

Characterization and wear properties of carbon nanotubes incorporated ceramic coatings on Ti6Al4V and Ti6Al7Nb alloys

S.K. Yazıcı, F. Muhaffel, Y. Yurekturk, M. Baydoğan*

Department of Metallurgical and Materials Engineering, Istanbul Technical University,
34469 Maslak – Istanbul, Turkey

* Corresponding e-mail address: baydogan@itu.edu.tr

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ABSTRACT

Purpose: of this paper is characterization and wear properties of carbon nanotubes incorporated ceramic coatings on Ti6Al4V and Ti6Al7Nb alloys.

Design/methodology/approach: Carbon nanotubes (CNTs) incorporated ceramic coatings were fabricated by micro arc oxidation (MAO) method to improve the tribological performance of Ti6Al4V and Ti6Al7Nb alloys for wear resistant applications. Titania and CNTs incorporated titania coatings were formed on Ti6Al4V and Ti6Al7Nb alloys via MAO process. Surface and cross-sectional morphology, phase composition, thickness and roughness of the ceramic coatings were investigated by using scanning electron microscopy (SEM), X-ray diffraction (XRD) and surface profilometer.

Findings: Wear behavior of bare titanium alloys and those of their oxidized surfaces (with and without CNTs addition) were evaluated by reciprocating wear test against 100Cr6 steel ball at dry sliding condition. XRD analyses of the oxidized samples demonstrated that coatings were consisted mainly of rutile and aluminum titanate. Surface morphologies of the coatings revealed that CNTs addition into the electrolyte led to generation of less porous, flat regions surrounded by relatively irregular-shaped pores on the surface of the coatings. Wear rate of CNTs incorporated coatings was decreased significantly compared to coatings generated without CNTs addition.

Research limitations/implications: CNTs addition into the base electrolyte sharply decreases wear rate of both alloys, and there is no significant difference between the wear rates of Ti6Al4V and Ti6Al7Nb alloys oxidized in CNTs added electrolyte.

Originality/value: Titanium and its alloys are attracting a great deal of attention especially in automotive and aerospace industries. However, titanium-based materials tend to have insufficient wear resistance in abrasive conditions. In an attempt to overcome this limitation, carbon nanotubes (CNTs) incorporated ceramic coatings were fabricated.

Keywords: Titanium alloy; Micro arc oxidation; Titania coating; Carbon nanotubes; Wear resistance

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PROPERTIES

1. Introduction

Titanium and its alloys are widely used in aerospace, automotive, chemical and biomedical industries due to their low density, high strength, high melting point and good corrosion resistance [1,2]. Among these properties, titanium and its alloys exhibit poor wear resistance due to severe adhesive wear mechanism against steel tools. Low surface hardness and low wear resistance of titanium alloys are substantial problems for the use of them in wear related applications. The mentioned disadvantages reduce the useful life of parts made of titanium alloys. However, as it has been indicated by the researches, it is possible to overcome these problems with various surface treatments. These methods include physical vapour deposition (PVD) [3], chemical vapour deposition (CVD) [4], conventional anodization [5] and micro arc oxidation (MAO) [6]. The most attractive one among these methods is MAO process which can generate smooth, hard and thick ceramic coatings on the surface of valve metals such as Al, Mg, Ti, Zr, and so on [7]. While the MAO technology exhibits a continuous growth on research and development, it is more economical and far better environmentally friendly technique than other technologies. As a key advantage of the MAO technique, all types of titanium alloys can be coated easily and superior surface properties can be achieved with MAO method. Typical MAO equipment consists of high power supply unit, cooling water, mixer, electrolyte bath, anode (sample), thermometer and cathode (stainless steel container). In principle, high voltage (or current density) between anode and cathode is applied in the electrolyte. This voltage is so high that it exceeds the breakdown voltage of the oxide layer and creates micro arcs on the surface of the material. With these arcs, the oxide layer on the sample surface can be generated rapidly due to intensive dissolution of base metal and subsequently oxidation of metallic ions on the surface [8]. The titania coating that is formed on titanium based materials through MAO process has many beneficial properties, such as high wear resistance and corrosion resistance, high surface hardness and even enhanced photo-catalytic properties [9]. Furthermore, some additives also can be incorporated into the MAO coatings. These additives can include ceramics (ZrO_2 , Al_2O_3 , TiB_2 etc.), organic compounds (tannic acid), polymers (PTFE) and carbon-related materials (carbon nanotubes) [10-12]. By the incorporation of these additives into the oxide coating, MAO coatings exhibit a dense and less porous microstructure, improved wear and corrosion resistance and higher hardness.

