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Morphological Investigations of Oxide Nanotubes Grown on Zircaloy-4 Cladding

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ABSTRACT

Self-organized, highly ordered and vertically oriented nanotubes have been fabricated on the surface of Zircaloy-4 (Zr-4) sheet using an electrochemical route. Anodization is carried out in ethylene glycol (EG) and glycerol electrolyte containing ammonium fluoride and de-ionized water. The morphology of nanotubes was studied using field emission scanning electron microscope (FESEM) and high resolution transmission electron microscope (HRTEM). Electron microscopy showed that self-organized nanotubes with regular ordered and extremely smooth wall morphology were obtained in glycerol based electrolyte. The diameter of the nanotubes could be tailored by anodization parameters. The TEM and SAED results revealed that the as-prepared nanotubes are closed at the bottom surface and have crystalline structure.

1. Introduction

Zircaloy-4 (Zr-4) is an important alloy mainly utilized in the nuclear power/fuel industry due to its excellent corrosion and hydride resistance efficiency as well as low absorption cross-section [1-2]. In a light water reactor, thermal energy produced is transferred to the surrounding water through the surface of cladding material. Therefore, in a way cladding surface plays an important role in the safe operation of a nuclear reactor under normal as well as extreme conditions. What happened at Japan's Fukushima Daiichi plant during 2011 accident was attributed to the core meltdown due to failure of core cooling water circulation system [1]. This resulted in rise of core assembly temperature to such levels that Zr-cladding became auto-oxidant producing excessive amounts of hydrogen (H_2) that ultimately generated severe explosions owing to accumulation of H_2 in reactor's containment area.

In order to address such safety issues, two pronged approach may be adopted; one is nano-engineering of cladding surface and second would be to adopt other passive systems for containment cooling [3]. Nano-engineering of cladding surface is intended to reduce the probability of oxidation reaction between Zr-cladding and water at high temperatures (due to loss-of-coolant accident, LOCA) hence unnecessary generation and accumulation of H_2 can be avoided. By nano-engineering, surface area of Zr-cladding can be increased for its novel and excellent performance thus lending more time for other safety systems to become operational under LOCA type emergency situations [4]. It has been shown that nano-structures or thin films grown on the surface of Zr-4 sheet exhibit superhydrophilic characteristics [5, 6] and manifold increase in its electrochemical corrosion resistance [7].

Among the existing techniques, anodization is a simple technique to grow various kinds of nanostructures on metals surface for different applications [8-14]. Nano-structures have also been fabricated on the surface of zircaloy in different aqueous electrolytes using anodization [5, 6, 15 - 17]. Here in this article, we report the fabrication and morphological study of highly ordered oxide nanotubes on the surface of Zr-4 using ethylene glycol (EG) based electrolyte. Consequently, no more oxidation occurs on the surface of cladding and hence no hydrogen is generated.

2. Experimental

The highly ordered oxide nanotube arrays were grown on the surface of Zircaloy-4 sheets by anodization technique. For this purpose, Zr-4 sheets (acting as working electrode) and platinum gauze (acting as counter electrode) of appropriate dimensions were used. The anodization process was carried out at room temperature by maintaining the electrodes at a constant *dc*-potential of 40 and 100 V in an electrolytic medium (EG/glycerol) with appropriate amounts of NH_4F and de-ionized water. The details of experimental procedure are described elsewhere [10]. The nanotube arrays thus obtained were washed thoroughly in de-ionized water, dried and

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annealed in air at ~450 ^{o}C for 2h for morphological investigations. A Hitachi S-4800 field emission scanning electron microscope (FESEM), and a high resolution transmission electron microscope (HRTEM) along with energy dispersive X-ray (EDX) attachment was employed for this purpose.

3. Results and Discussion

FESEM images of the oxide nanotubes grown on Zr-4 surface in EG based electrolyte at an electrode potential of 40 V are shown in Fig. 1. As grown oxide nanotubes can be clearly seen in Fig. 1a, with a measured diameter of ~20 nm (Fig. 1b). The height/length of the oxide nanotubes are approximately 5 µm, having straight wall morphology as shown in Fig. 1c but smoothness is different from that of TiO_2 nanotubes fabricated by the same anodization technique [9]. It is important to mention that sever charging phenomena has been observed during the SEM analysis, which is suppressed by coating a thick layer of Au. The thick Au layer deteriorates the surface morphology i.e., smoothness of the nanotubes as shown in the high magnification SEM image (Fig. 1d).

