THE EFFECT OF WEAR MECHANISM FOR PLASMA OXIDISED CP TI AND ITS ALLOYS ON TRIBOCORROSION PERFORMANCE

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Abstract

Commercially pure titanium (cp-Ti) and its alloys (Ti6Al4V, Ti45Nb, Ti6Al7Nb etc.) have an important use among biometallic materials. Recently developed alloying techniques and production methods have enabled many different titanium alloys to be used as biomaterials. Although harder and higher corrosion resistance than iron and its alloys, it is used as an invasive implant by applying various surface modifications to improve biodegradability performance. One of these processes is plasma oxidation process. With this process, corrosion resistance can be improved by obtaining more passive surfaces. There are many studies on these performance measurements in the literature. In this study, the effects of wear and corrosion mechanisms on the material in one cycle were investigated. Cp-Ti, Ti6Al4V and Ti45Nb were chosen as base materials. Samples were subjected to plasma oxidation for 600˚C-3 hours. Within the scope of this investigation, the adhesive wear mechanism on oxidized surfaces was compared with different types of abrasives, and its effect on corrosion performance was measured with the tribocorrosion test apparatus.

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Abrasion tests were carried out with two abrasive balls: tungsten carbide (WC) and silicon nitride (SiN) under 3 N load. Processes were carried out in two different media, dry and simulated body fluid (SBF). Potentiodynamic polarization scans were carried out using the scanning range of -0.28 V - 2 V in the presence of wear tests for tribocorrosion measurements. While abrasive wear mechanism is dominant in untreated samples, adhesive wear is at the forefront in coated samples. The effects that increase the corrosion resistance positively affected the performance of tribocorrosion. The high oxidation resistance of Ti and its alloys increased adhesive wear performance, and because of the higher corrosion resistance of Ti6Al4V and Ti45Nb, which were alloyed from these three material groups, their corrosion performance was higher than Cp-Ti.
Keywords: Cp-Ti, Ti6Al4V, Ti45Nb, Plasma oxidation, Tribocorrosion.

1. Introduction

Titanium and its alloys are frequently used in different industries such as the medical, aerospace, automotive, energy, and shipping industries [1]. Titanium and titanium alloys have high strength, low density, good biocompatibility, superior corrosion resistance and mechanical properties but they have low tribological properties such wear resistance [2]. It limits its widespread use due to its low wear resistance and high coefficient of friction.

The superior corrosion and biocompatibility properties of titanium and its alloys are due to the natural oxide film on the surface rather than the material itself. This oxide film is instantly created by air contact of the material and generally has a stable titanium dioxide (TiO_2) structure. Nevertheless, the low tribological properties of the natural oxide layer cannot guarantee the protection of titanium and its alloys to interact with the surrounding environment. Hence, surface modification is required to achieve good wear and tribocorrosion resistance.

The metallic materials surface such titanium alloys can be directly exposed to greater stresses, wear and environmental factors compared to their interior. For this reason, the surface properties of titanium alloy are improved by surface modification methods [3]. In order to improve the tribological properties of metallic materials, many different surface modification methods are used, such as chemical vapor deposition,

physical vapor deposition, sol-gel coating, heat treatment, plasma electrolytic oxidation and thermochemical processes [4].

TiO_2 coatings play an important role to gain superior electrochemical and tribological performance compared to other coatings. Ti02 films can be obtained by different methods such as micro arc oxidation, physical vapor deposition, chemical vapor deposition, anodizing, plasma oxidation and sol-gel dip coating [5,6]. Alsaran et al. [7] applied different oxidation methods (anodic oxidation, thermal oxidation and plasma oxidation) to Ti6Al4V alloy and they obtained TiO2 structure as a result of the study. As a result of all oxidation processes, they found that the hardness and wear resistance of the Ti6Al4V alloy improved compared to the untreated titanium alloy. Plasma oxidation process, which is a thermochemical process, is one of the most used methods for titanium and its alloys. In another study on thermal oxidation of Ti6Al4V alloy, it was found that the alloy oxidized for 60 hours at 600 ° C shows very good corrosion resistance and up to 25 times wear resistance in 0.9% NaCl solution [8].

