PROTECTIVE CERAMIC STRUCTURES BASED ON OXIDES DEVELOPED ON ZR-2.5NB BY PLASMA ELECTROLYTIC OXIDATION (PEO) IN SODIUM ALUMINATE SOLUTION

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Abstract
The electrolytic plasma oxidation method was used to form ceramic coatings on Zr-2.5Nb substrates using various sodium aluminate aqueous solutions (15 g/l and 30 g/l). The Plasma Electrolytic Oxidation (PEO) process was carried out at different times and for constant voltage (5 and 10 minutes, 200V). The ceramic coatings obtained by PEO were investigated by Scanning Electron Microscopy (SEM) and their corrosion behavior was evaluated. The study aimed to improve the corrosion resistance of Zr-2.5Nb through the development of protective ceramic structures of oxides using the PEO technique in sodium aluminate solution at various concentrations.

Keywords: *Zr-2.5Nb, PEO, SEM, EDS, Corrosion resistance*

Introduction

Zirconium-based alloys have been extensively studied in the literature due to their low neutron absorption cross-section, high corrosion resistance, superior mechanical strength, and creep resistance, which is essential for use in the nuclear field, especially in nuclear power plants reactors of CANDU type [1-2].

However, it is known that Zr-2.5Nb pressure tubes exhibit high corrosion rates when the oxygen is present in the water [3]. In addition, achieving a high degree of combustion requires severe operating conditions. The operating conditions (high pH, high temperatures) require some surface engineering techniques to obtain superficial layers that improve the behavior of Zr-2.5Nb alloys [4].

To improve the resistance to severe working conditions, it is necessary to understand the corrosion mechanisms of zirconium alloys [5-6] and to develop appropriate surface engineering techniques. Among others, the electrolytic plasma oxidation (PEO) technique is a suitable method for adjusting the surface properties. Protective oxide layers can be obtained by electrochemical oxidation of zirconium alloy in an electrolytic solution [4].

The novelty of the present work resides in the method developed to improve the corrosion resistance of the Zr-2.5Nb alloy using the electrolytic plasma oxidation technique in sodium aluminate solution for various concentrations.

Experimental section

The samples were taken from commercial pressure tubes made of Zr-2.5Nb alloy with the following nominal composition (at%): 2.5% Nb, 0.04% Fe, 0.06% Cr and the rest being Zr.

The samples were directly oxidized using voltage pulses in electrolytic plasma from two types of aqueous solutions:
- *Electrolyte E1*, containing 15 g/L $NaAlO_2$, with pH ≈12.2 and electrical conductivity of 18 mS/cm, and
- *Electrolyte E2*, containing 30 g/L $NaAlO_2$, with pH ≈12.9 and electrical conductivity of 22 mS/cm, respectively.

The PEO process was carried out by applying a potentiostatic regime. It was worked under magnetic stirring (200 rpm). The temperature of the electrolyte was kept below 20°C.

Fig. 1 shows the experimental facilities used to realize superficial structures based on Al, developed on Zr-2.5Nb alloy by PEO.

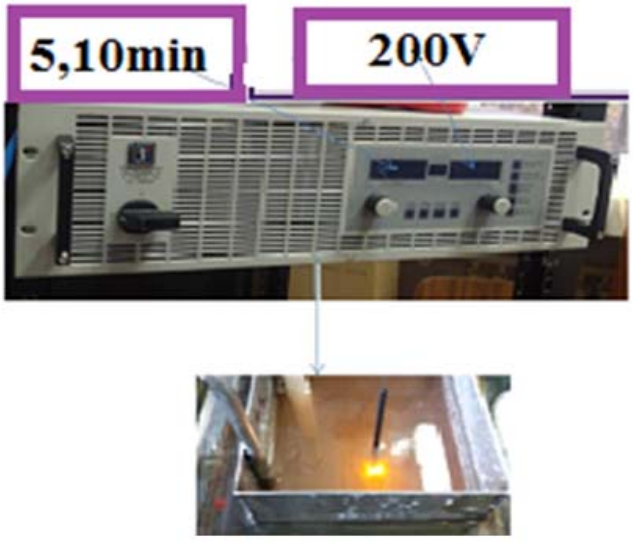


Fig. 1. The experimental facilities used for the realization of superficial structures on Zr-2.5Nb alloy by PEO

