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Effect of voltage on properties of microarc oxidation films prepared in phosphate electrolyte on Zr–1Nb alloy

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ABSTRACT

A thin protective film on Zr–1Nb alloy was fabricated by AC microarc oxidation (MAO) in phosphate electrolyte. The morphology, microstructure and phase constituents of MAO films under different discharge voltages were examined by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy. Their surface roughness and microhardness were measured. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were used to evaluate corrosion behaviors of films. The equivalent circuits of EIS plots for bare Zr–1Nb alloy and MAO films were proposed. It was found that all of films at different discharge voltages consisted of the monoclinic ZrO_2 and tetragonal ZrO_2 phases, but the content of monoclinic ZrO_2 was much higher than that of tetragonal ZrO_2 phase. Microhardness of MAO films is over 570 HV, which is higher than that of Zr–1Nb alloy substrate with 245 HV. The film fabricated in higher voltage shows lower corrosion current density and higher impedance, which displays better corrosion resistance. The EIS results identify that the inner compact layer of MAO films plays a key role in improving the corrosion resistance of Zr–1Nb alloy.

1. Introduction

Zirconium alloys have much low neutron absorption coefficient, good corrosion resistance and high temperature mechanical properties, which are important structural materials in the nuclear industry and chemical industry. In the nuclear reactor, zirconium alloys can withstand high temperature and high pressure water corrosion. The hydrogen absorption, neutron irradiation damage and corrosion will deteriorate mechanical properties of zirconium alloys [1–3]. Thus, the appropriate surface treatment to improve the corrosion resistance of zirconium alloys has important practical significance.

Microarc oxidation (MAO), named as plasma electrolytic oxidation (PEO), is a in-situ ceramic film growth technology on non-ferrous metals to improve their wear, corrosion and insulating properties [4,5]. A lot of researches about microarc oxidation of aluminum, magnesium and titanium alloys have been reported [6–12]. Their oxidation process, microstructure and performance have been quite understood. However, MAO research on zirconium alloys is relatively less, and the oxidation process and film properties are still in the early exploration [13–21]. Yan [14] fabricated a thick Al_2O_3/ZrO_2 coating up to 100 μm on pure Zr by DC microarc oxidation in $NaAlO_2$ electrolyte. Zhou [15] and our group [16] prepared a thick ceramic film by AC microarc oxidation in silicate electrolyte, which is composed of tetragonal phase (t-ZrO_2) and monoclinic phase (m-ZrO_2), and the corrosion resistance of zirconium alloy was improved. Besides t-ZrO_2 and m-ZrO_2 phases, MAO thick coating on zirconium alloy also contained a small amount of c-ZrO_2 (cubic phase). Chen [18] employed a pulsed DC power supply to obtain a m-ZrO_2 thin film of 5 μm thick in the sodium silicate solution, and it was found that its wear resistance and corrosion resistance were better than that of the autoclave precast film, showing that MAO films on zirconium alloys had good application prospect. Ya [20] tried to add the Ce contained compound into silicate solution and increased the content of t-ZrO_2 phase in MAO film on Zr-4 alloy. It was declared that Ce element could get into the oxide film to improve the film performance. In addition, for the fuel cladding of zirconium alloy in nuclear reactor, the preparation of a protective oxide film cannot obviously decrease the strength and thermal conductivity properties of fuel cladding, thus the protective film on zirconium alloys in nuclear reactor is required to be thin and compact. Phosphate electrolyte is one of conventional solutions for microarc oxidation. Cheng [21] fabricated a thick ZrO_2 film up to 60 μm in silicate and pyrophosphate electrolytes using an AC power supply, but its porosity was high. So it is interesting to explore the microarc oxidation process and properties of a compact thin film on zirconium alloy in phosphate electrolyte.

In this paper, a thin protective film on Zr–1Nb alloy was fabricated by AC microarc oxidation in phosphate electrolyte. The morphology, microstructure, phase constituents and microhardness of MAO films at different discharge voltages were examined, and their electrochemical corrosion behaviors were evaluated.

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2. Experiment procedure

The as-received Zr–1Nb sheet of 1.4 mm thick annealed at 853 K for 24 h was cut into the coupons with 15 mm×25 mm dimensions. The specimens were polished with 1000# emery paper and then the chemical polishing was finished in a mixture acid with volume ratio of HNO_3:HCl:H_2O = 45:45:10. The Zr–1Nb specimens were fixed in the center of the 10 L stainless steel container in diameter of 25 cm and depth of 30 cm. The specimens and 304 stainless steel electrolytic bath were used as the anode and cathode, respectively. The microarc oxidation treatment was carried out in 2 g/l Na_3PO_4 aqueous solution with additive by using a home-made bipolar power supply (WHYH-100 kW). The electrolyte temperature was controlled below 303 K. The specimens were oxidized by choosing three different anode voltages of +300 V, +340 V and +400 V with the same cathode voltage of −50 V and the oxidation time of 15 min. After MAO treatment, the specimens were washed in running water and dried in warm air. The three specimens of anode voltage of +300 V, +340 V and +400 V were named as Z1, Z2 and Z3, respectively.