In a study examining the effect of oxidation of Ti6Al7Nb, Ti13Nb13Zr and Ti15Zr4Nb alloys on the corrosion properties, it was found that the oxide film structure formed on the surface depends on the structure of the alloy and aluminum oxide (Al2O3) phase is also encountered in the aluminum containing alloy. It has been interpreted that in the process conditions where the oxide film is dense and porous, the corrosion resistance improves, but the cracks observed in the surface film in TiNbZr alloys cause negative effects [9].

The aim of this study is to investigate the wear and tribocorrosion behavior of titanium alloys such as Cp-Ti, Ti6Al4V and Ti45Nb using different counterparts such as SiN and WC. In addition, the effect of surface condition was investigated by applying plasma oxidation process to these materials.

2. Experimental Details

In this study, three groups of titanium alloys were used: Cp-Ti, Ti6Al4V and Ti45Nb. The samples were grinded by 800 mesh to 1200 SiC emery paper grit and then they were polished with 3 μm grain size alumina powder. After polishing with alumina powder, the samples were cleaned with alcohol. For plasma oxidizing process, the samples were placed as cathode into plasma chamber which was evacuated to 2.5 Pa. In

order to samples' surfaces cleaning, hydrogen sputtering was performed under 500 V for 15 min with a pressure of $5x10^2$ Pa at 100 ℃. The plasma oxidizing treatment was carried out under 70% O_2-30% Ar and at 600˚C for 3 h.

The tribological properties of the samples were determined using reciprocation tribo-test device tester with 6 mm diameter and silicon nitride (SiN) and tungsten carbide (WC) balls as a counterpart. Experiments were carried out in both dry and Simulated Body Fluid (SBF) environments using normal loads of 3 N and speed of 0.5 Hz. In the wear tests with SBF, solution suggested by Kokubo and Tamada was used and its content was ion concentrations-mM 142.0 Na^+, 147.8 Cl^-, 4.2 HCO^{-3}, 5.0 K^+, 1.5 Mg^{2+}, 2.5 Ca^{2+}, 1.0 HPO_4^{-2} ,0.5 SO_4^{-2}, 7.4 pH [10].

In tribocorrosion experiments, open circuit potential changes of the samples (OCP) were measured and potentiodynamic polarization with wear measurements after the sample and electrolyte reached equilibrium. During the potentiodynamic polarization measurement, the wear test was carried out simultaneously. Potentiodynamic polarization scans were carried out using the scanning range of -0.28 V - 2 V in the presence of wear tests for tribocorrosion measurements. The experiment was carried out in SBF solution. Test measurements in a corrosion cell were made using the Ag / AgCl reference electrode (RE), the graphite rod as the counter electrode (CE) and the working electrode (WE) test sample.

The worn surfaces were investigated by FEI QUANTA-FEG 50 scanning electron Microscopy (SEM). The phase analyses were carried out using PANalytical EMPYREAN X-ray diffractometer using CuKα (λ= 1.5406 Å) radiation

3. Results and Discussion

XRD spectra of plasma oxidized Cp-Ti, Ti6Al4V and Ti45Nb samples are given in Fig.1. When the figure 1 is examined, it can be seen that the oxidation process of the Ti45Nb alloy at 600 ° C for 3 hours does not create a significant oxide phase except for the small amount of rutile and magnet phases (Ti_nO_{2n-1}), but the phase β (110) shifts to the left. The formation of the reflection angle means that the lattice parameters have changed. The reason for this is that oxygen atoms diffusing to the surface of the material settle in the interstitial, creating pressure stresses and widening the lattice structure. The Ti6Al4V alloy has an alpha + beta (α+β) structure, and as a result, the alpha phase is

dominantly observed in XRD spectra, as well as the beta and rutile phase. Rutile titanium dioxide (R) peaks can be clearly seen in plasma oxidized samples. As a result of this observation, the presence of oxygen atoms chemically bound to Ti atoms during plasma oxidation processes is revealed.

