

# Investigation of zirconia tetragonal phase coatings formed by plasma electrolytic oxidation

S V Savushkina<sup>1,4</sup>, A A Ashmarin<sup>1</sup>, A V Apelfeld<sup>2</sup>, A M Borisov<sup>2</sup>,  
A V Vinogradov<sup>2</sup>, M N Polyansky<sup>1</sup> and N L Bogdashkina<sup>3</sup>

<sup>1</sup> Keldysh Research Center, Onezhskaya str. 8, 125438 Moscow, Russia

<sup>2</sup> Moscow Aviation Institute (National Research University), Volokolamskoe sh. 4, 125993 Moscow, Russia

<sup>3</sup> Institute of Physical Chemistry and Electrochemistry of RAS, 119991 Moscow, Leninsky pr., 31-4

E-mail: sveta\_049@mail.ru

**Abstract.** Zirconia coatings were formed on zirconium-niobium alloy (1 % Nb) by plasma electrolytic oxidation (PEO) in silicate-hypophosphite electrolyte with Y<sub>2</sub>O<sub>3</sub> nanopowder additives. The structure, elemental composition and layer-by-layer phase composition of the PEO coatings were investigated using methods of scanning electron microscopy (SEM), X-ray microanalysis, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS). PEO coatings formed in an electrolyte with 6 g/L Y<sub>2</sub>O<sub>3</sub> nanoparticles additive contain predominantly tetragonal *t*-ZrO<sub>2</sub> phase and have the superficial layer mainly consisting of electrolyte components and their compounds, including yttria and yttrium silicate. Moreover, stabilization of the *t*-ZrO<sub>2</sub> phase in the PEO coating leads to increase its hardness up to 4.6 GPa.

## 1. Introduction

Zirconia coatings are most often produced by thermal spraying and electron-beam deposition methods [1, 2]. The method of plasma electrolytic oxidation (PEO) also allows forming ZrO<sub>2</sub> coatings that have a high adhesion strength and low thermal conductivity [3–5]. It makes them promising for using as thermal barrier layers in thermal barrier coatings to prevent overheating of heat-stressed units of aerospace, etc. Zirconia PEO coatings usually contain a monoclinic *m*-ZrO<sub>2</sub> phase or a mixture of *m*-ZrO<sub>2</sub>, tetragonal *t*-ZrO<sub>2</sub>, and cubic *c*-ZrO<sub>2</sub> phases [5–7]. The partially stabilized tetragonal zirconia *t*-ZrO<sub>2</sub> with 7–8 % doping of Y<sub>2</sub>O<sub>3</sub> is the most suitable for obtaining of the effectively working thermal barrier coatings [2, 8]. Y<sub>2</sub>O<sub>3</sub> forms a solid solution with ZrO<sub>2</sub>. It prevents the phase transformations during thermal cycling that often lead to the destruction of the coating. Moreover, *t*-ZrO<sub>2</sub> has higher hardness than *m*-ZrO<sub>2</sub> that increases the wear resistance of PEO coatings. Incorporation of stabilizing oxides in zirconia coatings can be achieved by carrying out the PEO process in suitable slurry electrolytes [9, 10].

In present work the layer-by-layer study of the structure, elemental and phase composition of PEO coatings with a thickness up to 120 μm formed in a silicate-hypophosphite electrolyte with additions of Y<sub>2</sub>O<sub>3</sub> nanoparticles and consisting mainly of the tetragonal modification of zirconia was carried out.

## 2. Experimental setup and characterization techniques

PEO coatings were formed on specimens fabricated from zirconium-niobium alloy (1 % Nb). PEO process was carried out in electrolytes comprising 9 g/L sodium silicate, 5 g/L sodium hypophosphite



and 4 or 6 g/L  $Y_2O_3$  nanopowder with particle size of  $\sim 30$  nm. Slurry electrolytes were treated using a homogenizer with a power of 20 W for 3 min at ultrasonic vibration frequency of 40 kHz to stabilize the suspended state of suspension. The PEO process was carried out for 60 min under the AC electrical mode at equal values of anode and cathode currents and total current densities 20 or 30  $A/dm^2$ .

