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EFFECT OF APPLIED VOLTAGE AND SUBSTRATE PREPARATION ON SURFACE MODIFICATION OF ANODICALLY OXIDIZED TITANIUM

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In the present work, anodic oxidation (AO) treatment was used to modify surface of commercially-pure (CP) titanium. C.P-Ti ASTM grade 2 specimens, in two shapes of disc and plate were prepared for this work. Disc titanium specimens were ground, polished and etched, while plate ones just etched. Afterwards anodic oxidation treatment performed in phosphoric acid electrolyte at 100, 200, and 300V. Crystalline structures of the substrate and grown films were evaluated using X-ray diffraction (XRD). Scanning electron microscopy (SEM) micrographs represented that by increasing the applied anodic voltage, the pore size increased, while the number of pores decreased. Energy-dispersive X-ray Spectroscopy (EDS) analysis was performed to assay compositions of the prepared films. Roughness measurement of surface before and after anodic oxidation treatment indicated that etched plate samples had higher surface roughness than disc specimens. Moreover roughness measurements represented that by applying higher voltage during anodic oxidation treatment, surface roughness increased due to arc-generation at high applied voltages, especially for those which anodized at 300V.

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Keywords: Anodic oxidation, Titanium, Anodic voltage, Surface preparation

1. Introduction

Ti and Ti-based alloys as metallic biomaterials are extensively used because of high strength, durability, biocompatibility, resistance to corrosion in physiological medium, light weight, and reasonably cost [1-5]. Naturally stable titanium oxide layer within nanometric thickness which formed onto titanium surface has not desirable mechanical properties, hence, a variety of surface treatments have attempted to form dense, uniform and rough titanium oxide layer [4]. Some methods such as preoxidation [6], etching [7-9], air-borne [8] and bonding coating have been used to modify the surface of titanium and titanium-based alloys [9].

Anodic oxidation (AO) treatment provides the deposition of ceramic coatings on the surface of metals, such as Ti, Al, Mg, Ta, W, Zn, and/or their alloys. Such metals in their natural state are protected by thin, tight, self-healing and adherent dielectric oxide films, which resist the current passage in the anodic direction [10]. Anodic oxidation is considered one of the most useful methods for surface modification because it can produce porous, uniform, relatively thick and adherent titanium oxide films on titanium and titanium-based alloys at ambient temperatures. It can incorporate chemical elements from the electrolyte in order to improve protective properties of titanium substrate [11]. This technique basically makes full use of the anodic oxidation of titanium by applying a positive voltage to titanium substrate used as the anode immersed in an electrolyte. In particular, when an applied voltage is increased beyond a certain point, micro-sparks created as a result of dielectric breakdown of titanium oxide surface layer [12]. The characteristics of metal oxide coatings are mainly determined by the substrate material, electrolyte composition, applied

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anodic voltage, current density behaviour, and electrolyte temperature. Current density which is directly related to the total charge transferred through a unit sample surface area during anodic oxidation may have an important effect in oxide ceramic coating formation. Moreover, distribution of the anode current in whole surface of substrate has an important effect on uniformity of the grown surface film and surface properties [13]. Anodic oxidation process can be carried out either at constant current (galvanostatic process) or at constant voltage (potentiostatic process). If the anodizing is carried out at voltages above the breakdown dielectric potential limit, the oxide will no longer be resistive enough to prevent further current flow and oxide growth. At such high voltages, the process will lead to increased gas evolution and sparking. During anodic oxidation of titanium metal, oxygen gas evolution is usually observed, which contributes to reduce the current efficiency of the growth process [14]. In this work the deposition of titanium oxide ceramic films by using anodic oxidation treatment and the effect of applied anodic voltage and as well as surface preparation on surface modification of anodically oxidized titanium is studied.

2. Experimental procedure

2.1. Materials

In this work, cast commercially-pure Titanium (CP-Ti); ASTM Grade 2, used as metallic substrate. Samples were cut into 14mm diameter discs with a thickness of 5mm. Additionally the rectangular samples of dimension 12×12×2 mm were used. As a pre-treatment, the disc samples were ground by 1200 grit size SiC paper and afterwards polished with colloidal silica suspension, 1μm. After polishing, the specimens were pickled by the mixture of aqueous hydrofluoric and nitric acids (HF/HNO_3) for 10 s (the mole ratio HF/HNO_3 equalled 1:8). The rectangular specimens just pickled by HF/HNO_3 (1:8) for 10s. Finally, the samples were rinsed by ultrasonic rinsing in propanol and distilled water for 10 and 5min., respectively and dried.