During the treatment, the voltage was slowly increased until the spark-discharge voltage was reached, and then rapidly increased to the effective voltage (U) of 200 V. As a result, the oxidation times in the micro-arc (τ) were 5 and 10 minutes, respectively, and the electrolyte temperature was maintained below 20°C. The values of the operating parameters are listed in Table 1.

Table 1. Labeling of samples and values of operating parameters for oxidation in electrolytic plasma of Zr-2.5Nb alloy using E1 and E2 electrolytes

Sample code	$NaAlO_2$ (g/l)	U (V)	τ (min)
E1_P1	15	200	5
E1_P2	15	200	10
E2_P1	30	200	5
E2_P2	30	200	10

Results and discussion

SEM / EDS results regarding the surface morphology of layers formed by plasma oxidation of Zr-2.5Nb alloy

Figs. 2 and 3 show examples of secondary electron SEM images at low and high magnification, respectively, of samples from the plasma oxidation of the Zr-2.5Nb alloy. Micrographs at low magnification indicate the presence of micro-cracks. The coating layers are porous and unevenly distributed, with different crystal sizes. At high magnification, acicular particles with lengths of the order of microns are observed.

Through EDS elemental analysis, the distribution of chemical elements on the surfaces was determined. In the layers' composition, the chemical elements Zr, Al, O, and Na were detected, highlighting a slight variation in the composition at different points.

Figs. 4-7 show the SEM images of samples *E1_P1, E1_P2, E2_P1*, and *E2_P2*, respectively, as well as the mass concentrations of chemical elements associated with different points of the analyzed surfaces.

SEM images (see Fig. 8) of cross-sections through *E1_P1, E1_P2, E2_P1,* and *E2_P2* samples, respectively, allowed the determination of the thickness of the oxide layers. As can be seen from Table 2, the layers are uneven and have thicknesses in the range 9 - 23 μm.

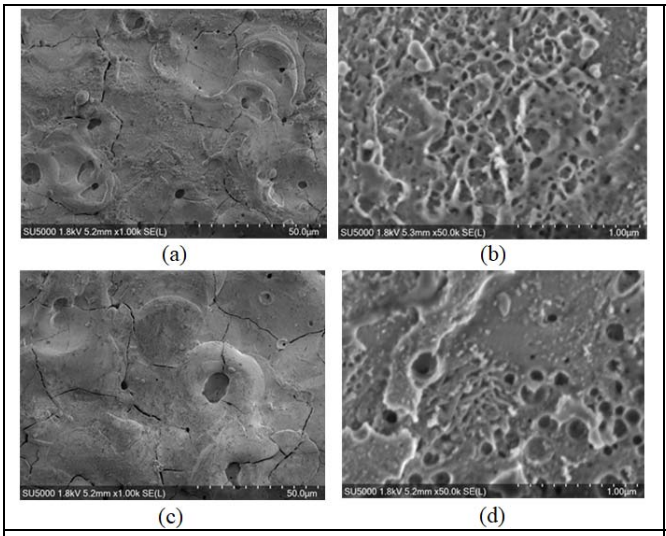


Fig. 2. SEM micrographs of the coatings from oxidized samples E1_P1 (a, b) and E1_P2 (c, d) (a, c) at low magnification (×1 k); (b, d) at high magnification (×50 k)

