



# The influences of microdischarge types and silicate on the morphologies and phase compositions of plasma electrolytic oxidation coatings on Zircaloy-2

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## ABSTRACT

Plasma electrolytic oxidation coatings were formed in alkaline silicate electrolyte on Zircaloy-2. The evolution of the types of discharges, the microstructures, phase compositions and the corrosion resistance of the coatings were studied by real time imaging, SEM, XRD, and electrochemical tests. Characteristic solidification structures were revealed in the PEO coatings, the formation of the solidification structures is related to the long lasting discharges during the PEO process and the very low thermal conductivity of zirconium oxide. Thermal effect in the coatings and silicate content in the electrolyte affect the phase compositions of the coatings.

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## 1. Introduction

Zirconium alloys display a low neutron absorption cross-section, together with satisfactory mechanical properties and excellent corrosion resistance, making them one of the best structural materials for water-cooled nuclear power reactors. The alloys are used widely for fuel cladding tubes and pressure tubes. However, they are subject to a several types of degradation, including water-side corrosion, nodular corrosion and hydrogen uptake, because of the severe environmental conditions during the operation of nuclear reactors [1–6]. Consequently, appropriate surface treatment methods are required to improve the surface properties of the alloys and to restrict hydrogen ingress.

Plasma electrolyte oxidation (PEO) is a relatively new surface treatment process that has evolved from conventional anodizing, but demands much higher voltages [7]. This technique has been successfully used to improve the corrosion resistance and wear resistance of aluminum, magnesium and titanium by formation of functional ceramic coatings [8–16]. PEO is also potentially an effective way of protecting and functionalizing zirconium alloys, although much less information is available on PEO of zirconium alloys [17–21]. Matykina et al. [17] studied the microstructure of coatings on Zirlo™ and Xue et al. [18] examined coatings on a Zr-6 wt.% RE alloy and discussed its corrosion properties. Pauporte et al. [19] studied the growth of zirconium oxide films in the

micrometer rang in 0.1 M (NH<sub>4</sub>)<sub>2</sub>B<sub>4</sub>O<sub>7</sub> solution. Klappkiv et al. [20] produced 100–120 μm PEO coatings on zirconium alloys, with the microhardness of ~800 MPa. In a more recent study, Chen et al. [21] compared the wear and corrosion properties of thin PEO coatings on a Zr-2.5% Nb alloy with those of a commercial, autoclaved black oxide coating.

Although the microstructure and phase compositions of the PEO coatings on zirconium alloys have been considered in several papers, contrasting results are evident. In Xue's work [18], thick ceramic coatings were fabricated on zirconium alloy under an AC regime in silicate solution. The coatings were mainly composed of monoclinic ZrO<sub>2</sub> and tetragonal ZrO<sub>2</sub> phases, but the tetragonal ZrO<sub>2</sub> content was much lower than the monoclinic ZrO<sub>2</sub> content. In a previous paper of the present authors [22], PEO of Zircaloy-4 in silicate and pyrophosphate electrolytes with a 50 Hz square wave-form AC current regime was studied in detail. The coatings formed in silicate electrolyte comprised a porous inner layer and a more compact outer layer, with characteristic solidification structures being evident following treatment for extended times. The coatings contained monoclinic and tetragonal ZrO<sub>2</sub>, the latter being mainly present in the outer layer, and the content of tetragonal ZrO<sub>2</sub> was relatively high. In contrast, extensively cracked coatings, which consist wholly of m-ZrO<sub>2</sub>, resulted from the use of pyrophosphate electrolyte.

During the PEO process, micro-discharge characteristics, both individual and collective, determine the thermal and chemical conditions on the oxidizing surface and thus play an important role in the phase formation, structure and stress state of the ceramic

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layers that are generated [23]. Some researchers have used imaging techniques to study the microdischarge behavior during PEO of various substrates, such as aluminium [23,24], titanium [25], in which the spatial distribution, size, population density and lifetime of the microdischarges can be acquired. More recent progress in the study of discharges has been obtained by the application of optical emission spectroscopy (OES) to characterize the PEO plasma [26–32]. Based on the OES results, and with an assumption of local thermodynamic equilibrium (LTE) [33], plasma electron temperatures can be calculated using the relative intensities of spectral lines of particular atomic or ionic species [26]. The estimations of discharge temperatures during PEO vary widely, from 800–3000 to 3000–6000 K and even 10,000–20,000 K [7]. The latest studies of Hussein et al. [29] reported plasma electron temperatures for an aluminum alloy to be in the range of 4000–7000 K for a unipolar current mode and 4000–5500 K for a bipolar current mode.

Although the electron temperatures of the PEO plasma can be determined by OES, the real thermal conditions of the oxide coatings during the PEO process are difficult to determine, with related work on the topic being very limited. Yerokhin et al. [23] forwarded approximate evaluations of the thermal process in the oxide layer on aluminum under discharge conditions, with the temperature developed in a microdischarge zone of the coating appearing to be related to the current density passing through a microdischarge, the microdischarge duration and the physical and chemical properties of the coating material (e.g. thermal conductivity and thermal diffusivity of alumina).

