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The characterization of the oxide based coating synthesized on pure zirconium by plasma electrolytic oxidation

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ABSTRACT

The pure zirconium metal was coated by plasma electrolytic oxidation in silicate containing basic electrolyte for the cumulative periods of 5, 10, 20, 30, 45, 60, 90, and 120 min successively for the total coating duration of 120 min. The phase content, surface morphology and chemical composition of the PEO coating were characterized by XRD, SEM and profilometry after each coating time successively. The equiaxed clusters unique to Zr were formed on the surface of the coating. The number of plasma channels decreased but the sizes and intensities of the sparks increased by increasing the process duration and consequently the amount of materials ejaculated through these channels increased. The thickness and the surface roughness of the coating were increased by the process duration. The presence of cracks and pores resulted in a lower value of microhardness of the coating compared to the theoretical value of ZrO_2. The plasma channels containing Si rich and radially grown Zr rich crystals were clearly observed from the cross sectional examination of intentionally created fracture surface. The characterizations carried out upon successive coating and successive removal of this coating confirmed that monoclinic ZrO_2/tetragonal ZrO_2 ratio was not changing with coating thickness.

1. Introduction

Zirconium metal and its alloys are used as structural materials in water-cooled nuclear power reactors, fuel cladding tubes and pressure tubes [1–4]. These materials are also substantially used as biomaterial, particularly in surgical and dental–orthopedic implants, because of their biocompatibility and sufficient strength [5–8]. However, usage of zirconium and its alloys in these aggressive environments result in short service life [9–11]. Hence, various surface modification techniques were applied to improve the surface properties such as corrosion and wear. Zirconium oxide films were synthesized by ambidextrous techniques which included physical or chemical deposition processes, spray coating, dip coating and sol–gel techniques [12–16]. However, these coating techniques resulted in either non-crystallite oxide films or not well-adhered films which needs post-heat treatment to obtain well-adhered crystalline coating [12–15]. These treatments usually may evoke cracking, spallation of the film or change in the properties of base material of zirconium. Plasma electrolytic oxidation (PEO), also called microarc oxidation (MAO), is a promising electrochemical surface treatment process for producing well-adhered and crystalline oxide films on zirconium and its alloys at room temperature (RT) in eco-friendly alkaline based electrolytes [1,3,17–21]. Although the surface modification of light metals including Al, Ti, Mg and their alloys by PEO are widely investigated, the studies on PEO of zirconium and its alloys are limited [20,22–28]. The studies were mainly concentrated for researching the properties of PEO coatings synthesized on Zr alloys as biomaterials. The recent studies were also focused towards understanding the process of PEO coating on Zr alloys and growth kinetics of oxide film on the substrates. However, the mechanism of the oxide film formation and phase transformation (if it was the case) was not fully understood with the studies carried out so far. The microstructure and compositions of the PEO coatings on Zr alloys have been considered in several studies [1,2,4,7,16,29–32]. However, these studies have not resulted in a consensus on the PEO phases' formation. So, in this study an attempt was made to understand the oxide formation mechanism on commercially pure zirconium by increasing PEO duration step by step and characterization by XRD, SEM, and profilometry up to the coating duration of 120 min under the constant bath conditions and with the same electrical parameters. Additionally, the accumulated coating was mechanically removed step by step and characterized successively for the purpose.

2. Experimental

The pure zirconium (99.6%) sample with the dimensions of 40 mm ×35 mm × 1 mm was prepared from pure zirconium sheets (Dad Chemicals). The surface of the sample was ground using 600–1200 grit SiC paper and then polished using 3–1 μm diamond paste. After grinding and polishing, the substrate sample was cleaned in an ultrasonic bath of ethanol for 5 min.

The surface roughness of the sample was determined using Veeco Dektak 8 profilometer by scanning a certain area of 2 mm × 5 mm (40 scan) on the surface of the sample prior to the PEO process. An

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electrolyte for PEO coating was prepared by dissolving high purity 12 g/l Na_2SiO_3 and 2 g/l KOH in distilled water (pH = 12.9). The process was carried out by means of a homemade PEO unit with an asymmetric AC power supply (50 Hz) with the maximum capacity of 100 kVA. The coating formation voltages were of 480 V (positive peak value) and 120 V (negative peak value) and maintained constant during the PEO process.

The current density was maintained approximately 0.25 A/cm^2 for the sample. The electrolyte was stirred with pressurized air and the temperature of the bath was kept at 23 °C ± 3 by circulating cold water around the electrolyte cell during the process.