The coatings structure was examined by scanning electron microscope (SEM) Quanta 600 with X-ray microanalysis system TRIDENT XM 4. The thickness of the coatings was measured by eddy current thickness gauge and on the cross-sections using SEM. The elemental composition of the coatings surface layer was investigated using X-ray photoelectron spectroscopy (XPS) on a Quantera device after preliminary surface cleaning by argon ions for 3 min. X-ray diffraction analysis of PEO coatings was carried out layer-by-layer in  $\beta$ -filtered copper radiation ( $\lambda_{K\alpha 1,2} = 1.54178$  Å) on a X-ray diffractometer EMPYREAN. The hardness of the coatings was measured on the microhardness tester Micromet 5114 with a load on indenter of 0.25 N. The time from the start of the load application to its nominal value was 5 s. The exposure under the load was 10 s.

### 3. Results and discussion

SEM investigations of surface coating ( $\sim 70$   $\mu m$  thickness) formed in the electrolyte with 4 g/L  $Y_2O_3$  nanoparticles additive showed a typical structure for PEO coatings on zirconium alloys. It consists of crater-shaped areas with size up to 70  $\mu m$  with the predominance of the elements of zirconia (Zr, O) and inter-crater areas with the predominance of the elements of electrolyte components (Si, P, Na, Y, O) (figure 1(a)) [5]. Some crater-shaped areas have in their centers pores with the diameter up to 10  $\mu m$  preserved after extinction of microdischarges. Most of the crystallites in such areas are elongated and directed to the craters center.

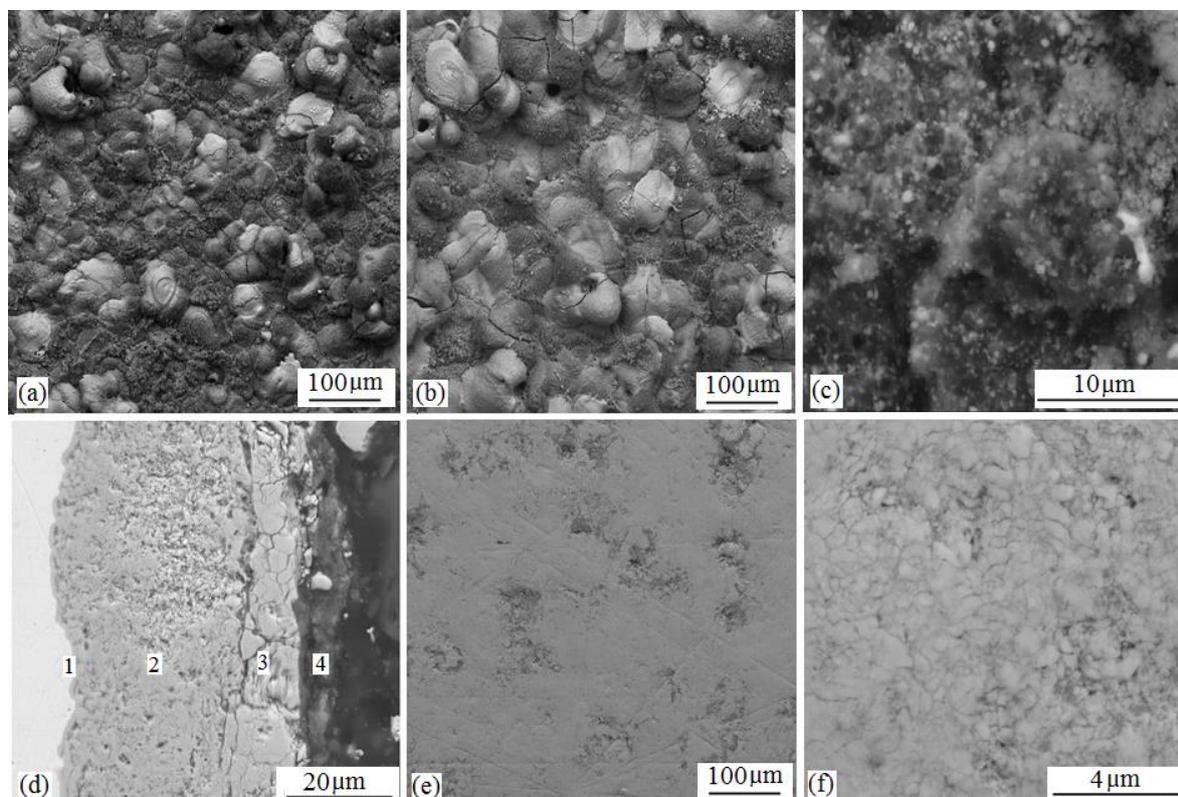
When increased the concentration of nanopowder  $Y_2O_3$  in the electrolyte up to 6 g/L the size of these areas enlarged up to 100  $\mu m$  (figure 1(b)). The thickness of the coating increases to  $\sim 100$   $\mu m$ . The net of microcracks mainly outgoing from the centers of the craters is formed on the surface of the coating.

