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# Surface charge and corrosion behavior of plasma electrolytic oxidation film on $Zr_3Al$ based alloy

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ABSTRACT

The surface charge of $Zr_3Al$ based alloy and its plasma electrolytic oxidation (PEO) film were measured in different solutions by streaming current method. Their corrosion property was evaluated by electrochemical impedance spectroscopy (EIS) analysis. The correlation between their surface charge and corrosion behavior was discussed. The results showed that LiCl solution and NaCl solution behaved as inert electrolyte for PEO film. In addition, the low negative zeta potential reduced the adsorption of chloride ions and made the PEO film less susceptible to chloride attack. The PEO film with proper surface charge can also protect $Zr_3Al$ alloy from the attack of hydrogen ions and lithium ions.

## 1. Introduction

Many researches have been focused on intermetallics involving aluminum and transition metals (Ni, Ti, Zr and Hf) due to their relative low density, high melting points, elevated temperature strength, excellent resistance to corrosion and oxidation [1]. Zr alloys are widely used in nuclear reactor as fuel cladding material because of its low thermal neutron capture cross-section [2]. However, the strength and corrosion resistance of $\alpha$-Zr is not high enough in modern technological application such as higher fuel burn-up, extended recycled times and higher reactor temperature. This problem might be overcome by addition of Al, which results in the transformation from $\alpha$-Zr to $Zr_3Al$ phase [3]. The strength of Zr-Al alloys is higher than that of traditional zirconium alloys. Therefore, the $Zr_3Al$ intermetallic compound has potential application in the nuclear energy field [4]. Unfortunately, it is difficult to produce a single-phase $Zr_3Al$ material. There are always some residual $\alpha$-Zr, $Zr_2Al$ or both phases in $Zr_3Al$ based alloy [5]. As described by Schulson [6], a requirement for corrosion resistance of $Zr_3Al$ alloy was the absence of the corrodible $\alpha$-Zr phase. In addition, excess aluminum as impurity is harmful to the corrosion resistance of Zr alloys under most environments, which even results in catastrophic oxidation in steam or water [7].

Surface modification technologies have been widely applied to enhance the wear and corrosion resistance of metals. It is expected to improve the corrosion resistance of $Zr_3Al$ based alloy through appropriate surface modification treatment. Li [8] fabricated the anticorrosive Ni-P coating on $Zr_3Al$ based alloy by electroless plating. In recent years, plasma electrolytic oxidation (PEO) or microarc oxidation (MAO) was used to fabricate a protective film on Zr alloys [9–14]. It was found that the PEO surface treatment could greatly improve the corrosion resistance of Zr alloys. However, it was rarely reported about the PEO treatment on $Zr_3Al$ intermetallic. So it is worth expecting in fabricating a protective PEO film on $Zr_3Al$ based alloy.

In the corrosion process, the ions in electrolyte play an important role in the corrosion deterioration of metal properties. However, these ions are closely related to the surface charge on metal-electrolyte interface. Using the Helmholtz Smoluchowski equation [15], the surface charge density can be expressed by the zeta potential. Therefore, the zeta potential is an important parameter to evaluate the corrosion process. Kendig [16] found that the oxyanions of hexavalent chromium rendered anodic film of aluminum negative zeta potential. The negative zeta potential discourages the chloride adsorption under the effect of electrostatic force, which makes anodic film less susceptible to chloride attack. Sato [17] and Natishan [18] also reported that the negative zeta potential on surface of Al is beneficial to hinder the adsorption of chloride. McCafferty [19–21] reported that the critical pitting potential is a linear function of the isoelectric point (IEP) of the implanting element oxide in the ion-implanted aluminum. However, the correlation between zeta potential and corrosion behavior of Zr alloys is rarely reported.

