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Effect of incorporating carbon nanotubes into electrolyte on surface morphology of micro arc oxidized Cp-Ti

Selim Kaan Yazıcı [a], Faiz Muhaffel [a], Murat Baydogan [a,b,*]

[a] Istanbul Technical University, Department of Metallurgical and Materials Engineering, Maslak Istanbul 34469, Turkey
[b] Istanbul Technical University, Prof. Dr. Adnan Tekin Material Sciences and Production Technologies Applied Research Center, Maslak Istanbul 34469, Turkey

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ABSTRACT

In the present study, effect of carbon nanotubes (CNTs), as electrolyte additives in the micro arc oxidation (MAO) process, on surface morphology of commercially pure titanium (Cp-Ti) was investigated. MAO process was carried out under constant bipolar voltage pulses using two different positive and negative voltage combinations. Results showed that CNTs were successfully incorporated into the coating surface especially within the pores generated by the discharge channels during the MAO process as confirmed by SEM examinations. As the applied voltage and CNTs concentration in the electrolyte were increased, size of micro pores on the surface also increased and their numbers decreased. Higher amount of CNTs addition in the electrolyte resulted in a corresponding decrement in the coating thickness after the MAO process.

1. Introduction

Titanium and its alloys are widely used engineering materials in aerospace, chemical, biomedical, and automotive industries due to their relatively low density, high strength/weight ratio, biocompatibility, and high corrosion resistance [1–3]. Biocompatibility and corrosion resistance of titanium-based materials arise from native oxide layer (TiO_2) formed at the surface [4]. However, this native oxide layer provides insufficient protection against wear and fretting as well as corrosion in aggressive environments. In addition, these materials exhibit low hardness and high coefficient of friction. It is therefore aimed to improve surface properties of titanium-based materials by numerous surface modification techniques such as physical vapor deposition (PVD) [5], gas nitriding [6], chemical vapor deposition (CVD) [7], conventional anodization [8], and micro arc oxidation (MAO) process [9]. Among these techniques, the MAO process is an attractive one which generates hard, dense, and thick oxide coatings on the surface of valve metals such as Al, Mg, Nb, Zr, and Ti and their alloys, and employ high hardness, excellent wear resistance as well as enhance corrosion resistance of the substrates [10–14]. Additionally, high adhesion strength between the substrate and the coating is another advantage for extreme environments compared to conventional anodization [15]. Another approach to improve surface properties of oxide coatings formed by the MAO process is to incorporate mainly ceramic-based materials into the oxide coating [16–19]. These complex structures of oxide coatings further enhance tribological and corrosion behaviors of the material and provide high hardness to the surface.

CNTs have been major constituents of nano technological research since they were discovered by Iijima in 1991 [20]. Due to their unique properties such as high thermal and electrical conductivity, high chemical stability, and high energy storage capability, applications of CNTs tend to increase steadily [21].

There are numerous works in the literature focusing on various factors affecting structural and morphological properties of oxide coatings generated by the MAO process [22–26]. These include electrical parameters such as applied voltage, current density, frequency, and pulse characteristics as well as total processing time of the process and composition of the electrolyte [27–29]. Despite to this fact, incorporation of CNTs as electrolyte additives in the MAO process is very limited. In such works, Lee et al. [30,31] studied effect of CNTs incorporation into the oxide coatings formed on the surface of 7075 aluminum alloy by the MAO process. They found that incorporation of CNTs reduced pore density on the surface and improved corrosion resistance of the oxide coating in 3.5 wt.% NaCl solution. On the other hand, to our knowledge, there is no published work focusing on the effect of CNTs as electrolyte additives on surface properties of titanium-based materials. This work is therefore aimed to investigate effect of CNTs added into the electrolyte during the MAO process on structural and morphological properties of Cp-Ti.