When the total current density was increased up 30  $A/dm^2$  the square of the areas enriched by the elements of electrolyte components was significantly grown, and the thickness of coating reached  $\sim 120$   $\mu m$ . On the surface of PEO coatings there are conglomerates of nanoparticles with size up to 0.3  $\mu m$ . Some of them are incorporated into the coating and some are electrophoretically deposited on its surface and are welded to it by micro-arc discharges (figure 1(c)).

On the cross-section of the PEO coating formed in the electrolyte with 4 g/L  $Y_2O_3$  nanoparticles additive at a current density of 20  $A/dm^2$  four layers can be distinguished (figure 1(d)). The barrier layer (1) is located at the boundary with the zirconium-niobium alloy. It is dense and has a thickness of  $\sim 1$   $\mu m$ . The main median layer (2) occupies the most of coating thickness and is characterized by a crystalline structure. The outer layer of the coating (3) occupying up to a third of its thickness is dense but has large pores and microcracks at the junctions of the large crystallites. This layer is characterized by a high content of silicon that incorporates into the coating from sodium silicate dissolved in the electrolyte. On the outer layer of the coating there is the superficial layer (4) with the thickness up to 5  $\mu m$ . The thickness of this layer is inhomogeneous and it is the thinnest in the crater-shaped areas of the coating surface. X-ray microanalysis showed that the yttrium content in the median layer is approximately two times lower than in the superficial layer of coating. This indicates that part of the  $Y_2O_3$  nanoparticles are deposited in the surface layer. As a result they were not incorporated inside the coating and not formed a solid solution with zirconia. It is found that the yttrium content grows in the top layer of the PEO coating with an increase of  $Y_2O_3$  nanopowder concentration in the electrolyte from 4 to 6 g/L and with an increase current density from 20 to 30  $A/dm^2$ .

Figure 1(e) shows the polished structure of the median layer at the boundary with the barrier layer of coating. It has the islands consisting of yttrium and silicon in addition to zirconium and oxygen as X-ray microanalysis shows. The size of islands is comparable to the size of craters on the coating surface. It means that Y and Si incorporate precisely through these craters from the electrolyte into the coating. The median layer is characterized by the structure of heteraxial crystallites with dimensions

up to 0.3  $\mu\text{m}$  (figure 1(f)). Such structure has formed during the PEO process as a result of the permanent influence of microdischarges on the already formed coating material.



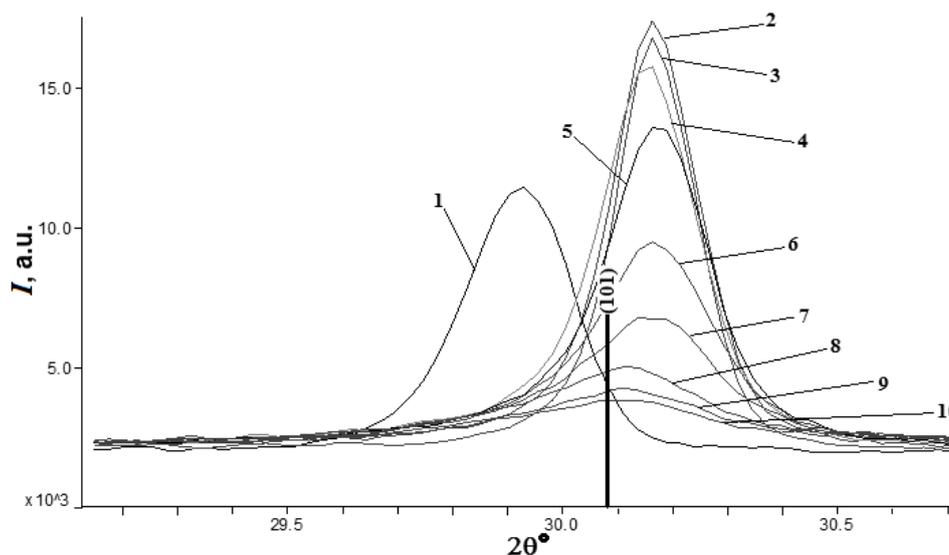
**Figure 1.** The backscattered electron images of PEO coatings formed at current density 20 A/dm<sup>2</sup> in slurry electrolyte with Y<sub>2</sub>O<sub>3</sub> nanopowder additives 4 g/L (a) and 6 g/L (b), (c); the layer structure on the cross-section of the coating formed in electrolyte with 4 g/L Y<sub>2</sub>O<sub>3</sub> nanoparticles additive at current density 20 A/dm<sup>2</sup> (d) with barrier layer (1), median layer (2), outer layer (3) and superficial layer (4); the polished structure of the median layer of the coating formed at current density 20 A/dm<sup>2</sup> in electrolyte with 6 g/L Y<sub>2</sub>O<sub>3</sub> nanoparticles additive at the boundary with the barrier layer (e) and its crystalline structure (f).

