

Wear behavior of the plasma and thermal oxidized Ti-15Mo and Ti-6Al-4V alloys

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Abstract. Titanium and its alloys widely used in load bearing applications. Titanium alloys are capable of providing lower elastic modulus and better corrosion resistance with alloying processes. In spite of the modified mechanical properties, the surface degradation is still the main critical defect. Ti-15Mo alloy is one of the alpha+beta titanium alloys with acceptable mechanical and chemical superiority. Recent researches in literature show that the wear performance of base Ti-15Mo is relatively low as compared to Ti-6Al-4V, using in high performance applications. Plasma oxidized surfaces increase the tribological and chemical performance of titanium alloys. In this study the Ti-15Mo alloy and Ti-6Al-4V alloys were compared in terms of wear performance. To obtain alloys with similar microstructure they were solution treated at 800°C 1H and then air-cooled. The plasma and thermal oxidations were applied at 650°C for 1 hour. Wear performance of oxidized surfaces investigated in dry conditions. Oxidized surface characterized with XRD, SEM, 3D profilometer and hardness measurements. Wear volume calculated with 3D profilometer. Results show that oxidizing increased the surface roughness and improved the wear performance of Ti15Mo alloy. The plasma and thermal oxidized Ti-15Mo showed a remarkable increase in wear resistance.

1. Introduction

Titanium and its alloys are important structural materials due to their high specific strength and good corrosion resistance. Thus, they have been widely used in many applications ranging from aerospace and defense systems to biomedical industries. However, their wear resistance is very poor due to the unstable oxide film formed on the surface by the effect of tribo-chemical reaction leading to rapid oxidative wear loss. In this regard, various surface modification techniques including thermochemical processes and thin film coatings have been applied commonly to improve wear resistance.

In recent years, on the other hand, some new-generation techniques including anodizing [1,2], ion implantation [3], dc-diode plasma oxidation [4], plasma electrolytic oxidation [5], reactive dc-sputtering [6,7] and thermal oxidation (TO) [8,9] have recently gained interest from researchers. The thermal oxidation and plasma oxidation (PO) techniques are especially promising methods because of their ease-to-use and effectiveness in some specific applications. Both techniques are based on



diffusional processes that form a thick oxide layer and a diffusional region between the oxidized layer and the bulk material. However, the plasma oxidation technique, has some advantages over the thermal oxidation such as lower temperatures and shorter times required for processing. In general, these techniques have been used especially on the oxidation of pure titanium and Ti-6Al-4V alloy [10-12]. In recent years, alpha+ beta / beta-type titanium alloys including Zr, Nb, Ta and Mo have been developed and used due to their higher corrosion resistance and also low elastic modulus. However, the wear resistance of such alloys is still a main obstacle to be employed in broader applications where the tribological effects are the major concerns.

Therefore, the main purpose of the current study is to improve the wear resistance of alpha+beta type titanium alloys by applying both plasma and thermal oxidations. In this study, the wear performance of plasma and thermal oxidized Ti-15Mo and Ti-6Al-4V alloys was investigated and compared in terms of their wear properties.

2. Experimental Procedure

In this study, Ti-6Al-4V and Ti-15Mo alloys were used for the oxidization processes. Table 1 represent the chemical composition of the alloys.

Table 1. Chemical composition (%) of Ti-16-4V and Ti-15Mo.

Elements	Al	V	Mo	Fe	Ti	Other
Ti-6Al-4V	6	4.1	-	<0.30	Balance	0.45
Ti-15Mo	-	-	15	<0.20	Balance	0.40

Ti-6Al-4V and Ti-15Mo alloys were obtained from their commercial grades. To obtain the same initial conditions, they were solution treated at 800°C for 1 hour and then, air cooled to room temperature. The process was performed under argon atmosphere. Electron Discharge Machine (EDM) was used to cut the disks with thickness of 5 mm and diameter of 10 mm from the ingot. The surfaces were prepared by mechanical grinding using SiC paper up to 1200 mesh followed by polishing using alumina in 1 µm grain size.

The disk samples were treated for 1 hour at 650°C (which is below the Beta transus temperature) in both thermal and plasma oxidation processes. The thermal oxidation treatments were carried out in an atmosphere-controlled furnace with an oxygen flow rate of 10 ppm. Prior to the plasma oxidation treatments, hydrogen sputtering was applied to the surface of all samples for 15 min under a voltage of 500 V and a pressure of 5×10^2 Pa for eliminating of any contaminants on the surfaces. The plasma treatments were performed in a mixture of 50% Ar – 50% O₂ for 1 hour under the same pressure of sputtering.