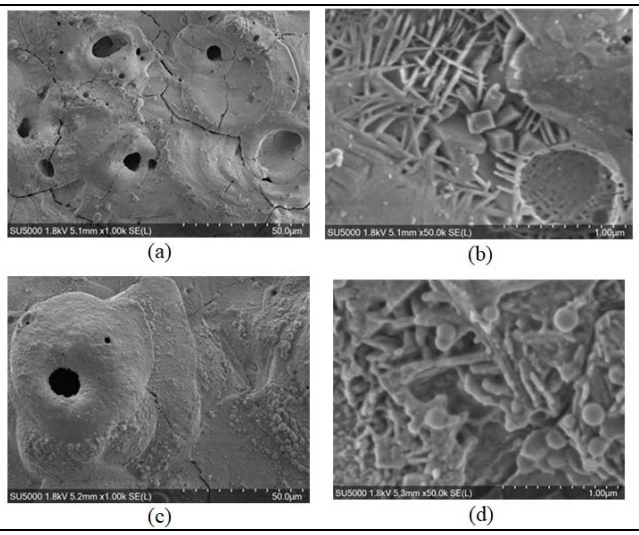
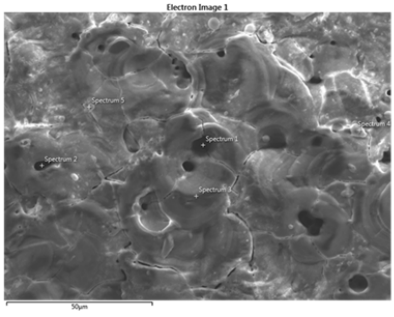
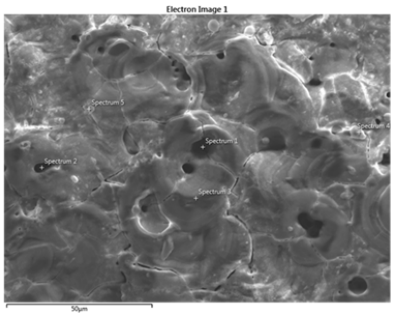


Fig. 3. SEM micrographs of the coatings from oxidized samples E2_P1 (a, b) and E2_P2 (c, d) (a, c) at low magnification (×1 k); (b, d) at high magnification (×50 k)



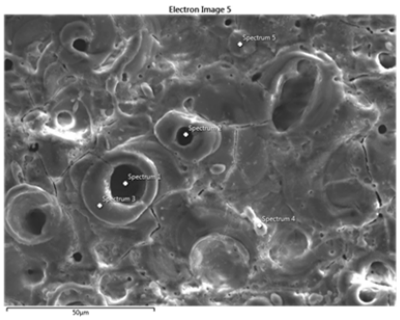
Position no.	1	2	3	4	5
O	36.88	37.67	36.12	38.28	40.89
Na	0.18	0.57	0.15	0.06	0.40
Al	11.94	12.42	11.05	12.00	13.2
Zr	49.55	47.01	50.67	48.08	43.97
Nb	1.45	2.33	2.01	1.58	1.54
Total	100.00	100.00	100.00	100.00	100.00

Fig. 4. SEM micrographs of PEO coatings for E1_P1 formed in E1 electrolyte (200 V, 5 min) and the elemental composition (wt%) at selected points on the surface



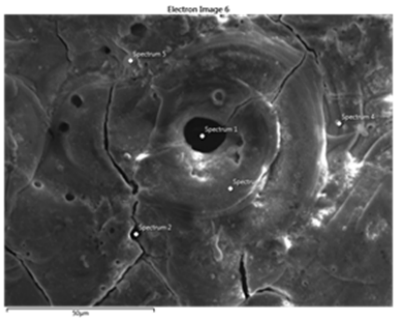
Position no.	1	2	3	4	5
O	36.88	37.67	36.12	38.28	40.89
Na	0.18	0.57	0.15	0.06	0.40
Al	11.94	12.42	11.05	12.00	13.2
Zr	49.55	47.01	50.67	48.08	43.97
Nb	1.45	2.33	2.01	1.58	1.54
Total	100.00	100.00	100.00	100.00	100.00

Fig. 5. SEM micrographs of PEO coatings for E1_P2 formed in E1 electrolyte (200 V, 10 min) and the elemental composition (wt%) at selected points on the surface



