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Archives of Applied Science Research, 2013, 5 (5):1-7
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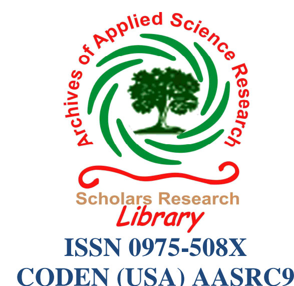

ISSN 0975-508X
CODEN (USA) AASRC9

Anodic oxide films of Zr-4 in 0.1M ammonium oxalate by AFM studies

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ABSTRACT

The surface of zircaloy-4 anodized at a constant current density of 8 mA.cm^{-2} in 0.1M ammonium oxalate at a potential 0–79 V, was characterized by means of surface science technique AFM. It was found that during anodization by temperature effect (various temperatures ranging from 273K to 333K using galvanostatic technique. the surface oxide grows with modifying the topography. The incorporation of oxalate dianions from the electrolyte to the surface during the anodizing process changes the topology. Anodized oxide films grown with relatively high voltages, the zirconia (ZrO_2) formed over the Zr-4 in 0.1M ammonium oxalate at 333K appeared less rougher and protruded when compared with 288K and 318K. Anodic oxide films were homogeneous and rough with nanosized grains. When the anodization voltage was 79V the average roughness (Ra) of the zirconia film reached 3.9nm, and it is increased to 8.8nm (288K) and fallen down to 2.3nm (333K) and the oxide formed changed abruptly to become as less roughness as that formed on non-anodized.

Keywords: Zircaloy-4; Topology; Atomic force microscopy; Anodic zirconium oxide.

INTRODUCTION

The kinetics of anodic film formation on zirconium in various electrolytes has been reviewed [1]. Anodization of zirconium has been studied in 1N Na_2SO_4 at various temperatures 279–338K [2]. The influence of temperature on the kinetics of anodization of Zr, Ti and Nb in 40% H_2SO_4 and 0.1M sodium salicylate has been reported earlier [3–5].

Panasa Reddy [6] in his experiments found that the change in temperature has a marked influence on the kinetics of anodization of zircaloy–4 in 40% H_2SO_4. The ionic current density was found to decrease with the increase in temperature, whilst the differential field of formation was independent of temperature. The breakdown voltage was found to increase with the increase in temperature.

Jun Wang and Zhiqun Lin [7] studied the effect of electrolyte temperature and the applied anodization potential. Since a change in temperature was found to influence the kinetics of anodization significantly [8,9], a detailed study of effect of temperature was studied in 0.1M L-ascorbic acid, 0.1M sodium methoxide and 0.1M potassium malonate with zircaloy-4 and niobium and the results are compared with the earlier work[6,10,11]

Wilkins studied the growth of thin uniform oxide films on Zr at high temperatures. He made an attempt to study the effect of electrolyte, composition on the anodization. The electrolytes used were 0.2M H_2SO_4 and 1% KOH.

In this work, the electrochemical oxidation of Zr-4 was focused. The electrochemical experiments were performed at various temperatures in Kelvin. We have studied the electrochemical behavior of Zr-4 through constant current density i.e. 8mA.cm^{-2}. Thus specified experiments were performed and the surface characterization of materials employed in a topic of main importance since the surface plays a key role in the response to the valve metal presence. It was found that both the topography and the chemical surface composition have a strong influence in the early stages.

The surface interaction is with a broad range from a few microns, where the surface topography changes the effective contact area between 273K to 333K 3.9 to 2.3 nanometers. So the anodized oxide films roughness decreased. Where the influence of chemical species present on the surface can modify. The ''native'' zirconium oxide film thickness reported from different authors varies between 2 to 5nm [12-14].

The thickening of the film may improve the barrier effect against corrosion, and may also change the surface topography of zircaloy-4. Anodizing is a simple and economic process to obtain a uniform surface oxide film despite the geometry of the specimen. The anodic oxide thickness can be controlled by controlling the processing parameters such as current density, anodizing potential or electrolyte and the resulting oxide surface film attain strong bonding and adherence with the underlying metal substrate [12-16].