The wear tests were performed with a reciprocating linear motion of 1 Hz frequency and 4 mm amplitude, a ball-on-plate configuration was used in a tribometer (UMT II, Bruker, Germany). The wear tests were carried out by rubbing a 5 mm alumina ball on the sample surface under 10 N loads for the duration of 1 hour. The oxidation process was performed on 3 samples in one chamber for both thermal and plasma oxidation treatment. Also the wear tests were performed at least 3 times on two different samples to obtain reliability. Before the wear tests, the surface of the plasma oxidized samples was also polished with alumina in 1 µm grain size for removing the any peeling formed.

The phase structure of the oxidized surfaces was determined by using an X-ray diffraction spectrometer (XRD) with Co tube (Explorer, GNR, Italy). A Scanning Electron Microscope (FEI Quanta FEG 250, USA) was also utilized for the evaluation of processed surface and sub-surface morphologies. The wear volume was obtained from 3D profilometer (Bruker Contour GT) and Vision64 software. The surface and cross-sectional hardness of the samples were measured in a microhardness tester (Shimadzu HMV-G, Japan) under a normal load of 25 g for a dwell time of 15 second.

3. Results and Discussion

3.1. Structure analysis

Figure 1 and figure 2 show the representative X-ray diffraction patterns for untreated (AR), PO and TO treated Ti-6Al-4V and Ti-15Mo samples. Both AR alloys consist of alpha + Beta microstructures. (Alpha (α) (JCPDS cards #44-1294) and Beta (β) (JCPDS cards #44-1288)). As seen, both anatase (A) (JCPDS cards #21-1272) and rutile (R) (JCPDS cards #21-1276) phases formed on both oxidized alloy surfaces. The intensity of the rutile phases formed by plasma oxidation is higher than that of phased formed by thermal oxidation. This may be due to the relatively high thickness of the layer formed by plasma oxidation and the plasma kinetics (Fig 4). It is known that the rutile phase is more stable compared to the anatase phase [13, 14]. Therefore, more stable structures can be achieved during plasma oxidation at chosen temperatures.

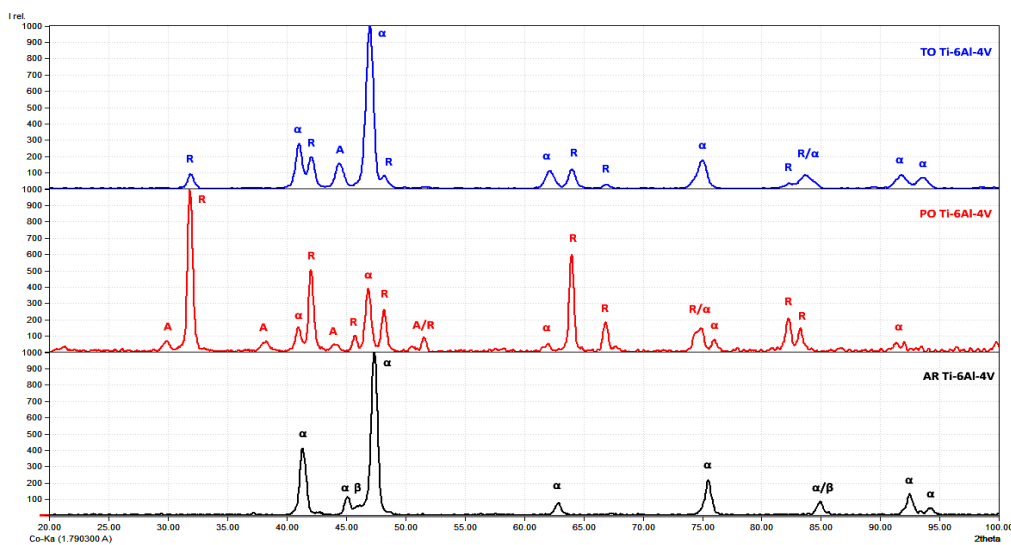


Figure 1. XRD patterns of the Ti-6Al-4V alloy samples after plasma and thermal oxidations (α : Alpha, β : Beta, A: Anatase, R: Rutile).