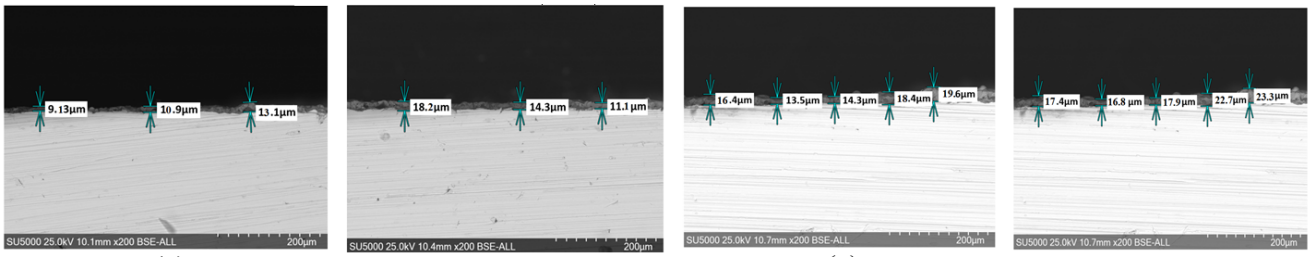
Position no.	1	2	3	4	5
O	40.04	33.60	31.32	34.82	32.98
Na	0.92	0.51	0.22	1.90	0.54
Al	13.57	15.19	17.46	18.79	13.77
Zr	43.61	47.63	48.40	43.19	50.99
Nb	1.86	3.07	2.60	1.30	2.12
Total	100.00	100.00	100.00	100.00	100.00

Fig. 6. SEM micrographs of PEO coatings for E2_P1 formed in E2 electrolyte (200 V, 10 min) and the elemental composition (wt%) at selected points on the surface



Position no.	1	2	3	4	5
O	41.41	37.94	37.88	38.33	37.57
Na	0.38	0.27	0.16	0.20	0.24
Al	17.05	18.50	20.67	28.64	30.22
Zr	40.31	41.71	39.32	31.67	30.71
Nb	0.85	1.58	1.97	1.16	1.26
Total	100.00	100.00	100.00	100.00	100.00

Fig. 7. SEM micrographs of PEO coatings for E2_P2 formed in E2 electrolyte (200 V, 10 min) and the elemental composition (wt%) at selected points on the surface



(a) (b) (c) (d)

Fig. 8. Cross-sectional SEM images for the samples: (a) E1_P1, (b) E1_P2, (c) E2_P1, (d) E2_P2

Table 2 Oxide layer thickness values of PEO-treated samples in E1 and E2 electrolytes

Sample	*E1_P1*	*E1_P1*	*E1_P1*	*E1_P1*
(µm)	9-13	11-18	13-19	16-23

Corrosion protection study

In Fig. 9, one can see a comparison of the potentiodynamic polarization curves for the Zr-2.5Nb alloy (untreated sample), the commercial Zr-2.5Nb alloy with black oxide (m-ZrO_1), naturally formed as a thin film, and for *E1_P1, E1_P2, E2_P1 and E2_P2*, the PEO coated samples.

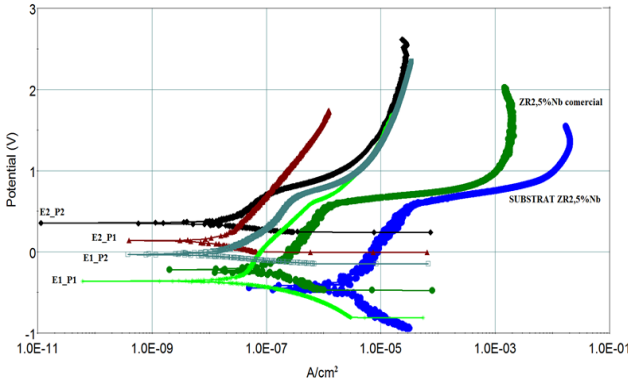


Fig. 9. Polarization curves of the tested samples: untreated Zr-2.5Nb alloy, commercial Zr-2.5Nb and PEO coated samples (E1_P1, E1_P2, E2_P1, E2_P2)

The values of corrosion parameters (corrosion potential (E_{corr}), corrosion current density (j_{corr}), and corrosion velocities (v_{corr})) were calculated for the tested samples.