Concerning the characteristic solidification structures formed on the zirconium PEO coatings [22], which feature clusters of equiaxed grain in the central region and a ring of radially-orientated, elongated grains, to the best of the authors' knowledge similar solidification structures have not been reported in PEO coatings of other metals, and were not present in PEO coatings on Zircaloy-4 formed in pyrophosphate electrolyte. Long-lasting melted zones were assumed to be existed at the coating surface and the formation of the characteristic solidification structures was explained by the different temperature gradients and grain growth rates at different locations in the melting pool in the subsequent solidification process [22]. The formation of the long-lasting melting zones was attributed to a persistent discharge at a particular location. However, the reason that why similar structures are not formed with aluminum and magnesium alloys remains a subject of discussion.

In this paper, PEO coatings on a zirconium alloy are further investigated. The coatings on Zircaloy-2 alloy are prepared with a pulsed bipolar current regime in silicate electrolyte, with particular consideration of the coating morphology and phase composition and their relationship to the sparking behavior.

## 2. Experimental

### 2.1. Materials

The composition of as-received Zircaloy-2 alloy was as follows: (in wt.%) Fe 0.19, C 0.02, Sn 1.31, Hf < 0.01, Cr, 0.089, Ni < 0.002, and Zr balance. The alloy was cut into specimens of dimensions of  $10 \times 10 \times 5$  mm, which were then sealed with epoxy resin to leave an exposed area of  $1 \text{ cm}^2$ . Before PEO treatment, the working surface was successively ground to 2000 grit abrasive paper, then degreased in acetone, rinsed in distilled water and dried in a stream of warm air.

### 2.2. PEO treatment

PEO treatment was carried out in a 1 l glass vessel, equipped with magnetic-stirring and water-cooling, using a 5 kW pulsed

DC source, and a stainless steel plate was used as the counter electrode. The alkaline electrolyte comprised 8 g/L  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  and 1 g/L KOH; analytical grade reagents were employed. A constant current mode was employed, with the initial positive and negative current densities set at 0.4 and 0.3 A/cm<sup>2</sup> respectively. The waveforms of the current were a pulsed bipolar form, with the frequency and the duty ratio of the positive and negative currents kept at 1000 Hz and 20% respectively.

### 2.3. Imaging of the discharges

The discharges at different stages of PEO were recorded with a commercial digital camera (Cannon Powershot G5), with the shutter speed set to 1/1000 s or 1/2000 s. The images were later analyzed to determine the appearances and dimensions of the discharges.

### 2.4. Coating characterization

The surface and cross-section morphologies of the PEO coatings were examined by environmental scanning electron microscopy (ESEM) in a QUANTA 2000 instrument (FEI, USA), or by field emission scanning electron microscopy in a JEOL JSM6700F instrument, both equipped with energy-dispersive X-ray spectroscopy (EDS, EDAX Inc.). For cross-sectional observation, the specimens were ground with successive grades of SiC paper, followed by diamond finishing to 1  $\mu\text{m}$ .

Phase compositions of the coatings were determined with a Rigaku D/MAX 2500 X-ray diffractometer (Cu-K $\alpha$  radiation). The scans were performed with a step size in  $\theta$  of 0.02° and a range of  $2\theta$  from 10° to 80°.

The electrochemical behaviors of the Zircaloy-2 alloy substrate and the PEO coated-substrates were determined by recording of potentiodynamic polarization curves using a CHI660 electrochemical workstation. A naturally-aerated 0.5 M NaCl solution was selected for the corrosion tests in a conventional three-electrode test cell, with a platinum counter electrode, a saturated calomel reference electrode and the specimen as the working electrode. The variation of the open circuit potential with time was recorded during immersion in the solution. After 60 min immersion, the potentiodynamic polarization curves were recorded at a scan rate of 1 mV/s, from 500 mV below the open circuit potential toward the anodic direction until the current density reached relatively high values.

## 3. Result and discussion

### 3.1. Voltage–time curves and time-dependent appearance of discharges developed

The voltage–time curves during PEO of Zircaloy-2 alloy at 1000 Hz, 20% positive and negative duty ratio for 1800 s are presented in Fig. 1. The voltage values displayed are the peak values of the voltage waveform as shown on the panel of the power source. The results indicate that the positive and negative voltages rise rapidly in the initial stages of PEO with rates of  $\sim 53$  and  $\sim 8$  V/s respectively, and then there is an inflexion point on the curves, after which the rate of voltage rise becomes slower; the final positive and negative voltages were 649 and 249 V respectively.

Sparks are a characteristic feature of the PEO processes, with the distribution and types of the sparks having important effects on the surface morphology and phase composition of the resultant coatings. Fig. 2 shows the microdischarge appearances at various stages of the PEO process for the condition of Fig. 1. All the images in Fig. 2 were recorded with a shutter speed of 1/1000 s except for (g) and

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