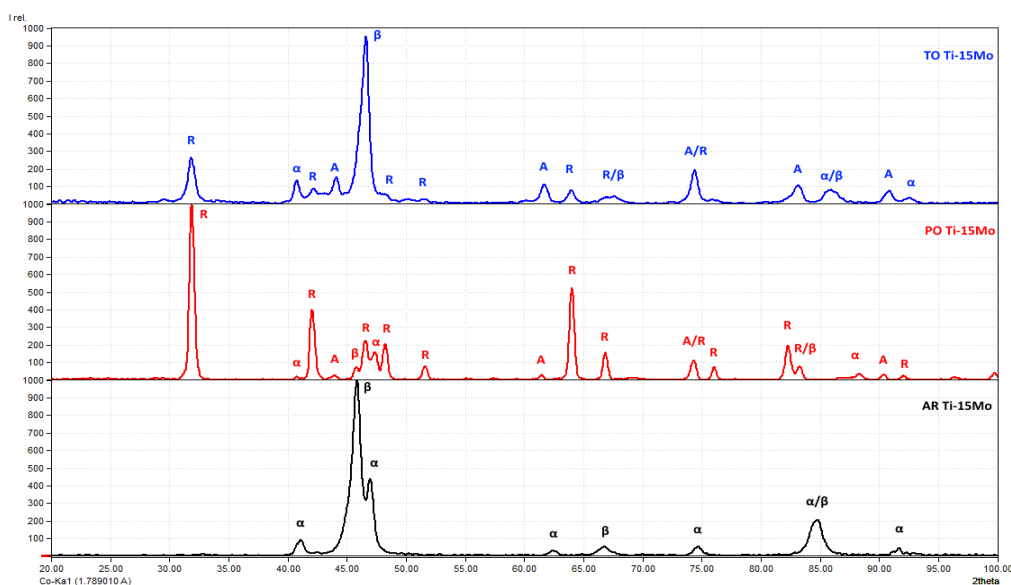


Figure 2. XRD patterns of the Ti-15Mo alloy samples after plasma and thermal oxidations (α : Alpha, β : Beta, A: Anatase, R: Rutile).

3.2. Mechanical Properties

The surface morphologies of the samples after oxidation processes are shown in figure 3. It is seen from the SEM micrographs that the surface morphology of the samples changed completely after oxidation treatments. While the PO treatment caused a more porous surface morphology, the TO treatments did not change the surface morphology of both alloys. The high magnification micrographs of Ti-15M shows a net-shaped microporous structure, which was formed after the PO.

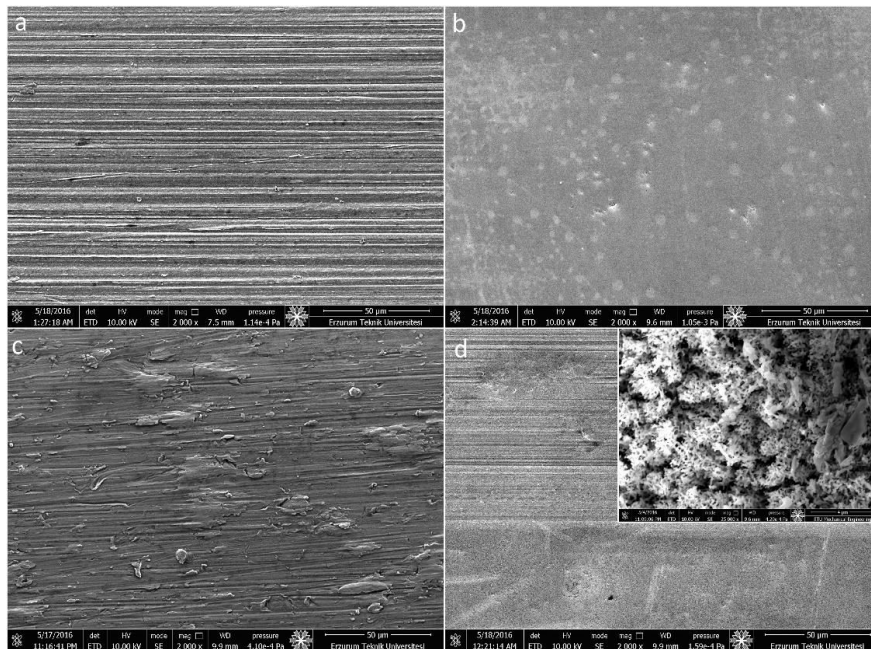


Figure 3. SEM images of Plasma and Thermal treated Ti-6Al4V and Ti-15Mo alloys (a: TO Ti-6Al4V, b: PO Ti-6Al4V, c: TO Ti-15Mo, d: PO Ti-15Mo and detailed view).