In this study, Ti6Al4V and Ti6Al7Nb alloys were micro arc oxidized in an alkaline solution with or without carbon nanotubes (CNTs) addition into the electrolyte. As a result of this process, formed oxide coating was investigated regarding the effect of carbon nanotubes on surface morphology, mechanical properties and dry sliding wear behaviour.

2. Material and method

2.1. Micro arc oxidation

Disc shaped Ti6Al4V and Ti6Al7Nb samples having 8 mm diameter and 4 mm thickness were cut, ground by SiC abrasive papers up to #1200 and then subjected to the MAO process at the constant voltage mode. A 30 kW bipolar power supply with a stainless steel container serving as the cathode, was used in the MAO process. The first group of samples were oxidized for 5 min in an aqueous electrolyte (base electrolyte) containing $NaAlO_2$ (VWR International LLC) and KOH (VWR International LLC) with the applied voltage of 300 V in the positive half cycle and 60 V in the negative half cycle. The second group of the samples was oxidized under same MAO conditions but with the addition of 2 g/L of CNTs into the base electrolyte. The pulse frequency and duty cycle were 833 Hz and 33%, respectively. During the process, the temperature of the electrolyte was below 30°C by the external cooling system. After the MAO treatment samples were washed with distilled water and dried in air.

2.2. Characterization

Surface morphology and microstructure of the coatings were examined by scanning electron microscope (SEM, Hitachi, TM-1000). The phase composition of the coatings was identified by X-ray diffractometer (XRD, GBC, MMA 027) using Cu $K\alpha$ radiation ($\lambda = 0.154$ nm) at 35 kV and 28.5 mA with a scan range between 10-90° at a step of 0.020° and a scanning speed of 2°/min. Elemental distribution on the wear tracks was analyzed by Electron Probe Micro Analysis (EPMA, Cameca SX-100) Mean surface roughness (Ra) of the samples was measured by using a surface profilometer (Veeco Dektak, 6M). The coating thickness was determined by the cross-sectional observations performed in SEM.

2.3. Wear tests

Dry sliding wear tests of untreated and coated samples were performed by a reciprocating wear tester (Tribotech Oscillating Tribotester) operating in ball-on-disc configuration at room temperature. In this configuration, a 100Cr6 ball with a diameter of 6 mm was sliding forward and backward against the samples with a sliding speed of 4 mm/s. Normal load of the test, sliding amplitude (wear track length) of the reciprocating motion and overall sliding distance were 3 N, 2 mm and 25 m, respectively. During the wear tests, the temperature and the relative humidity were maintained as $23 \pm 2^\circ\text{C}$ and $32 \pm 3\%$, respectively. The friction force was continuously measured during the tests and divided by the normal load to calculate friction coefficient. Width and depth of the wear tracks were measured by a surface profilometer (Veeco Dektak 6M) to calculate worn volume of the samples and wear rate. Following the wear tests, wear tracks and wear scars on counterface (100Cr6 ball) were examined by an optical microscope (Leica ICC50HD) and a scanning electron microscope (SEM, Hitachi TM-1000).

3. Results and discussion

3.1. Characterization

XRD patterns of Ti6Al4V, Ti6Al7Nb, Ti6Al4V-CNTs and Ti6Al7Nb-CNTs samples are presented in Fig. 1. The coatings are mainly composed of aluminium titanate (Al_2TiO_5) and rutile (TiO_2) as the stable phase of titanium oxide at high temperatures. Intensity of titanium peaks is higher than that of other phases due to penetration of X-rays into the substrates and varied from sample to sample depending on coating thickness. Aluminium titanate was incorporated into the coatings during MAO treatment from the species in of the electrolyte. Interestingly, it was observed that CNTs addition into the electrolyte increased the formation of aluminium titanate on the surface coating. While CNTs addition into the electrolyte induced an intensive sparking and increase in current density, the phase transformation from aluminium and titanium oxides to aluminium titanate encouraged.

The surface morphologies of the coatings formed on Ti6Al4V and Ti6Al7Nb with and without CNTs addition into the electrolyte during the MAO process are shown in Fig. 2. Ti6Al4V and Ti6Al7Nb samples exhibited similar surface characteristics with micro-pores distributed on the surface and no surface cracks were visible on the surfaces of both samples. Micro-pores formed during the sparking stage during the MAO process and generally called as micro-discharge channels. The porous surface characteristics

strictly depends on discharging nature involved in the MAO mechanism. With the addition of CNTs, the micro-pores number decreased sharply, while flat regions occurred on the surfaces of Ti6Al4V-CNTs and Ti6Al7Nb-CNTs samples. The mentioned flat regions were generated through the ejection of more molten oxide due to very high temperature inside the channels sealed the smaller discharge channels and then cooled down as flat regions on the surface. It is suggested that the rapid contingence of CNTs particles on the surface induced an increase in high local temperature which caused smooth regions on the surface of CNTs incorporated samples. Similar observations were obtained in the previous study about CNTs incorporation in MAO coatings on Cp-Ti samples [12].

