

Stabilization of the high-temperature phases in ceramic coatings on zirconium alloy produced by plasma electrolytic oxidation

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Abstract. The composition and structure of ceramic coatings obtained on Zr-1%Nb alloy by plasma electrolytic oxidation (PEO) in aqueous electrolyte comprising 2 g/L KOH, 6 g/L NaAlO₂ and 2 g/L Na₂SiO₃ with addition of yttria nanopowder, have been studied. The PEO coatings of thickness ~20 μm were studied using scanning electron microscopy, X-ray microanalysis and X-ray phase analysis. Additives in the electrolyte of yttria nanopowder allowed stabilizing the high-temperature tetragonal and cubic zirconia in the coating.

1. Introduction

Plasma electrolytic oxidation (PEO) of zirconium alloys for obtaining ceramic coatings is the subject of many modern researches. For example, PEO of zirconium has been studied for biocompatible zirconium implants [1], for water corrosion protection of fuel elements of nuclear power reactors [2–4]. Due to low thermal conductivity and high thermal resistance, zirconium oxides are widely used as the top thermal barrier layers of thermal barrier coatings [5,6]. The possibilities of PEO for the thermal barrier coatings production were recently presented in [7–9]. Using zirconia PEO coatings at high temperatures requires stabilization of the high-temperature ZrO₂ phases. At transition of high-temperature tetragonal *t*-ZrO₂ to low-temperature monoclinic *m*-ZrO₂, the volume of material increases by 5–7%. It can lead to cracks and destruction of the coating. Stabilization of high-temperature phases is possible with additives of oxides CaO, MgO, Y₂O₃, Al₂O₃, etc. [10–11]. They form a solid solution with ZrO₂ and prevent phase transitions. The additives of these oxides allow retaining the metastable *t*-ZrO₂.

The aims of the present study were synthesis and investigations of oxide coatings on Zr-1%Nb alloy produced by plasma electrolytic oxidation in the electrolyte comprising an addition of yttria nanopowders. It is assumed that during PEO oxide nanoparticles can be incorporated into the structure of the coatings that will stabilize high-temperature phases of zirconia.

2. Experimental setup and characterization techniques

PEO coatings were formed on Zr-1% Nb alloy pipes with diameter of 8 mm. Specimens were ultrasonic degreased in acetone and ethanol, then rinsed in distilled water and dried on warm air. The

coatings were formed by PEO in the electrolytes comprising 2 g/L KOH, 6 g/L NaAlO₂ and 2 g/L Na₂SiO₃ with addition of yttria nanopowder. Nanopowder particles were 10 ÷ 30 nm in diameter. Nanopowder was added to the electrolyte in amount of 2, 5, 8 and 10 g/L. The electrolytes were prepared in an ultrasonic bath with aim of uniform nanopowder distribution. PEO was carried out at an alternating current, and oxide coatings thickness of ~ 20 μm were obtained during 60 minutes of PEO with average current density of 10 A / dm².

During PEO, the current *I* flowing through the electrolytic bath and the voltage drop *U* on it were periodically measured. A typical *I-U* curve for one period of the alternating current with the frequency of 50 Hz is shown in figure 1. Rising branches 1 and 3 of *I-U* curve correspond to increase of the anodic and cathodic voltage, and falling branches 2 and 4 correspond to anodic and cathodic voltage decrease.

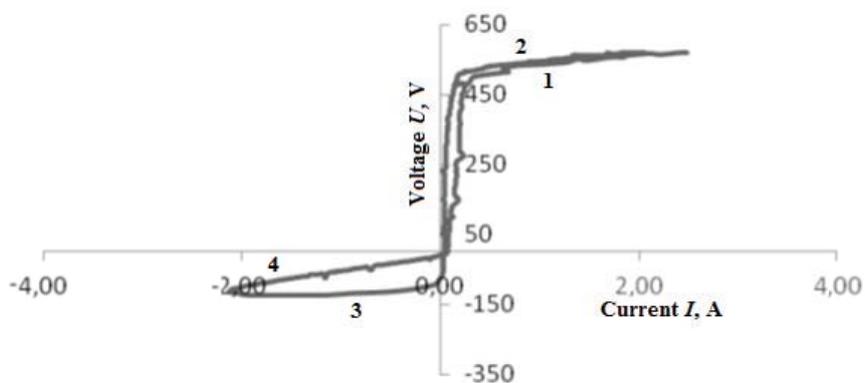


Figure 1. *I-U* curve that has been recorded after 1180 s of PEO.

