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Effect of Aquo-Glycolic Media of Anodic Oxides on Zr-4 by AFM with Micro and Nanostructures

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Abstract

The surface of zircaloy-4 anodized at a constant current density of 4mA.cm-2 in 0.05M ammonium oxalate and ethylene glycol at a potential 0–187V, was characterized by means of surface science technique AFM with micro and nanostructures. It was found that during anodization by aquo-glycolic media the surface oxide grows with an in homogeneous coverage on zr-4 surface modifying the topography. The incorporation of oxalate dianions from the electrolyte and ethylene glycol solvent to the surface during the anodizing process changes the topology. Anodized oxide films grown with relatively high voltages, the oxide formed over the Zr-4 in 0.05M AO+75%EG appeared rougher and protruded. Anodic oxide films were homogeneous and rough with nanosized grains. When the anodization voltage was 187 V the average roughness (Ra) of the anodic film reached 5.9nm, and the oxide formed changed abruptly to become as rough as that formed on non-anodized in micro and nanometers.

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

Introduction

Zircaloy-4 is a valve metal , which is a zirconium alloy containing Sn, Fe, Cr and O is mainly used in the Nuclear industry, especially in pressurized water reactors [1] as fuel cladding integrity has to be ensured for its entire working life in the reactor core. Anodizations of Zr-4 have been studied in electrolyte [2].The good in performance of zircaloy-4 is mainly due to the presence of protective oxide layer in oxygenated electrolytes.

Xiuli Yang et al [3] investigated anodization behavior of ammonium sebacate solution in ethylene glycol, and in several H_3PO_4 –containing electrolytes. A new mechanism is proposed for the formation of porous anodic films. The model emphasizes the close relationship between pore generation and oxygen evolution. PO_4^{3-} ions incorporated in the anodic films behave as the primary source of avalanche electrons. It is the avalanche electronic current through the barrier film that causes oxygen evolution during anodization. When growth of anodic oxide and oxygen evolution occur simultaneously at the anode, cavities or pores are formed in the resulting films.

This film diminishes the corrosion rate, minimizing the metal ion release to the aquo-glycolic media. In this work, the electrochemical oxidation of Zr-4 was focused. The electrochemical experiments were performed at room temperature. We have studied the electrochemical behavior of Zr-4 through constant current density i.e. 4mA.cm^{-2} and at room temperature. 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 aquo-glycolic media interactions is with a broad range from a few microns, where the surface topography changes the effective contact area between the 0% ethylene glycol and 25%EG,50%EG,75%EG–3.9to5.9nanometers.

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 [4-6].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 [4-8]. The ammonium oxalate is an interesting electrolyte in ethylene glycol 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 between 0–187V. It is also determined the surface changes that occur when the modified surfaces are anodized in a 25%, 50%, 75% ethylene glycol solution.

Anodic films were obtained in the range 0–187V [9]. 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 voltage was increased the films thickened. The interpretation for the abrupt changes was that the oxide was rearranging which had accumulated during earlier growth. This was implicated for the 0–187V (3.9–5.9nm) films because the anodization changed with the time the films anodized in a dilute 0.05M AO to 0.05M AO+75%EG.

In the current work, AFM was used to characterize the outside free surfaces 0–187V (3.9–5.9nm) 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 [10-12]. 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 [13]. The results of fractal analysis contain different information about the texture than do the results of Conventional analyses.

Experimental

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 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.

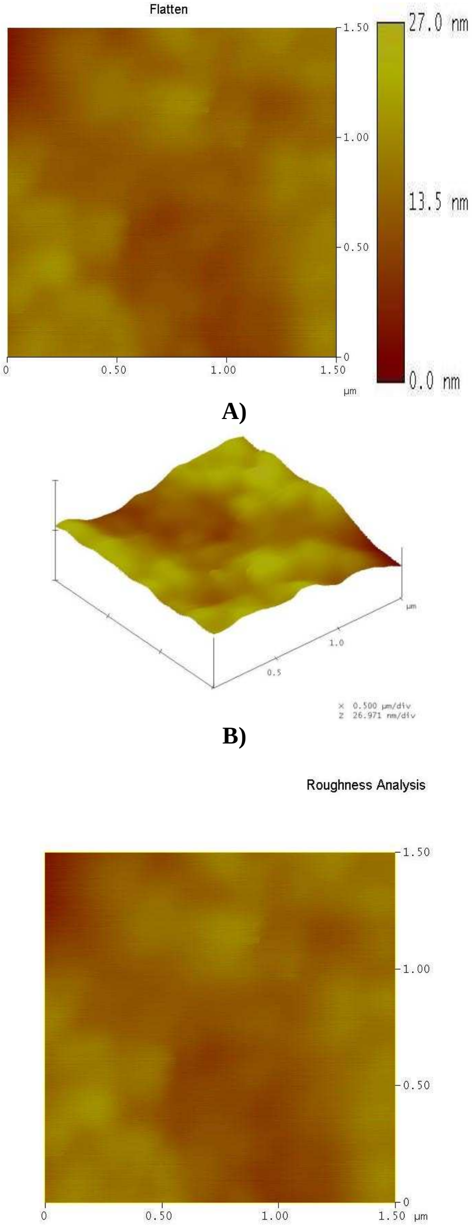
Anodic oxides of varying thickness were produced with the constant current used was a stabilized DC regulated power supply unit built by Physitech, Hyderabad. The unit employed had a provision to supply constant current 0–200mA. The current passed was measured accurately on a digital milliammeter. A 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, 89,139,157,187V, 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 4mA.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.