The ammonium oxalate is an interesting electrolyte between 273K to 333K because during the anodizing treatment the oxalate dianions may be incorporated into the growing film. The anodic film thus formed would increase the corrosion resistance with the environment. Anodic films can be grown quickly and characterized relatively easily with surface science technique atomic force microscopy. This work presents the study of the topological and chemical evolution of zircaloy-4 surface when anodizing at a potential 0–79 V. It is also determined the surface changes that occur when the modified surfaces are anodized between 273K to 333K.

Anodic films were obtained in the range 0–79 V [17]. This paper is a report of a complementary AFM investigation of the surface topology of oxide films grown anodically on Zr-4. The purpose of this work was to use AFM. As non-anodized specimen was smooth, in contrast as the anodization voltage was decreased from 79V to 60V the thin films formed. The interpretation for the abrupt changes was that the oxide was rearranging which had accumulated during earlier growth. This was implicated for the 0V–79 V (2.0 to 2.3nm) films because the anodization changed with the time the films anodized in a dilute 0.1M ammonium oxalate between 273K to 333K.

In the current work, AFM was used to characterize the free surfaces 79V to 60V (3.9 to 2.3nm) anodic oxides on Zr-4. A major goal was to determine if the topological/textural changes in the oxide surface to parameterize the surface fractal dimension, which can be calculated from the AFM measurements. Many different methods of fractal analysis have been applied to measured surface textures [18-20]. The ability of fractal analysis to extract different kinds of information from measured textures compared to the common, conventional analysis justifies their use. In general, the ranking of surfaces based on common, conventional height parameters, like roughness average (Ra) or root mean square roughness (Rms) should not be the same as the ranking based on any kind of fractal analysis. In contrast to the common, conventional height parameters, many geometric properties of surfaces tend to increase with decreasing scale of observation, which is consistent with their fractal nature(for example, the angles of inclination and the apparent areas [21]. The results of fractal analysis contain different information about the texture than do the results of Conventional analyses.

MATERIALS AND METHODS

Materials and surface modification treatment

Zr-4 was of 98% nominal purity supplied in the form of annealed sheet by Nuclear Fuel Complex, Hyderabad, as gift samples were used. Thinning of this annealed sheet was done by Defence Metallurgical Research Laboratory, Hyderabad. From the initial sheet, the foil samples used were cut with the aid of a punch into a flag shaped specimen of 1cm^2 working area on both side and 1 ½ cm long tag.

The alloy chemical composition is presented in Table 1 and the microstructure is shown in **Fig. 1.** They were chemically polished. The procedure for the chemical polishing was described earlier [22]. The chemical polishing mixture consisted of acids such as HF, HNO3 and H2O in a definite volume ratio 3:3:1. The samples were

thoroughly cleaned in distilled H2O, wiped with tissue papers, and exposed to dry before the experiment. An electrical contact, conveniently isolated from electrolyte was mounted on each zircaloy-4 sample.

Anodic oxides of varying thickness were produced with the constant current used was a stabilized DC regulated power supply unit built by Physitech, Hyderabad. The unit employed had a provision to supply constant current 0–200mA. The current passed was measured accurately on a digital milliammeter. A DP-DT switch was included in the circuit so that the current could be set prior to use. The potential directly across the cell was measured by a digital voltmeter (1000V) and set to various limiting voltages (0, 79. 74, 72, 65, 60V etc.) or digital multimeter. Digital LCR meter supplied by Physitech, Hyderabad was used at 1 KHz for the capacitance measurements. The oxides were grown under constant current density of 8mA.cm^{-2}. When the potential across the interface reached the set point, the current was allowed to decay for approximately 30 sec and then the dc power source was shut off.

Table- 1: Amount of the principal impurities present in Zr-4(as part per million).

