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# Tribological properties of PEO nanocomposite coatings on titanium formed in electrolyte containing ketoconazole

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ABSTRACT

Nanocomposite coatings were formed on commercial pure titanium through plasma electrolytic oxidation (PEO) process in a phosphate-based electrolyte containing ketoconazole and alumina nanoparticles. The procedure was performed by direct current and current density was kept constant. The effects of concentration of ketoconazole in the electrolyte on growth of coatings, absorption of alumina nanoparticles, morphology, chemical structure and mechanical behavior of coatings were studied by means of Fourier-transform infrared spectroscopy, scanning electron microscopy, nanoindentation and pin-on-disk wear test. Existence of ketoconazole in the electrolyte was observed to increase alumina nanoparticles absorption within coatings and consequently decrease porosity. Mechanical behavior of coating indicated that the rate of hardness to Young's modulus was increased and consequently wear resistance of coating was improved.



## 1. Introduction

Titanium and titanium-based alloys are widely applied in aerospace, petrochemical and biomedical industries due to their distinguished properties such as high strength to weight ratio, high melting temperature, appropriate mechanical properties, high resistance against corrosion and biocompatibility [1]. To further improve titanium function in terms of mechanical properties, corrosion resistance and biocompatibility, the rather new method of plasma electrolytic oxidation has recently been paid a great deal of attention [2]. The parameters of coating process which may be varied to achieve the best desired properties mainly consist of the electrolyte effect and electrical parameters of the PEO process. Among these parameters, due to the role of their components in sparking process as well as introduction of elements into the coating and affecting its properties, the electrolyte and its additives are of great importance in the PEO process. Recent studies regarding electrolyte and PEO process are mostly attributed to the electrolyte additive effect [3,4]. It was reported that addition of cerium nitrate to the PEO electrolyte on titanium leads to formation of a coating with proper biocompatibility properties [5]. Existence of sodium vanadate in the PEO electrolyte on titanium was seen to improve photo-catalytic properties [6]. Also, existence of iron sulfate in the PEO electrolyte on titanium causes a change in color to yellow and red [7]. Considering the application of corrosion inhibitors as electrolyte additives in other conversion coating processes like anodizing [8,9], their use in PEO process has also recently attracted attentions. Oleinka et al. [10] investigated the effect of corrosion inhibitors in PEO process on aluminum-based alloys, They reported that existence of corrosion inhibitors raised hydrophobization. Another major advantage of PEO coating process in comparison with other conversional coating processes such as anodizing is that the former is environmentally friendly [11,12]. Hence, it is better to employ non-toxic materials such as medicinal inhibitors as additives to the electrolyte to improve corrosion and wear resistance properties of PEO-coatings on titanium. Ketoconazole is an antifungal drug with chemical formula of $C_{26}H_{28}Cl_2N_4O_4$ and its molecular weight is 531.431 g/mol [13]. The effect of ketoconazole as corrosion inhibitors was previously investigated. The results revealed that ketoconazole acts as an inhibitor for the corrosion of mild steel in 0.1 M $H_2SO_4$ [14]. Accordingly, application of ketoconazole, a medicinal inhibitor, as a non-toxic additive to the electrolyte which is readily accessible and inexpensive in PEO coating on titanium surfaces (as they are mainly used in medical and dental applications, it is necessary to use non-toxic materials in the coating process) may become a matter of considerable interest.

On the other hand, there are various methods to improve mechanical properties of PEO-coatings on titanium including addition of hard ceramic nanoparticles suspended in an electrolyte

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[15], combination with other coating processes [16], application of new electrolyte compounds [17], performance of secondary heat treatments on the coatings, etc [18]. The present work is aimed to investigate the effect of ketoconazole, the medicinal inhibitor, as an additive to the electrolyte (together with α-$Al_2O_3$ nanoparticles) on absorption of nanoparticles from the suspension, chemical structure, morphology and mechanical properties of the oxide coatings obtained on commercially pure titanium (CP-Ti) surfaces through plasma electrolytic oxidation process.

## 2. Experimental procedure

### 2.1. PEO coating

A sheet of commercially pure titanium (ASTM-Grade 2) with dimensions of 50 mm × 50 mm × 1 mm was selected as the substrate material. Prior to the coating process, samples were polished until Ra < 1 µm, cleaned in acetone via ultrasonic, washed by deionized water and dried in warm air. The PEO process was carried out by means of a 20 kW DC power supply under constant current density of 20 mA/cm$^2$ and for 12 min in an aqueous solution. In this process, the substrate (anode) is placed in a cell made of stainless steel (cathode) with a recirculating water-cooling system. Since the effect of ketoconazole alone was to be considered in this project, the simplest electrolyte (single-component) was used. The electrolyte utilized in PEO process was composed of 8 g/lit sodium phosphate heptahydrate with/without 25 g/lit α-$Al_2O_3$ nanoparticle and ketoconazole additive in deionized water. The nanoparticle was analyzed by transmission electron microscopy (TEM, JEOL-2010) (Fig. 1). The average size of alumina nanoparticles was 22 nm. Several primary tests were carried out to acquire the concentration range of ketoconazole. It was observed that at concentrations higher than 4.5 g/lit, sparks immediately reached a destructive state and the coating process would not be performed soundly; hence, the maximum concentration of ketoconazole was set to be 4.5 g/lit. In order to investigate the effect of ketoconazole additive in alumina nanoparticle suspension, samples with ketoconazole concentration of 0, 1.5, 3 and 4.5 g/lit were provided. The denominated title for each sample is given in Table 1. The electrolyte temperature during the coating process was kept at 25 °C. All samples were washed with deionized water after the coating process and dried in warm air.