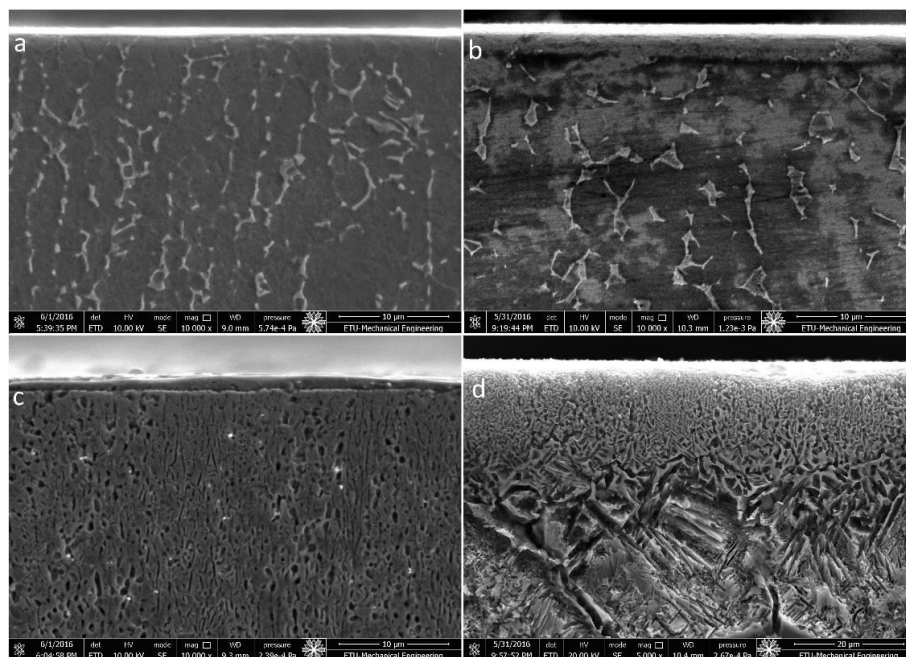


Figure 4. Cross-sectional SEM images of Plasma and Thermal treated Ti-6Al4V and Ti-15Mo alloys (a: TO Ti-6Al4V, b: PO Ti-6Al4V, c: TO Ti-15Mo, d: PO Ti-15Mo).

The cross-sectional views of the samples, oxidized by PO and TO, are shown in figure 4. It is seen that the sample surfaces are not completely covered by an oxide film during TO. Also the oxidized layer thickness of TO sample is lower than that of PO counterpart. After PO, an oxide layers in thickness of 2-2.5 μm and 20-25 μm were obtained for Ti-6Al-4V and Ti-15Mo, respectively. In addition, beneath the oxide layer, a thick diffusion region formed for both alloys. Furthermore, the oxide layer formed on the Ti-15Mo sample has a different morphology with a grid-shaped appearance connecting with the well-developed grain boundaries inside the diffusional region.

After the TO, a remarkable oxide layer formed on Ti-15Mo surfaces, unlike Ti-6Al-4V. On the other hand, the PO led to a thick oxide layer on the surfaces of both alloys. However the oxide layers obtained from PO were partially peeled off, as reported by other researchers [15-16]. Therefore, the diffusion layers were determined by microhardness measurements and the SEM analyses.

