Investigation of zirconia plasma electrolytic oxidation coatings by nuclear backscattering spectrometry

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Abstract. Zirconia coatings of a thickness up to 110 µm were obtained by plasma electrolytic oxidation (PEO) in silicate-alkaline and silicate-hypophosphite electrolytes. Layer-by-layer structure and total porosity of the coatings were investigated using proton nuclear backscattering spectrometry (NBS). The PEO coating obtained in the first electrolyte has a thick transition layer with decreasing oxygen content with the depth increasing. The coating formed in the second electrolyte has a thick layer of zirconia and a thin transition layer. When analyzing the NBS spectra, the thickness is determined without taking porosity into account (so called mass thickness). The total porosity of the coatings was evaluated by determining the difference between their geometric and mass thicknesses: 15 and 22%, respectively. The critical load of disruption is higher for the PEO coating formed in the silicate-hypophosphite electrolyte.

1. Introduction

Ceramic-like zirconia coatings obtained by plasma electrolytic oxidation (PEO) are promising for use as heat-protective coatings, biocompatible, corrosion-resistant [1–3]. The electrolyte composition largely determines the properties of the PEO coating. PEO coatings are characterized by layered structure comprising thin barrier layer, a main oxide layer and an upper layer that also contents elements of the electrolyte components [4]. Such structure contributes to low thermal conductivity of the coating. It can reach 0.2 W/(m K) for PEO zirconia coatings that makes them promising for use as thermal barrier layers [5]. Nuclear backscattering spectrometry (NBS) allows layer-by-layer profiling of elemental composition. The NBS is based on the nuclear backscattering of the accelerated charged particles by the atomic nuclei and deceleration of the particles in the material [6]. The depth of analysis reaches 100 µm.

Diagnostics based on nuclear reactions are very sensible but require individual selection of the type and energy of probing particles for each analyzed element. Rutherford backscattering spectrometry (RBS) and NBS methods are free from these drawbacks. If the proton energy $E$ is lower than the Coulomb barrier energy $E_b$, protons undergo elastic scattering described by the Rutherford cross section. However, the sensitivity of RBS method to light elements is
often insufficient for identifying them in a material that also comprises heavier elements. This is caused by the quadratic dependence of the Rutherford scattering cross section from a nuclear charge. If \( E > E_b \), the protons can undergo not only elastic but also inelastic scattering and initiate further nuclear reactions involving the emission of charged particles. At such energies, the dependence of the cross section on the scattering angle, energy and mass number of the target nucleus differs from the Rutherford case and is extremely individual for each nucleus. In this NBS case, the proton backscattering spectra as a rule are nonmonotonic unlike the RBS spectra. Proton NBS (at scattering angles larger than 90°) has a higher sensitivity to light elements (B, C, N, O) owing to broad resonances of excitation functions for the elastic scattering of 5 to 8 MeV protons on nuclei of these elements. Differential cross sections for proton backscattering on C, N and O in this energy region is almost 100 times larger than the corresponding to Rutherford scattering cross sections [5–7].

In this work zirconia PEO coatings were obtained in silicate-alkaline and silicate-hypophosphite electrolytes. Their layered structure and total porosity were investigated using nuclear proton backscattering spectrometry. The critical loads of the coatings disruption were estimated.

2. Experimental setup and characterization techniques
PEO coatings were formed on specimens fabricated from zirconium–niobium alloy (1 wt %Nb) in electrolyte containing 2 g/l potassium hydroxide and 9 g/l sodium silicate and in electrolyte containing 5 g/l sodium hypophosphite and 9 g/l sodium silicate under the ac electrical mode and total current density 22 A/dm². The temperature of the electrolyte was 21–27 °C. In result of the PEO process analysis the treatment durations were limited to 60 minutes in the first electrolyte and to 100 minutes in the second electrolyte. Layer-by-layer structure investigations of the coatings were carried out by nuclear backscattering spectrometry using the 120 cm-cyclotron of the Institute of Nuclear Physics at Moscow State University [6] at proton energy of 7.6 MeV, beam diameter of 3 mm and scattering angle of 160°. The spectra were analyzed by modeling in the NBS program. The coatings total porosity was estimated by comparing its mass thickness (without taking into account the porosity) and the geometric thickness, which was determined using a scanning electron microscope (SEM). The coating structure was examined using SEM Quanta 600 and Empyrean PANalytical x-ray diffractometer (CuKα radiation). The critical load of coatings destruction was evaluated using a scratch tester Revetest Xpress (CSM Instruments SA). 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
NBS spectra of protons with energy of 7.6 MeV of the PEO coatings formed in silicate-alkaline and silicate-hypophosphite electrolytes are shown in figure 1. The initial proton energy of 7.6 MeV corresponds to the 300-th channel of the analyzer. The right sides of the spectral peaks with the largest energies of protons elastically scattered from Zr, O and Si atoms (approximately 265-th, 220-th and 240-th channels, respectively) characterize proton scattering from atomic nuclei of the surface layer. The left parts of the spectral peaks are inherent to proton scattering at atomic nuclei on the internal side of the coating. The peak width is determined by the thickness of the atomic layer of the given element. Modeling of NBS spectra showed 4 layers in the coating. The upper layer has a thickness of about 4 µm with a silicon content of 30 at %. The next 35 µm thick layer is corresponding to zirconia. The third 14 µm thick layer is characterized by high zirconium content and the lower 8 µm thick layer contains 60 at % of zirconium and 40 at % of oxygen. The presence of a lower layer can be caused by the heterogeneity of the coating thickness, since NBS layer-by-layer analysis data are averaged over the proton-beam
Figure 1. Experimentally measured (open circles) and calculated (full circles) NBS spectra of 7.6 MeV protons for PEO coatings on alloy of Zr with 1 wt % of Nb formed in (a) silicate-alkaline and (b) silicate-hypophosphite electrolytes.