Material	Element	ppm
Zircaloy-4	Cr	1100
	Fe	2200
	O	1200
	Sn	14400

Atomic force microscopy (AFM) was employed to characterize the morphology of the nanoparticles using a Digital Instrument Nanoscope IV (Veeco Instruments, Santa Barbara, CA). Measurements were carried out in contact mode at room temperature, in air, using Digital Instruments micro fabricated Si_3N_4 tips on 100μm triangular cantilevers with a manufacturer's quoted spring constant of 0.58N/m. The microscope was vibration damped. Commercial phosphorous (n-) doped silica tips on an I-tape cantilever with a length of 115–135 mm and resonance frequency of about 260 kHz were used. Tapping-mode AFM allows the imaging of the soft samples at high resolution without damaging the sample. The AFM scans were square regions with side lengths of 1.5μm x 1.5μm for the thick films; each scan consisted of 512 lines sampled 512 points per line. Slow scans were necessary for the thicker films to avoid the artifacts ('streaks' in the scan direction). The analysis was repeated on at least 5 images of each sample, and at least in 2 samples for each anodizing condition, verifying the variation of the roughness parameters for each condition.

AFM 2D and 3D images of the topography of the surface before anodization

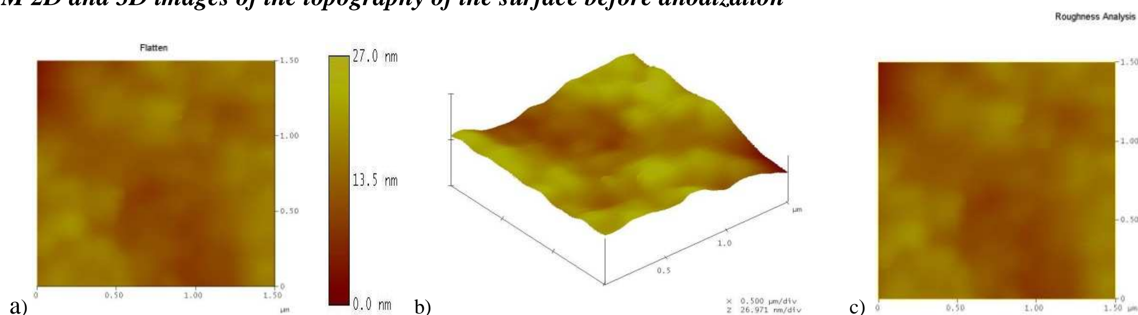

Fig-1: The micro and nanostructures of the underlying metal can be seen in these AFM images (non-anodized zircaloy-4), a) 1.5 μm x 1.5μm with z-axis maximum (see scale bar) (b) 1.5 μm x 1.5μm height image with a height scale 26.9 nm/div, c) the Ra and Rms are 2.0 nm and 2.4 nm of the initial formed non-anodized oxide film.

For each sample, five images were taken at different locations on the surface to account for local variability. Two scanning heads were used (J and D) to accommodate the variations in scan size. The AFM measurements are presented as images, either plan view, in which the height is represented by grey scale shading, or in3-D, for which the scale of the 'z' axis is expanded relative to the x and y scales to aid viewing. All of the heights used to produce the images were obtained without filtering.

RESULTS AND DISCUSSION

An AFM image of the starting surface is shown in Fig-1. The valve metal microstructure underlying the oxide shown in Fig-1. The areas associated with the elongated grains that comprise the main component of the alloy. The topologies of the zirconia surfaces were measured with AFM in 0.1M ammonium oxalate at 273K for high voltage anodized films (i.e. 0–79 V, 3.9nm); see, for example, Fig-2.

AFM 2D and 3D images of the topography of the surface after anodization

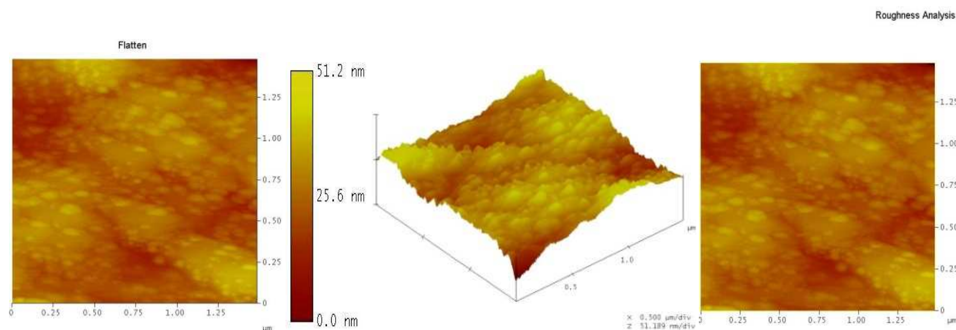

Fig-2: AFM images of 79V (273K) anodic oxides a) 1.5 µm x 1.5µm with z-axis maximum (see scale bar) b) 1.5 µm x 1.5µm height image with a height scale of 45.3 nm/div and c) the Ra and Rms are 3.9 nm and 4.9nm.