2.2. Anodic oxidation (AO) treatment of C.P titanium substrate

The anodic oxidation treatment was carried out by a DC power supply (GW Instrument) at constant voltage. Anodically oxidized samples were fabricated using a platinum plate and titanium specimens as the cathode and anode, respectively. The anode/cathode ratio was 1:2. The electrolyte was phosphoric acid (H_3PO_4, 1M) at a pH of 3. The applied voltage was 100, 200 and 300V during 1min with agitation and without agitation. The agitation speed was 300 rpm at room temperature during anodic oxidation treatment. The surface area of titanium samples that exposed to the electrolyte solution was $0.5cm^2$. The current variation was recorded at intervals of 0.25s during the constant applied voltage until anodization process was terminated by a computer interfaced with a DC power supply. After the anodic oxidation, two different regions could be clearly distinguished on the sample: one region containing only bared titanium and the other one containing a circular region covered by an electrochemically produced oxide film. Fig. 1 shows the schematic diagram of anodic oxidation treatment used in the present work.

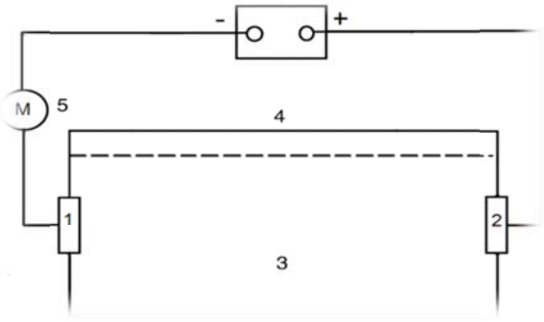


Fig. 1. Schematic diagram used in present work for anodic oxidation system.
(1) cathode, (2) anode, (3) electrolyte, (4) electrobath, (5) multimeter,
(2) and (6) DC power supply.

After anodic oxidation process, the samples were rinsed with distilled water and dried. Table 1 shows the experimental conditions that used in this study.

Table 1. Anodization conditions used in the present work (1M H_3PO_4 electrolyte, t= 1min.).

Anodic potential (V)	Anodic oxidation treatment			
	Disc samples		Plate samples	
	Without agitation	With agitation	Without agitation	With agitation
100	✓	-	✓	✓
200	✓	-	✓	✓
300	✓	-	✓	✓

2.3. Surface roughness measurement

Roughness parameters can be calculated in either two-dimensional (2D) or three-dimensional (3D) forms. 3D roughness parameters are calculated for an area of the surface instead of a single line. In this work, the surface roughness calculated via Amplitude parameters (3D roughness parameters). Amplitude parameters are the most important parameters to characterize the surface topography. Arithmetic average height parameter (R_a); which calculated in this work for surface roughness measurement, is defined as the average absolute deviation of the roughness irregularities from the mean line over one sampling length.

2.4. Surface morphology and Chemical composition of surface oxide film by using SEM/EDS

The surface micro-morphologies of the titanium oxide films formed by the anodic oxidation treatment were observed by NanoSEM-FEI Nova 200 and 5 kV used as acceleration voltage at secondary mode. Anodized titanium samples were sputter-coated with gold. Energy-dispersive X-ray Spectroscopy (EDX) was performed by using Pegasus X4M (EDS/EBSD) connected to SEM to assay differences in composition and preferential chemical attack on particular phases.

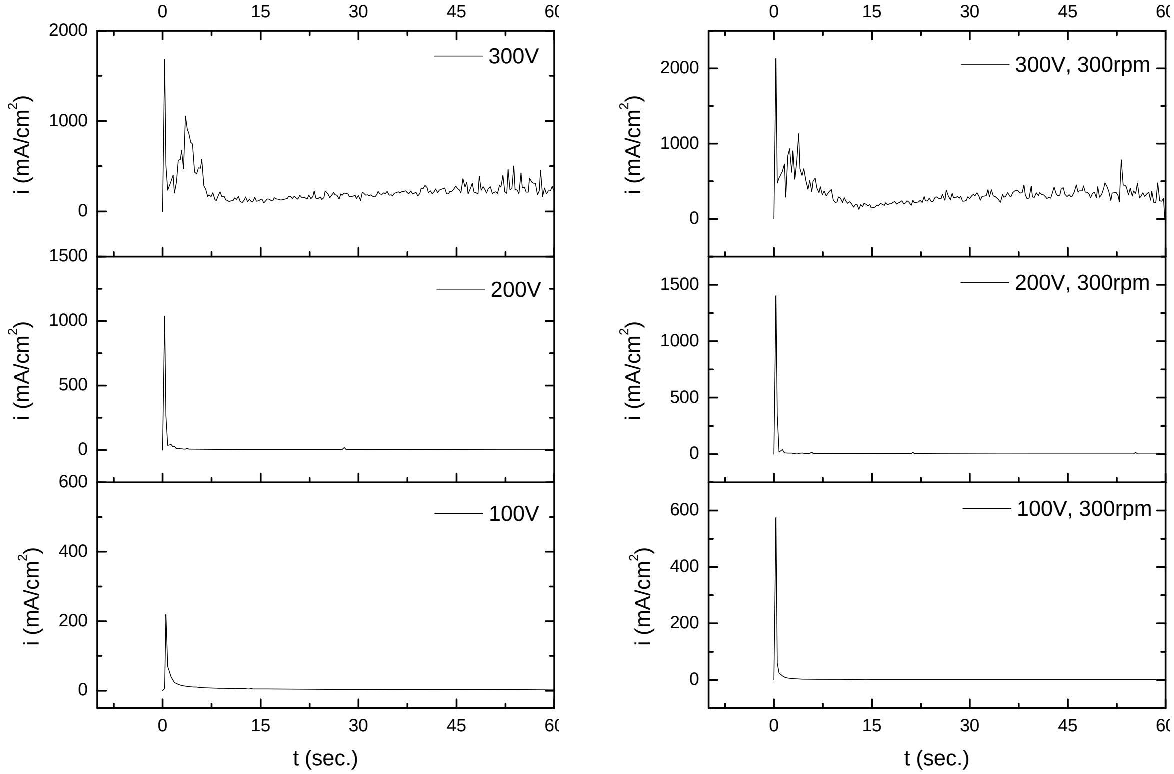
2.5. X-ray diffraction (XRD) of anodically oxidized C.P titanium substrate