The surface hardness of solution treated and air-cooled (AR) Ti-6Al-4V and Ti-15Mo alloys were measured to be 480 ± 22 and 357 ± 17 $\text{HV}_{0.025}$, respectively. Hardness distribution through the cross-section of Ti-6Al-4V and Ti-15Mo after TO and PO samples is shown in figure 5. In general, the hardness profile demonstrates that both PO and TO processes significantly increase the hardness of the surface and sub-surface. It is caused by the distortion of the lattice system by the effect of oxygen atoms. The hardness profile is almost the same for both alloy samples under PO process. Both alloy exhibit almost the same profile in terms of hardness and the thickness of diffusional layer. After TO, while the Ti-15Mo is higher surface hardness compared to that of Ti-6Al-4V, it has lower thickness of diffusional layer. These results are consistent with the cross-sectional images (figure 4). It can be said that while the surface hardness of oxidized sample is related to its phase structure, the depth or thickness of the diffusional layer depends on the diffusional capacity of oxygen inside the alloy. As seen from the XRD results (Fig 1 and 2), the intensity of the rutile phase is higher in Ti-15Mo alloy than the TO Ti-6Al-4V in accordance to hardness measurements. However, the thickness of the diffusion layer of Ti-15Mo is relatively low due to the presence of Mo atoms which prevent the easy penetration of oxide atoms through the surface. After the plasma and thermal treatments, the samples were cooled to the ambient temperature in an oven or a plasma chamber. The slow cooling rate leads to decreasing of the base metal hardness. The hardness of base metals reduced to 400 ± 12 and 338 ± 18 $\text{HV}_{0.025}$ for the Ti-6Al-4V and Ti-15Mo alloys, respectively.

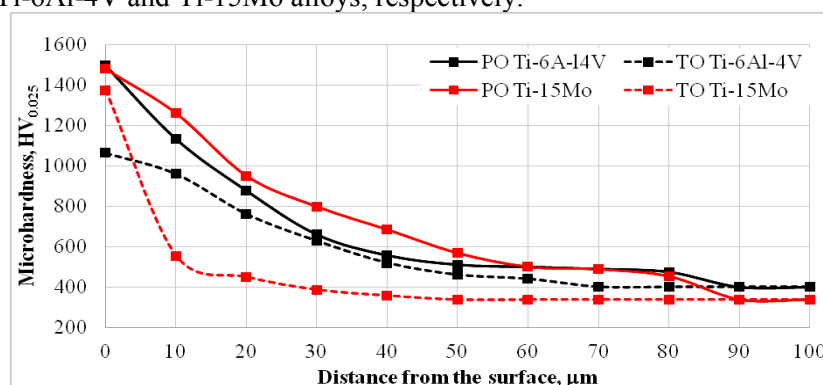


Figure 5. The change in microhardness as a function of depth below the surface of PO and TO Ti-15Mo and Ti-6Al-4V.

Friction test results of untreated and oxidized Ti-6Al-4V and Ti-15Mo are given in figure 6 and figure 7, respectively. Both alloys in the as-received states exhibit more stable friction coefficient during sliding time compared to oxidized counterparts. The average friction coefficient of AR Ti-6Al-4V and Ti-15Mo are in the steady state conditions are 0.4 and 0.8, respectively. The friction coefficient of AR Ti-6Al-4V surface gradually increased throughout the rubbing period (Fig 6). On the other hand, the friction coefficient of AR Ti-15Mo was generally stable. Also, a slight decrease was observed at about 1800 sec. and 3200 sec (Fig 7).

At the start of the friction tests, an increase in the friction coefficient of all samples was observed due to mechanical contact. Later, it remained steady-state as the surface became smoother. The PO treatment led to lower friction coefficient value for Ti-6Al-4V in the beginning of rubbing, it reached to higher value after about 400 seconds. Subsequently a frictional fluctuation was observed, due to formation of debris. The more stable friction coefficient of PO may be ascribed to lower debris produced during rubbing of PO (Fig 6) [17]. The difference between the frictional behaviour of Ti-6Al-4V may imply differences in surface morphologies caused by varying processes.

In general, the Ti15Mo had higher friction coefficient than the Ti-6Al-4V and the oxidation processes did not have significant effect on friction coefficient. The PO surface suddenly reached the same value with AR Ti-15Mo after about 150 seconds. The TO gradually attained the same value with others as well (Fig 7).