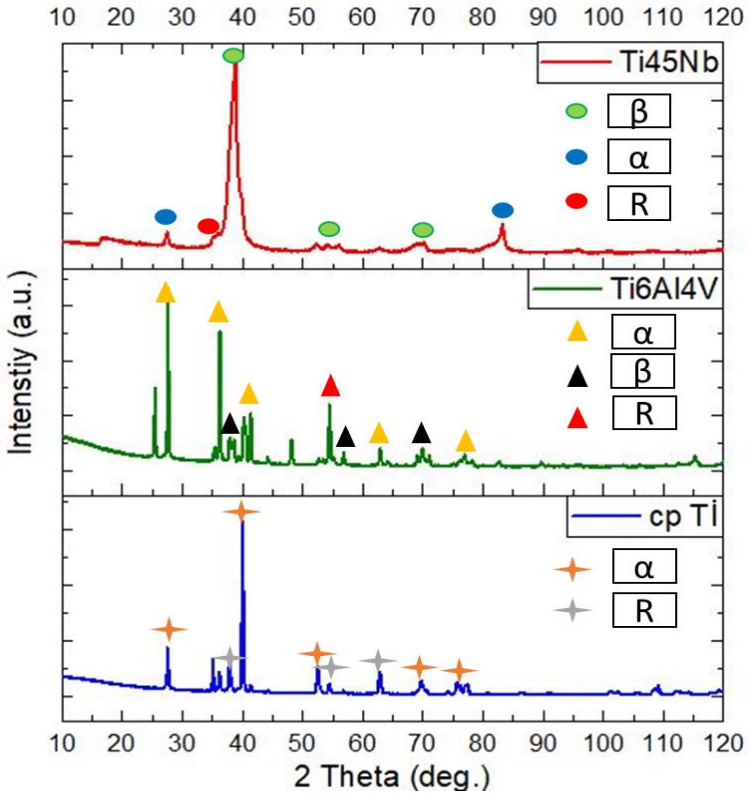

Fig. 1 XRD spectra of plasma oxidized Cp-Ti, Ti6Al4V and Ti45Nb samples

The CoF vs. time graph for Cp-Ti, Ti45Nb and Ti6Al4V titanium alloys are given Fig. 2-4. A lower coefficient of friction was obtained due to the lack of direct contact between the pin and the surface of the material. As a result of the plasma oxidation process, the surface roughness increases as the surface of the sample is constantly exposed to ion bombardment. The increase in the roughness of the century also creates an increase in the friction coefficient value [12,13].

As a result of the plasma oxidation process, the hardness value of the material increases. The reason for this situation is that oxygen atoms located in the intermediate places in the cage structure expand the cage and create pressure residual stresses. pressure now brings the plastic strain resistance along with the stresses. Thus, the wear resistance of the material is increased [11,12,13].