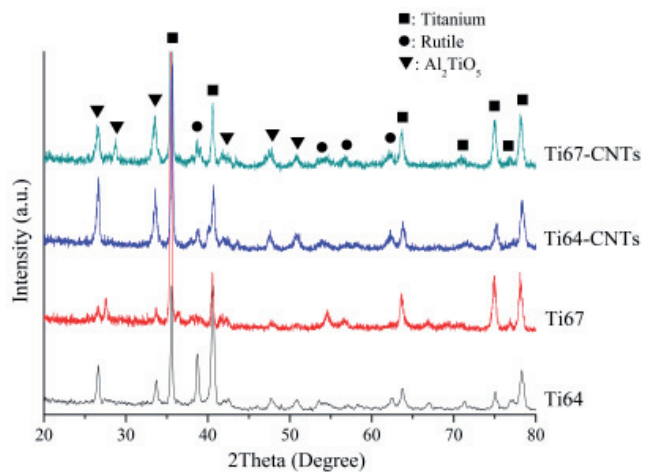


Fig. 1. XRD patterns of MAO coatings formed with and without CNTs addition into the electrolyte

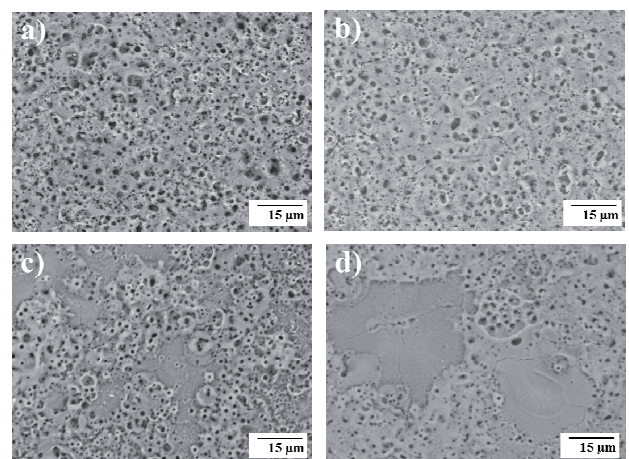


Fig. 2. Surface SEM micrographs of a) Ti6Al4V, b) Ti6Al7Nb, c) Ti6Al4V-CNTs and d) Ti6Al7Nb-CNTs samples

Cross-sectional microstructures of the coatings formed on titanium alloys with and without CNTs addition into the electrolyte during the MAO process are shown in Fig. 3. It is observed that the microstructure of the cross-sections of the coatings had a dense and uniform structure with no significant evidence of cracking. There was no spallation or discontinuity at the coating-substrate interface which showed that the adhesion of the coatings to the substrate is good. The porosity of the coatings treated in CNTs containing electrolyte increased slightly, especially for the Ti6Al4V sample. The variation of thickness of the coatings (Fig. 4) on the samples prepared in CNTs containing electrolyte was not so uniform as the samples prepared in the base electrolyte (without CNTs addition). This may be due to the intensive melting of oxide phases on the coating surface and therefore, the growth of the coating is not relatively inhomogeneous due to high current density on the surface.

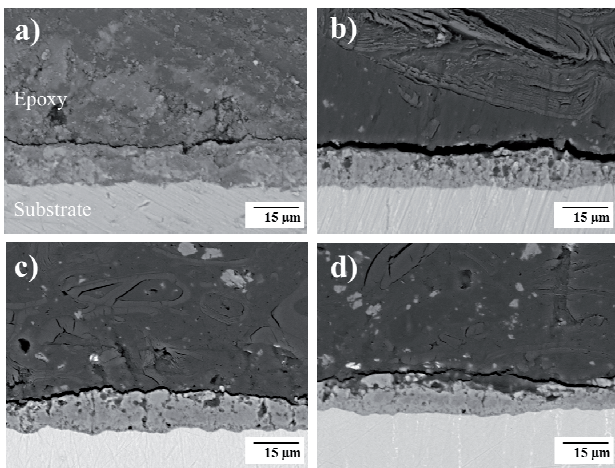


Fig. 3. Cross-sectional SEM micrographs of a) Ti6Al4V, b) Ti6Al7Nb, c) Ti6Al4V-CNTs and d) Ti6Al7Nb-CNTs samples