* Corresponding author. Tel.: +90 212 285 30 96; fax: +90 212 285 71 78.
E-mail addresses: yazicisel@itu.edu.tr (S.K. Yazıcı), muhaffel@itu.edu.tr (F. Muhaffel), baydogan@itu.edu.tr (M. Baydogan).

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2. Material and methods

Grade 4 quality Cp-Ti discs (8 mm in diameter and 4 mm in thickness) were cut and ground using SiC abrasive paper up to #1200. Afterwards, the samples were cleaned in acetone and distilled water and then dried in air, successively. The base electrolyte was an aqueous solution of 15 g/L sodium aluminate ($Na_2Al_2O_4$, Alfa Aesar) and 2 g/L potassium hydroxide (KOH, Alfa Aesar). Multi-walled carbon nanotubes (MWCNTs, Grafen Chemical Industries™) used in this study were produced via catalytic carbon vapor deposition (CCVD) process and have an average diameter of 9.5 nm and a length of ~1.5 μm. The purity and BET surface area of MWCNTs are reported by the manufacturer as >90% and about 250 m^2/g, respectively. CNTs were added into the base electrolyte with concentrations of 2 and 4 g/L. The samples which were oxidized in CNTs containing electrolytes were referred as CNTs-2 and CNTs-4 according to their CNTs concentration, while the samples oxidized in the base electrolyte (without CNTs) were named as MAO. A 30 kW power supply with a stainless steel container serving as the cathode, was used in the MAO process and the sample was connected as the anode. During the process, temperature of the electrolyte was controlled around 30 °C by an external cooling system. A constant voltage mode was used in the present study. Power supply was capable of applying successive bipolar square pulses, and all oxidation processes were performed by applying positive voltages in the range of 300 and 375 V and negative voltages of 60 and 75 V for a total processing time of 5 min. Following the MAO process, samples were washed ultrasonically with ethanol and distilled water and then dried in air at room temperature.

Surface morphology of the samples was examined by scanning electron microscopes (SEM, Hitachi TM-1000, JEOL JSM 6335F FEG and Philips XL 30 SFEG). Qualitative phase analysis of the coatings was performed by an X-ray diffractometer (XRD, GBC MMA 027) using Cu K_α radiation at 35 kV and 28.5 mA. The samples were scanned over 2θ angles of 20–80° at a step of 0.02° and a scanning speed of 2°/min. The XRD patterns were identified utilizing PANalytical X'Pert High Score software based on the International Centre of Diffraction Data JCPDS- ICDD database. Mean surface roughness (R_a) of the samples was measured by using a surface profilometer (Veeco, Dektak 6 M). At least 10 measurements were performed for each sample, and the results were averaged. The mean coating thickness of the samples was determined by a thickness gage operating according to eddy current principle (Fischer, Dualscope MP20E-S). At least 5 measurements were applied on different locations over the surface of each sample, and the results were averaged. Raman spectroscopy analyses were performed by using Renishaw inVia Raman spectrometer with a constant excitation wave length of 514.5 nm.

3. Results and discussion

XRD patterns of MAO, CNTs-2, and CNTs-4 samples oxidized at a positive voltage of 300 V are shown in Fig. 1. It was identified that the coating formed in the electrolyte without CNTs addition (MAO sample) was composed of mainly titanium dioxide (TiO_2, JCPDS #73-1765) in the form of rutile and weak peaks of aluminum titanate (Al_2TiO_5, JCPDS #41-0258) were also identified. Peaks corresponding to titanium (Ti, JCPDS #1-1198) come from the underlying substrate due to low thickness and porosity in the coating [23,32]. Any peak related to CNTs was not detected, possibly because of low amount of CNTs in the coating structure. In a similar work performed by Lv et al. [33] graphite grains in different size were added into electrolyte in the micro arc oxidation process and they could not observed any carbon related peak in the XRD patterns. It was mentioned that absence of carbon-based peaks can be explained by irregular distribution of graphite powders.

