



Full Length Article

Characterization of Al₂O₃/ZrO₂ composite coatings deposited on Zr-2.5Nb alloy by plasma electrolytic oxidation



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ABSTRACT

Plasma electrolytic oxidation (PEO) process was employed in a galvanostatic regime on Zr-2.5Nb alloy in NaAlO₂ aqueous electrolyte solutions within a concentration gradient of 5–30 g/L in order to produce Al₂O₃/ZrO₂ composite coatings. The composition and microstructure of the oxide layers were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS). Vickers microhardness, scratch adhesion and potentiodynamic polarization measurements were used to assess the mechanical and electrochemical properties of the PEO coatings. The experimental findings suggest a strong correlation between the electrolyte concentration and the coating layers. By increasing the concentration of NaAlO₂ in the electrolyte solution, significantly increased tetragonal crystal structure, particle size, hardness, adhesion strength and corrosion resistance occur with pore size decrease. Best values for the hard and adherent coating were ~1500 HV and ~60 N critical load. The corrosion current densities for the plasma electrolytic oxidized samples are lower than the black oxide coated Zr alloy.

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1. Introduction

Although zirconium and zirconium-based alloys have been extensively used as fuel cladding and pressure tubes in water-cooled nuclear power reactors due to their low neutron absorption cross-section, high corrosion resistance, high-strength and creep resistance properties [1–4], previously conducted studies reported evidence of mechanical and chemical changes occurring during extremely harsh operating environment. Large strains, deformation and fracture, cladding expanding, low tensile properties such as ductility and toughness [5,6] along with hydrogen adsorption and oxygen diffusion in metal [7–9], were associated with the environmental degradation of the Zr nuclear alloys. In addition, well-known important issues related to higher fuel burn-up, extended recycle, high pH operation and higher operating temperatures [4,10] have emphasized the in-reactor aggressive environment conditions and therefore, corrosion and wear protective coatings were developed and deposited on Zr-2.5Nb alloy [10,11]. On the other hand, plasma electrolytic oxidation (PEO) is a suitable method for obtaining increased wear and corrosion

resistant layers by growing protective oxide coatings on the metal surface [10,11]. In our previous study [11], tetragonal ZrO₂ phase stabilization in coating layers by the aluminum oxide matrix yielded favorable corrosion resistance as compared to commercial black oxide coating, in contrast to the reported findings of Wang [4] and Chen [12] regarding the PEO-treated Zr-2.5Nb alloy in Na₂-SiO₃ and KOH electrolyte solution, indicating only an enhanced wear and corrosion resistance of Zr-2.5Nb coated alloy, without any promising reference to the black oxide coating. Taking into consideration that few studies have been addressed the electrolytic plasma oxidation process of Zr-2.5Nb alloy [4,10,12,13], the present paper aims to provide further insight into tetragonal ZrO₂ phase enhancement associated with an increased resistance to wear and corrosion obtained through an electrolyte concentration gradient. Additionally, according to Hui et al. [14] similar developed PEO oxide coatings on Zr-2.5Nb demonstrate promising application potential in supercritical water-cooled reactors. These findings will contribute to understanding, controlling and stabilizing the ZrO₂ tetragonal phase of newly formed coated material important for the nuclear community. This work is intended as a continuation of our recent study [11] related to improving the surface wear and corrosion resistance properties of Zr-2.5Nb alloy by means of plasma electrolytic oxidation in various sodium alumi-

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nate electrolyte concentrations, ranging from 5 to 30 g/L under galvanostatic regime, in contrast to the previous potentiostatic operation mode.

2. Experiment

2.1. Preparation of PEO coatings

Plasma electrolytic oxidation of Zr-2.5Nb samples was performed using a unipolar pulsed DC power source with 150 Hz frequency [15].

Electrolyte solutions containing sodium aluminate at concentrations of 5 g/L (E1), 10 g/L (E2), 15 g/L (E3), 20 g/L (E4), 25 g/L (E5) and 30 g/L (E6) were prepared using pure reagents and distilled water. The pH and electrical conductivity values of the prepared electrolytes were between 12.0 and 13.1 and 6.1 and 30.2 mS/cm, respectively.

The Zr-2.5Nb samples having rectangular shape (1.4×2.0 cm) were preliminary prepared for the PEO treatment according to the procedure described elsewhere [11].

For the micro-arc oxidation process of zirconium alloys, the galvanostatic regime has been used applying a fixed current density of 0.35 A/cm^2 . The actual value of current intensity was slowly increased until spark discharges occurred (U_{sp}), after which it was rapidly increased to 2 A and maintained at this value throughout the micro-arc oxidation process. In each electrolyte, samples were oxidized in electrolyte plasma for 5 min (5 M) and 10 min (10 M) treatment time. Sample codes, the actual values of the voltage from which spark discharges take place (U_{sp}), variation intervals for the actual values of the voltages (U) and values of impulse amplitudes (U_{amp}) applied in the oxidation process are shown in Table 1. During PEO process, the electrolytes temperature was kept at 15°C .

