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# Synthesis and characterization of $Al_2O_3$/ZnO coatings formed by plasma electrolytic oxidation

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## ABSTRACT

Mixed $Al_2O_3$/ZnO coatings are prepared by conventional DC plasma electrolytic oxidation (PEO) of aluminum in boric acid and borax solution containing ZnO nanoparticles. Scanning electron microscopy equipped with energy dispersive x-ray spectroscopy, x-ray diffraction, and Raman spectroscopy were employed to monitor morphological, structural, and chemical changes of obtained oxide coatings. It was found that chemical and phase compositions strongly depend on PEO time. Photoluminescence and photodegradation of methyl orange served as a tool to estimate potential application of $Al_2O_3$/ZnO coatings. Photoluminescence measurements showed that clearly observable bands inherent to $Al_2O_3$ and ZnO are present in formed coatings, pointing at oxygen vacancies as the main source of photoluminescence. Longer PEO processing times proved beneficial for enhanced photocatalytic activity.

## 1. Introduction

Zinc oxide (ZnO), a wide band gap semiconductor (Eg = 3.37 eV) with large exciton binding energy, is an important material in various fields of application due to its low cost and excellent physical and chemical properties, such as high melting point (1975 °C), high thermal and chemical stability, a large piezoelectric coefficient, high electrochemical coupling coefficient, broad range of radiation absorption and high photostability [1]. For this reason, ZnO is an excellent candidate for solar cell [2], light-emitting diodes in the blue and UV regions [3], ultraviolet photoconductive detectors [4], piezoelectric transducers [5], photocatalyst [6], etc.

The aim of this work was to examine the possibility of formation of ZnO based coatings on aluminum substrate by plasma electrolytic oxidation (PEO) and to probe their photoluminescent (PL) and photocatalytic properties. PEO is an economic, efficient, and environmentally friendly processing technology capable of producing in-situ oxide coatings on some metals (aluminum, magnesium, titanium, zirconium, tantalum, etc.) as well as on their alloys [7]. The PEO process is coupled with the formation of plasma, as indicated by the presence of microdischarges on the metal surface when the supplied voltage is higher than a critical value (known as the breakdown voltage) [8]. The microdischarging results in localized high temperature ($10^3$ K to $10^4$ K) and high pressure (~$10^2$ MPa), and various processes including plasma-chemical, electrochemical, and thermodynamical reactions occur at the microdischarge sites [9]. These processes allow the formation of oxide coatings that contain crystalline and amorphous phases with constituent species originating both from metal and electrolyte. Having in mind that such severe conditions exist on the surface during the PEO process, we assumed that the deposition of ZnO nanoparticles from electrolyte is possible and that obtained oxide coatings may be interesting for various applications.

## 2. Experimental details

Rectangular samples cut from the commercially available aluminum (99.9% purity) were used as working electrodes in the experiment. The dimensions of the samples were 25 mm × 10 mm × 0.25 mm. The working electrodes were sealed with insulation resin leaving only active surface with an area of 1.5 $cm^2$ accessible to the electrolyte. Before the anodization, samples were degreased in acetone, ethanol, and distilled water, using ultrasonic cleaner, and dried in a warm air stream. During the anodization, the electrolyte circulated through the chamber–reservoir system and the temperature of the electrolyte was maintained at (20 ± 0.5) °C. Water solution of 0.1 M boric acid ($H_3BO_3$) + 0.05 M borax ($Na_2B_4O_7 \cdot 10H_2O$) was used as a supporting electrolyte. Commercially available ZnO powder was used as a source of nanoparticles and added to the supporting electrolyte in the concentration of 2 g/L ZnO. The average size of ZnO nanoparticle was estimated to be around 28 nm (calculated by Williamson–Hall method using obtained XRD patterns). Anodizing was carried out at a current density of 150 mA/$cm^2$.

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After the anodization, samples were rinsed in distilled water to prevent additional deposition of electrolyte components during drying.

Scanning electron microscope (SEM) JEOL 840A equipped with energy dispersive x-ray spectroscopy (EDS) was used to characterize morphology and chemical composition of formed oxide coatings. The crystallinity of oxide coatings was analyzed by x-ray diffraction (XRD), using a Rigaku Ultima IV diffractometer in Bragg–Brentano geometry, with Ni-filtered CuKα radiation ($\lambda = 1.54178$ Å). Diffraction data were acquired over the scattering angle 2θ from 20° to 80° with a step of 0.020° and acquisition rate of 2°/min.

Micro-Raman spectra were collected at room temperature using the TriVista 557 Raman system equipped with a nitrogen-cooled CCD detector in the backscattering configuration. The $\lambda = 532$ nm line of solid state laser was used as an excitation source.

PL spectral measurements were taken on a Horiba Jobin Yvon Fluorolog FL3-22 spectrofluorometer at room temperature, with a Xe lamp as the excitation light source. The obtained spectra were corrected for the spectral response of the measuring system and spectral distribution of the Xe lamp.