To assess whether the chemical treatment changed the amorphous nature of the native oxide layer, treated samples were investigated by using a Bruker D8 Discover diffractometer equipped with a parabolic mirror for production of parallel ray. Cu (K_α radiation, λ= 0.15406 nm) used as the ray source and scintillation detector. The configuration goniometer was $\theta/2\theta$. The incident beam angle was 0.5º and the range of 2θ was 20-80º. Ni filter used for radiation of Cu K_β. Computer software package (EVA) was used for complete analysis of phase identification. EVA enables semi-quantitative analysis based on the reference-intensity-ratio (RIR) method using XRD patterns.

3. Results

3.1. Current-time curve for anodic oxidation of C.P titanium substrate

Fig. 2 represents the variation in current density versus the anodization time at 100,200 and 300V for agitated and non-agitated 1M H_3PO_4 electrolyte during anodic oxidation process of titanium samples at potentiostatic mode; respectively.



(a) (b)

Fig. 2. Current variation as a function of the anodization time for 100, 200 and 300V in potentiostatic mode: (a) without agitation and (b) with agitation (300 rpm).

As represented in Fig. 2(a), (b); after initial increasing of current density for all the titanium samples, decreasing of the current density are observed. For 100V applied voltage was not observed any spark and gas evolution during the anodic oxidation treatment for both non-agitated and agitated H_3PO_4 electrolyte which means applied voltage (100V) is lower than breakdown dielectric voltage for mentioned anodic conditions and so gas evolution may be insignificant [15]. The current density which is current per surface unit area of substrate during anodic oxidation has the main effect for the formation of titanium oxide coatings by anodic oxidation treatment [14]. During titanium anodization, the current density decreased which can contribute to the anodic titanium oxide growth [16].

For anodic oxidation of titanium samples at 200V for non-agitated and agitated H_3PO_4 electrolyte as shown in Fig. 2 (a), (b); after initial increasing of current density, decreasing of the current density observed. For this applied voltage some small sparks during the anodic oxidation treatment for both agitated and non-agitated condition observed and increasing of the current density contributes to breakdown voltage of the metal oxide. During titanium anodization process, the current density decreased which can contribute to the anodic oxide growth [16].

For anodic oxidation of titanium samples at 300V for non-agitated and agitated H_3PO_4 electrolyte as represented in Fig. 2(a), (b); after initial increasing of current density of titanium samples, decreasing of current density observed; and immediately increasing of the current density can be seen. During anodic oxidation process for all both agitated and non-agitated specimens, gas evolution and spark observed, which is stronger for agitated condition. This phenomenon called anodic spark deposition (ASD) or micro-arc oxidation (MAO) which is accompanied by visible light emission and by a high frequency noise discharges move randomly on the treated surface. The gas evolution related to water becomes unstable under high applied anodic voltage above the breakdown voltage and the increasing the current density after the stable decrease was related with breakdown of the titanium oxide [17]. The liberation of gaseous oxygen and/or metal oxidation occurs on the anodic surface depending on the electrolyte chemical activity in respect to the metal, the oxidation process can lead either to surface dissolution or to oxide film formation [18].