3.2. Wear characteristics

The wear rates and the mean thickness of the MAO coatings on Ti6Al4V and Ti6Al7Nb alloys with and without CNTs addition into the electrolyte are demonstrated in Fig. 4. The wear rates of the coatings of Ti6Al4V and Ti6Al7Nb were between 0.42×10^{-3} and $0.40 \times 10^{-3} \text{ mm}^3/\text{Nm}$ while the wear rate of Ti6Al4V-CNTs and Ti6Al7Nb-CNTs were determined as 0.05×10^{-3} and $0.07 \times 10^{-3} \text{ mm}^3/\text{Nm}$.

It is clearly observed that there were obvious plastic deformations on the worn track of the MAO coatings without CNTs addition. The coatings on them were spalled out and bare metal appeared as shown in Figs. 5a,b. Therefore, the wear mechanism of Ti6Al4V and Ti6Al7Nb is dominantly abrasive wear. The addition of CNTs into the electrolyte significantly improved the wear resistance of the MAO coatings (Fig. 4 and Fig. 5). The worn surface of the Ti6Al4V-CNTs and Ti6Al7Nb-CNTs samples exhibited very smooth appearance except some detachments on the coating shown as relatively darker areas presented in Figs. 5c,d.

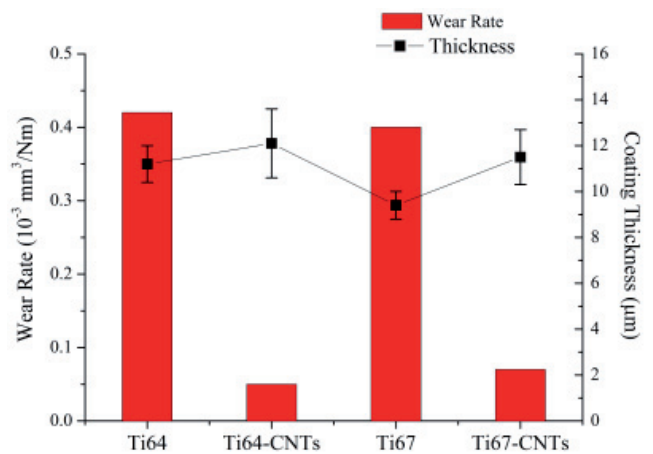


Fig. 4. Wear Rate and mean coating thickness of oxidized samples

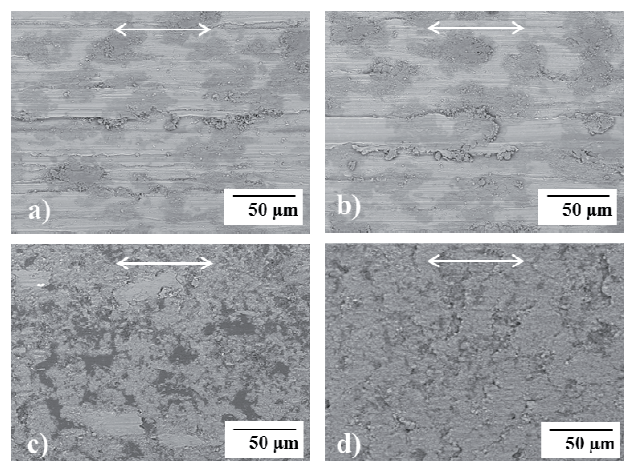


Fig. 5. Wear tracks of a) Ti6Al4V, b) Ti6Al7Nb, c) Ti6Al4V-CNTs and d) Ti6Al7Nb-CNTs samples