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

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

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.

Non-Anodized Zr-4



A)

B)

C)

Fig. 1. The micro and nanostructures of the underlying metal can be seen in these AFM images, 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.

Result And Discussion

An AFM image of the starting surface is shown in Fig. 1. The 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 oxide surfaces were measured with AFM in aqueous media (0.05M ammonium oxalate) for high voltage films (i.e. 0–89 V, 3.9nm); see, for example, Fig. 2. The AFM images for the Anodized aquo-glycolic, 0–139, films are indistinguishable from each other and the starting air-formed oxide. In addition, the oxide formed in aquo-glycolic media is ‘rougher’ than that non-anodized and anodized aqueous media. Images for thicker anodic oxides are shown in Fig. 3, 4, 5. The topologies of films formed with voltages up to 139 V are not the same as those shown in Fig. 2. For the 89 V film. For 139 V and higher films, local disruptions of the oxide become apparent, initially and eventually over the entire surface.

One explanation for the apparent initial enhanced anodic growth at 187 V are porous than those oxides found initially at 138 V. Anodic films formed on zircaloy; oxide is expected to be infiltrated with more ethylene glycol when anodized which would make the effective insulating thickness of the oxide less.

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

0.05M AO

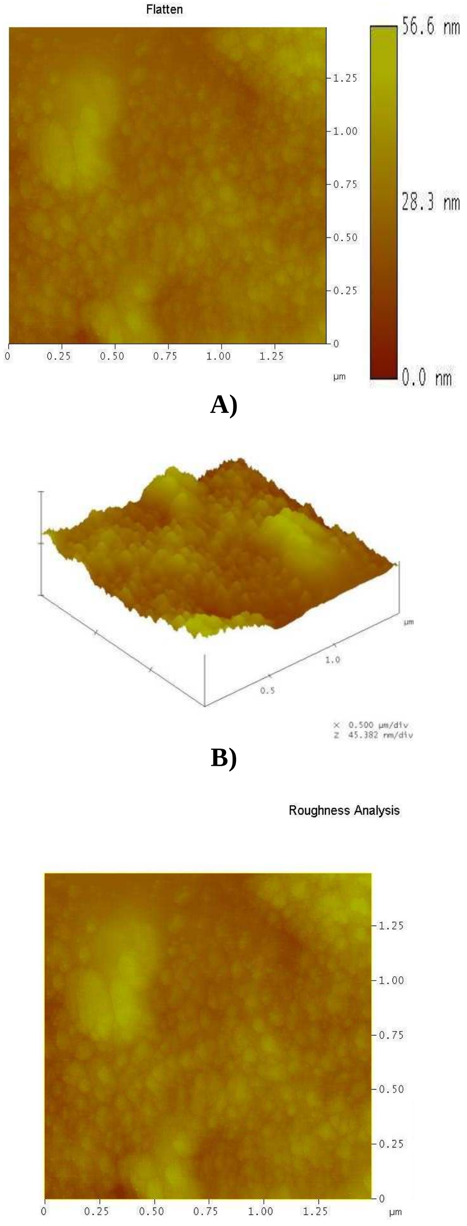


Fig.2 AFM images of 89V anodic oxides a) 1.5 µm x 1.5µm with z-axis maximum (see scale bar) b) 1.5 µm x 1.5µm height image with a height scale of 45.3 nm/div and c) the Ra and Rms are 3.9 nm and 5.1nm.