As shown, for both 100 and 200V agitated and non-agitated specimens, after increasing the initial current density, the decreasing of current density was observed. For agitated and non-agitated anodized specimens, after steady state of current density, the increasing of the current density observed that related to the spark during anodic oxidation process. For some agitated and non-agitated titanium anodized samples the decreasing the current density after initial increasing of the current density observed, while for others seen the increasing of the current density. The increasing of the current after steady state related to the breakdown voltage of the titanium oxide surface films [17]. Gas evolution, water evaporation and spark was considerable for all agitated and non-agitated titanium specimens that anodized at 300V because of breakdown voltage of the titanium oxide surface films in comparison with the samples that anodized at 100 and 200V.

The effect of agitation can be explained that the gas bubble entrapped on the anode surface will reduce the surface area of the anode that takes part in the electrochemical reaction, which in turn will have effects in current density increase and finally the anodic voltage will increase. Therefore, if agitation speed is sufficient to remove the attached gas bubbles on the anode surface, the anodic voltage would decrease. Moreover, if agitation speed can circulate the electrolyte enough, the electrical resistance will be reduced and the ion–electron reactions at the oxide film/electrolyte interface will be accelerated, and the current density increased, as shown in Fig. 2 (b). As a result, the agitation of the electrolyte solution during the anodic oxidation process can cause the distribution of anode current in the whole surface of specimen and consequently a strong effect on uniformity of the coating thickness and surface properties of grown anodic oxidation film [16].

3.2. Effect of surface preparation and anodic oxidation on surface roughness of Ti substrate

Fig. 3 represents the effect of surface preparation on surface roughness of titanium specimens before and after anodic oxidation treatment at potentiostatic mode in 1M H_3PO_4 during 1min. As shown, for four surface preparation methods, the specimens which etched by the mixture of aqueous hydrofluoric and nitric acids (HF/HNO_3), have the highest mean surface roughness (R_a), while the samples which ground and polished, have the lowest surface roughness before and after anodic oxidation treatment.

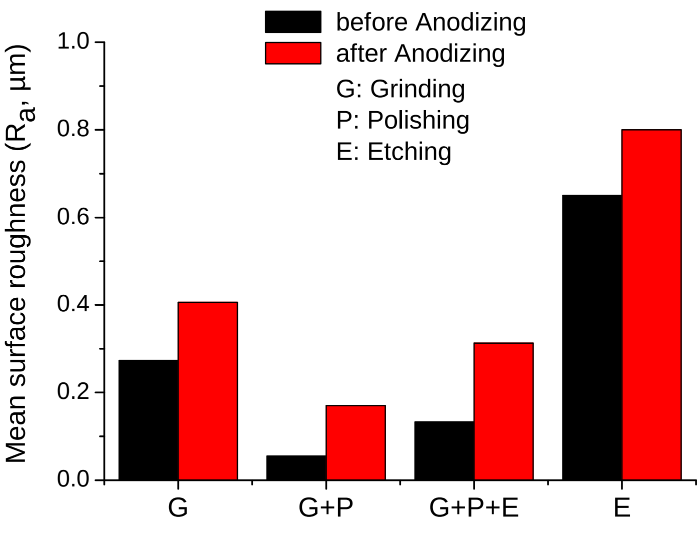


Fig. 3. Effect of surface preparation on surface roughness of titanium specimens before and after anodic oxidation at potentiostatic mode in 1M H_3PO_4 during 1min.

Adhesion is obviously related to the interface between both materials. Surface properties of titanium clearly have a big effect on adhesion strength of electrochemically deposited titanium oxide. The adherence between grown oxide ceramic and metal has been attributed to mechanical forces, van der waals forces, chemical bonding by bonding oxides and contracting forces by mismatch of expansion coefficients. Van der Waal's forces consist of bonding because electrical dipoles or dispersion effect without chemical interaction carrying out. Chemical bond is ordered by oxide layer formed on metal substrate which forms ionic, covalent, or metallic bonds with oxides onto the ceramic. Mechanical interlocking contains locking of one substance into pores, cavities, and surface roughness of other material to be the major factor for coating-substrate adhesion strength [19]. It seems that the etching pretreatment process because of higher surface roughness than other methods such as grinding or polishing, can achieve the adherent interface for titanium oxide-metallic substrate bonding.

The effect of anodic oxidation treatment on surface roughness of commercially-pure titanium is shown in Fig. 4. As represented, for all the CP titanium samples, after anodizing treatment, mean surface roughness increased. Moreover by increasing the applied voltage for anodic oxidation process of titanium samples, the mean surface roughness increased. Increment of the surface roughness with applied voltage during anodic oxidation treatment could be related to the electrical charge and as a result the increase in thickness of the titanium oxide film grown onto the samples [20]. By applying high voltage like 300V, the fusing effect caused the growth of oxide films on substrate metals via instantaneous ultrahigh heat generation during anodic spark deposition process [21].