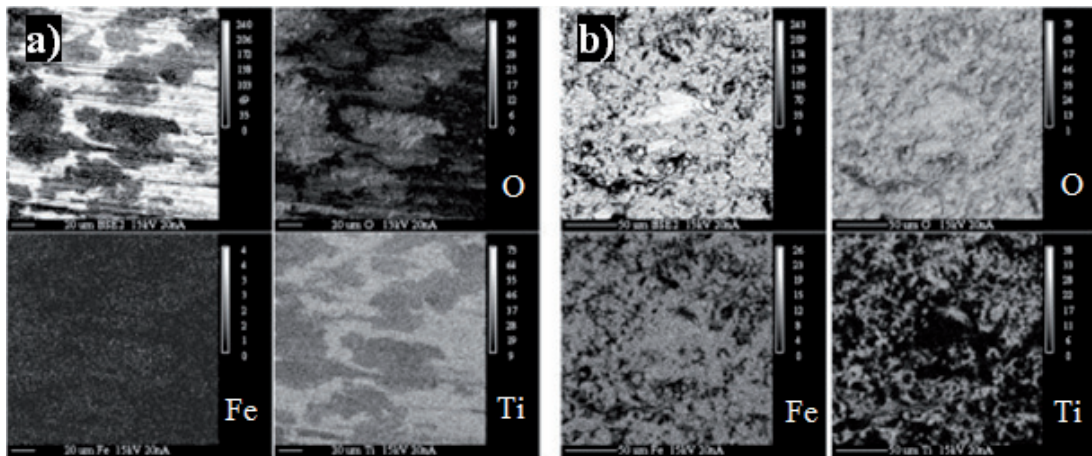


Fig. 6. EPMA mappings of wear tracks of a) Ti6Al4V and b) Ti6Al4V-CNTs samples for O, Fe and Ti on the surface

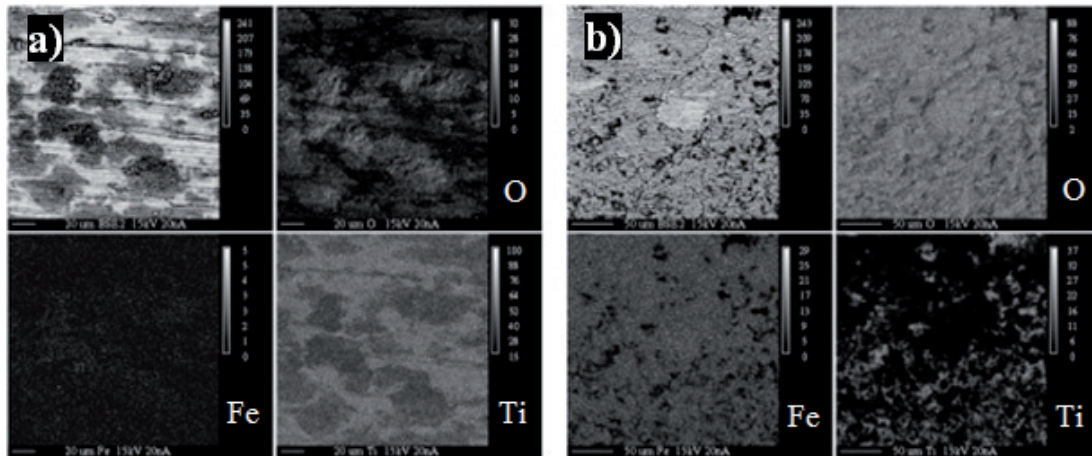


Fig. 7. EPMA mappings of wear tracks of a) Ti6Al7Nb and b) Ti6Al7Nb-CNTs samples for O, Fe and Ti on the surface

In accordance with the wear rates and SEM micrographs of worn surfaces, the chemical composition analyses performed by EPMA showed that higher oxygen concentration on wear tracks of Ti6Al4V-CNTs and Ti6Al7Nb-CNTs samples (Fig. 6 and Fig. 7) was detected compared to the coatings formed without CNTs addition. Presence of oxygen on the coatings indicates that oxide coating formed with CNTs addition was more durable during the wear tests than the coatings formed without CNTs addition. In addition, it was apparent that more iron was detected on CNTs incorporated samples, indicating more material transfer from counterface steel ball (100Cr6) to the wear track as a result of extensive wear of the steel ball.

4. Conclusions

Following conclusions can be drawn from this study, where Ti6Al4V and Ti6Al7Nb alloys were micro arc oxidized in an aqueous electrolyte solution containing NaAlO_2 and KOH with and without CNTs addition.

1. Surface coatings formed by micro arc oxidation in the base electrolyte consist of rutile form of titania and aluminium titanate.
2. CNTs incorporation into the base electrolyte leads to an intensive sparking and increases the current density during micro arc oxidation and encourages more aluminium titanate formation on the surface.

3. Surfaces of micro arc oxidized samples exhibit characteristic morphology of micro arc oxidation with uniformly distributed pores along the surface, while CNTs addition into the base electrolyte decreases number of pores on the surface and some flat regions around the pores were appeared.
4. CNTs addition into the base electrolyte did not significantly affect coating thickness.
5. Both Ti6Al4V and Ti6Al7Nb alloys oxidized in the base electrolyte have almost the same wear rate. CNTs addition into the base electrolyte sharply decreases wear rate of both alloys, and there is no significant difference between the wear rates of Ti6Al4V and Ti6Al7Nb alloys oxidized in CNTs added electrolyte.

Additional information

This paper will be presented at 15th International Materials Symposium (IMSP2014).

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