Figure 2. The SEM images in secondary electrons of PEO coatings: (a) the surface structure and (b) cross-section of the coating obtained in the silicate-alkaline electrolyte; (c) structure on the cross-section of the coating obtained in the silicate-hypophosphite electrolyte.

cross section 3 mm in diameter. NBS spectra of protons with energy of 7.6 MeV for the PEO coating formed in silicate-hypophosphite electrolytes are shown in figure 1(b). The coating is characterized by 2 layers. The thickness of the upper layer, containing silicon (20 at %) in addition to elements of zirconia, is 4 µm. The lower main layer has a thickness of about 81 µm and corresponds to the zirconia. Thus, the outer layer of both coatings contains element of the electrolyte components (Si) in different concentrations. The first coating is characterized by decrease in oxygen content with depth increasing and has a thicker transition layer. The second coating has a thick zirconia layer and a thin transition layer.

The surface structure of the both coatings is identical. It is characterized by crater-like regions some of them have pores in the center and regions with a fine globular structure, figure 2(a) [5,8]. The coatings thickness estimated on the cross-section by SEM is ≈ 70 µm for the coating obtained in the silicate-alkaline electrolyte, figure 2(b), and ≈ 110 µm for the PEO coating formed in the silicate-hypophosphite electrolyte, figure 2(c). The upper layer of coatings is heterogeneous in thickness and reaches 20 µm. It has large pores at the boundary with the lower layer that can explain the much smaller thickness of this layer, measured by the NBS.
Figure 3. The curves from the applied load on the indenter for the PEO coating obtained in the silicate-alkaline electrolyte (a) and silicate-hypophosphite electrolyte (b): 1—the residual depth $R_d$; 2—the penetration depth; 3—the friction coefficient $\mu$; 4—the acoustic emission signal.

method. When analyzing the NBS spectra, the thickness is determined without taking porosity into account; in this case, we deal with so called x-ray or mass thickness. Knowledge of the mass thickness ($h_{\text{NBS}}$) at the known geometrical thickness ($h_{\text{geom}}$) allows estimating the total porosity of the coating: $P = (h_{\text{geom}} - h_{\text{NBS}})/h_{\text{geom}}$. The obtained values of $P$ for PEO coatings formed in silicate-alkaline and silicate-hypophosphite electrolytes are 15 and 22%, respectively.

The critical load of coating disruption was determined by means of linear scratch testing using a diamond indenter of type “Rockwell S” with a tip radius of 2 $\mu$m at a load of 1 to 200 N and the loading rate of 100 N/min. The scratch length was 10 mm. The dependences of the friction coefficient $\mu$, the penetration depth $R_d$, the residual depth and acoustic emission signal on the indenter load of the coatings are presented in figure 3. Comparison of these dependences, see
Figure 4. The SEM images of scratches for the PEO coating obtained in the silicate-alkaline electrolyte (a) and silicate-hypophosphite electrolyte (b).

Figure 3(a), with the SEM image of the obtained scratch in figure 4(a) has showed that the load of coating disruption is approximately 80 N for the PEO coating formed in the silicate-alkaline electrolyte. PEO coating formed in the silicate-hypophosphite electrolyte has the critical load of disruption of approximately 150 N, as one can see in figures 3(b) and 4(b). At the beginning of the test the acoustic emission signal increase for the both coatings can be associated with the upper coating layer destruction at a critical load of approximately 20 N. With increasing the indenter penetration depth and the load, the friction coefficient increases from 0.1 to 0.3 for the first coating and from 0.1 to 0.4 for the second coating. Its further increase is due to the influence of the specimen material.

Microhardness of coatings varies from 2.5 to 3.5 GPa. X-ray diffraction analysis (XRD) is showed the presence of a monoclinic modification of zirconia for two types of coatings. Silicon, which is present in outer layer of the coatings, appears to be mainly in the form of amorphous materials, since no peaks were resolved in the XRD patterns for silicon-containing phases.

4. Conclusion
Zirconia coatings with a thickness up to 110 µm were obtained by plasma electrolytic oxidation in silicate-alkaline and silicate-hypophosphite electrolytes. Layer-by-layer structure and total porosity of the coatings were investigated using proton nuclear backscattering spectrometry at a proton energy of 7.6 MeV. PEO coating obtained in the first electrolyte has a thick transition layer with decreasing oxygen content with the depth increasing. The coating formed in the second electrolyte has a thick layer of zirconia and a thin transition layer. The total porosity of the coatings is 15 and 22%, respectively. The critical load of disruption is higher for the PEO coating formed in the silicate-hypophosphite electrolyte. Both coatings contain a monoclinic modification of zirconia and do not differ in microhardness.

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