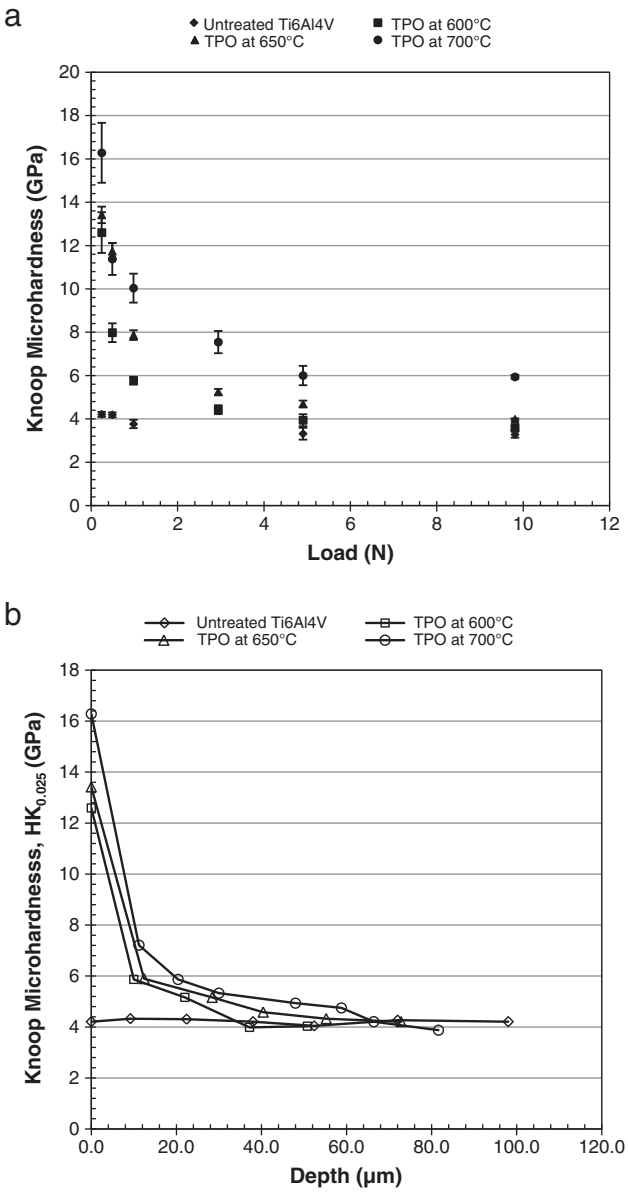

Fig. 6. a) Surface hardness with load and b) Knoop microhardness profiles of samples TPO-treated at 600 °C, 650 °C and 700 °C. The first hardness value (drawn at 0 μm depth) was measured at the surface of the TPO-treated samples.