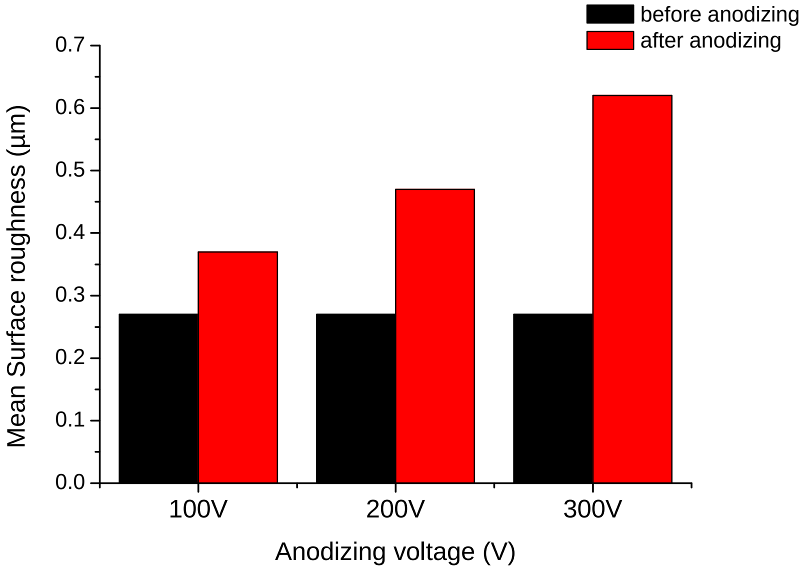


Fig. 4. Surface roughness (R_a) variation of ground titanium samples before and after anodic oxidation in 1M H_3PO_4 at potentiostatic mode.

3. The colours of the anodic titanium oxide films

Colouring of the resultant titanium anodic oxide films was the most prominent optical change during potentiostatic anodizing. Table 2 shows various colours of the anodic oxide film prepared by anodic oxidation treatment at potentiostatic situation.

Table 2. The variation of anodized titanium surface colour at different voltages (anodization conditions: 1M H_3PO_4 electrolyte, t= 1min.)

Anodization voltage	100V	200V	300V
Anodized surface color	Green	Purple+Gray	Gray

Different colouring of the titanium oxide films is in relation to the different anodic forming voltage and consequently different anodic forming growth constant, anodic forming rate and different thickness of anodic oxide surface films. Moreover for the different colouring of the titanium oxide of the same thickness may be ascribed to the different crystal structures of anodic oxide, implying changes of the density of the anodic oxide films [21]. It has been proposed during electrochemical anodizing, electrical double layer forms at the oxide film/electrolyte interface, which consists of an excess or lack of electrons on metal side and of an excess or lack of ions on the electrolyte side. These couplings of electrons and ions during anodizing normally result in a certain gradient of the concentration distribution of the electrolyte at the oxide film/electrolyte interface, i.e., the inner layer of lower concentration and outer layer of the higher concentration [16]. Anodic oxidation of titanium is categorized by solid state diffusion in the oxide or by dissolution-deposition in the electrolyte [22].

Chemical reactions which conduct to oxidation at the anode can be as following equations:

$$\text{At Ti/Ti oxide interface: } Ti \rightarrow Ti^{2+} + 2e^{-} \quad (1)$$

$$\text{At Ti oxide/electrolyte interface: } 2H_2O \rightarrow 2O_2^{-} + 4H^{+} \quad (2)$$