The AFM images for the Anodized zirconia films at 0– 74V, 0–72V, 0–65V, 0–60V are indistinguishable from each other and the starting air-formed oxide. In addition, the anodic oxide formed at 288K (8.8nm) is 'rougher' than that non-anodized and anodized anodic oxide film at 273K, 318 and 333K. Images for anodic oxides are shown in Fig-3, 4, 5. The topologies of zirconia films formed with voltages up to 60V are not the same as those shown in Fig-2.

One explanation for the apparent initial enhanced anodic growth at 72V are porous than those oxides found at 60V. Anodic films formed on zircaloy−4; oxide is expected to be infiltrated at 333K when anodized which would make the effective insulating thickness of the oxide less.

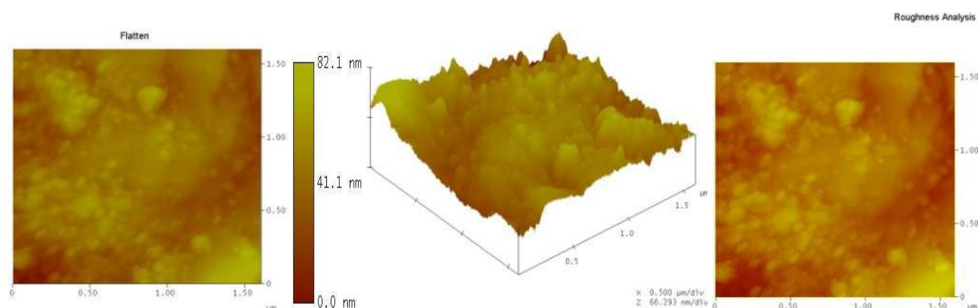

Fig-3: AFM images of 74V (288K) anodic oxides a) 1.5 µm x 1.5µm with z-axis maximum (see scale bar) b) 1.5 µm x 1.5µm height image with a height scale of 77.2 nm/div and c) the Ra and Rms are 8.8nm and 11.2nm

During anodization the electric field across the anodic oxide of 318K zirconia would be greater than 333K zirconia and because the oxide growth rate is proportional to the field strength [23]. Zirconium oxide can grow relatively uninterrupted because of the large size of the grains

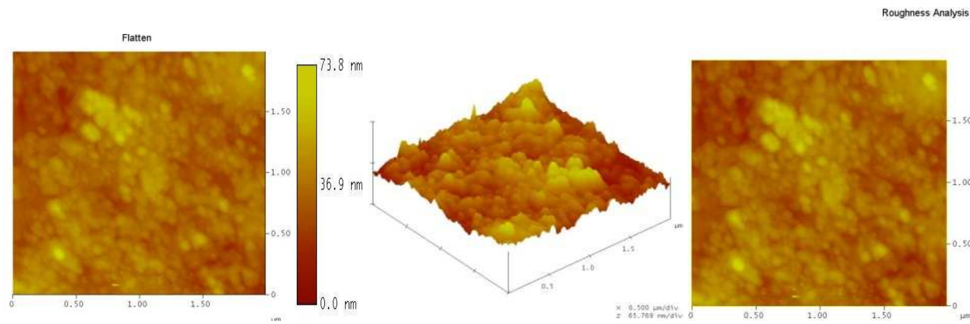

Fig- 4: AFM results showing images of 65V (318K) anodized oxides initially formed dark coloured protrusions. a) 1.5 µm x 1.5µm with z-axis maximum (see scale bar) b) 1.5 µm x 1.5µm height image with a height scale of 38.6 nm/div and c) the Ra and Rms are 5.5 nm and 7.0 nm