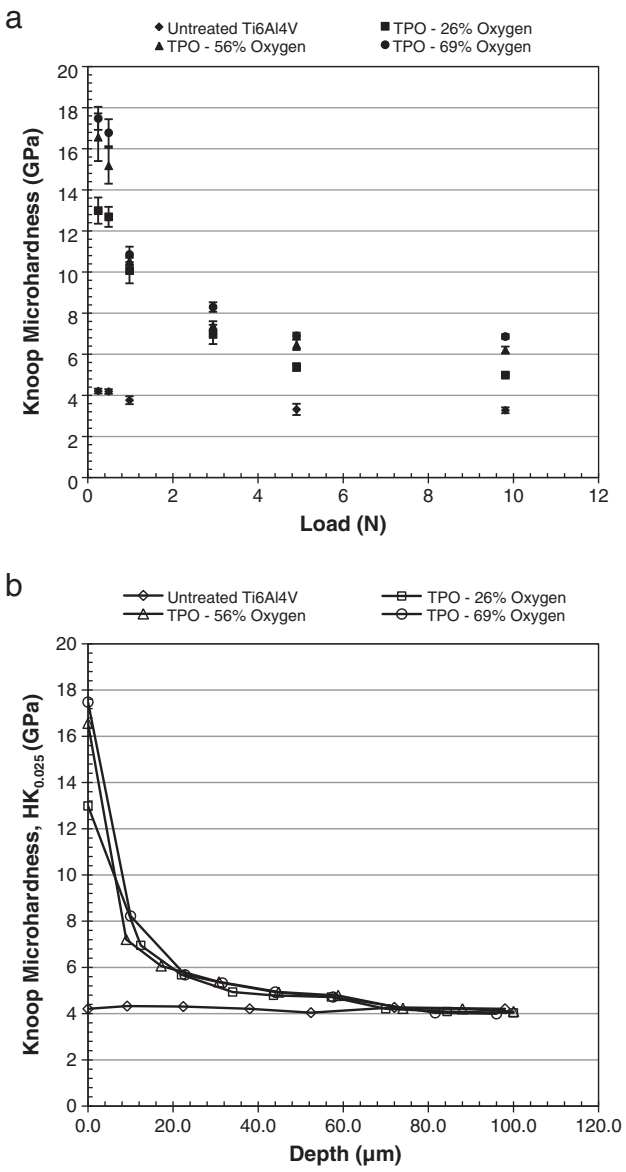

Fig. 7. a) Surface hardness with load and b) Knoop microhardness profiles of samples TPO-treated at varying oxygen concentrations. The first hardness value (drawn at 0 μm depth) was measured at the surface of the TPO-treated samples.

Hardness measurements obtained for samples treated in experiment 3 indicated that a harder oxygen diffusion zone was generated at the high current density (Fig. 8a). Moreover, the hardness-depth profiles revealed that a shallower case resulted when a low current density was used during the process (Fig. 8b); with the thickness of the hardened layer dropping from 60 μm at a current density of 1.5 mA/cm^2 to 40 μm when the current density was reduced to 0.5 mA/cm^2.

3.4. Reciprocating sliding wear measurements

Reciprocating sliding wear tests indicated that, in all cases, the TPO processes significantly improved the tribological properties of Ti6Al4V alloys, with the TPO-treated samples exhibiting much better wear performance compared to the untreated material. Furthermore, no flaking or spalling of the oxide compound layer was observed during testing which suggest that the hard layer was well-adhered to the substrate. As the treatment temperature increased from 600 to 700 °C, the wear performance improved considerably (Fig. 9). This was more noticeable when moving from 600 °C to 650 °C with a much smaller volume loss recorded for the latter at sliding distances of over 1250 m. Increasing the oxygen content during the process was also found to be beneficial, although negligible improvement occurred when it was increased from 56 to 69% (Fig. 10). The results also showed that samples treated at the high current density exhibited better wear performance than the ones treated at the low current density (Fig. 11). The reciprocating wear results appear to be in close agreement with the reported hardness results. For all TPO-treated samples, the coefficient of friction, measured after reaching a steady state regime, was found to be in the range of 0.9–1.0, a marked increase from that of the untreated Ti6Al4V substrate (0.45).

3.5. Scratch adhesion testing

Scratch tests were carried out on a sample TPO-treated in experiment 3 at a current density of 1.5 mA/cm^2. The results revealed that 46 ± 3 N is the critical load at which the oxide layer is completely removed from the substrate. The high critical load recorded confirmed that good adhesion of the oxide compound layer to the underlying