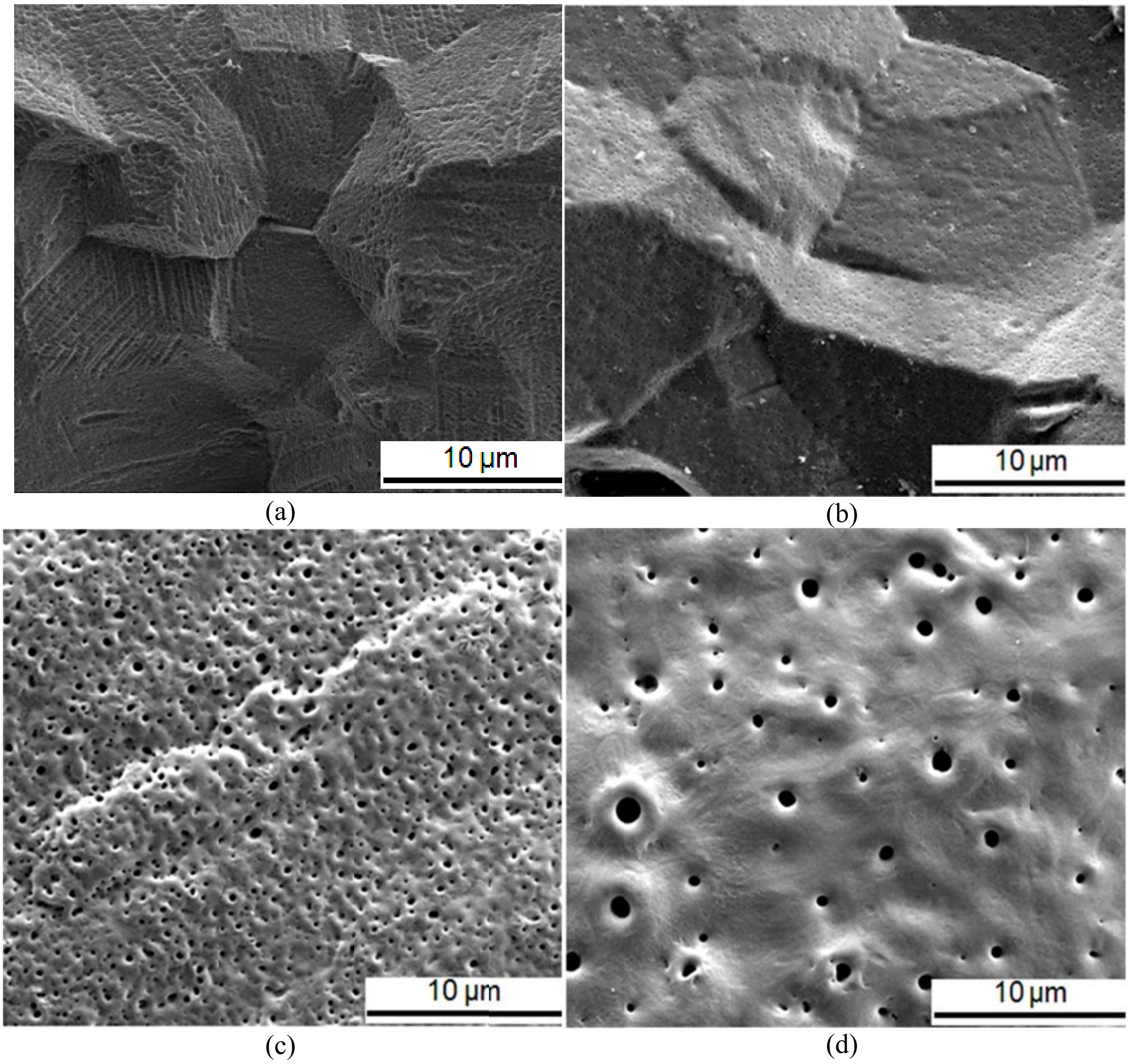
$$2H_2O \rightarrow O_2\,(\text{gas}) + 4H^{+} + 4e^{-} \quad (3)$$

$$Ti^{2+} + 2O_2^{-} \rightarrow TiO_2 + 2e^{-} \quad (4)$$

Titanium and oxygen ions formed in these reduction-oxidation (redox) reactions are driven through the oxide by externally applied electric field, conducting to growth of the oxide. Since anodic titanium oxides have a high resistivity relative to the electrolyte and the metallic parts of the electrical circuit, the applied voltage drop will mainly occur over the oxide film of the anode. As long as the electric field is strong enough to drive the ions through the oxide, a current will flow and the oxide will continue to grow depending on electrolyte and other process conditions of anodic oxidation [23].

3.4. Surface morphology of anodized CP-Ti by using SEM

SEM micrographs of surface-etched titanium and titanium anodized at potentiostatic mode in 1M H_3PO_4 during 1min. at 100, 200, and 300V shown in Fig. 5.