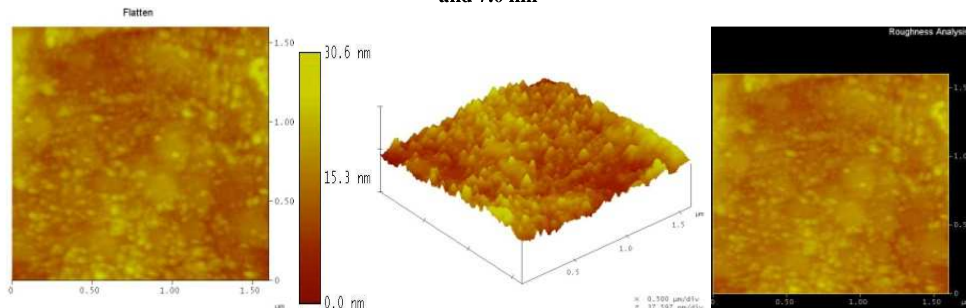

Fig- 5: AFM results showing images at higher voltage 60V (333K), a) 1.5 µm x 1.5µm with z-axis maximum (see scale bar) b) 1.5 µm x 1.5µm height image with a height scale of 91.4 nm/div and c) the Ra and Rms are 2.3nm and 2.9nm

For zircaloy-4 used in this study oxidize predominantly to ZrO_2 (zirconia) which has a higher metal oxide [24]. The structure of the anodic oxide is consistent with the surface morphology determined by AFM. The topography of the zircaloy-4 surface changes with anodization in 0.1M ammonium oxalate at 288K to 318K, Ra and Rms decreased, as can be observed in Fig.3, 4 but comparing the non-anodized surface the ones anodized surface at 74V, 65 V is increased the surface roughness [25–28].

The zirconia roughness parameters Ra and Rms were determined from AFM images. These parameters are often used to study the topography of effect of temperature was (anodization voltage fallen down) to 333K from 273K. Roughness is an important characteristic of effect of temperature anodized oxide surfaces is decreased [29].

The zirconia Ra parameter corresponds to the average of a set of individual measurements of a surface protrusions; peaks and valleys on the surface. Rms is the root mean square average of the profile height deviations from the mean line, recorded within the evaluation length. The evolution of those roughness parameters with anodizing potential in a sampling scale 1.5µm x 1.5µm is presented in Fig-6. A continuously decrease of roughness with decreasing potential was determined as shown in Table-2. The zirconia grain size, Ra and Rms were resulted in figures. Ra and Rms resulted useful parameters to evaluate the surface topography evolution in our study, since the differences in the parameters with the anodizing potential were reproducible and repetitive on different images of the same sample and also on different samples with the same anodizing potential treatment. However, both parameters are very sensitive to the sampling scale, and therefore, the comparison of the values obtained in our study with the ones reported by other authors becomes difficult. The reported values for zircaloy-4 materials with several surface modification processes ranges from a nanometers to below 2 micrometers, but the sampling scale also varies from one reporter to other, and even is not reported in numerous cases.

Table- 2

Temperature	Material	Electrolyte	Ra (nm)	Rms (nm)	Anodization voltage (V)
	Non-anodized Zr-4	0	2.0	2.4	0
273K	Anodized zirconia	0.1M AO	3.9	4.9	79
288K	Anodized zirconia	0.1M AO	8.8	11.2	74
303K	Anodized zirconia	0.1M AO	-	-	72
218K	Anodized zirconia	0.1M AO	5.5	7.0	65
333K	Anodized zirconia	0.1M AO	2.3	2.9	60