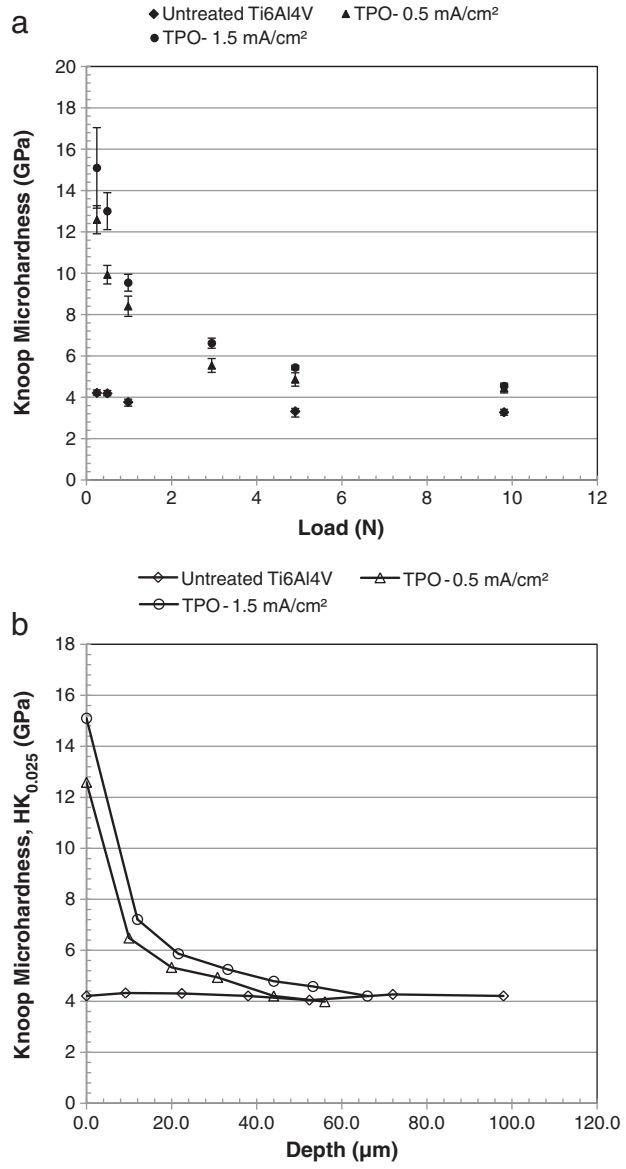

Fig. 8. a) Surface hardness with load and b) Knoop microhardness profiles of samples TPO-treated at different plasma densities. The first hardness value (drawn at 0 μm depth) was measured at the surface of the TPO-treated samples.

Ti6Al4V alloy substrate is achieved with the TPO process. SEM micrographs of the scratch track showed that at lower load (less than 40 N), some cracks are present in the oxide compound layer but no chipping or flaking of the hardened layer was observed (Fig. 12a). With increasing load, more cracks were observed which eventually resulted in flaking and complete removal of the oxide layer as shown in Fig. 12b.

4. Discussion

From the analysis carried out on all TPO-treated samples, it is clear that changing key process parameters affects the structure and properties of the hardened layer generated. SEM analyses showed that a thin oxide layer was formed at the surface of all Ti6Al4V samples after a 4-hour TPO treatment. The thickness of the oxide layer varies depending on the substrate temperature used during processing. Increasing the substrate temperature to 700 °C accelerates the oxidation rate [6], enabling the formation of a substantially thicker oxide compound layer on the surface. XRD results indicate that, as the substrate temperature is increased, the oxide layer structure undergoes a series of phase changes from a mixture of Anatase and Rutile at 600 °C

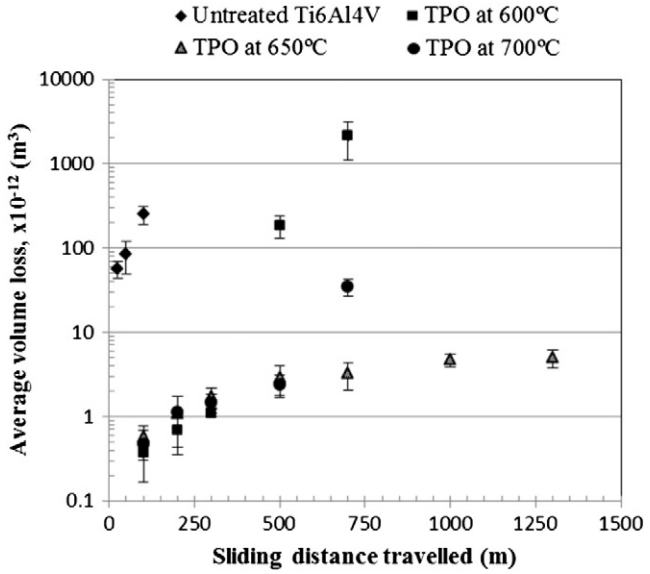

Fig. 9. Wear plots of average volume loss versus sliding distance travelled for samples TPO-treated at different substrate temperatures. A logarithmic scale was used on the y-axis for clarity purpose.