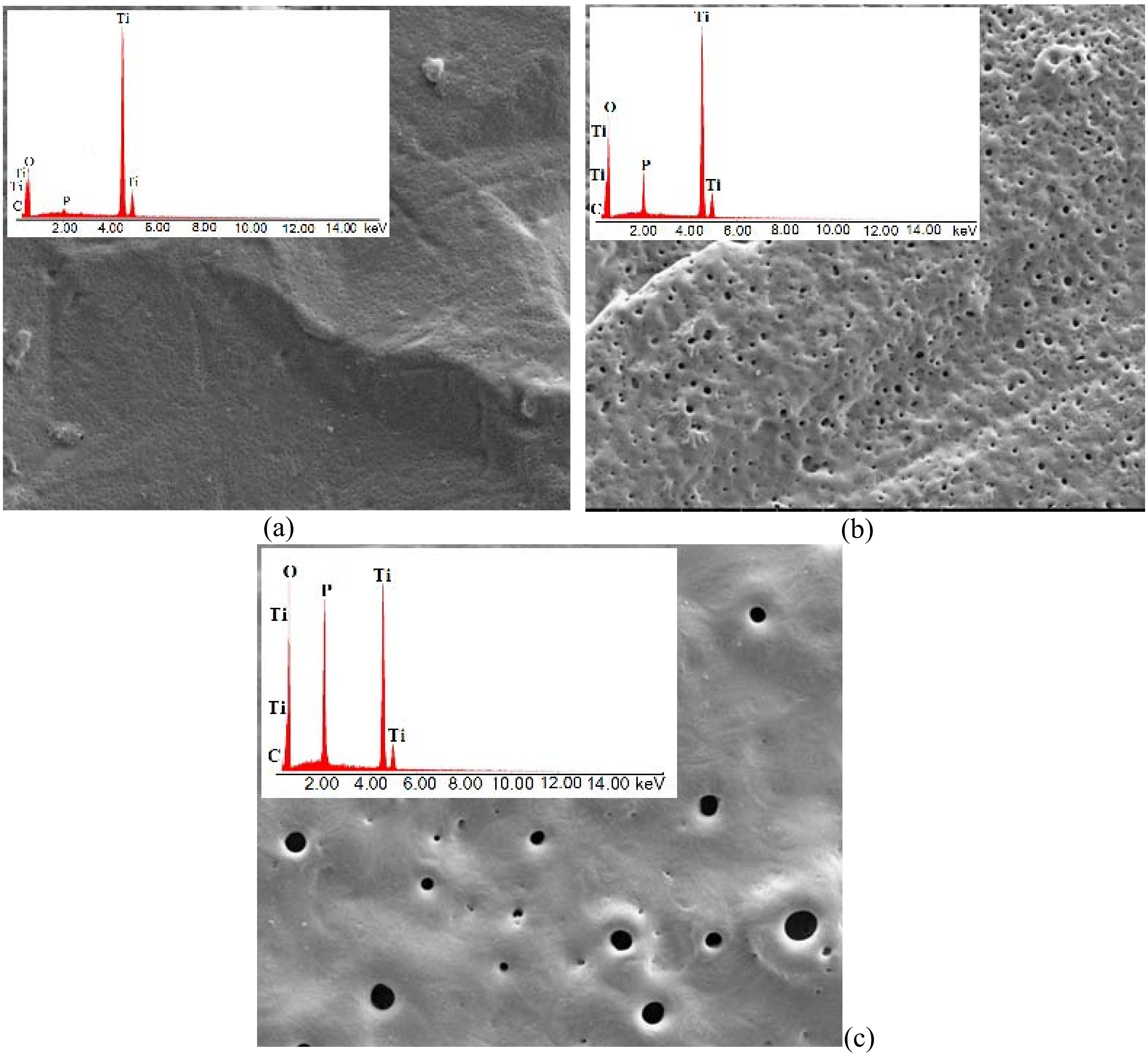
(a) (b) (c) (d)

Fig. 5. SEM micrographs of (a) surface-etched and anodized titanium at potentiostatic mode in 1M H_3PO_4 during 1min at (b) 100V, (c) 200V and (d) 300V; respectively.

By increasing applied voltage of anodization, the size of pores increases, while the number of pores decreases due to connecting of small pores together [24], as shown in Fig. 5(b), (c) and (d). Moreover, by increasing the anodization voltage, the thickness of surface oxide film increases, for instance the sample which anodized at 100V, the topography of surface still can be seen, while for specimen anodized at 300V, the surface covered by oxide layer. The oxide films prepared at higher electrolyte concentration and/or applied potential have a more porous surface with bigger pore size. The main formation mechanism of titanium oxide at high anodic potentials occurs due to O^{2-} ions inward migration (metal–film interface), and Ti^{4+} ions outward migration (film–electrolyte interface). The application of high anodic potentials in aqueous medium gives the water unstable. If O_2 forms inside the film the pressure of the gas can break down the oxide film and alter its morphology. Another mechanism of oxide film formation is the dielectric rupture. The high electric field generated inside the oxide film, which appears at higher potentials, may be attributed to pore formation (Fig. 5d). This phenomenon accounts for morphology of outer oxide layer. The pores located at outer film surface are filled with the electrolyte, making these sites preferential to the charge transfer and producing O_2 bubbles at film–electrolyte interface [25]. At higher potential than 200V the anodizing process was conducted to increased gas evolution and additionally frequent sparking phenomena. At the same time, anodic pore cell structure began to nucleate at the surface, and the irregular arrays of cell structure have gradually changed to regular morphology [26] as represented in Fig. 5d. The shape, size, and densities of pores formed by anodic oxidation process depend on the current density as well as applied voltage during anodizing [27] as it can be observed clearly in Fig. 5b, c, and d.