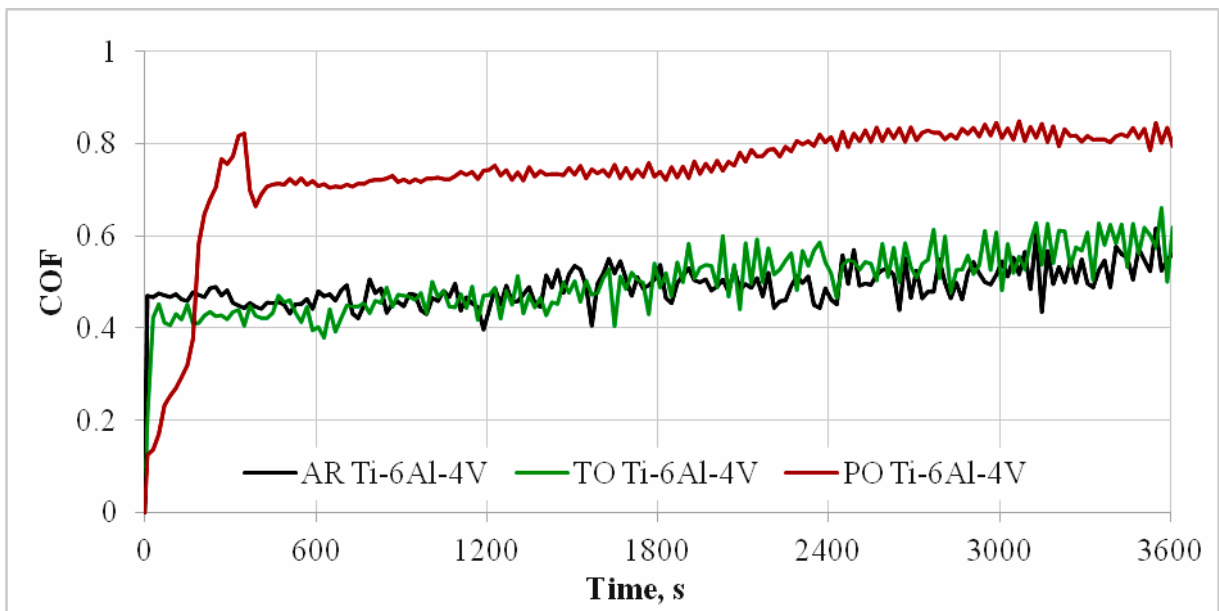


Figure 6. The change in friction coefficients of Ti-6Al-4V alloy samples oxidized by TO and PO as a function of sliding time.

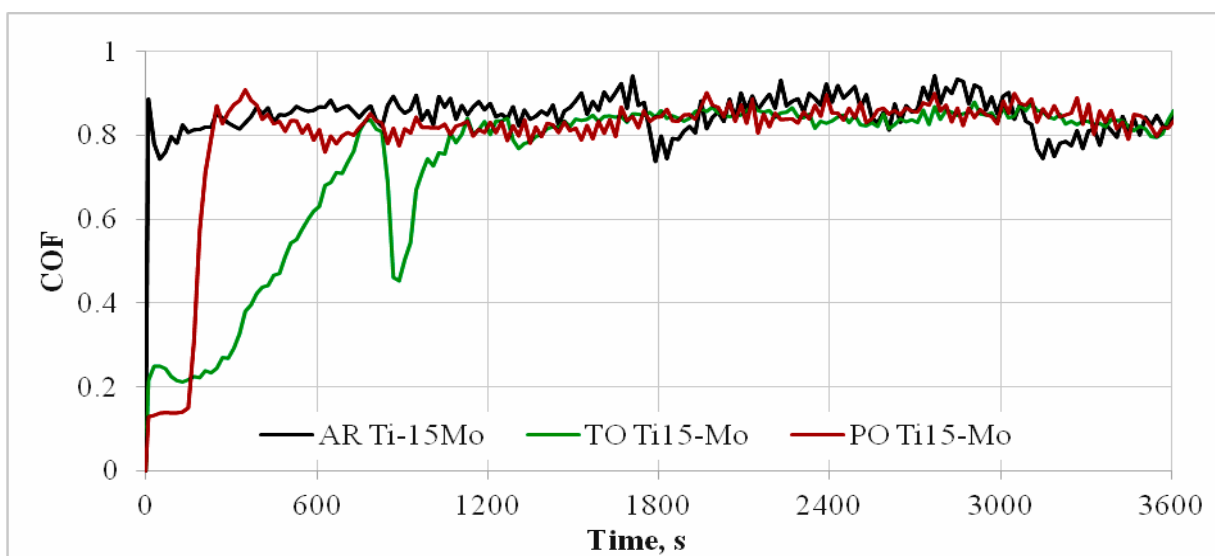


Figure 7. The change in friction coefficients of Ti-15Mo alloy samples oxidized by TO and PO as a function of sliding time.