It can be seen that the anodic voltage at first increases very rapidly with current increase that corresponds to ignition of the discharge, and then the *I-U* curve rises very slowly as in the case of normal glow gas discharge. At the large thickness of PEO coatings the rise of the *I-U* curve is also seen which is characteristic for anomalous glow discharge [12]. Transition of the discharge to the arc in the anode half-cycle of PEO is not observed. The difference of rising and falling branches of *I-U* curve indicates the formation of the anodic oxide film during the pulse of anodic voltage. Short-lived microdischarges moving along the metal surface in the anodic and cathodic half-cycles have significantly different character. The cathodic branches of the *I-U* curve correspond to the arc discharge. The voltage in cathodic half-cycles is not higher than 100 V. During PEO, the *I-U* curves do not undergo qualitative changes. The growth of the coating leads to increase of voltage of the discharge ignition. Detailed analysis of the evolution of the *I-U* curve revealed some changes for consecutive stages of PEO including anodizing, luminescence, sparking, and burning of microdischarges [13].

The structure of the coatings was studied using scanning electron microscopy (SEM), X-ray microanalysis and X-ray diffraction phase analysis (XRD).

3. Results and discussion

PEO coatings formed without yttria nanopowder additives are characterized by lenticular zirconium-enriched and silicium-enriched regions with fine globular structure (figure 2, a, b). In the center of some zirconia regions pores with a diameter of 20 μm are located. X-ray microanalysis shows that zirconium-enriched regions are composed of zirconia and silicium-enriched regions comprise SiO₂. The lenticular regions are typically composed of grains 0.2–0.4 μm in size (figure 2, c).

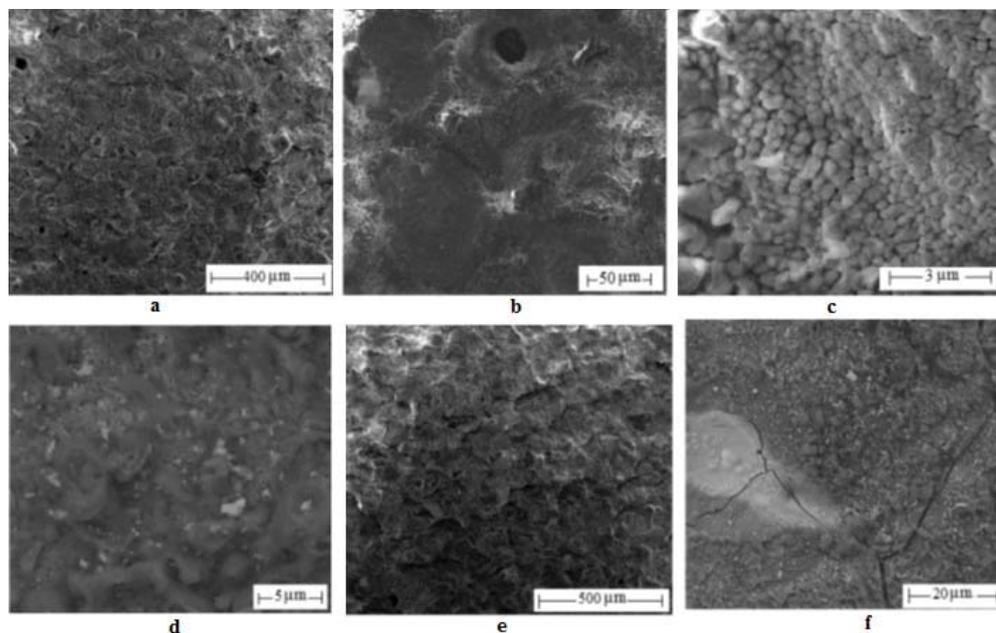


Figure 2. The SEM images of PEO coatings on Zr-1% Nb alloy without (a, b, c) and with additives of Y_2O_3 nanopowder of 5 g/L (d, e) and of 8 g/L (f).

If 2 g/L of yttria nanopowder is added in the electrolyte, the structure of PEO coating does not change significant, but if 5 g/L are added, conglomerates of yttria nanoparticles are observed on the surface (figure 2, d). X-ray microanalysis showed that the concentration of yttrium in the coating is higher than 3 at%. With 8 g/L additives of yttria in electrolyte the structure of PEO coatings became more rough (figure 2, e). Microcracks in the regions of zirconia and silica were observed (figure 2, f), also there were significant amount of conglomerates of yttria nanoparticles on the surface. X-ray microanalysis showed the content of yttrium in the coating was more than 8 at%.

X-ray diffraction analysis of the PEO coatings obtained without addition of yttria nanopowder showed monoclinic and tetragonal phases of zirconia in an equal amount (figure 3).