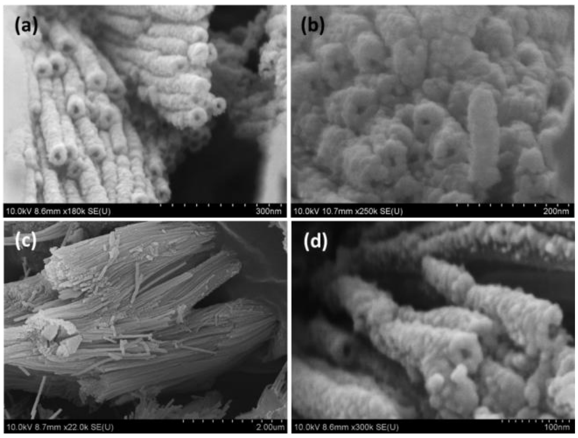

Fig. 1. FESEM images (a-d) of the as-grown Zr-4 oxide nanotubes prepared in ethylene glycol (EG) electrolyte showing (a, b) the top surface morphology and (b-d) cross-sectional view

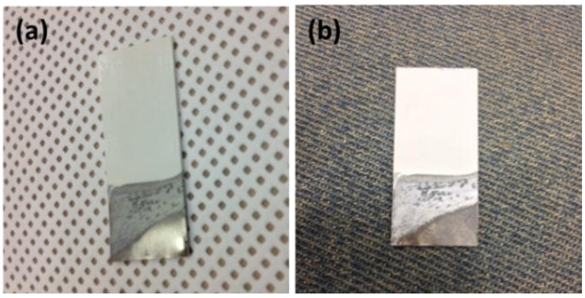

Fig. 2: Digital images of Zr-4 oxide nanotubes along with Zr-4 substrate prepared in ethylene glycol (EG) electrolyte: (a) before annealing, (b) after annealing

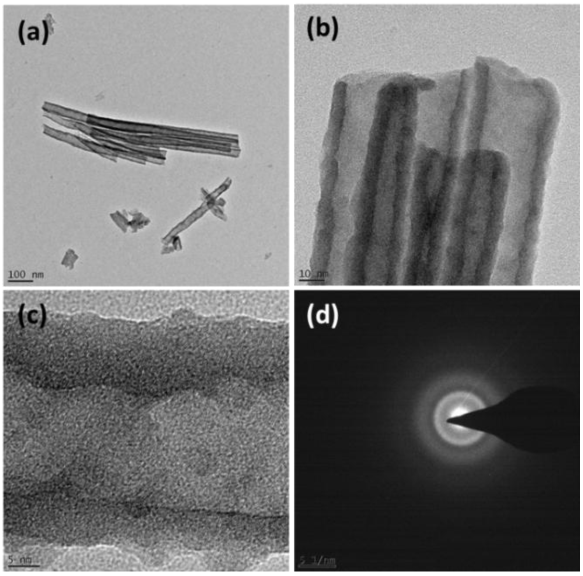

Fig. 3: TEM images (a-c) showing the formation of Zr-4 oxide nanotubes in EG electrolyte, and (d) SAED pattern of Zr-4 oxide nanotubes.

