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Characterization of the plasma electrolytic oxidation of titanium in sodium metasilicate

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ABSTRACT

Plasma electrolytic oxidation (PEO) of titanium in sodium metasilicate at 200 mA/cm^2 is investigated using real-time imaging and optical emission spectroscopy. It has been detected that during the PEO process the size of microdischarges becomes larger, while the number of microdischarges is reduced. The species and their ionization states present in PEO microdischarges are identified. The species originate both from titanium anode and from the electrolyte. The spectral line shape analysis of hydrogen Balmer line H_β (486.13 nm) indicates the presence of two types of microdischarges during PEO. The discharges are characterized by relatively low electron number densities of $N_e = 3.8 \times 10^{15}$ cm^{-3} and $N_e = 4.5 \times 10^{16}$ cm^{-3}. For electron temperature (T_e) measurement we used Ti I lines at 398.18 nm and 501.42 nm and obtained T_e in the range of 3700 ± 500 K. Surface coatings formed by PEO process were characterized by AFM, SEM-EDX and XRD. The main elemental components of PEO coatings are Ti, Si and O. The PEO coatings are partly crystallized and mainly composed of anatase, rutile, and amorphous SiO$_2$.

1. Introduction

Titanium and its alloys are important engineering materials featuring high strength-to-weight ratio, good corrosion resistance, high melting point, good mechanical behavior, and a good biocompatibility. Because of these properties they are becoming significantly important in many industries such as aerospace, automobile, biomedical, energy, military and biomedicine. [1–3]. However, low wear resistance and high friction coefficient limit their extensive applications. Anodization of titanium and its alloys are one of the methods used for forming protective oxide coatings that can help to overcome these deficiencies. In recent years, high-voltage anodization, so-called plasma electrolytic oxidation, has proved to be a very useful technique for the formation of protective oxide coatings [4–8].

Plasma electrolytic oxidation (PEO), also called microarc oxidation (MAO) or anodic spark deposition (ASD), is an economic, efficient, and environmentally benign technology capable of producing a stable oxide coating on the surface of lightweight metals (aluminum, magnesium, zirconium, titanium, etc.) or metal alloys [9,10]. Oxide coatings have controllable morphology and composition, excellent bonding strength with the substrate, good electrical and thermal properties, high microhardness, and high-quality wear and corrosion resistance.

PEO process is coupled with the formation of plasma, as indicated by the presence of microdischarges on the metal surface, accompanied by gas evolution [11,12]. The anodic gas consists predominantly of oxygen with minor fractions of other elements [13]. Various processes including chemical, electrochemical, thermodynamical, and plasma-chemical reactions occur at the discharge sites, due to increased local temperature (10^3 K to 10^4 K) and pressure (~10^2 MPa). These processes are responsible for modifying the structure, composition and morphology of obtained oxide coatings. The oxide coatings formed by PEO process usually contain crystalline and amorphous phases with constituent species originating both from metal and electrolyte.

Understanding the microdischarge phenomena is important for characterization of the PEO process. Distribution and types of microdischarges have important effects on the formation mechanism, composition, morphology, and various properties of the resultant oxide coatings. Given the liquid environment, optical emission spectroscopy (OES) is the best available technique for PEO plasma characterization. The most popular application of OES for PEO diagnostics is spectra characterization and observation of temporal evolution of spectral lines in the visible and near UV spectral region. The main difficulty in an application of OES for PEO characterization comes from space and time inhomogeneity of microdischarges appearing randomly across the anode surface. Despite numerous articles using OES for the characterization of

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the PEO process on metals, mostly on aluminum [14–22] and magnesium [22–26], there is a deficiency of data on the OES characterization of the PEO process on titanium and titanium alloys [27,28].

The present paper describes PEO process of titanium in sodium metasilicate. Since the occurrence of plasma electrolytic oxidation is both electrolyte and metal sensitive we have decided to use sodium metasilicate solution because of good experience we had in our previous investigations of the PEO process on magnesium and its alloys [25,26]. At the same time, electrolytes containing sodium metasilicate are among the most commonly used electrolytes for the formation of oxide coatings by PEO process on lightweight metals. Microdischarge characteristics during PEO process of titanium were investigated by optical emission spectroscopy and real-time imaging. Atomic force microscopy (AFM), scanning electron microscopy (SEM-EDX) and x-ray diffraction (XRD) served as tools for examining surface morphology, chemical and phase composition of obtained oxide coatings.

2. Experimental

In the experiment, oxide coatings were formed on titanium samples of dimensions 25 mm × 5 mm × 0.25 mm and 99.5% purity. Before the anodization, samples were degreased in acetone, ethanol and distilled water, using ultrasonic cleaner, and dried in a warm air stream. The oxidation process was carried out in an electrolytic cell with flat glass windows [29]. Platinum wires were used as cathodes. For anodization of titanium we used water solution of 10 g/l $Na_2SiO_3 \cdot 5H_2O$. The electrolyte was prepared by using double distilled and deionized water and PA (pro analysis) grade chemical compound. Anodizing was carried out at current density of 200 mA/cm^2. During the anodization, the electrolyte circulated through the chamber–reservoir system. The temperature of the electrolyte was maintained during the anodization process at (294 ± 1) K. After anodization, the samples were rinsed in distilled water to prevent additional deposition of electrolyte components during drying.