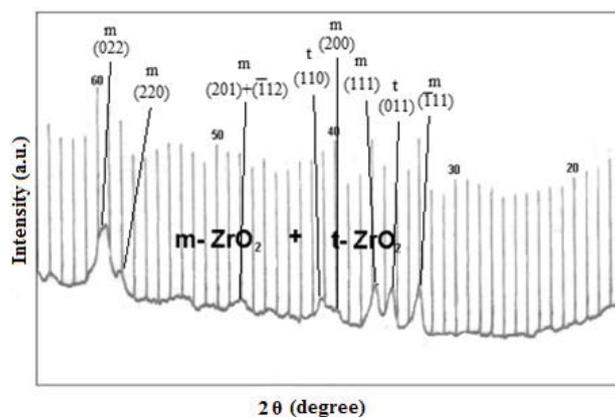


Figure 3. XRD pattern of the PEO coatings formed in electrolyte comprising 2 g/L KOH, 6 g/L $NaAlO_2$ and 2 g/L Na_2SiO_3 without additives of yttria.

If 2 g/L of Y_2O_3 nanopowder is added to the electrolyte, the ratio of monoclinic and tetragonal phases becomes 1: 4. If the concentration of Y_2O_3 nanopowder in the electrolyte rises to 5 g/L, only peaks of tetragonal phase are observed (figure 4, a). Finally, if the concentrations of Y_2O_3 nanopowder in electrolyte becomes 8 and 10 g/L, only peaks of cubic phase are observed in the XRD pattern (figure 4, b). Phase transformations obtained in this work correlate with the equilibrium diagram $ZrO_2 - Y_2O_3$. Increase of the yttria concentration leads to sequential formation of the monoclinic, tetragonal and cubic ZrO_2 phases. The transition monoclinic to tetragonal ZrO_2 phase takes place at 1170 °C. The cubic phase of zirconia is formed at 2370 °C [14]. The phase transitions to the tetragonal or cubic zirconia in PEO coatings can be explained by presence of yttria in the electrolyte in the form of a slurry. It can be assumed that yttria nano-particles decompose in microdischarges during the PEO process that results in dissolution of yttria in zirconia.

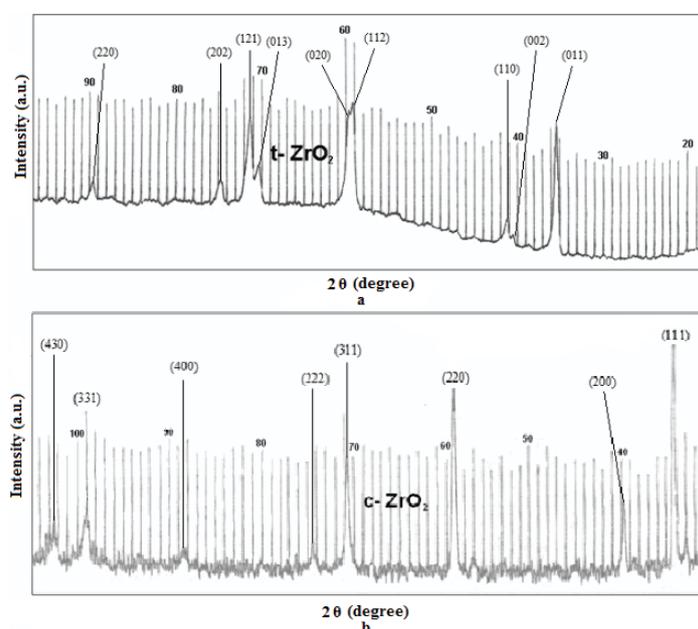


Figure 4. XRD patterns of the PEO coatings formed in the electrolyte comprising 2 g/L KOH, 6 g/L $NaAlO_2$ and 2 g/L Na_2SiO_3 with 5 g/L (a) and 8 g/L (b) additives of yttria nanopowder.

The presence of tetragonal zirconia in the PEO coating without yttria nanopowder in the electrolyte may be due to effect of stabilization of this phase by alumina due to presence of $NaAlO_2$ in the electrolyte. Stabilization of zirconia by alumina is known, for example, in the coatings obtained by magnetron sputtering [15].

4. Conclusions

The composition and the structure of ceramic coatings obtained on Zr-1%Nb alloy by plasma electrolytic oxidation in aqueous electrolyte, comprising 2 g/L KOH, 6 g/L $NaAlO_2$ and 2 g/L Na_2SiO_3 with addition of yttria nanopowder, have been studied.

It has been shown that additions of yttria nanopowder in the electrolyte allowed stabilizing the high-temperature tetragonal zirconia in the PEO coating. If 7 g/L of yttria nanopowder is added in the electrolyte, the high-temperature cubic phase of zirconia dominates in the PEO coatings.

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