As seen from the results, the PO process has a significantly effect on the wear resistance of Ti-6Al-4V alloy. The highest wear resistance (or the lowest wear rate) was obtained after PO treatments of both alloys. In general, high hardness means high wear resistance as expected. The thermal oxidation led to slightly thin oxide layer on Ti-6Al-4V alloy. The hardness measurements and cross-sectional SEM images claim the diffusion zone increased the surface hardness.

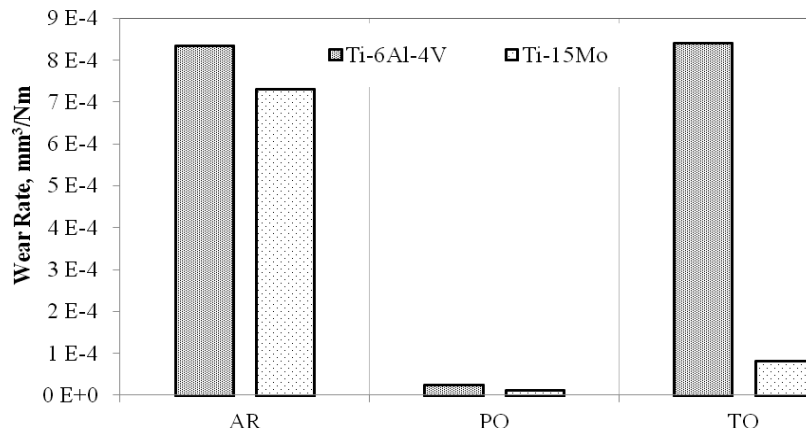


Figure 8. Wear rates of Ti-15Mo and Ti-6Al-4V alloys in the AR, PO and TO conditions.

SEM images of both Ti-15Mo and Ti-6Al-4V alloys are shown in figure 9. As considering the width of wear scars, the Ti-15Mo sample exhibited higher wear resistance in all conditions compared to Ti-6Al-4V alloy. Also, it is clearly seen that the PO decreased the wear rates of both alloys as presented in figure 8. The lowest width of the wear track is obtained from the Ti-15Mo sample oxidized by PO. As indicated on the figure 9f, the wear track was wider at the beginning of rubbing and then became narrower. This observation may comply with frictional behaviour after about 130 seconds (Fig 7).

In generally, adhesive, abrasive and oxidative wear mechanisms seem to be operative in all samples.

When SEM images of AR and TO Ti-6Al-4V and their frictional behaviour are considered, it suggests a similar wear mechanism. The rough, wide and deep wear track implies that this can be adhesive mechanism (Fig 9). According to 3D surface profile, the wear track depth of both PO alloys remained in the diffusion layer and an improvement of load-bearing capacity was observed (Fig 10).

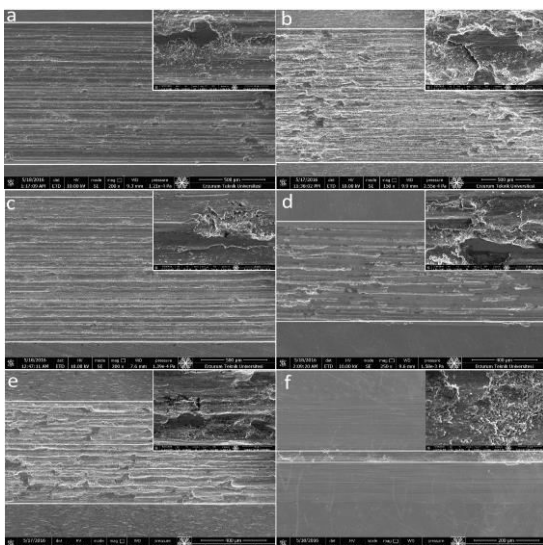


Figure 9. SEM images showing the wear tracks and worn surfaces of Ti-15Mo and Ti-6Al-4v alloys: (a: AR Ti-6Al-4V, b: AR Ti-15Mo c: TO Ti-6Al-4V, d: PO Ti-6Al-4V, e: TO Ti-15Mo, f: PO Ti-15Mo).