The XPS analysis (spot area of 100  $\mu\text{m}^2$ ) identified the absence of zirconium in the superficial layer unlike the other layers the other layers of PEO coatings. This layer totally consists of the elements of electrolyte components: 71 at. % O; 9 at. % P; 9 at. % Si; 5 at. % Na; 6 at. % Y. The analysis of XPS peak of yttrium showed that it consists of several sub-peaks. This suggests that yttrium is presented in the PEO coatings in the form of various compounds such as Y<sub>2</sub>O<sub>3</sub>, yttrium silicate Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, etc. The thickness of the superficial layer is less than 1  $\mu\text{m}$  in the crater-shaped areas and up to 5  $\mu\text{m}$  in the inter-crater areas.

The XRD analysis of the outer layers of PEO coatings formed in the slurry electrolyte with the concentration of Y<sub>2</sub>O<sub>3</sub> nanoparticles 4 g/L showed *t*-ZrO<sub>2</sub> and *m*-ZrO<sub>2</sub> phases. In the electrolyte without Y<sub>2</sub>O<sub>3</sub> additives the *m*-ZrO<sub>2</sub> phase usually forms. When added 6 g/L of Y<sub>2</sub>O<sub>3</sub> nanopowder in the electrolyte *t*-ZrO<sub>2</sub> phase is predominate in the composition of the outer coating layer. When the current density of the PEO treatment increases up 30 A/dm<sup>2</sup> Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> reflexes additionally appear in XRD pattern. Apparently, the microarc discharges power gets sufficient to form yttrium silicate as a result of fusing Y<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> formed in the process of thermolysis of the sodium silicate.

The layer-by-layer XRD analysis was carried out by successive mechanical removal the certain thickness layers from the surface of coating. The residual thickness of the coating was monitored by the eddy current thickness gauge. For quantitative phase analysis powder reference samples with

different mass content of tetragonal and monoclinic  $ZrO_2$  phases were prepared. Dependence  $I(101)t/I(111)m$  on the mass content of  $m-ZrO_2$  in the samples was used to determine the content of  $t-ZrO_2$  in the PEO coatings [10]. Figure 2 shows the change in the intensity of the tetragonal phase reflex  $I(101)t$  at layer-by-layer XRD analysis of the PEO coating. At depths of  $\sim 50 \mu m$  (peaks 1, 2 and 3 on figure 2) only the  $t-ZrO_2$  phase was identified. In the next layer (peak 4) traces of the  $m-ZrO_2$  phase were found. Its content increases up to 5 % at the distance from the surface of  $\sim 60 \mu m$  (peak 5) and up to 45 % (peak 7) at the depth of  $\sim 80 \mu m$ . Then the content of the  $m-ZrO_2$  phase increases up to 70 % (peak 8) and reaches 85 % at the depth of  $\sim 100 \mu m$  (peak 9).



**Figure 2.** The intensity of the reflex  $I(101)t$  obtained by layer-by-layer XRD analysis of the PEO coating formed at current density  $20 A/dm^2$  in the electrolyte with  $6 g/L Y_2O_3$  nanoparticles additive: 1–10 – peaks corresponded the coating layers.

The presence of the  $m-ZrO_2$  phase in the inner layers of PEO coating can be explained by insufficient temperature for  $m-ZrO_2 \rightarrow t-ZrO_2$  polymorphic transformation as a result of better heat removal near metal substrate. Because of low thermal conductivity of zirconia increasing of PEO coatings thickness gets worse the heat transfer from the action zones of microarc discharges in the median layer. The local temperature grows in the layer and it leads to formation of the high-temperature  $t-ZrO_2$  phase, as noted in [10]. This is promoted by yttria that forms a solid solution with zirconia. The particles  $Y_2O_3$  can enter directly from the electrolyte, as well as in the microdischarges action areas from the superficial layer enriched with yttria. At the initial stages of the PEO process this layer is practically absent, that reduces the  $Y_2O_3$  delivery into the coating, and therefore, there are no conditions for the  $t-ZrO_2$  phase formation. Enlargement of the areas enriched by the electrolyte components including yttria occurs with increasing of current density and PEO process duration.