to mainly Rutile at 700 °C. Hardness plots confirmed the presence of an oxygen diffusion zone lying immediately underneath the oxide compound layer. During TPO treatment, interstitial oxygen diffusion within the titanium lattice hinders plastic flow enabling solid solution hardening of the substrate. The thickness of the diffusion layer was measured to be around 60 μm at 700 °C, decreasing to approximately half this value when the substrate temperature is reduced to 600 °C. As the TPO temperature increases, so does the surface hardness measured at a given indentation load. This is related to increases both in compound layer thickness and in diffusion zone depth with increasing temperature. At 0.245 N indentation load, high hardness values were measured on all TPO-treated samples regardless of the substrate temperature used, which further confirms the presence of a hard oxide compound layer on their surface. The wear results, which indicate significant improvements in wear performance with increasing substrate temperature, are in good agreement with the hardness data reported. The TPO-treated samples appear to wear slowly as long as the oxide layer is present. The gradual removal of the oxide layer is evident from the wear plots which showed a minimal increase

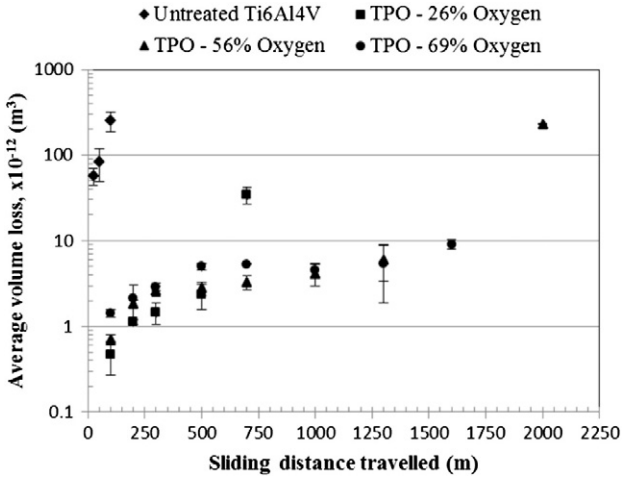

Fig. 10. Wear plots of average volume loss versus sliding distance travelled for samples TPO-treated at different oxygen concentrations. A logarithmic scale was used on the y-axis for clarity purpose.

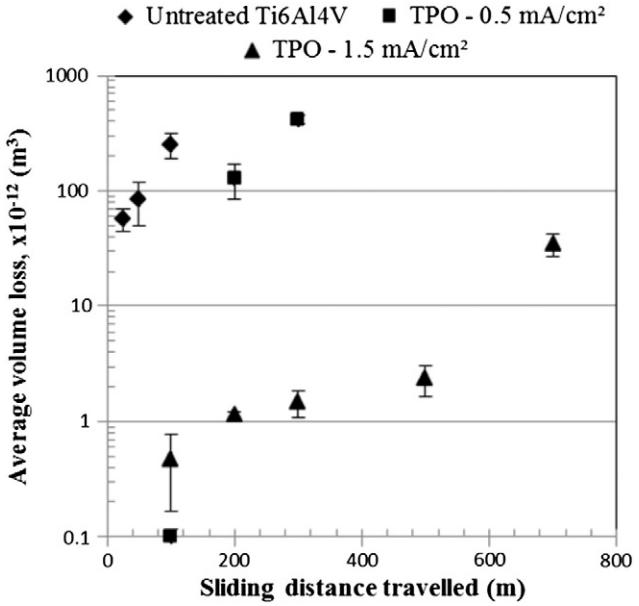

Fig. 11. Wear plots of average volume loss versus sliding distance travelled for samples TPO-treated at different plasma densities. A logarithmic scale was used on the y-axis for clarity purpose.

in average volume loss with increasing sliding distances, at the start of the test. However, once the oxide compound layer is removed, the abrasive particles in the wear track, running against the softer oxygen diffusion layer, accelerate the wear rate [2]. This was observed for the sample TPO-treated at 600 °C, which showed negligible wear up to sliding distances of 500 m when a noticeable increase in average volume loss occurs as a result of the removal of its thin oxide compound layer.

