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## Electrochemical study of Zr–1Nb alloy with oxide coatings formed by plasma electrolytic oxidation

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**Abstract.** Plasma electrolytic oxidation (PEO) coatings were formed on Zr–1Nb alloy in electrolyte containing 9 g/L sodium silicate, 5 g/L sodium hypophosphite, and 6 g/L submicron yttrium oxide powder at current densities 20, 30, and 40 A/dm<sup>2</sup>. The coatings surface morphology was studied by scanning electron microscope. The electrochemical behavior of coated and uncoated samples was investigated after 1- and 7-days exposure in 10 % HCl. The samples with PEO coatings formed at 30 A/dm<sup>2</sup> current density had the best corrosion protective properties after 1-day exposure in 10 % HCl. After 7-days exposure in 10 % HCl the samples with PEO coatings formed at 30 and 40 A/dm<sup>2</sup> current densities showed greater corrosion resistance than samples with PEO coatings formed at 20 A/dm<sup>2</sup> current density and uncoated samples.

### 1. Introduction

Plasma electrolytic oxidation (PEO) of zirconium and its alloys is the subject of many modern studies. PEO coatings are promising for the protection of reactor structural materials against corrosion, accelerated oxidation at high temperatures, embrittlement and absorption of oxygen and hydrogen [1, 2]. Zirconium and its alloys with PEO coatings are also promising in orthopedics and dental prosthetics [3]. Due to the low thermal conductivity the possibilities of PEO coatings application as thermal barrier coatings are also considered [4–6].

PEO is electrochemical process using the energy of electrical microdischarges functioning on the surface of the materials being treated [7]. During PEO process electrolyte components can be incorporated into the coatings, forming oxides and various compounds with components of base material. Also, powders of insoluble compounds can be added in the slurry electrolytes to provide certain properties to the coatings: wear resistance, corrosion resistance, heat resistance, etc. For example, the addition of nanoparticles of such oxides as Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and ZrO<sub>2</sub> in PEO electrolytes improves the corrosion resistance of zirconium alloys (up to 10<sup>3</sup> times compared with uncoated alloys) [1].



In present work PEO coatings were formed on Zr–1Nb alloy in electrolyte with yttrium oxide submicron particles addition. Yttrium oxide additives can increase the corrosion protective properties of the PEO coatings, as well as lead to tetragonal and cubic  $\text{ZrO}_2$  phases stabilization in oxide layer on zirconium alloys that improve its thermal stability and hardness.

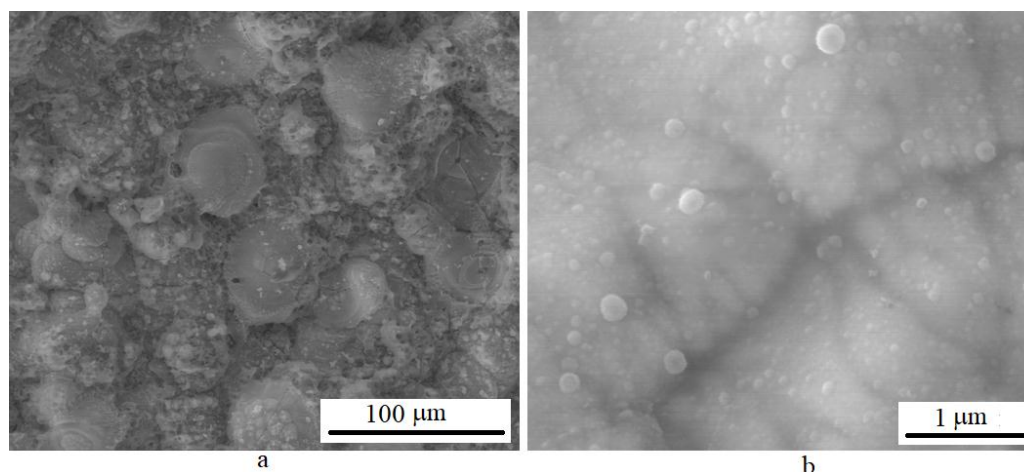
## 2. Experimental setup and characterization techniques

PEO coatings were formed on Zr–1Nb alloy in the electrolyte containing 9 g/L sodium silicate, 5 g/L sodium hypophosphite, and 6 g/L submicron yttrium oxide powder. Slurry electrolyte was treated for 3 min using a homogenizer at ultrasonic vibration frequency of 40 kHz to stabilize the suspension. Plasma electrolytic oxidation was carried out for 60 min at AC electrical mode and equal values of anodic and cathodic currents and sum current densities 20, 30, and 40 A/dm<sup>2</sup>.