The flowchart of the experimental procedure is given in Fig. 1. The zirconium sample was firstly coated by PEO process for 5 min. The coated sample was cleaned by distilled water and then in an ultrasonic bath of ethanol for 5 min and dried by warm air. Then, the thickness of coating was determined by Eddy Current (Fischer) using 10 measurements from different locations. Rigaku D-MAX 2200 X-Ray diffractometer (40 kW, 40 mA), with a Cu K_α radiation over a 2θ range from 10° to

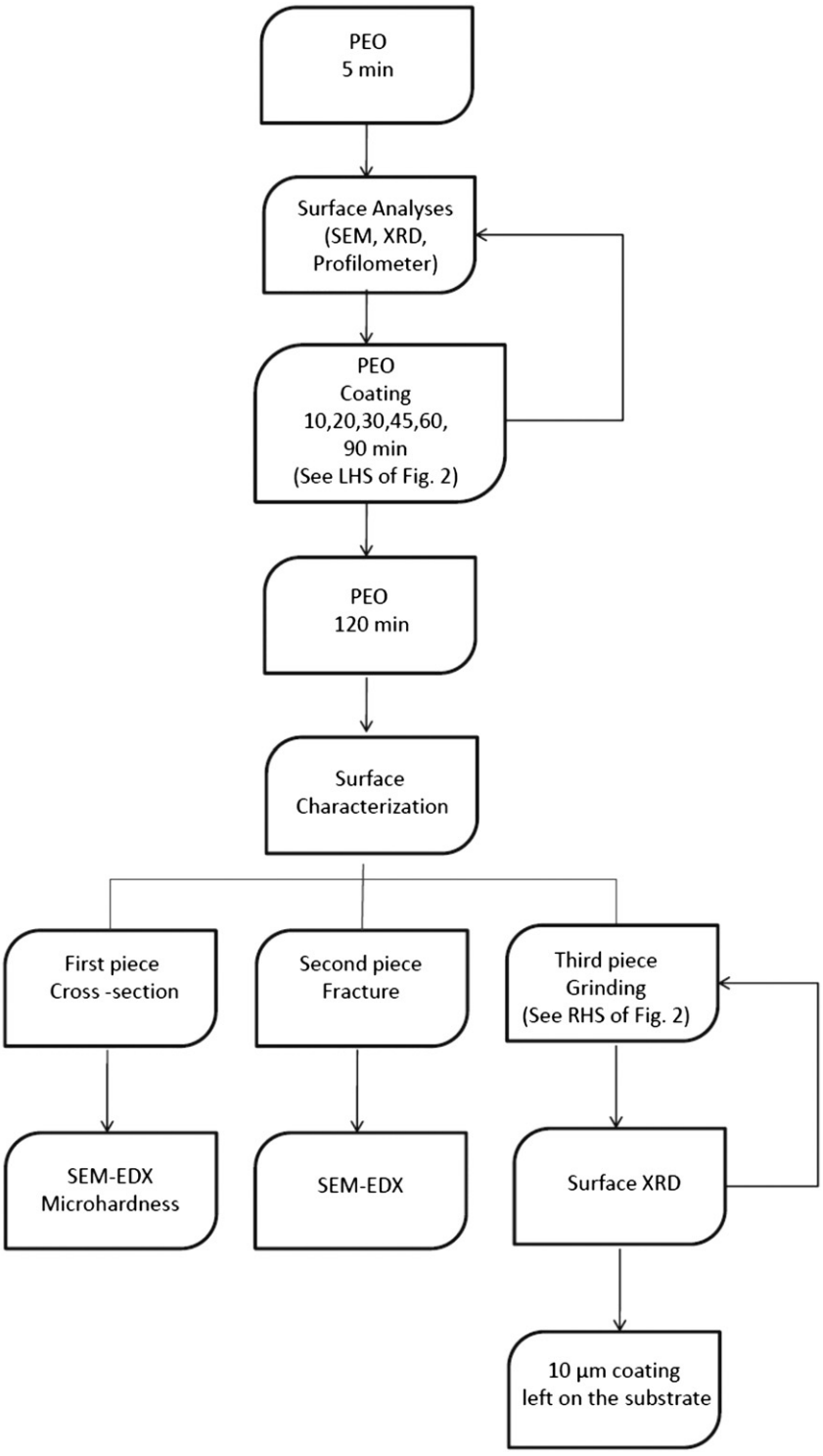

Fig. 1. The flowchart of the experimental procedure of PEO coating of pure Zr.