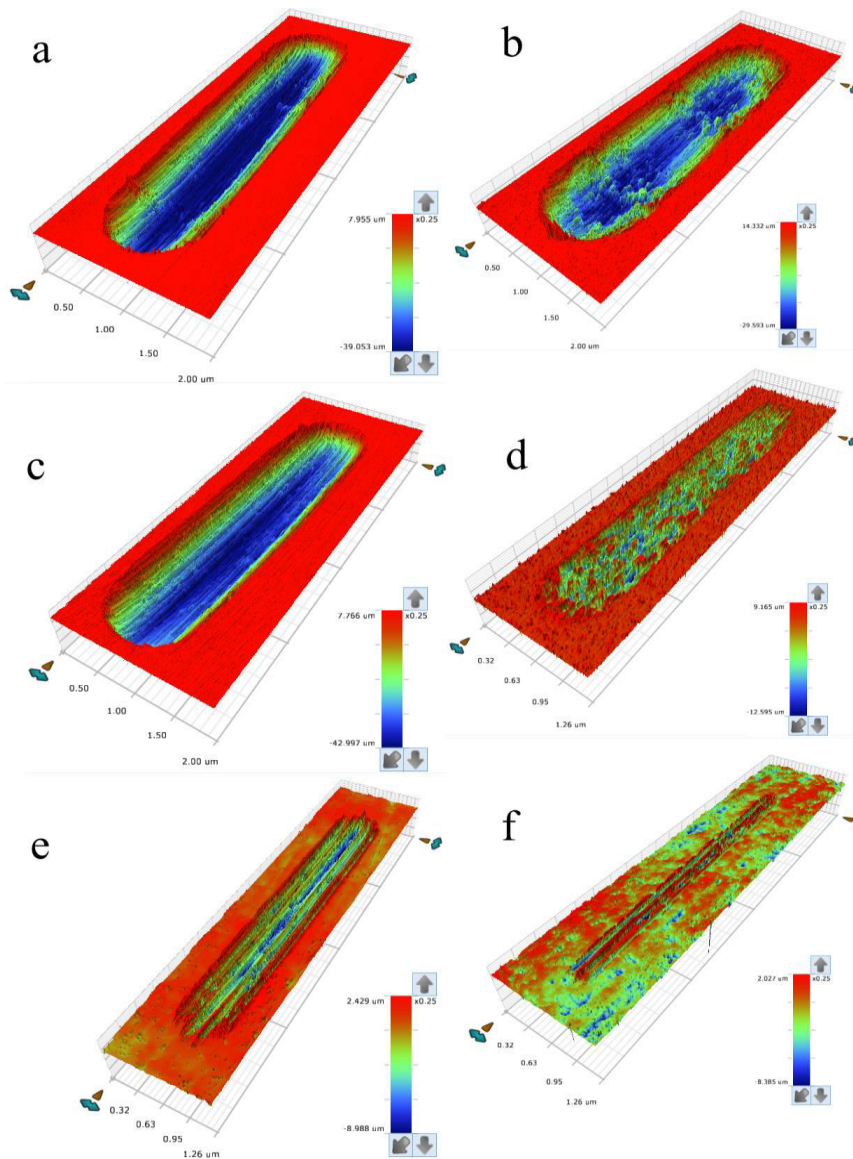


Figure 10. 3D profilometer images showing the wear tracks and worn surfaces of Ti-15Mo and Ti-6Al-4V alloys: (a: AR Ti-6Al-4V, b: AR Ti-15Mo c: TO Ti-6Al-4V, d: PO Ti-6Al-4V, e: TO Ti-15Mo, f: PO Ti-15Mo).

4. Conclusions

Thermal and plasma oxidation treatments were applied to alpha+beta type Ti-15Mo and Ti-6Al-4V alloys, and their tribological properties as well as structure and hardness were investigated.

- An oxide layer consisting of anatase and rutile phases formed on the surfaces of Ti-15Mo and Ti-6Al-4V after both plasma oxidation and thermal oxidation treatments. After plasma oxidation treatment, the intensity of rutile phase and the thickness of oxidized layer were higher for both Ti-15Mo and Ti-6Al-4V samples than after thermal oxidation.
- The surface hardness and the thickness of diffusion layer of both alloys after plasma oxidation were higher compared to thermal oxidized.

- The Ti-15Mo alloy exhibited higher wear resistance compared to Ti-6Al-4V alloy under all conditions. Wear resistance of both Ti-15Mo and Ti-6Al-4V alloy oxidized by plasma oxidation was higher than the thermally oxidized.

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