The oxygen content used during TPO also influences the thickness of the oxide layer produced. Due to the high solubility of oxygen in titanium, the oxide compound layer nearly doubles in thickness when the oxygen concentration is increased from 26% to 69%. At the high oxygen content, the thickness of the oxide compound layer was found to be around 1.7 μm; a similar value was reported in the literature for conventional plasma oxidation [11]. XRD data showed that the oxide structure, consisting mainly of Rutile with a few Anatase peaks, did not significantly change as the oxygen concentration increased. High surface hardness was measured with increasing oxygen content, although negligible changes to the thickness of the oxygen diffusion layer occurred. The highest surface hardness was measured at around 17.5 GPa on the sample TPO-treated with 69% oxygen, considerably higher than the hardness achieved on samples subjected to plasma oxidation at 750 °C with 75% oxygen [2]. Reciprocating sliding wear data confirmed the effectiveness of oxygen at improving the tribological properties of titanium, with the highest oxygen concentration providing only a small volume loss (9.05×10^{-12} m^3) over large sliding distances (1600 m).

The third process parameter investigated in this study was the cathode current density which was controlled during the TPO process by adjusting the current passing though the tungsten filament. As shown by XRD analysis, the current density affects the structure of the oxide layer generated which is mainly Rutile at low current density changing to a mixture of Rutile and Anatase phases at higher substrate current densities. A noticeable increase in hardness was recorded at the high current density even though the oxide layer structure in that case, consisted of a mixture of Rutile and Anatase phases. The high hardness recorded is associated with the increase in thickness of the oxide compound layer at high current densities. The hardness measured is that of the oxide layer generated, with very little or no contribution from the underlying softer oxygen diffusion layer. At low current densities (0.5 mA/cm^2), with the formation of a thin oxide compound layer, there is more contribution from the softer oxygen diffusion layer, hence the lower hardness values observed. From the hardness profiles, it is clear that, at the high current density, with more oxygen arriving and diffusing into the material, the total thickness of the treated layer increases from 40 to 60 μm. The high surface hardness combined with a deeper diffusion zone achieved at a current density of 1.5 mA/cm^2, considerably improved the wear performance of Ti6Al4V alloys. Moreover, scratch adhesion testing performed on this particular sample confirmed that with the TPO process (unlike conventional thermal oxidation [6]); the oxide compound layer generated is well-adhered to the Ti6Al4V alloy substrate.

TPO treatments carried out at high temperature, high oxygen content and high current density enable the formation of a thick and hard oxide layer which significantly enhances the tribological properties of Ti6Al4V alloys.

5. Conclusions

Ti6Al4V alloys were subjected to Triode Plasma Oxidation treatments in order to improve their tribological properties. The effects of selected process parameters were investigated in this study. From the results, the following conclusions can be drawn:

- All TPO-treated samples exhibit much improved mechanical and tribological properties compared to the untreated material.
- The oxygen-rich layer generated during TPO consists of a thin oxide compound layer at the surface with a thicker oxygen diffusion zone lying underneath it.
- The thickness of the oxide compound layer increases with increasing substrate temperature, oxygen content and current density.
- The hard, thick and well-adhered oxide layer generated on the surface of Ti6Al4V alloys TPO-treated at high substrate temperature, high oxygen content and high current density significantly improves the tribological properties of the material.

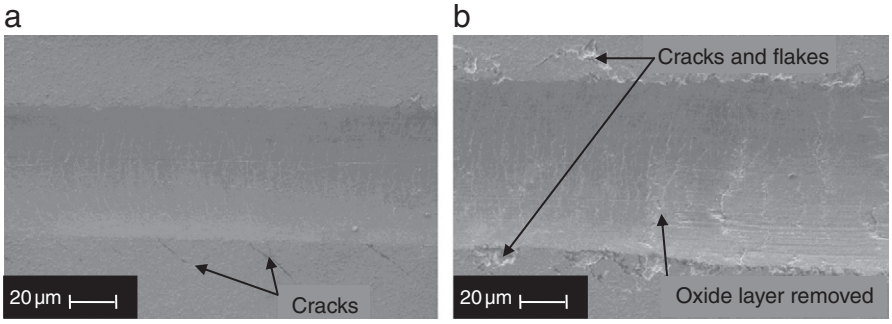

Fig. 12. SEM photomicrographs (×2500) of a scratch track at a) lower load (below 40 N) and b) around 46 N load when the oxide compound layer is removed.

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