Plasma electrolytic oxidation treatment mode influence on corrosion properties of coatings obtained on Zr-1Nb alloy in silicate-phosphate electrolyte

R G Farrakhov¹, V R Mukaeva¹, A R Fatkullin², M V Gorbatkov¹, P V Tarasov³, D M Lazarev¹, N Ramesh Babu⁴ and E V Parfenov¹, ⁵, ⁶

¹ Department of Theoretical Basis of Electrical Engineering, Ufa State Aviation Technical University, 12 Karl Marx Street, Ufa, 450008, Russia
² Department of Natural Sciences and General Engineering, Kumertau Campus of Ufa State Aviation Technical University, 22A Maxim Gorky Street, Kumertau, 453300, Russia
³ Department of Engineering Technology, Ufa State Aviation Technical University, 12 Karl Marx Street, Ufa, 450008, Russia
⁴Department of Metallurgical and Materials Engineering, National Institute of Technology, Tiruchirappalli, NIT Quarters, Tiruchirappalli, 620015, India
⁵ Academy of Sciences of Republic of Bashkortostan, 15 Kirov Street, Ufa, Russia
⁶ E-mail: evparfenov@mail.ru

Abstract. This research is aimed at improvement of corrosion properties for Zr-1Nb alloy via plasma electrolytic oxidation (PEO). The coatings obtained in DC, pulsed unipolar and pulsed bipolar modes were assessed using SEM, XRD, PDP and EIS techniques. It was shown that pulsed unipolar mode provides the PEO coatings having promising combination of the coating thickness, surface roughness, porosity, corrosion potential and current density, and charge transfer resistance, all contributing to corrosion protection of the zirconium alloy for advanced fuel cladding applications.

1. Introduction
Zirconium and its alloys are widely used as nuclear energy materials owing to their excellent neutron transparency, high mechanical strength, creep resistance, corrosion resistance in boiling water and steam environment. The major application of zirconium alloys both in PWR and BWR type reactors is fuel cladding tubes which enclose nuclear fuel and emit neutrons into coolant water which heats up and transfers energy from the reactor [1].

Nuclear reactor safety is the major concern; therefore, the fuel cladding failures should be minimized by application of advanced energy materials and appropriate corrosion resistant coatings. One of the failure mechanisms associated with Zr alloy cladding tube is hydrogen embrittlement which follows from ZrH₂ formation within the tube due to pickup of the hydrogen resulting from the Zr water corrosion [2]. During the life cycle, the Zr alloy components gain ZrO₂ oxide layer on its surface as a result of the water corrosion reaction; this layer protects from further corrosion; however, simultaneously with its growth, the hydrogen pickup also takes place. Therefore, alternative oxidation techniques are developed in order to produce protective zirconia coatings [3, 4].
Plasma electrolytic oxidation (PEO) is one of the promising methods to develop oxide ceramic coatings on aluminum, titanium, magnesium and zirconium and their alloys. PEO of Zr alloys is currently gaining more attention since the methodology of the process modeling, optimization and mechanism understanding have been rigorously developed for Al and Ti alloys [5, 6].

This paper is devoted to investigation into the influence of the PEO treatment mode: DC, pulsed unipolar, pulsed bipolar, on the corrosion properties of the coatings obtained on Zr-1Nb alloy in silicate and phosphate containing electrolyte widely used for plasma electrolytic oxidation of various alloys, in order to choose the best mode for further coating optimization.

2. Experimental

2.1. Plasma electrolytic oxidation

In this study, reactor grade Zr-1wt%Nb zirconium alloy plate (GOST E110) was used. The material is supplied after a vacuum annealing; no texture differences appear in the plate; the grain size is 5-7 μm [7]. The samples were cut out of the plate to the size 20x20x0.8 mm; the sample roughness was 0.1 μm. The PEO process was performed in a 6 liter tank at the electrolyte temperature of 20±1 °C kept constant by heating and cooling system under microcontroller regulation (TRM202, Owen, Russia). The treatment time was 10 min. The electrolyte was composed of 1 g l⁻¹ KOH, 2 g l⁻¹ Na₂SiO₃ and 2 g l⁻¹ Na₃P₂O₇, all of purity grade.

The plasma electrolytic oxidation was realized using 50 kW automated equipment providing PC process control and data acquisition for voltage, current and electrolyte temperature. The following PEO treatment modes were used: DC at constant current density \( j = 10 \text{ A} \cdot \text{dm}^{-2} \); pulsed unipolar (PUP) at the same average current density and duty cycle \( d_p = 50 \% \); and pulsed bipolar (PBP) at positive / negative pulse voltages \( U_p / U_n = 550 / 100 \text{ V} \), and duty cycles \( d_p / d_n = 50 / 30 \% \). For the pulsed modes the frequency was \( f = 500 \text{ Hz} \). For the constant current density modes the maximal voltage achieved was 600 V.