0.05M A0+25%EG

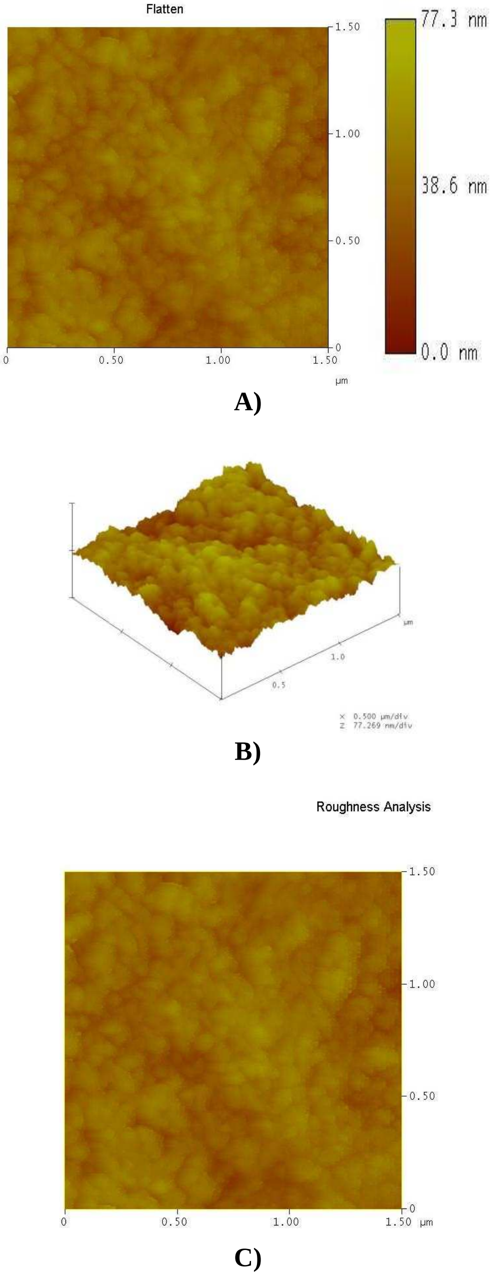
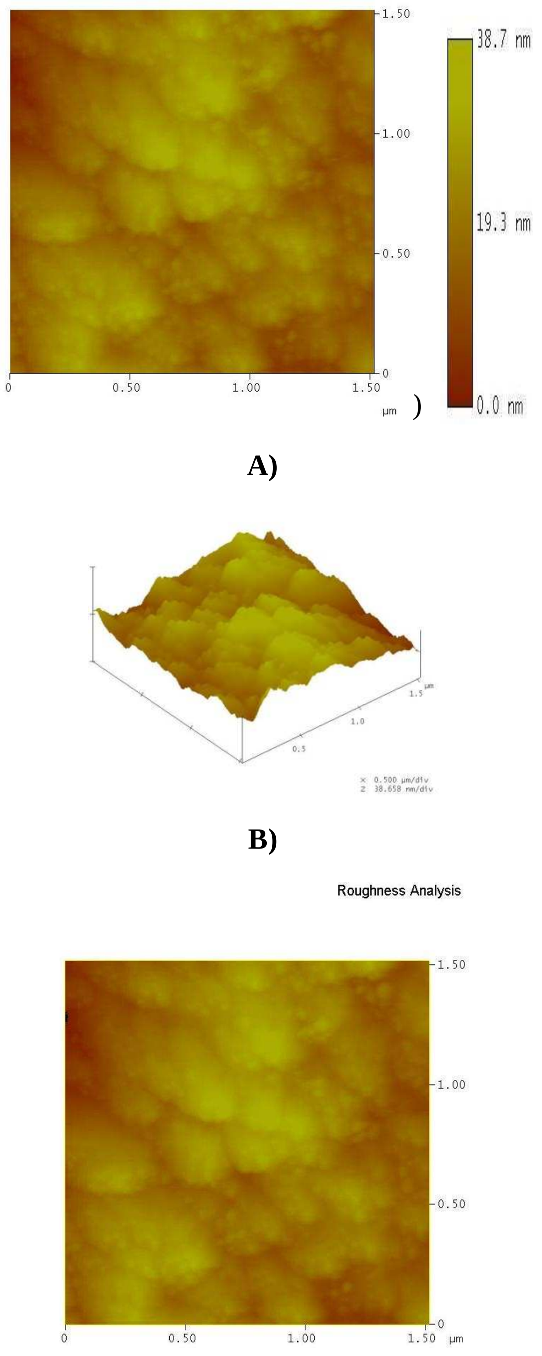


Fig.3 AFM images of 139V anodic oxides a) 1.5 µm x 1.5µm with z-axis maximum (see scale bar) b) 1.5 µm x 1.5µm height image with a height scale of 77.2 nm/div and c) the Ra and Rms are 4.8nm and 5.9nm.

During anodization the electric field across the aquo-glycolic oxides would be greater, and, because the oxide growth rate is proportional to the field strength [14].

Anodic oxides can grow relatively uninterrupted because of the large size of the grains.