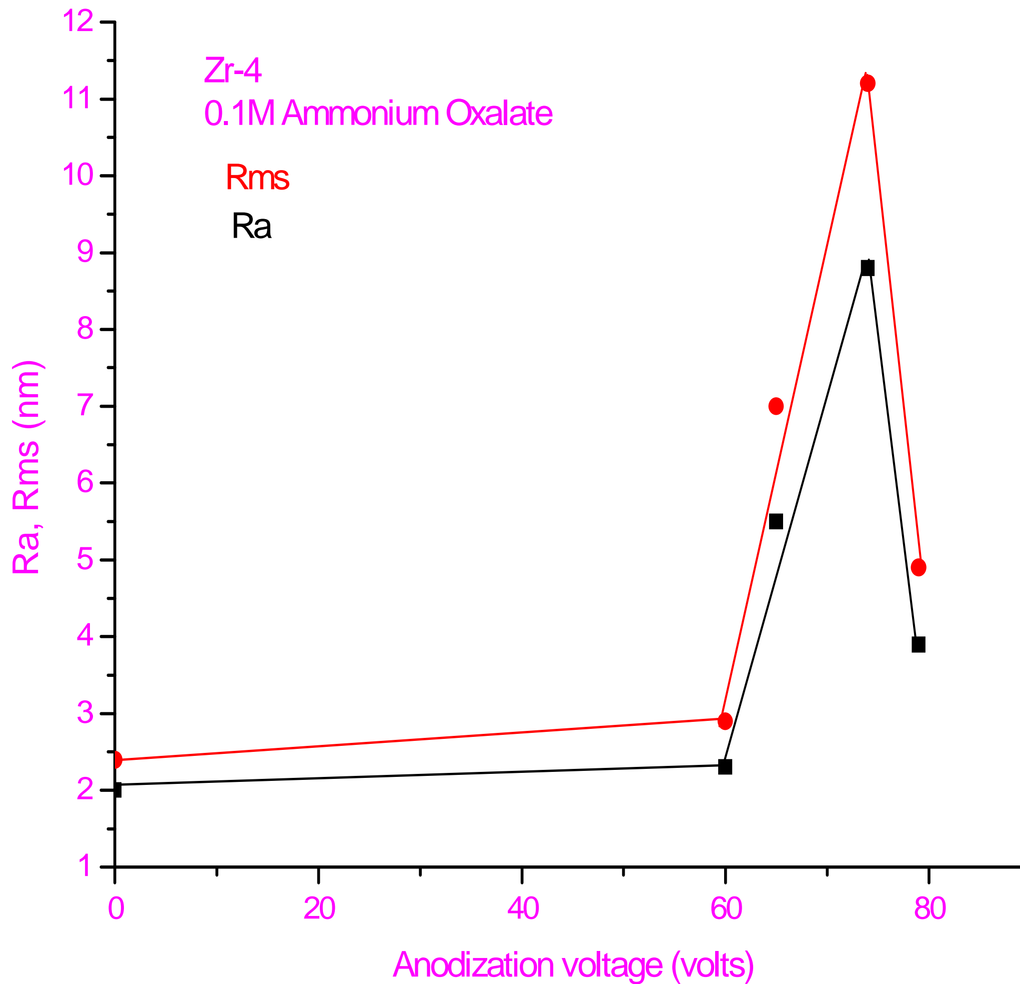

Fig-6: Evolution of roughness parameters Ra and Rms with anodization voltage determined from AFM images in a sampling scale

CONCLUSION

Anodization in 0.1M ammonium oxalate the chemical and roughness of Zr-4 are simultaneously modified. AFM measurements have been used to characterize the topology of oxide surfaces grown anodically on Zr-4. When decreasing the anodization voltage the Ra and Rms increased and then started to decrease when we raised the temperature from 273K to 333K. The fractal dimensions of the zirconia surfaces calculated from the AFM measurements indicated that the anodized oxides associated at 60V were less roughness than at 79V. Protrusions, hills and valleys were seen to grow for anodization voltages. There growths are believed to be the result of 0.1M

ammonium oxalate decreasing the effective in insulating oxide thickeness. Zirconia films formed with voltages 65V and 74V were rough with micro and nanometers over the anodized surface zirconia.

Acknowledgements
The authors convey their sincere thanks to Head, Department of Chemistry, University College of science, Osmania University for keen interest and encouragement. The authors are also grateful to Vice-Chancellor Prof.S. Satyanarayana, Osmania University, HYDERABAD, funding throughout this research work. One of the authors (J.P) expresses her gratitude to Ex-Heads, Profs Parameshwar murthy and S.Sondu of OUCS, Hyderabad. The authors are special thankful to scientists, INDIAN INSTITUTE OF CHEMICAL TECHNOLOGY, HYDERABAD, NUCLEAR FUEL COMPLEX,HYDERABAD and DEFENCE METALLURGICAL RESEARCH LAB (DMRL), HYDERABAD for generous help in providing AFM images, Zr-4 annealed sheet & thinning rolled of annealed sheet.

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