3.5. Chemical composition of surface oxide films by using EDS analysis

EDS analysis for the anodic surface layer formed at potentiostatic mode in 1M H_3PO_4 at 100, 200, and 300V shown in Fig. 6. EDS analysis represents the presence of titanium (Ti), oxygen (O) and phosphorus (P) in the anodized oxide film. Additionally by increasing the voltage of anodic oxidation process, the quantity of oxygen and phosphorus element increases, as can be observed. EDS spectra shows 0.53, 2.56, 7.03 (at. %) of phosphorus in anodic oxide film which treated at 100, 200 and 300V, respectively. Anodic oxidation can incorporate anions from the electrolyte into the coating and it is expected that phosphorus from the electrolyte would get deposited in all the coatings. Increasing levels of phosphorus in the coating can conduct to amorphous nature [28].



(a) (b) (c)

Fig. 6. EDS analysis for anodic surface layer formed at potentiostatic mode in 1M H_3PO_4 (a) 100V, (b) 200V, and (c) 300V; respectively.

3.6. X-ray diffraction (XRD) of anodized surface films

Fig. 7 represents grazing-angle X-ray diffraction patterns of titanium samples anodized at potentiostatic mode in 1M H_3PO_4 during 1min. at 100, 200, and 300V; respectively.

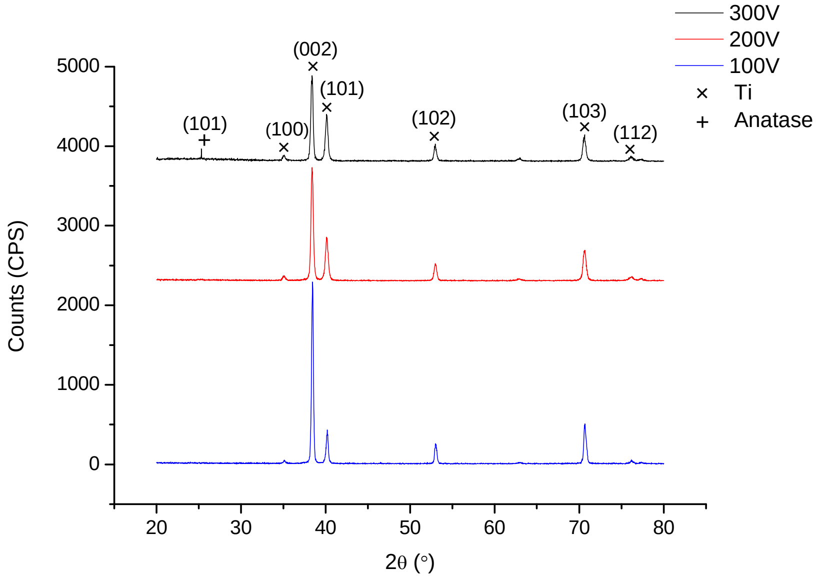


Fig. 7. Grazing-angle XRD patterns of titanium samples anodized at potentiostatic mode in 1M H_3PO_4 during 1min at 100, 200, and 300V; respectively.

The XRD peaks include titanium, amorphous titanium oxide which Ti is the main crystal phase in the XRD pattern for all the anodized samples. Anatase, the crystalline titanium oxide, TiO_2; just can be seen for specimen that anodized at 300V. The diffraction lines of the film obtained at 2θ 35.94 (2.555 A°), 38.442 (2.341 A°), 40.171 (2.243 A°), 53.005 (1.7262 A°), 62.951 (1.4753 A°), 70.663 (1.332 A°), and 76.221 (1.2481 A°) correspond well to the Ti phase (PDF 44-1294). One additional peaks at 2θ: 25.3198 (3.5169 A°) can be assigned to the anatase phase of TiO_2 (PDF 89-4203). Titanium dioxide may present both amorphous and crystalline structures, depending on anodic oxidation parameters. Crystalline oxides, that is, anatase and rutile, present several exceptional aspects, like photocatalytic behaviour, super hydrophilicity and biocompatible properties, which can be useful for biomedical application of Ti-based alloys [29]. Species which derived of electrolyte can incorporate into the anodic oxide fills and even may stabilize the amorphous structure inside the grown anodic oxide films [30].

4. Conclusions

In this work, titanium oxide coatings were grown onto commercially-pure titanium (C.P-Ti, ASTM Gr.2) at potentiostatic method from phosphoric acid electrolyte at different voltages. Four different surface preparation methods were used. Roughness measurement of surface before and after anodic oxidation treatment indicated that etched plate samples had higher surface roughness than disc specimens. Moreover roughness measurements represented that by applying higher voltage during anodic oxidation treatment, surface roughness increases. Regarding to current-time curves during anodic treatment, by applying 300V anodic voltage, gas evolution and spark observed more than 100 and 200V, which relate to the breakdown potential. SEM micrographs show by increasing the applied voltage during anodic treatment, the pore size increases, while the number of pores decreases. EDS analysis represents the presence of titanium, oxygen and phosphorus in anodized oxide film. Additionally by increasing the voltage of anodic oxidation process, the quantity of oxygen and phosphorus element increased.

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