Investigation of the surface morphology and thickness cross-sections of PEO coatings measurements were carried out using a Quanta 600 scanning electron microscope (SEM). The electrochemical behavior of uncoated and coated samples was investigated in 10 % HCl. Experimental curves were obtained by polarization from the cathodic to the anodic region with the sweep rate of 1 mV/s after 1- and 7-days exposure in 10 % HCl. The studies were carried out in standard three-electrode cell with silver chloride (Ag/AgCl) reference electrode. Polarization was carried out using a PI-50-1 potentiostat.

## 3. Results and discussion

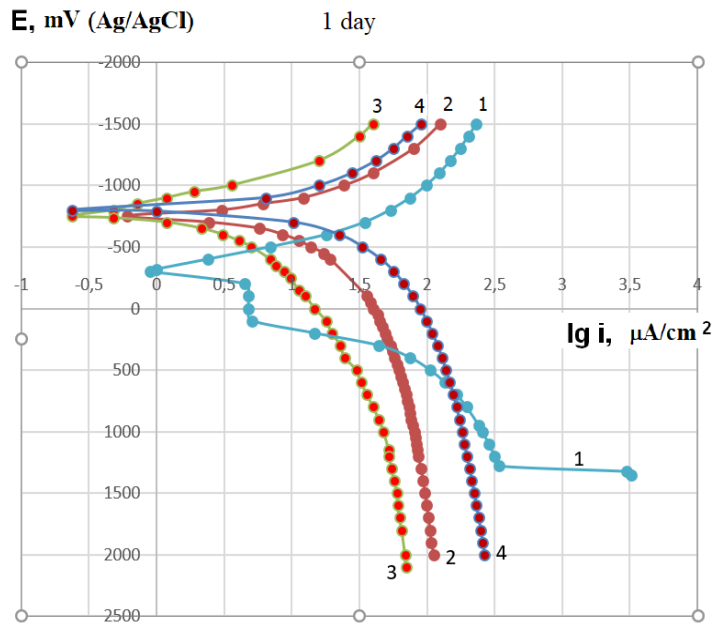
Cross-sections SEM study showed that PEO coatings average thickness formed at current density 20, 30 and 40 A/dm<sup>2</sup> is ~40, ~110 and ~170  $\mu\text{m}$  with accordingly. The surface layer of PEO coatings is characterized by crater-like regions, regions of globular structure (figure 1, a) and incorporated in coating yttrium oxide submicron particles up to 300 nm in size (figure 1, b). Figure 1b shows that the yttrium oxide particles quite uniformly cover the PEO coating surface, that can decrease open porosity. In addition, yttrium oxide can melt and form a solid solution with zirconia when it enter in areas of micro-discharges functioning, whose temperature reaches several thousand degrees. In this case the stabilization of the high-temperature zirconia phases occurs [8].



**Figure 1.** SEM images in backscattered electrons of PEO coating formed at current density of 30 A/dm<sup>2</sup>: **a** – morphology of the coating surface; **b** – submicron particles on the coating surface.

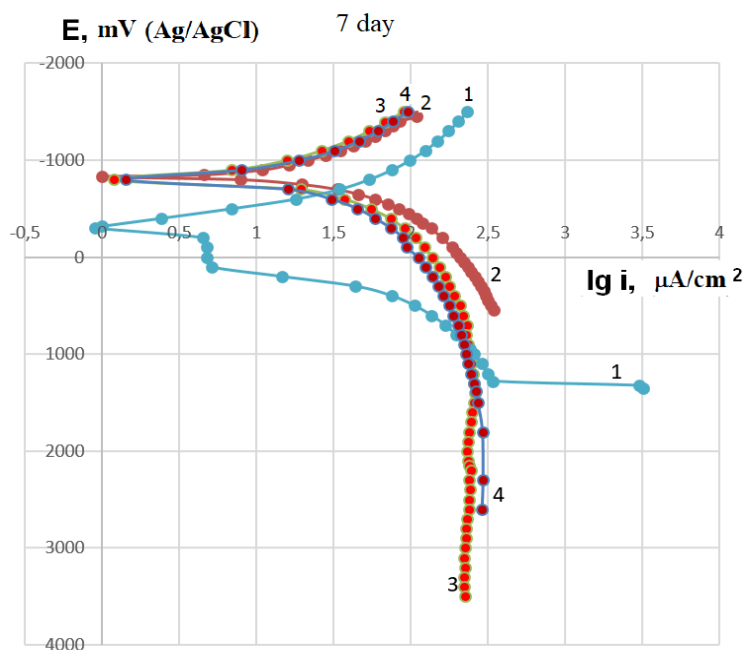
Polarization studies of PEO coated samples after 1-day exposure in 10 % HCl showed values of corrosion currents below the sensitivity of the potentiostat. For uncoated Zr–1Nb alloy the polarization curve has a passive state area from –250 to +100 mV. Then the anodic polarization current density increases and there is the sharp increase in current due to pitting after +1.3 V (figure 2, curve 1). For the PEO coated samples pitting was not observed. The samples with PEO coatings formed at 30 A/dm<sup>2</sup> showed lowest values of both anodic and cathodic polarization current densities after 1-day exposure