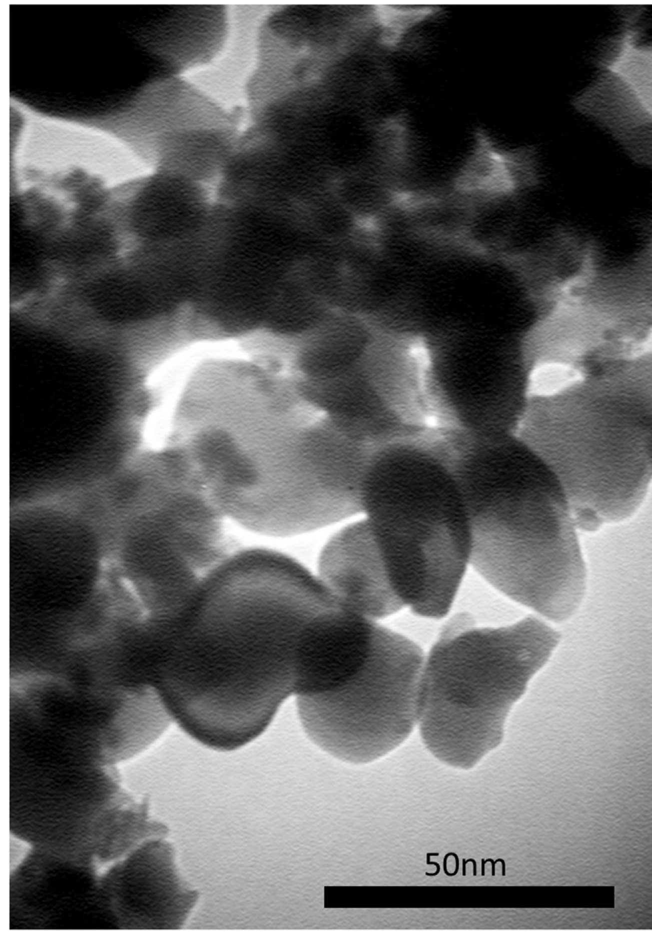


**Fig. 1.** TEM micrographs of alumina nanoparticles.

**Table 1**
Samples code in different phosphate-based electrolytes.

| | K-0 | KA-0 | KA-1.5 | KA-3 | KA-4.5 |
|---|---|---|---|---|---|
| Ketoconazole (g/Lit) | 0 | 0 | 1.5 | 3 | 4.5 |
| Alumina (g/Lit) | 0 | 25 | 25 | 25 | 25 |

### 2.2. Characterization of the oxide coating

Voltage variation during the sparking was automatically recorded by means of avomoter (Digital multimeter; APPA 505). Samples were weighed before and after the coating (AND, GR-202, precision ±50 µg balance). Fourier-transform infrared spectroscopy (FTIR) was performed on KBr pellets using a FTIR spectrophotometer (Spectrum 100, Perkin Elmer) in the range of 4000–400 cm$^{-1}$. The elements distribution of coatings surfaces were provided through energy dispersion X-ray spectroscopy (EDS; Oxford Instruments). The morphology of surfaces and cross sections was also studied by field emission scanning electron microscopy (SEM; Philips XL 30 and SIGMA/VP, Zeiss). A nanoindentation testing system (Nanoindentation Tester CSM) with a Berkovich diamond indenter was used to perform nanoindentation tests on five different locations of coating surface. For this purpose, the samples were cut, mounted and mechanically polished down to the average roughness of 0.02 µm. The maximum load and its loading and unloading rates were adjusted to be 3 and 6 mN/min, respectively. Load–displacement curves were recorded and elastic recovery was calculated. Hardness and elastic modulus were determined using the Oliver and Pharr method [19]. In order to study the wear resistance of the coatings, pin-on-disk test method was employed where the pin was 40 mm in length and 5 mm in diameter. The disk was a composite made of polymer in matrix and SiC as reinforcing particles. Normal load was 24 N, angular velocity was 50 rpm and wear distance for specimens with and without nanoparticle was 200 and 50 m, respectively.

## 3. Results and discussion

### 3.1. Voltage–time curves

Voltage–time graphs (started from the sparking) of all samples coated under different conditions are illustrated in Fig. 2. The voltage variation trends over time are almost the same for all samples and consist of two regions. Over the first region, slope of the voltage–time curve is steep; while, the trend becomes plateau in the second region. The overall variations of voltage–time curves indicate the nature of oxide films and various possible reactions over different stages of the coating process. It may be observed that addition of nanoparticles to the electrolyte caused the voltage