Spectral luminescence measurements during PEO of titanium were taken on a spectrometer system based on the intensified charge coupled device (ICCD). Optical detection system consisted of a large-aperture achromatic lens, a Hilger spectrometer with diffraction grating of 1200 grooves/mm (wavelength range of 43 nm), and a very sensitive PI–MAX ICCD thermoelectrically cooled camera (233 K) with high quantum efficiency, manufactured by Princeton Instruments. The system was used with several grating positions with overlapping wavelength range of 5 nm. In all experiments the image of the anode surface was projected with unity magnification to the entrance slit of spectrograph. The optical-detection systems were calibrated using a standard tungsten strip lamp (OSRAM Wi-17G). The obtained spectra were adjusted to the spectral response of the measuring system.

Real-time images during PEO were recorded utilizing a video camera Sony DCR-DVD110 (800 K pixels CCD, 40× optical zoom and 40 mm lens filter). The information obtained was split into separate frames and the image of individual frames was processed using our custom made software, which counts microdischarges in selected frame and determines spatial density of discharges including their dimensional distribution.

The topography and roughness of oxide coatings were characterized using an atomic force microscope (AFM; Veeco Instruments, model Dimension V). Micrographs were obtained in tapping mode under ambient conditions, using TAP300 tips (resonant frequency 300 kHz, force constant 40 N/m). Roughness data were obtained using diNanoScope software (version 7.0).

Scanning electron microscope (SEM) JEOL 840A equipped with X-ray energy dispersive spectroscopy (EDX) was used to characterize morphology and chemical composition of formed surface coatings. The crystallinity of samples was analyzed by X-ray powder diffraction (XRD), using a Phillips PW 1050 powder diffractometer in Bragg-Brentano geometry, with Ni-filtered Cu Kα radiation ($\lambda = 1.54178$ Å). Diffraction data were acquired over scattering angle 2θ from 10° to 80° with a step of 0.050° and acquisition time of 1 s/step.

3. Results and discussion

3.1. Spectroscopic and real-time imaging characterization of PEO process

Fig. 1 shows typical voltage versus time and luminescence intensity versus time characteristics during anodization of titanium samples in 10 g/l $Na_2SiO_3 \cdot 5H_2O$ at current density of 200 mA/cm^2. The relatively uniform growth of a compact barrier oxide film, at constant current density, is characterized by an almost linear increase in the anodization voltage. This stage of anodization is followed by apparent deflection from linearity in voltage–time curve, starting from so-called breakdown voltage. After the breakdown, voltage continually increases, but the voltage–time slope decreases and a large number of small size microdischarges appear, evenly distributed over the whole sample surface.

The appearance of microdischarges at various stages of PEO process of titanium is shown in Fig. 2. First microdischarges are visible after 15 s, accompanied by low acoustic emissions. During the PEO process the size of microdischarges becomes larger, while the number of microdischarges is reduced. It can be seen that relatively small microdischarges, with average cross-sectional area ≈ 0.03 mm^2, are dominant in the early stage of PEO process. The population of small microdischarges decreases during PEO. On the other hand, large microdischarges become noticeable with extended PEO time and after about 3 min large microdischarges with average cross-sectional area ≥ 0.13 mm^2 are dominant, while small microdischarges are being hardly observed on the surface.

The increased size and decreased spatial density of microdischarges during PEO is related to the number of discharging sites through which higher anodic current is able to pass. The surface topography of oxide coatings in various stages of PEO process (Fig. 3) shows that the number of micropores decreases, while their size increases during PEO process. Also, thicker coatings have higher surface roughness. In the initial stage of PEO, the discharge channels are well distributed and oxide coatings exhibit

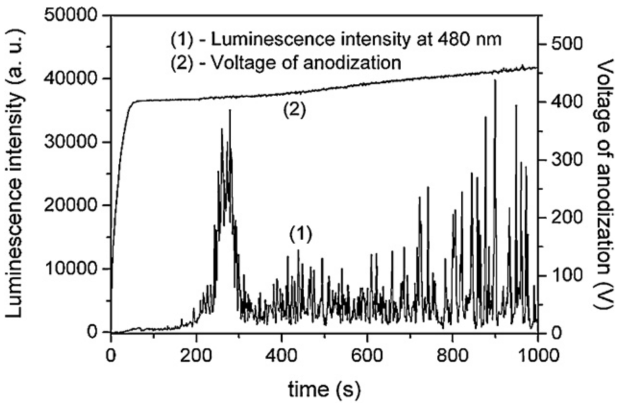

Fig. 1. Time variation of voltage of anodization and luminescence intensity at 480 nm during galvanostatic anodization of titanium in sodium metasilicate.