In Fig. 2 are shown the digital photos of the as-grown (Fig. 2a) as well as annealed (Fig. 2b) Zr-4 oxide nanotubes produced on the surface of Zr-4 sheet. The evaporation of trapped electrolyte after annealing [18] results in change of color of the nanotubes as seen in these images. Fig. 3(a-c) shows HRTEM images of the nanotubes along with selected area electron diffraction (SAED) pattern. The measured internal diameter and wall thickness of the nanotubes from the TEM images were ~20 nm and ~7 nm, respectively. The wall morphology of the nanotube is not very smooth and variation in the wall thickness can be observed. The HRTEM image (Fig. 3c) and SAED pattern (Fig. 3d) show that as-grown Zr-4 nanotubes are crystalline similar to our results of TiO_2 nanotubes [19]. The morphology i.e., diameter and wall-smoothness of the nanotubes was tailored by anodizing Zr-4 sheet in glycerol based electrolyte. In Fig. 4 are given FESEM images of the highly ordered and self-organized Zr-4 oxide nanotubes fabricated in glycerol based electrolyte at a *dc*-potential of 100 V. The Zr-4 oxide nanotubes are closed at the bottom surface with smooth walls morphology (Fig. 4b) with an average internal diameter of ~35 nm and a wall thickness of ~15 nm. The cross-sectional image (Fig. 4c) reveals very straight and extremely smooth wall morphology of the Zr-4 oxide nanotubes. This may be associated to the difference in viscosity of electrolyte [10] as the viscosity of EG and glycerol at 25 ˚C is 16 cP and 945 cP, respectively. The inner diameters of the nanotubes can be clearly seen in the SEM image (Fig. 4c). It is important to mention that sever charging phenomena previously observed during SEM characterization of Zr-4 oxide nanotubes in spite of thick Au-coating was greatly suppressed by plasma cleaning technique. Thick conducting coating for SEM analysis generally

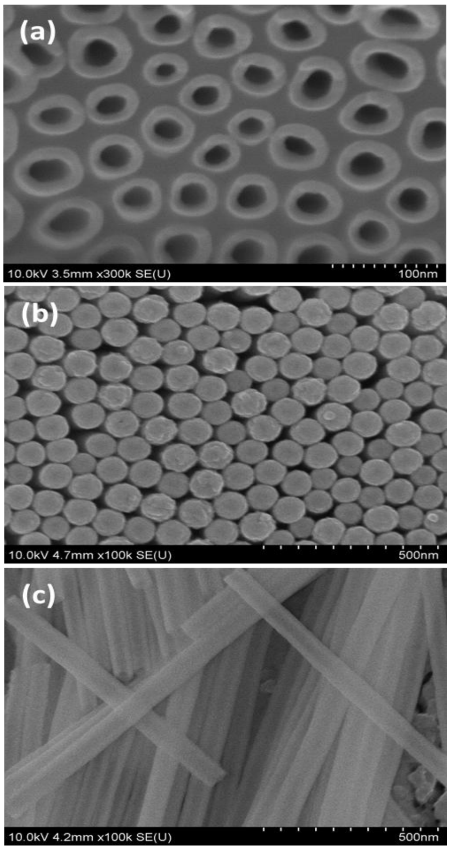

Fig. 4: FESEM images (a-c) of the as-anodized Zr-4 oxide nanotubes prepared in glycerol electrolyte: (a) the top surface, (b) bottom surface morphology, and (c) cross-sectional view.

deteriorates the morphology of the nanotubes and hides many desirable features. This may be attributed to the removal of organic species by plasma cleaning. The organic species usually remain trapped in the nanotube arrays during the process of anodization. TEM images (Fig. 5) of the Zr-4 oxide nanotubes confirm the SEM results that closed bottom nanotubes with extremely smooth walls morphology are formed. The bottom walls morphology is also very smooth and a few nm gap between the nanotubes can be seen, thus confirming the SEM results (Fig. 5b). TEM image of the single Zr-4 oxide nanotube (Fig. 5b) shows that the inner diameter of the nanotube is about 35 nm with average wall thickness of around 15 nm. The crystalline structure of the nanotubes has been confirmed from the XRD results. Fig. 5 shows XRD pattern of the annealed Zr-4 oxide nanotubes. It clearly reveals the formation of crystalline cubic and monoclinic phases of ZrO_2 (baddeleyite). Fig. 6 gives EDX spectrum of the Zr-4 nanotubes obtained using TEM, showing the peaks of major elements like Zr and O along with C and Cu which resulted from TEM grid. EDX spectrum confirms the formation of Zr-4 oxide.