It can be seen that all samples coated by PEO oxidation, as well as the commercial Zr-Nb alloy sample (which has black oxide on the surface) have more positive E_{corr} than the plain Zr-Nb alloy, and j_{corr} and v_{corr} are much lower (by 1- 2 orders of magnitude) compared to the Zr-Nb alloy.

In addition, the protective layers formed on samples *E2_P1* and *E2_P2* show the best corrosion resistance.

The corrosion potential of the untreated Zr-Nb sample (with a clean surface, without black oxide) is - 0.447 V, and the corrosion current density is 0.34 μA/cm^2. After PEO treatment, the corrosion potential changes in the positive direction of the values with the decrease of the corrosion current density (see Fig. 9), which shows an increase in corrosion protection.

Therefore, all the PEO-coated samples, as well as the commercial black oxide-coated sample, had a much lower j_{corr} corrosion current compared to the untreated Zr-2.5 Nb alloy, as it can be seen from Table 3.

Table 3 Corrosion parameter values calculated from potentiodynamic polarization curves for: untreated Zr-2.5Nb, commercial Zr-2.5Nb with black oxide, and PEO coatings formed in E1 and E2 electrolytes

Samples	**E_{corr} (mV)**	**$v_{corr}\times10^4$ (mm/an)**	**$j_{cor}r\times10^3$ (μA/cm^2)**
Zr-2.5Nb alloy (substrate)	-447	40.43	340
Commercial Zr-2.5Nb alloy coated with black oxide	-358	4.408	37.5
E1_P1	-361	0.77	6.7
E1_P2	-35	0.51	4.2
E2_P1	138	0.3	2.3
E2_P2	355	0.28	1.9

Conclusions

The work refers to developing protective ceramic coatings on the surface of the Zr-2.5Nb alloy, formed by electrolytic plasma oxidation technoques.

For the plasma oxidation of the Zr-Nb alloy, two types of aqueous sodium aluminate solutions were used: 15 g/L NaAlO2 (E1electrolyte) and respectively 30 g/L NaAlO2 (E2 electrolyte). The anodic oxidation of PEO consisted of pulses with slowly increasing voltage until the occurrence of electric spark discharge, after which it was rapidly increased to 200 V. The treatment times in the microarc were 5 and 10 minutes, and the electrolyte temperature was kept below 20 °C. Two samples were experimented with in each electrolyte, a total of 6 samples, including the commercial Zr-2.5Nb alloy sample (with the surface covered with a black oxide) and the Zr-2.5Nb sample with the surface free of oxides - as an element of comparison.

The obtained ceramic coating is a composite containing zirconium and aluminum oxides. SEM images and EDS elemental analyses show that the deposited layers are porous and contain Zr, Al, and O, uniformly distributed on the surface.

The SEM micrographs of the cross-section illustrate the presence of micron-sized grains. The compositional distribution of the elements determined by EDS confirms the presence of Zr, Al, and O. By processing the SEM images of the cross-section, it was possible to determine the thickness of the oxide layers obtained by anodic oxidation in the plasma; for different samples, the layers are uneven and have thicknesses of 9-23 μm.

The corrosion behavior was studied by potentiodynamic polarization curves drawn for: the Zr-2.5Nb alloy with the surface free of oxides (as a comparison sample), the commercial Zr-2.5Nb alloy (with the surface covered with an black oxide, m-ZrO_2) and all oxidized PEO samples in E1 and E2 electrolytes. The commercial Zr-Nb alloy has a corrosion potential of about 90 mV more positive and a corrosion current an order of magnitude lower. Also, for all oxidized PEO samples, the corrosion potential changes positively. Corrosion current density values for the PEO-treated samples are lower by 1-2 orders of magnitude compared to the untreated sample. The best corrosion resistances are shown by the samples treated by PEO in E2 electrolyte for a process duration of 10 min and (slightly weaker) by the sample treated in E2 electrolyte for 5 min.

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