During the plasma electrolytic oxidation process of all samples in this study, the form of impulses [11] remained practically unchanged and the values of impulse amplitudes have varied in the ranges shown in Table 1.

2.2. Characterization of PEO coatings

XPS measurements were performed with an Escalab 250Xi system (Thermo Scientific) equipped with a monochromated Al K α (1486.6 eV) X-ray source and a base pressure in the analysis chamber of 10^{-8} Pa. The acquired spectra were calibrated with respect to the C1s line of surface adventitious carbon at 284.8 eV. An electron flood gun has been used to compensate the charging effect in insulating samples.

XRD analysis was used to examine the crystal composition of the oxide layers employing a Rigaku Ultima IV diffractometer with CuK α radiation.

For the qualitative phase analysis, the X-ray diffractograms were obtained by scanning the $(2\theta) = 15\text{--}90^\circ$ range with 0.05° step and 10 s step-time using Bragg-Brentano (θ - θ) focusing scheme.

For the estimation of monoclinic and tetragonal ZrO $_2$ phase volume fractions inside the coating, employing Toraya equation [16],

high-resolution diffraction data were collected in the $(2\theta) = 27\text{--}33^\circ$ range with 0.02° step and 10 s step-time.

The crystallite sizes and micro-deformations of the polycrystalline t-ZrO $_2$ phase were estimated from the pure-specimen integral breadth of the (1 0 1) and (2 0 2) diffraction lines using multiple-order analysis. (1 0 1) X-ray diffraction line was acquired in the $(2\theta) = 29.5\text{--}31.3^\circ$ range and the (2 0 2) diffraction line was collected in the $(2\theta) = 61.5\text{--}65^\circ$ range, both with 0.02° step and 10 s step-time. For an accurate microstructural analysis, instrumental broadening was taken into account by measuring the (1 1 0) and (2 2 0) reflection of LaB $_6$ (SRM 660b) standard powder acquired in the angular range of $29.5\text{--}31.5^\circ$ and $62.5\text{--}64^\circ$, respectively, in the above-mentioned experimental conditions.

SEM/EDS investigations were carried out using a HITACHI SU5000 field emission scanning electron microscope equipped with an energy-dispersive X-ray analyzer (EDS, Oxford Instruments, Oxford, UK) operated at an accelerating voltage of 30 kV.

Adhesion strength of the coatings to the substrate was performed using a Teer ST-30 scratch tester equipped with a 0.2 mm radius diamond tip. The applied load was ranging from 0 to 100 N across the coated surface with a scratch speed of 10 mm/min.

The hardness of the coating layers was measured with a Vickers microhardness tester (AHOTEC 700 FM) under an applied load of 1000 gf and a dwell time of 15 s, using a diamond Knup indenter, the average microhardness being tabulated and reported.

The electrochemical measurements were accomplished with a PARSTAT-2273 potentiostat/galvanostat (Advanced Electrochemical System, Princeton Applied Research) in the voltage range -0.5 to $+2$ V with a 0.5 mV/s scan rate in an aqueous LiOH (0.2 M) solution using a conventional three-electrode electrochemical cell configuration.

3. Results and discussions

3.1. XPS analysis

The presence of Al $_2$ O $_3$ /ZrO $_2$ based composite coatings formed through the plasma electrolytic oxidation process was well-established from the XPS high-resolution spectra. Accordingly, the Al2p XPS superimposed spectra (Fig. 1a) for all the involved samples indicate a similar surface chemical behavior, confirming the occurrence of newly obtained aluminum oxide films on Zr-2.5Nb substrate. Furthermore, spectral deconvolution of Al2p photoelectron line (Fig. 1b) emphasizes the aluminum oxidation process generated by plasma electrolysis treatment of Zr-2.5Nb alloy and hence, the characteristic feature located at 74.5 eV can be attributed to Al $_2$ O $_3$ [17,18]. Moreover, due to the overlapping binding energy positions of both aluminum oxide and hydroxide, the contribution of Al(OH) $_3$ cannot be completely ruled out [17,18]. The surface chemistry of the substrate has been addressed by recording the Zr3d and Nb3d photoelectron lines. After deconvolution procedure, by constraining the doublet area ratio and the spin orbit parameter for both zirconium and niobium, the presence of fully oxidized Zr $^{4+}$ (ZrO $_2$) and Nb $^{5+}$ (Nb $_2$ O $_5$) chemical species [17,18] was indicated (Fig. 1d and f). A possible explanation

Table 1
Sample codes and plasma electrolytic oxidation conditions in E1-E6 electrolytes.

Sample code	U_{sp} (V)	U (V)	U_{amp} (V)	Sample code	U_{sp} (V)	U (V)	U_{amp} (V)
E1_5M	280	380–400	650–670	E4_5M	120	250–270	510–570
E1_10M	280	390–410	650–690	E4_10M	120	250–300	500–590
E2_5M	160	260–280	550–580	E5_5M	100	200–240	470–525
E2_10M	160	240–320	540–630	E5_10M	100	200–280	470–580
E3_5M	140	230–260	530–560	E6_5M	90	200–220	470–520
E3_10M	140	240–290	530–610	E6_10M	90	200–240	460–560

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