in 10 % HCl (figure 2, curve 3). The highest anodic polarization current densities are for the samples modified by PEO at 40 A/dm<sup>2</sup>. The cathodic polarization current densities for the samples modified at 20 A/dm<sup>2</sup> and 40 A/dm<sup>2</sup> are close.



**Figure 2.** Polarization curves after 1-day exposure in 10 % HCl for uncoated sample (1) and with PEO coatings formed at current densities: 20 A/dm<sup>2</sup> (2), 30 A/dm<sup>2</sup> (3), 40 A/dm<sup>2</sup> (4) (for uncoated sample – immediately after immersion in 10% HCl).

After 7-days exposure in 10 % HCl the PEO modified at 30 and 40 A/dm<sup>2</sup> samples showed more corrosion resistance than ones treated at 20 A/dm<sup>2</sup> current density (figure 3). They have a higher thickness (~110 and ~170 μm) compared with the coating formed at 20 A/dm<sup>2</sup> (~40 μm). With increasing of exposure time in 10 % HCl the values of the anodic current densities on the polarization curves increase (figure 3). Such behavior is typical for all coatings and may be associated with the gradual destruction of the barrier layer under the coatings due to their through porosity.



**Figure 3.** Polarization curves after 7-days exposure in 10 % HCl of uncoated sample (1) and samples with PEO coatings formed at current densities: 20 A/dm<sup>2</sup> (2), 30 A/dm<sup>2</sup> (3), 40 A/dm<sup>2</sup> (4) (for uncoated sample – immediately after immersion).

Thus, increasing of PEO process current density up to 30 and 40 A/dm<sup>2</sup> leads to higher corrosion protective properties of oxide coatings on Zr–1Nb alloy. It may be due to forming of denser barrier

layer forming as a result of higher local temperatures in discharges during PEO process. Increasing of current density also leads to more intensive incorporation of submicron yttrium oxide particles into the PEO coating structure and stabilization of the tetragonal and cubic  $\text{ZrO}_2$  phases as was shown in [8]. It was also reported in [1–2] that electrophoretic interaction could be responsible for the migration of yttrium oxide nanoparticles towards the anode during PEO process. Addition of yttrium oxide nanoparticles in PEO electrolyte leads to increasing of the corrosion resistance of coated zirconium alloys by several orders of magnitude [1]. The obtained in present work data suggest the similar effect for submicron particles.

#### 4. Conclusions

PEO coatings were formed on Zr–1Nb alloy in the electrolyte containing 9 g/L sodium silicate, 5 g/L sodium hypophosphite and 6 g/L submicron yttrium oxide powder at current densities 20, 30 and 40 A/dm<sup>2</sup>. The corresponding average coating thicknesses were ~40, ~110 and ~170 μm. The electrochemical behavior of coated and uncoated samples was investigated after 1- and 7-days exposure in 10 % HCl. The samples with PEO coatings formed at 30 A/dm<sup>2</sup> had the best corrosion protective properties after the 1-day exposure in 10 % HCl. After 7-days exposure in 10 % HCl the samples PEO modified at 30 and 40 A/dm<sup>2</sup> showed greater corrosion resistance that may indicate the presence of denser barrier layers under PEO coatings and more intensive incorporation of submicron yttrium oxide particles into their structure compared with the coatings formed at 20 A/dm<sup>2</sup>.

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