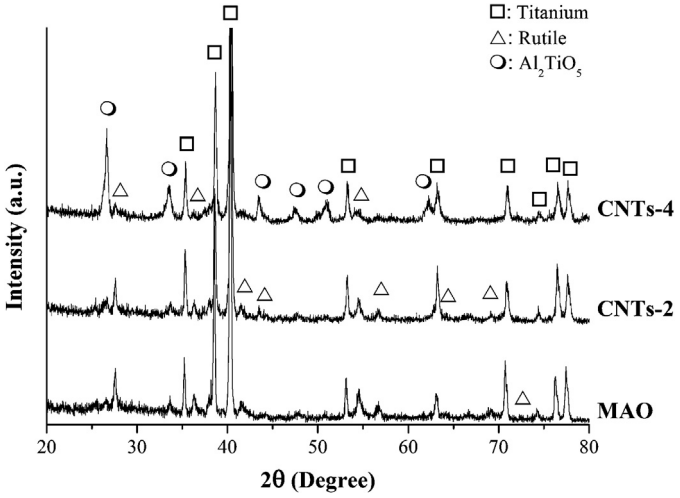

Fig. 1. XRD patterns of MAO, CNTs-2, and CNTs-4 samples oxidized at 300 V.

As shown in Fig. 1, CNTs addition into the electrolyte promoted the formation of Al_2TiO_5 as a complex phase rather than TiO_2. In addition, higher concentration of CNTs in the electrolyte (CNTs-4) induced more Al_2TiO_5 formation as clearly observed from the peak intensities of Al_2TiO_5, while TiO_2 peaks nearly disappeared. In alkaline aluminate electrolytes, mainly OH^- and AlO^{2-} anions generate the anodizing current [32]. Aluminate anions can partly interact with water and/or form complex anions such as $Al(OH)_4^-$ or $Al_n(OH)_{4n+2}^{(n+2)-}$ because of their relatively unstable nature. Elemental Ti transforms into Ti^{4+} ions by applied high voltage on anode. During MAO process, Ti^{4+} and aluminate ions firstly form TiO_2 and aluminum oxide (Al_2O_3) phases. In the further steps of MAO process, surface plasma discharges tend to generate more complex (Ti—O—Al) containing compounds such as Al_2TiO_5 due to elevated temperature on the surface. Oxidation reactions in alkaline aluminate electrolyte can be described according to following reactions [32,34]:

$$Ti \rightarrow Ti^{4+} + 4e \quad (1.1)$$

$$Ti^{4+} + 2OH^- + 2H_2O \rightarrow TiO_2 + 2H_3O^+ \quad (1.2)$$

$$Ti^{4+} + 4AlO_2^- \rightarrow TiO_2 + 2Al_2O_3 \quad (1.3)$$

$$TiO_2 + Al_2O_3 \rightarrow Al_2TiO_5 \quad (1.4)$$

Fig. 2 shows XRD patterns of CNTs-4 samples with respect to different positive voltage levels (300 and 375 V). XRD patterns demonstrated that Al_2TiO_5 peaks became more dominant with a corresponding decrement of Ti peaks due to thickening of oxide coating, as the applied voltage increased.

Surface SEM micrographs of MAO, CNTs-2, and CNTs-4 samples oxidized at 300 and 375 V are presented in Fig. 3. Surface of the samples exhibited characteristic nature of MAO process. As CNTs concentration in the electrolyte or applied voltage were increased, average diameter of the pores generated by the micro discharges during the MAO process also increased, and number of pores decreased. Pores became much more irregular in shape and reached up to nearly 20 μm in diameter for CNTs-4 sample oxidized at 375 V. Montazeri et al. [35] reported that as the applied voltage increases higher energy sparks are formed at the surface and this leads to the formation of larger pores at the end of micro arc oxidation. It should be noted that some plateaus (smooth regions) around the pores were also observed from SEM micrographs of the samples, which is probably due to rapid solidification of the molten

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