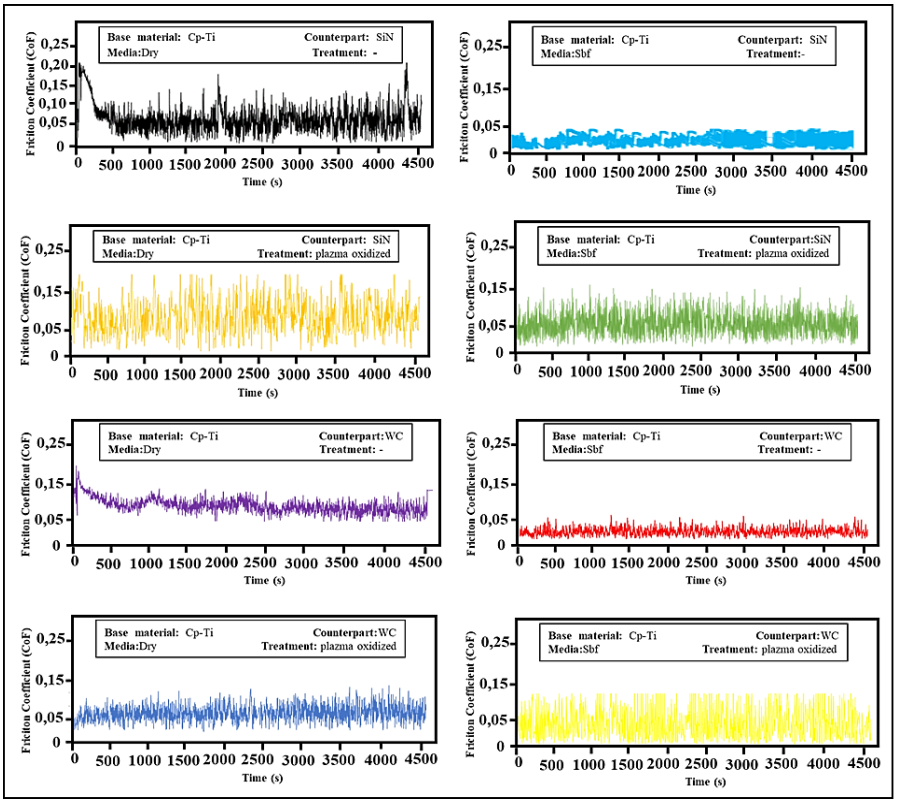

Fig. 2 The Coefficient of friction vs. time graph for Cp-Ti,

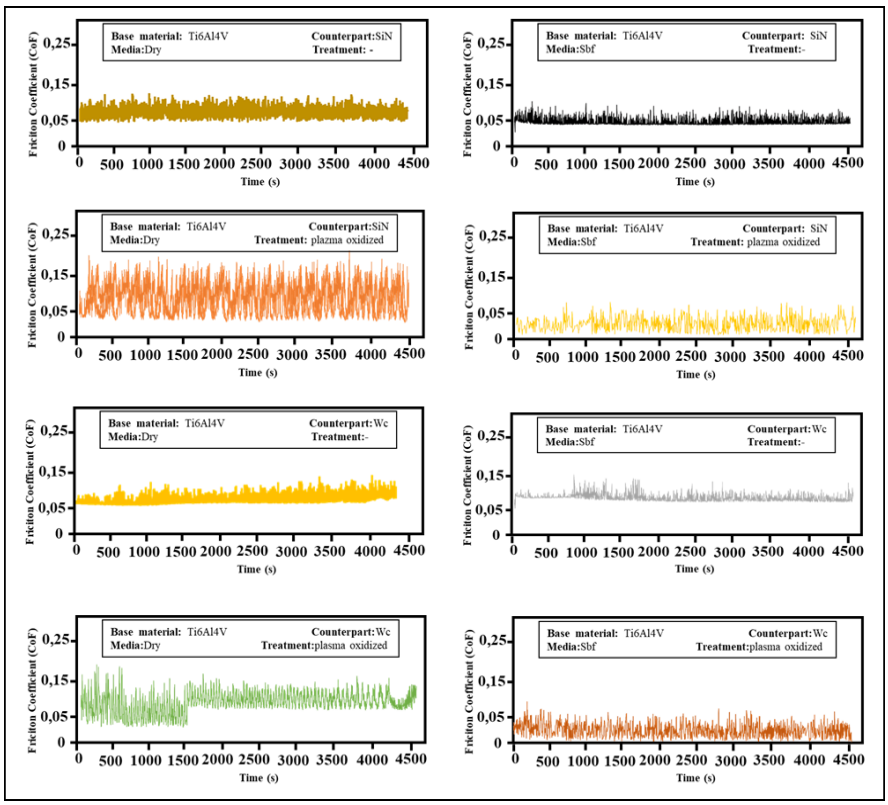

Fig. 3 The Coefficient of friction vs. time graph for Ti6Al4V

SEM images of worn surfaces under dry sliding and SBF solution are shown in Fig. 5. When wear widths are examined, it is narrower in SBF solution compared to dry condition. If the Sem images are investigated carefully, the adhesion mechanism is dominant. Also, wear debris create a third particle effect between the ball and the sample surface.

When the tribocorrosion sem images were examined (Fig. 5e-f) oxidative wear mechanism was observed due to the formation of oxide on the surface of the material compared to others and the adhesive adhesive mechanism is dominant.