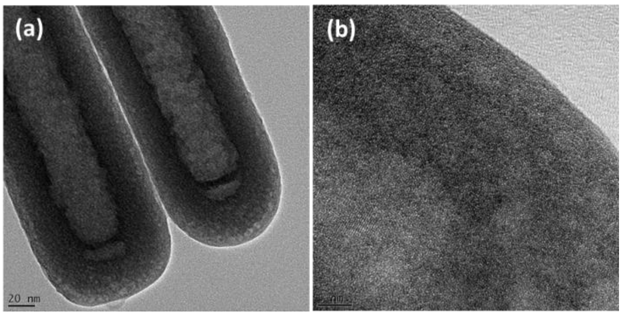

Fig. 5: TEM images showing the formation of Zr-4 oxide nanotubes in glycerol electrolyte.

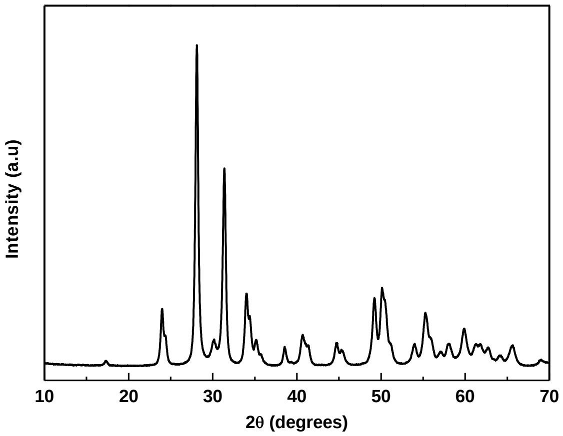

Fig. 6: X-rays diffraction (XRD) pattern of the annealed sample confirms the formation of Zr- 4 oxide nanotubes.

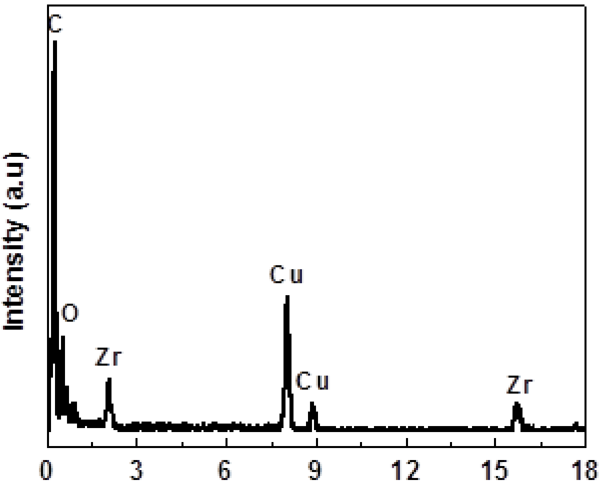

Fig. 7: Energy dispersive X-ray spectrum showing the formation of Zr- 4 oxide nanotubes in glycerol electrolyte.

The possible formation mechanism of Zr-4 oxide nanotubes is the following: When voltage is applied via power supply, all the surface atoms of Zr-4 loss their outermost electrons and form Zr-4 cations. Oxide layer grows at the surface of Zr-4 due to the interaction of Zr-4 cations with O_2- and OH− available in the electrolyte from water. Initially a compact oxide layer formed on the surface of Zr-4, however soon after its formation, peroration is initiated in the oxide layer due to the chemical attacked of fluorine. Moreover some of the Zr-4 cations are ejected (field-assisted dissolution) directly to the electrolyte forming soluble fluoride complexes at the oxide/electrolyte interface. The formation of nanotube morphology is due to the volume expansion of Zr-4 substrate as result of O atoms incorporation into Zr-4.

4. Summary

In summary, self-organized and highly ordered anodic Zr-4 oxide nanotubes with extremely smooth wall morphology were fabricated on Zr-4 sheets in organic viscous electrolytic medium. The anodization was carried out in EG and glycerol based electrolytes. It is shown that size and morphology of oxide nanotubes can be easily be manipulated by growth conditions during the anodization process. Results show that nanotubes with rough wall morphology were formed in ethylene glycol based electrolyte while glycerol based electrolyte produced nanotubes with extremely smooth wall morphology. This is ascribed to the viscosity of the electrolyte. The nanotubes are closed at the bottom surface. This kind of morphology may be useful for enhancing the safety level of the nuclear power plants.

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