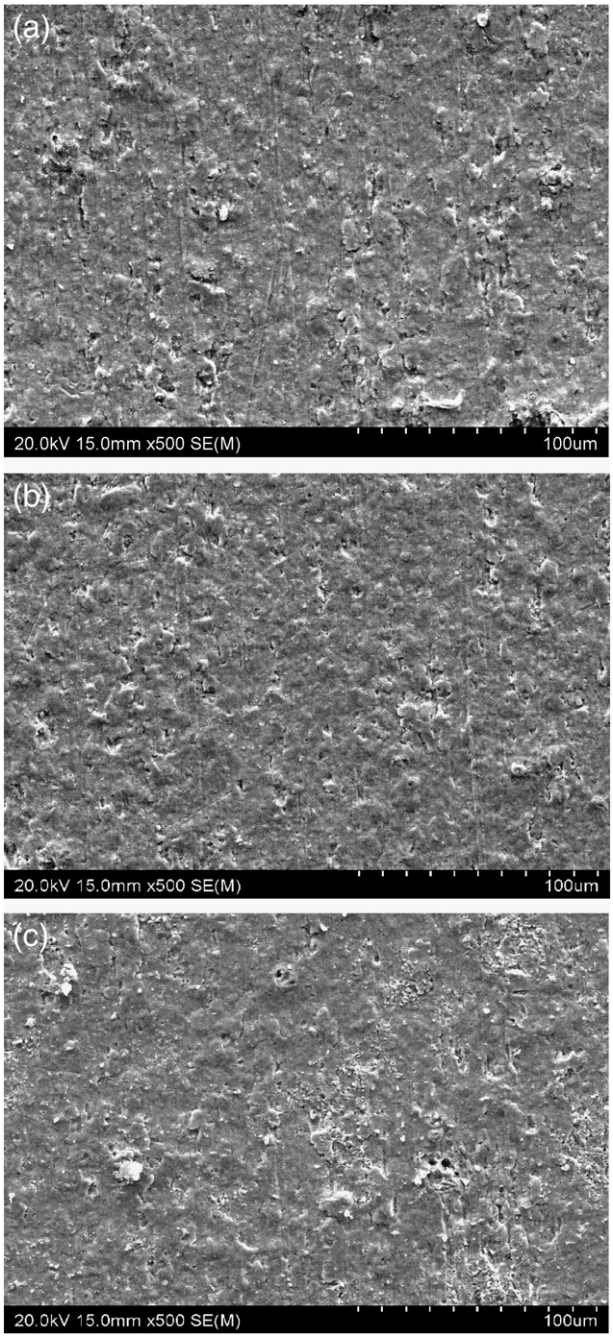

Fig. 1. Surface micrographs of coatings formed in different voltages. (a) +300 V, −50 V; (b) +340 V, −50 V; and (c) +400 V, −50 V.

The surface morphology and cross-sectional microstructure of MAO films were analyzed by Hitachi S-4800 scanning electron microscope (SEM). The phase constituents of films were examined by X'Pert PRO MPD X-ray diffraction (XRD) and LabRAM Aramis Raman spectroscopy. The step size of XRD is 0.33° ranged from 10° to 90° with 20 s scan step time and the laser wave length of 633 nm was selected for Raman spectroscopy analyses. The surface roughness (R_a) of MAO films was measured by TR200 roughness meter and the microhardness of the film surface was determined using a HX-1 Vickers microhardness tester with 50 g load and 15 s dwell time.

Electrochemical tests were carried out using a PARSTAT 2273 electrochemical workstation in 0.5 M LiOH solution at 293 K in order to evaluate the corrosion behaviors of bare Zr–1Nb alloy and MAO films. The electrochemical measurements were employed using a three-electrode cell with the sample as a working electrode (0.5 cm^2 exposed area), the saturated calomel electrode (SCE) as reference electrode and the platinum coil as counter electrode. Potentiodynamic polarization tests of bare Zr–1Nb alloy and MAO films were carried out at a scan rate of 1 mV/s. Meanwhile, electrochemical impedance spectroscopy (EIS) tests were performed at the open circuit potential with an AC amplitude of 10 mV over the frequency range from 1 MHz to 0.01 Hz. EIS plots were fitted using the ZSimpWin software.

3. Results and discussion

3.1. Morphology and microstructure of MAO films

Fig. 1 shows surface morphologies of coated Zr–1Nb alloy treated at different anode voltages with the same cathode voltage. They present a smooth surface with some minor holes. Distinct from the surface morphology of MAO films in Refs. [16] and [22], the surface of films in Fig. 1 is rather smooth. The residual holes are very small, which is beneficial in improving the corrosion resistance of Zr–1Nb alloy.

As shown in Fig. 2, the surface roughness of MAO films is in the range of 0.17 μm–0.35 μm, which is close to the roughness of the bare Zr–1Nb substrate. The roughness of films increases with the increase of applied anode voltage, which is related to spark discharge. As increasing the anode voltage, the spark discharge on the surface of Zr–1Nb alloy become more and more violent, and the spraying melt from the spark discharge channel results in higher roughness. In addition, it is found that the roughness of sample Z1 is slightly lower than that of bare Zr–1Nb alloy. That is because the spark discharge prefers to take place in the defects such as scratch and holes on Zr–1Nb alloy surface, where the

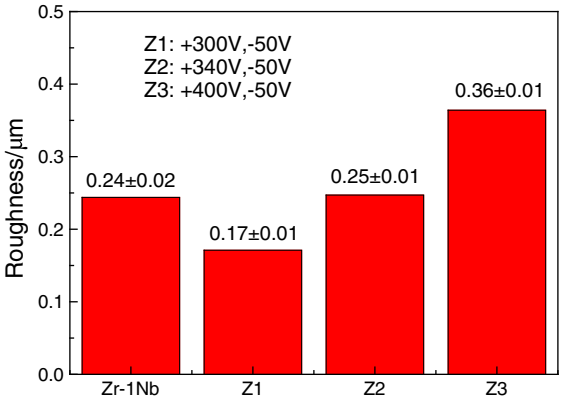

Fig. 2. Surface roughness of bare Zr–1Nb alloy and MAO films.