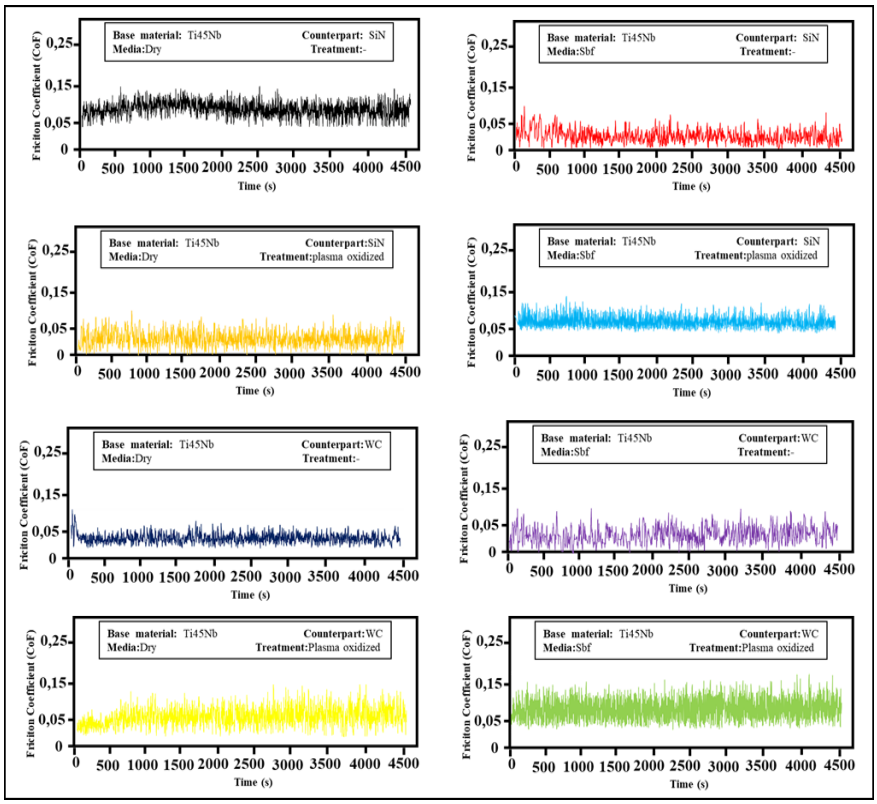

Fig. 4 The Coefficient of friction vs. time graph for Ti45Nb

Adhesive wear mechanism was observed especially after oxidation process. Easy breakage of the white layer formed as a result of the plasma oxidation process during wear causes an increase in wear rate and friction coefficient.