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In addition, the 1500 ppm $B^{3+}$ as $H_3BO_3$ and 2.3 ppm $Li^+$ as LiOH mixed solution is a typical coolant water in nuclear reactor. $B^{3+}$ can capture the thermal neutrons and LiOH as pH control agent can adjust pH value of coolant water in nuclear system [22]. So it is necessary in evaluating the surface charge and corrosion behavior of $Zr_3Al$ based alloy in $B^{3+}$ and $Li^+$ mixed solution in order to investigate its potential application in nuclear reactor.

In this paper, a protective PEO film on $Zr_3Al$ based alloy was tentatively fabricated by plasma electrolytic oxidation technology. Zeta potentials of the $Zr_3Al$ based alloy and its PEO film in different solutions including KCl, NaCl, LiCl solutions and 1500 ppm $B^{3+}$ + 2.3 ppm $Li^+$ mixed solution were measured by streaming current method. Their corrosion resistance in different solutions was evaluated by electrochemical impedance spectroscopy (EIS). The correlation between zeta potential and corrosion behavior of PEO film was also discussed.

## 2. Experiment procedure

The as-received $Zr_3Al$ based alloy (Zr-6Al-0.1B) was cut into pieces with dimensions of 20 mm × 10 mm × 1 mm. Each piece sample was ground with *SiC* abrasive paper, ultrasonically cleaned in ethanol and dried by hot air. Plasma electrolytic oxidation (PEO) was carried out in a stainless container. The alloy sample and stainless container were served as anode and cathode, respectively. The aqueous solution contained 6 g/l $Na_3PO_4 \cdot 12H_2O$ and 1 g/l KOH with 20 ml/l glycerin additive. The applied positive/negative voltages were +480 V and −60 V, respectively. The electrolyte temperature was controlled below 30 °C by a water cooling system. After 15 min PEO treatment, a thin oxide film was covered on $Zr_3Al$ based alloy. Table 1 gives the electrolytes for EIS and zeta potential measurements.

The surface and cross-sectional morphologies of PEO film on $Zr_3Al$ based alloy were observed by scanning electron microscopy (SEM, Hitachi S-4800) with energy dispersive spectroscopy (EDS). The phase component of PEO film was analyzed by X-ray diffractometer (XRD, Philips PW-1830) with Cu $K_a$ irradiation. Surface charge properties could be characterized as zeta potential. Zeta potentials of the $Zr_3Al$ based alloy and its PEO film in various solutions in Table 1 were measured by streaming current method using an electro-kinetic analyser (EKA, Anton Paar, Austria). The pH variation was achieved by adding either 0.05 M HCl or 0.05 M NaOH. Its titration was at first lowered stepwise by addition of HCl from the initial pH value to pH 2.5. Then the titration was carried out by addition of NaOH from the initial pH to pH 10 after renewing the electrolyte. Three zeta potential values at each pH were obtained to confirm experimental reproducibility. The corresponding pH value to the zero net surface charge was referred to as the isoelectric point (IEP).

**Table 1**
The electrolytes for EIS and zeta potential measurements.

| Sample | EIS electrolytes | Zeta potential electrolytes | Inert electrolytes | IEP |
|---|---|---|---|---|
| $Zr_3Al$ alloy | 0.1 M LiCl | 0.001 M–0.1 M LiCl | 0.001 M–0.01 M LiCl | 5.2 |
| | 0.1 M NaCl | 0.001 M NaCl | | 5.41 |
| | | 0.01 M NaCl | | 4.27 |
| | | 0.1 M NaCl | | 6.62 |
| | | 2.3 ppm $Li^+$ | | 4.02 |
| | 2.3 ppm $Li^+$ + 1500 ppm $B^{3+}$ | 2.3 ppm $Li^+$ + 1500 ppm $B^{3+}$ | | 4.94 |
| PEO film | 0.1 M LiCl | 0.001 M–0.1 M LiCl | 0.001 M–0.1 M LiCl | 4.6 |
| | 0.1 M NaCl | 0.001 M–0.1 M NaCl | 0.001 M–0.1 M NaCl | 4.6 |
| | | 2.3 ppm $Li^+$ | | 4.46 |
| | 2.3 ppm $Li^+$ + 1500 ppm $B^{3+}$ | 2.3 ppm $Li^+$ + 1500 ppm $B^{3+}$ | | 4.32 |