For photocatalytic activity evaluation, the photodegradation of aqueous methyl orange (MO) solution at room temperature was used as a model reaction. The concentration of MO solution was 8 mg/L. Samples of 15 mm × 10 mm active surface area were immersed into 10 mL of MO solution and placed on the holder, 5 mm above the bottom of the reactor, with magnetic stirrer located under the holder. Prior to illumination, the solution and the catalyst were magnetically stirred in the dark for 30 min to achieve adsorption–desorption equilibrium. The MO solution was then irradiated under lamp that simulates solar radiation (Solimed BH Quarzlampen), with a power consumption of 300 W, housed 25 cm above the top surface of the solution. Illumination intensity on the top of the photocatalytic reactor was 850 lx. A fixed quantity of MO solution was removed every 2 h to measure the absorption and then concentration, using UV–VIS spectrometer (Thermo Electron Nicolet Evolution 500). After each measurement of MO concentration, probe solution was returned back to the photocatalytic reactor. MO has a maximum absorbance at 464 nm, which was used as a wavelength for monitoring MO degradation. The absorbance was converted to MO concentration in accordance with a standard curve showing a linear relationship between the concentration and the absorbance at this wavelength. Prior to the photocatalysis, MO solution was tested for photolysis in the absence of the photocatalyst in order to examine its stability. The lack of change in MO concentration after 12 h of irradiation revealed that degradation was only due to the presence of the photocatalyst. The reproducibility of the results was verified by performing each test several times.

## 3. Results and discussion

### 3.1. Morphology, chemical, and phase composition of $Al_2O_3$/ZnO coatings

Time variation of anodization voltage of aluminum at 150 mA/cm$^2$ in electrolyte containing 0.1 M $H_3BO_3$ + 0.05 M $Na_2B_4O_7 \cdot 10H_2O$ + 2 g/L ZnO is shown in Fig. 1. From the beginning of anodization, the voltage increases roughly linearly with time to about 400 V with average slope of 34 V/s (stage I in Fig. 1) resulting in the constant rate of increase of the compact barrier oxide film thickness [10]. During this stage, the main part of the total current passing through the barrier oxide film is ionic current which forms oxide film. Throughout the anodization electrons are injected into the conduction band of the aluminum oxide film and accelerated by the electric field producing avalanches by an impact ionization mechanism [11]. When the avalanche electronic current reaches a certain critical value the breakdown of the barrier oxide films occurs. The point of dielectric breakdown can be identified by an apparent deflection from linearity in the voltage–time curve, starting from so-called breakdown voltage. At this point, a large number of small-sized microdischarges evenly distributed over the whole sample surface appear. After the breakdown, anodization voltage still increases, but the voltage-time slope decreases towards relatively constant value of the anodization voltage (Stage II in Fig. 1).

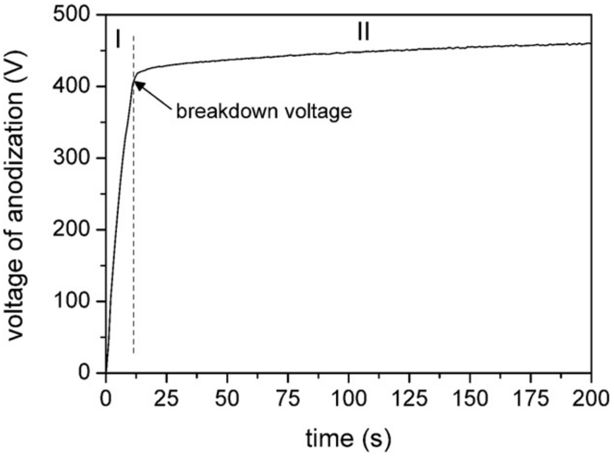

**Fig. 1.** Time variation of voltage during galvanostatic anodization of aluminum at 150 mA/cm$^2$ in electrolyte containing 0.1 M $H_3BO_3$ + 0.05 M $Na_2B_4O_7 \cdot 10H_2O$ + 2 g/L ZnO.

Multiple coexisting processes such as oxide formation, dissolution and dielectric breakdown are typical for PEO [12]. At the beginning of the anodization, oxide layer grows at the aluminum/oxide and oxide/electrolyte interfaces as a result of migration of $O^{2-}/OH^-$ and $Al^{3+}$ ions across the oxide assisted by a strong electric field. The proposed chemical reactions at the aluminum/oxide interface are [13]:

$$2Al + 3O^{2-}_{solid} \rightarrow Al_2O_3 + 6e^-, \tag{1}$$

$$Al \rightarrow Al^{3+}_{solid} + 3e^-. \tag{2}$$

Simultaneously, at the oxide/electrolyte interface the following reaction takes place:

$$2Al^{3+}_{solid} + 9H_2O \rightarrow Al_2O_3 + 6H_3O^+. \tag{3}$$

During the PEO process, components of the electrolyte are drawn into the discharge channels. Alongside, aluminum is melted out of the substrate, enters the discharge channels, and gets oxidized. In the following step, oxidized metal is ejected from the channels into the coating surface in contact with the electrolyte and in that way increases the coating thickness around the channels. At last, discharge channels get cooled and the reaction products are deposited onto its walls. The ZnO nanoparticles take part in this process through the electrophoretic and microdischarging mechanisms. Due to the electrophoretic effect, the ZnO nanoparticles move in the direction of anode and locally high temperature and pressure induced at the microdischarge sites result in deposition of the ZnO nanoparticles on the surface of oxide coatings.

SEM micrographs of the surface coatings obtained at various stages of PEO process are shown in Fig. 2. Numerous microdischarge channels with different diameters and shapes, as well as regions resulting from the rapid cooling of molten material, decorate the surface of the coatings. Results of the EDS analyses of surface coatings in Fig. 2 are shown in Table 1. Main elements of the coatings are Al, O, and Zn. The concentration of Zn increases with PEO time. Although one may expect incorporation of boron from the electrolyte into the surface coatings obtained by PEO [14], we were not able to detect its presence utilizing EDS analysis, possibly because its concentration is below the detection limit of our equipment. Fig. 3 shows SEM micrograph and EDS of two different regions on surface coating processed for 5 min (Table 2). Due to a high sparking strength in microdischarge channel oxide coating in the surrounding area is mainly composed of aluminum and oxygen (spectrum