0.05M AO+50%EG



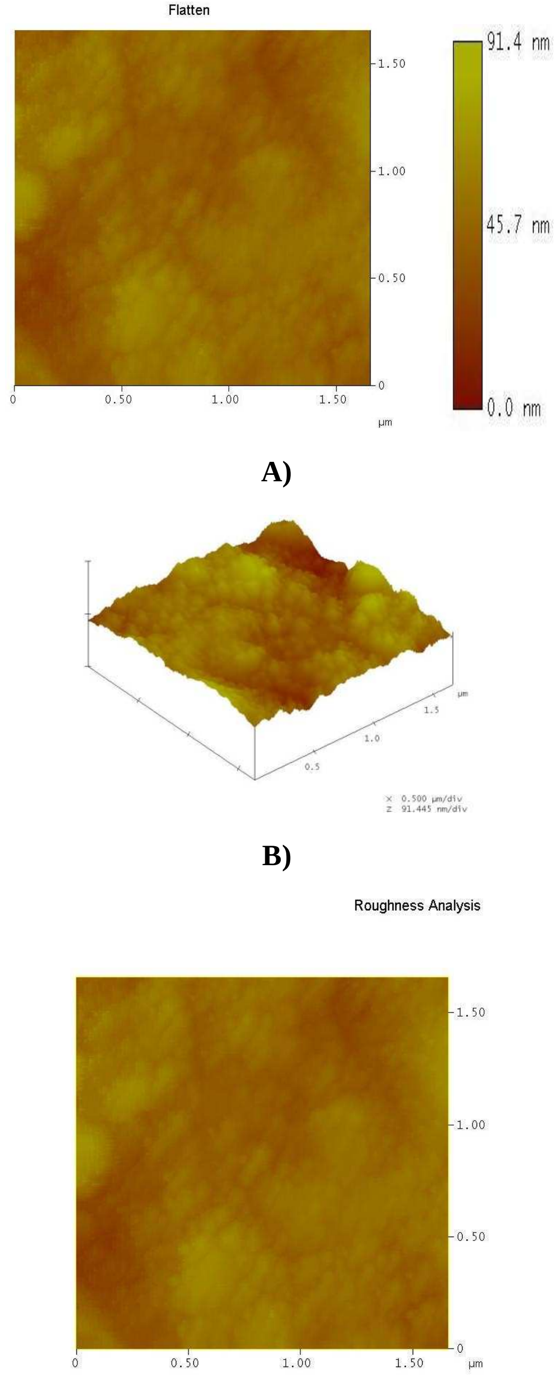
A)

B)

C)

Fig. 4 AFM results showing images of 157V 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 4.7 nm and 5.8 nm.

0.05M AO+75%EG



A)

B)

C)

Fig. 5 AFM results showing images at higher voltage 187V 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 5.9nm and 7.495nm.

In contrast, oxidation of the aqueous sheath will be more frequently interrupted by the oxidation of the aquo-glycolic sheath. The result is that the anodic films in aquo-glycolic should be more punctuated and, therefore, have much larger grain surface area for electrolyte during anodization. For zircaloy-4 used in this study oxidize predominantly to ZrO_2 which have a higher metal oxide [15]

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 0.05M A0+ ethylene glycol , as can be observed in Fig.3, 4 comparing the non-anodized surface the ones anodized at 157, 187 V [16-18]. The roughness parameters Ra and Rms were determined from AFM images. These parameters are often used to study the topography of aquo-glycolic media. Roughness is an important characteristic of aquo-glycolic media surfaces [19]

The Ra parameter corresponds to the average of a set of individual measurements of a surfaces 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 increase of roughness with increasing potential was determined. The 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.

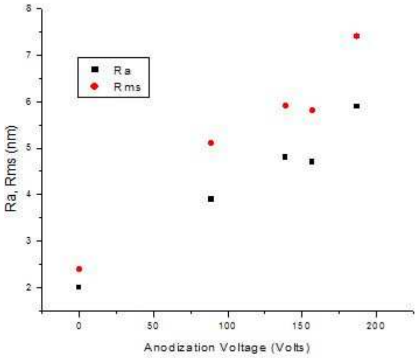


Fig.6. Evolution of roughness parameters Ra and Rms with Anodization voltage determined from AFM images in a sampling scale 1.5µm x 1.5µm.

Conclusion

During anodization in ammonium oxalate and ethylene glycol both, the chemical and roughness of zircaloy-4 are simultaneously modified. AFM measurements have been used to characterize the topology of oxide surfaces grown anodically on Zr-4. When increasing the anodizing voltage the Ra and Rms increased. The fractal dimensions of the surfaces calculated from the AFM measurements indicated that the oxides associated at 187V were much rougher than at 87V.Protrusions were seen to grow for anodized voltages. These growths are believed to be the result of ammonium oxalate and ethylene glycol decreasing the effective insulating oxide thickness. This in turn increases the local electric field during anodization,and hence, the oxidation rate. Films formed with voltages 157V and 187V were rough with micro and nanometers over the anodized surface and showed a significant rise in the overall anodized surface fractal dimension.

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