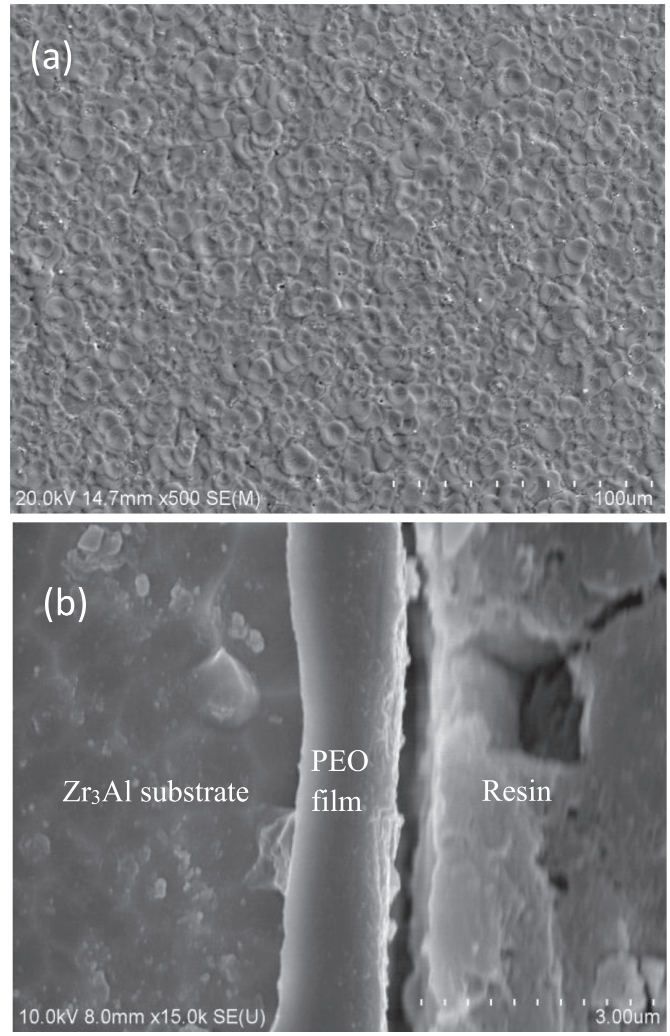


**Fig. 1.** (a) Surface morphology and (b) cross-sectional microstructure of PEO film on $Zr_3Al$ based alloy.

Electrochemical impedance spectroscopy (EIS) was carried out in different solutions to evaluate the corrosion property of the $Zr_3Al$ based alloy and its PEO film. All the experiments were started after 30 min immersion in corrosive solutions. After this time, a steady-state open circuit potential (OCP) corresponding to the corrosion potential ($E_{corr}$) of working electrode was obtained. The EIS tests were performed using an electrochemical workstation (PARSTAT 2273) in the frequency range from 1 MHz to 0.01 Hz. The electrochemical cell contained a saturated calomel reference electrode (SCE), a platinum coil counter electrode and the sample as the working electrode.

## 3. Experimental results

### 3.1. Microstructure and phase composition of PEO film

Fig. 1 shows the surface morphology and cross-sectional microstructure of PEO film on $Zr_3Al$ based alloy formed in phosphate solution. As indicated in Fig. 1a, the film has the typical surface characteristic of PEO film with the presence of the rapid solidified molten region described as "pancake" in Ref. 23. It is noticed that there are some micro-pores in the center of pancake structure. These micro-pores correspond to the residual discharge channels. However, the film in Fig. 1a is much smoother than the conventional PEO films on Zr alloys as reported in Ref. 24, meanwhile these micro-pores on its surface are