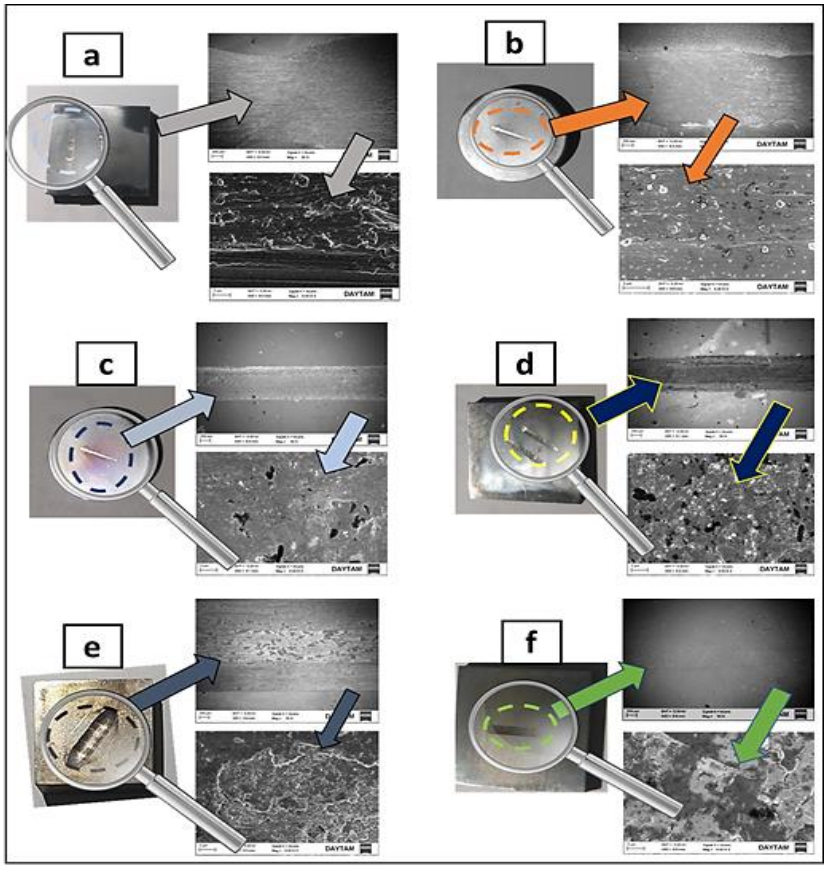

Fig. 5 The Coefficient of friction vs. time graph for a.) Ti45Nb alloy under dry condition with WC ball as counterpart b.) Cp-Ti alloy under SBF solution with SiN ball as conunterpart c.) Cp-Ti alloy under dry condition with SiN ball as counterpart d.) plasma oxidizing Ti6Al4V alloy under SBF solution with WC ball as counterpart e.) Ti45Nb alloy under tribocorrosion test f.) plasma oxidizing Ti45Nb alloy under tribocorrosion test

Current density-potential curves for all conditions of titanium and its alloys is given Fig.6. In tribo-corrosion analysis, after reaching the equilibrium in the open circuit potential, potentiodynamic scanning was performed. Even if this screening process was initiated in the cathodic region, the cathodic region was observed to be either absent or very small. This is because the passive oxide layer on the surface becomes active after the wear process begins.

In Figure 6, potentiodynamic polarization scanning curves of untreated and plasma oxidized Ti alloys under wear are given. The anodic polarization curves of the samples are in a densely wavy form. The current density varies with the track width under different conditions. Therefore, the width of these fluctuations can be associated with the

surface contact area of the sliding balls (SiN, WC). In addition, the permanent degradation of the natural oxide film during wear is one of the main causes of oscillation. The areas where the sliding ball moves away become passive again, while the areas it passes over become active again. Since the polarization and wear test was started simultaneously, the oscillation continued from the start of the test to the end. It is seen that the cathodic branch does not occur in the curves. In all conditions, the activation of the passive oxide layer after activation started and the removal of the scan start from the OCP value prevented the formation of cathodic branch.

The oscillations lasted at constant levels due to the fact that the natural oxide layer, which passivated the surface in the untreated samples, had a similar effect on the corrosion mechanism during the test and the absence of a second layer. However, the presence of excessive deviations in the oscillations where there are no constant levels of oscillations is observed in the oxide coated samples. The anodic branches of oxidized samples in the same scanning range have reached more noble potential values than untreated samples. TiO_2 ceramic films delayed the access of the electrolyte liquid to the base material with the increase of wear resistance. In addition to the formation of the TiO_2 phase in the Ti45Nb alloy, the presence of the Nb_2O_5 phase has increased the resistance of this alloy electrochemically.

4. Conclusions

In this study, alpha, alpha + beta, beta structure and titanium and its alloys, which have many applications, are oxidized in the atmosphere of 70% O_2 + 30% Ar at a temperature of 600 °C and 3 hours by the plasma oxidation process, which is a thermochemical method. Structural, tribological, tribo-corrosion properties of oxidized and untreated samples were examined and the results are summarized below.

- As a result of the plasma oxidation process, the surface roughness of the material increases and the friction coefficient increases.
- Oxygen atoms on the surface of the material expand the lattice structure and create pressure stresses. As a result of this situation, hardness value and wear resistance increase.
- When sem images are examined as a result of wear in alloys, the generally dominant mechanism is adhesive wear.

- Plasma oxidation surface treatment has generally improved tribological and tribocorrosion properties.
- Maximum tribocorrosion resistance was obtained from plasma oxidized Ti45Nb sample.
- No significant qualitative difference of SiN and WC wear balls of different hardness could be detected on tribocorrosion tests.

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