2.2. Surface characterization

The surface morphology was assessed using scanning electron microscope (SEM) JEOL JSM-6490LV. The surface roughness \( Ra \) was measured with TR 220 profilometer. The coating thickness \( h \) was measured using Defelsko Positector 6000 eddy current gauge with accuracy +/- 0.1 μm. X-ray diffraction was performed using Shimadzu XRD-6100 diffractometer in Cu-Kα radiation from 10 to 80 degrees 2θ, step size 0.02 degrees 2θ and step scan time 1 s.

To evaluate the corrosion properties, 1M LiOH solution was used, because lithium hydroxide is added to the coolant water in nuclear reactors. Elins P-5X potentiostate-impedancemeter was used (Elins, Russia). The open circuit potential (OCP) was measured for 2 hours to achieve a steady state value. The potentiodynamic polarization (PDP) tests were performed from –1.5 to +0.5 V with respect to OCP at the scan rate 0.25 mV/s. The corrosion potential \( E_{corr} \) and corrosion current density \( I_{corr} \) were obtained from Tafel parts of the PDP curves. The electrochemical impedance spectroscopy (EIS) was performed from 2·10⁻² to 1·10⁵ Hz at 10 mV perturbation with respect to OCP. The EIS spectra were fitted with EIS Spectrum Analyzer 1.0 using the equivalent circuit shown in Figure 1. As a reference, silver chloride electrode Ag/AgCl in saturated KCl with \( E_D = 200 \text{ mV} \) vs. standard hydride electrode was used; as a counter electrode, a Pt plate was used.

![Figure 1. Equivalent circuit used for the EIS analysis.](image-url)
3. Results and discussion

3.1. Influence of the PEO treatment mode on the coating morphology

Figure 2 shows the PEO coating morphology in top view and cross-sections for different treatment modes. The coating thickness and roughness are shown in Figure 3. The highest coating thickness comes out of the DC mode; this mode also provides the highest roughness. Numerous cracks can be seen in the cross-section for this mode. The opposite results appear for the PBP mode: it provides high thickness and low roughness. This suggests that the PBP mode appears to be promising; however, as follows from Figure 2, the coating has uneven morphology and cracks in the cross-section; moreover, in macro scale this mode yields burned edges of the samples. Therefore, the research into the PBP mode requires additional optimization. For the PUP mode, the coating has the middle value of the roughness and lowest thickness; no burned edges appear on the samples. In the cross-section the PUP coating appears solid, without cracks.

The coatings have porous structure (Figure 2) which is typical for the PEO process since the surface layer becomes intensively modified with numerous microdischarges contributing to zirconium oxidation, coating melting and resolidifying.

![PEO coating morphology: top view (a-c) and cross-sections (d-f) for different PEO treatment modes: DC (a, d), PUP (b, e), PBP (c, f).](image)

![PEO coating thickness $h$ (a), roughness $Ra$ (b) and porosity $\Pi$ (c) for different PEO treatment modes.](image)
The largest pore diameter reaches 10 µm, and the average pore size is 2 µm. SEM image analysis with ImageJ software shows quantitative difference in the coating porosity Π (Figure 3). DC PEO yields the highest porosity correlated to the highest roughness and coating thickness. Pulsed PEO of both types results in 1.5-fold lower porosity and more compact coatings [8]; the lowest value belongs to PUP mode due to the lowest coating thickness.

The results of X-ray diffractometry (Figure 4) show that the PEO coating contains crystalline ZrO₂ phase baddeleyite which is a monoclinic form of the oxide. The content of tetragonal ZrO₂ phase is quite small and does not exceed 2-3% as follows from its strongest peak at 30.2 degrees 2θ; therefore, in these experiments, the influence of this high-temperature oxide phase on the coating properties appears to be minor.

3.2. Analysis of corrosion properties for the PEO coatings obtained in different modes

Table 1 and Figure 5 show the electrochemical test results for the uncoated and PEO coated samples for different treatment modes. The OCP stabilizes quite fast – within 1 hour – and stays constant for all the treatment modes. According to the OCP values (Table 1), all the coated samples have nobler surface compared to the substrate due to passive oxide layer presence. The PUP mode provides the most difference with the uncoated sample.