The lattice parameters of  $t-ZrO_2$  phase in the superficial layer of PEO coatings are very different from those in the underlying layers. Apparently, this is due to residual stresses as a result of excess content of yttria in the upper layers of the coating. It is indirectly confirmed by the appearance of microcracks in the outer coating layer with increasing of  $Y_2O_3$  content in the electrolyte up to  $6 g/L$  (figure 1(b)).

The hardness of PEO coatings was measured on cross-sections in the median layer and on the polished surface of the median layer near the barrier layer. The increase of hardness when approaching to the barrier layer of the coating was seen. The hardness of the median layer near the outer layer was  $4.2 GPa$  and when approaching to the layer centre hardness was  $4.3 GPa$ . The hardness reached  $4.6 GPa$  near the barrier layer (figure 1(f)). It should be added, the hardness of PEO coatings formed in

the electrolyte without  $Y_2O_3$  nanopowder additives was 3.5 GPa, and the hardness of the Zr-Nb alloy was 1.7 GPa.

#### 4. Conclusions

The structure, elemental composition and layer-by-layer phase composition of the PEO coatings with the thickness up to 120  $\mu\text{m}$  formed on zirconium-niobium alloy (1 % Nb) in the silicate-hypophosphite electrolyte with  $Y_2O_3$  nanopowder additives were studied. The layer-by-layer XRD analysis of PEO the coatings in the electrolyte with 6 g/L  $Y_2O_3$  nanoparticles additive showed that more than half of their thickness contains predominantly *t*- $ZrO_2$  phase. When approaching to the barrier layer *m*- $ZrO_2$  phase begins to predominate. The lattice parameters of the zirconia tetragonal phase on the surface of the coating are very different from those in the underlying layers, that is associated with the residual stresses in the outer layer. Besides, a superficial layer mainly consisting of the electrolyte components and their compounds including  $Y_2O_3$  and  $Y_2Si_2O_7$  has been identified in the coating. Stabilization of the *t*- $ZrO_2$  phase in the PEO coating leads to increasing of its hardness up to 4.6 GPa.

#### Acknowledgments

The study was partially supported by Russian President Grant No. MK 524.2017.8.

#### References

- [1] Slifka A J, Filla B J, Phelps J M, Bancke G and Berndt C C 1998 *J. Thermal Spray Technol.* **7** 43
- [2] Zhao H, Yu F, Bennet T D and Wadley H N G 2006 *Acta Material.* **54** 5195
- [3] Cheng Y, Matykina E, Arrabal R, Skeldon P and Thompson G E 2012 *Surf. Coat. Technol.* **206** 3230
- [4] Savushkina S V, Polyansky M N, Borisov A M, Vinogradov A V, Lydin V B, Dankova T E and Agureev L E 2016 *J. Surf. Invest.: X-Ray, Synchrotron. Neutron. Tech.* **10** 406
- [5] Apelfeld A V, Borisov A M, Krit B L, Ludin V B, Polyansky M N, Romanovsky E A, Savushkina S V, Suminov I V et al. 2015 *Surf. Coat. Technol.* **269** 279
- [6] Chen Y, Nie X and Northwood D O 2010 *Surf. Coat. Technol.* **205** 1774
- [7] Zou Z, Xue W, Jia X, Du J, Wang R and Weng L 2013 *Surf. Coat. Technol.* **222** 62
- [8] Shin D I, Gitzhofer F and Moreau C J. 2007 *Mater. Sci.* **43** 5915
- [9] Borisov A M, Krit B L, Lyudin V B, Morozova N V, Suminov I V and Apelfeld A V 2016 *Surf. Engineer. and Applied Electrochem.* **52** 1 50
- [10] Apelfeld A V, Ashmarin A A, Borisov A M, Vinogradov A V, Savushkina S V and Shmytkova E A 2016 *Surf. Coat. Technol.* <http://dx.doi.org/10.1016/j.surfcoat.2016.09.071> (in press)