![Figure 4: XRD patterns for the substrate and coatings obtained in different PEO treatment modes](image_url)

Table 1. Open circuit potential for Zr-1Nb alloy samples, uncoated and coated by PEO in different modes.

| PEO treatment mode | \(-E_{OCP}\) (V) vs. Ag/AgCl electrode |
|--------------------|----------------------------------------|
| DC                 | 0.355                                  |
| PUP                | 0.189                                  |
| PBP                | 0.379                                  |
| no coating         | 0.482                                  |
The PDP test results are presented in Figure 5a. The uncoated sample has much higher values of the corrosion current. For the coated samples, at high polarizations, the PDP curves overlap, showing the similarity of the anodic and cathodic corrosion processes. The curve tips have different positions and depths, so \( E_{corr} \) and \( I_{corr} \) vary among the PEO treatment modes (Figure 5b, 5c). The PDP analysis shows that the corrosion current for all the coated samples is much lower than that for the substrate; this indicates an increase in the corrosion protection. As follows from \( E_{corr} \) values (Figure 5b), both DC and PUP modes provide surface passivation compared to the substrate, while PBP mode results in more active surface, probably, due to incorporation of the electrolyte cations \( K^+ \) and \( Na^+ \) into the coating during the negative pulse. Corrosion current \( I_{corr} \) appears to be in a good correlation with the coating porosity \( \Pi \) and coating thickness \( h \): DC mode yields the highest values, while PUP results in the lowest values. Excessive porosity and cracks in thicker coating welcome corrosive media into the coating impurities, thus, resulting in less surface protection.

Figure 6 shows the results of the EIS tests for uncoated and coated samples. The impedance modulus at the lowest frequencies, uncovering corrosion processes, shows the same tendency as the corrosion current. The coated samples exhibit two orders of magnitude higher impedance modulus; this indicates corrosion resistance improvement. The PUP mode provides the highest impedance modulus at the lowest frequencies; this can be explained by thinner coating having denser structure.

The fit results of the impedance spectra using the equivalent circuit shown in Figure 1 are presented in Table 2. Resistance \( R_1 \) stands for the electrolyte of the corrosive media; compared to \( R_2 \), its values are negligibly small. Resistance \( R_2 \) and constant phase element CPE describe the coating properties: charge transfer resistance and double layer impure capacitance, respectively.

![Figure 5](image-url)

**Figure 5.** Electrochemical test results for Zr-1Nb alloy samples, uncoated and coated by PEO in different modes: PDP curves (a); corrosion potential \( E_{corr} \) (b); corrosion current density \( I_{corr} \) (c); charge transfer resistance \( R_2 \) (d).
Figure 6. Complex (a) and Bode (b) plots of impedance spectra for Zr-1Nb alloy samples, uncoated and coated by PEO in different modes.

Table 2. Equivalent circuit elements describing EIS results for Zr-1Nb alloy samples, uncoated and coated by PEO in different modes.

| PEO treatment mode | $R_1$ (Ω·cm$^{-2}$) | $R_2$ (Ω·cm$^{-2}$) | CPE$_1$ | $Q$ (μF·cm$^{-1}$) | $n$ |
|--------------------|---------------------|---------------------|---------|-------------------|-----|
| DC                 | 120                 | 1.09·10$^7$        | 6.00·10$^{-7}$ | 0.80 |
| PUP                | 155                 | 2.29·10$^7$        | 1.30·10$^{-7}$ | 0.86 |
| PBP                | 160                 | 1.51·10$^7$        | 4.39·10$^{-7}$ | 0.75 |
| no coating         | 37                  | 7.15·10$^5$        | 2.64·10$^{-5}$ | 0.92 |

As seen from Figure 5d and Table 2, the value of $R_2$ generally increases for less porous and thinner coating; it is the highest for PUP mode. Moreover, the difference between PUP and PBP in $R_2$ is stronger than in porosity $P$. This suggests that the coating is not only less porous for PUP, but also more uniform as it can be seen in Figure 2. Also, this statement is supported by the CPE power $n$. Its value is closest to one – pure capacitor – for the uncoated substrate having ideal double layer with the highest “capacitance” $Q$ among the tested samples. The next higher value of $n$ belongs to the coating developed in PUP mode. Moreover, this coating has the lowest “capacitance” $Q$ among the coated samples suggesting that the specific surface area is lower; therefore, the coating is more compact, and it can provide better corrosion protection.

4. Conclusions
In this study, three treatment modes of plasma electrolytic oxidation (DC, PUP, PBP) were compared regarding development of corrosion resistant coatings on Zr-1Nb reactor grade alloy in a silicate-phosphate electrolyte. Based on the SEM morphology, cross-section and porosity assessment, coating thickness and roughness measurements, X-ray diffractometry, potentiodynamic polarization, and electrochemical impedance spectroscopy, it was shown that pulsed unipolar PEO treatment promises the best advances in developing corrosion resistant coatings for this alloy.
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