Added Iodide Ions (0.001M I^-) In 0.1M Sodium Hydroxide on the Anodic Polarized Zirconia by Faraday 1st Law and XRD

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Abstract

Anodization of zircaloy-4 in 0.1 M sodium hydroxide has been carried out. Kinetics of anodic oxidation of zircaloy-4 has been studied at a constant current density of 8 $mA.cm^{-2}$ and at room temperature. Thickness estimates were made from capacitance and faradaic data. The plots of anodization voltage vs. anodization time, Thickness by Capacitance vs. Thickness by Faradaic, and anodization rate, faradaic efficiency were calculated. Kinetics of anodic polarized oxide film formation was observed by the addition of millimolar concentration of anions (I^-). By the addition of iodide ions to the sodium hydroxide there was better improvement in the anodization rate, faradaic efficiency but there is not that much improvement in the field strength. The micro structural characterization of zirconia was studied by XRD. The anodic oxide layer is composed of cubic phase. The crystallite sizes are not stable in nanometers.

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KEYWORDS: Zircaloy-4, Anodic polarization by faraday 1st law, Faradaic efficiency, Added anions, powder XRD.

Introduction:

Zirconium based alloys are used as structural material in water-cooled thermal reactors [1, 2]. Zircaloy-4 is a alloy of 98% pure zirconium with other trace impurities. Zircaloy-4, due to their low cross section for thermal neutrons and because of their relatively good corrosion resistance against water and steam used in water cooled reactors. Anodization of zirconium alloys have been studied in some electrolytes [3-5]. Zirconium alloys are used in nuclear power plants for example as fuel cladding [6].

Lavanya et al [7] observed that only certain anions influence the kinetics of oxide film formation.

Sastry and Draper [8] studied the effect of chloride ions on the kinetics of anodization of zirconium in 0.1M KOH and observed that there is a consistent ratio of 10: 1 of [OH^-]: [Cl^-], above which the voltage sustained by any film already formed fell almost to zero and further anodization was not found to be possible.

The effect of halide ions, mainly fluoride and iodide ions, upon the kinetics of anodic oxide films formed on zircaloy-4 and niobium in 0.1M sulphamic acid, 0.1M ferrous ammonium sulphate, 0.1M LiOH were examined and it was known[9] that the presence of relatively small concentration of halide ions in the electrolyte change the efficiencies of the film growth.

Zirconia coatings are important materials for several electrical and structural high-performance applications.

In the present work, the report of the results of studies on the anodic polarization of zircaloy-4 in 0.1 M sodium hydroxide at 8mA.cm^{-2} and the effect of added anions (iodides). I have calculated the anodization rate, faradaic efficiency of anodic polarized zirconia. The anodized oxide films have been characterized by X-ray diffraction (XRD). At present the X-ray diffraction are standard ones in the microstructure characterization of materials. X-ray diffraction methods enable qualitative and quantitative phase analysis and also microstructure characterization (crystallite sizes, lattice distortions, dislocation densities, staking faults and twins probability).
Wanklyn [10] and Misch and Ruther [11] have shown anodic oxide films on zirconium are crystalline. Two modifications are well established, the cubic and monoclinic.

Panagopoulos [12, 13] examined the structure of Zr oxide growth in alkaline phosphate and sulphate solutions by using electron and X-ray diffraction techniques. He found the oxide to be cubic at thickness up to 1000Å or 100nm and a mixture of cubic and monoclinic at larger thickness.

Materials and Methods:
Zircaloy-4 was of 98% nominal purity, supplied in the form of plate by **Nuclear Fuel Complex, Hyderabad** as gift samples. Thinning of this Zr-4 plate was done by **Defence Metallergical Research Lab, Hyderabad**. Cutting of the thinned sheet was done at **tools and techniques, Hyderabad.** The chemical composition of zircaloy-4: 0.07 wt. % chromium; 0.23 wt. % iron; 1.44 wt. % tin and balance is zirconium.
In the present work, the foil samples used were cut with the aid of a punch into flag-shaped specimens of 1 cm2 working area on both side and 1 ½ cm long tag .The chemical polishing mixture consisted of acids such as HNO3, HF and water in a definite volume ratio of 3:3:1.

Electrochemical conditions
The counter electrode was a sheet of Platinum [14] (2x3 cm, weight 3.000 gm). The working electrode was the Zr-4 [15] sample. For anodizing, a double walled glass cell 100mL capacity was used. The experiments were performed in an electrolyte, 0.1 M sodium hydroxide and added anions (iodides) in 0.001M concentration.
All experiments were carried out at a constant current density of 8 mA.cm^{-2}. The experimental procedure for the anodization is given elsewhere [16]. The kinetic results calculated are formation rate in Vs^{-1}, faradaic efficiency (η) % from the conventional plots V vs. t, D_c vs. D_F.

Characterization
X-Ray diffraction (XRD) experiments were recorded using a Philips (X' Pert) diffractometer
with Cu/40Kv/30mA and K_α radiation (wavelength λ=0.1542 nm) were used to characterize the crystalline phase and size of samples. Divergence type is fixed,

Divergence (0.4785°) and receiving (0.10mm). The X-ray data collection was recorded in 10– 80° 2Θ range with 0.02° step. The time of data acquisition was chosen to obtain the intensity of the most intense diffraction line of 700counts for non-anodized material and 3000counts for zirconia X-ray patterns [17]. The average crystallite size, D (or t, thickness) is estimated using Scherrer equation [18].This equation is limited to nano-scale particles. The dislocation Density (δ) which represents the amount of defects in the crystals is estimated from the equation, $\delta = 1/ D^2$. Strain (ε) of the thin film is determined from the following formula: $\varepsilon = \beta \cos\theta/4$. XRD measurements were performed at room temperature.

Results and Discussion:

Anodic polarization of zircaloy-4 was done in various electrolytes (acidic, basic and neutral). The anodization rate, the faradaic efficiency were calculated.

Effect of substitution

The kinetics of zircaloy-4 anodized in 0.1 M sodium hydroxide. The effect of added anions was studied in 0.1 M sodium hydroxide to check whether there was enhancement in the kinetics of film formation [19, 20].

Effect of added anions

Experiments were carried out in 0.1 M sodium hydroxide + 0.001 M (I^-) anions to check the effect of the added anions. The addition of iodide ions resulted in improvement of the kinetics of anodic polarization to better extent. It is observed that the oxide film formed on the alloy consisting of two discrete layers in 0.1M sodium hydroxide appear as a single layer in presence of added anions. The results are given in **Table 1** and the plots are shown in **Figures a & b.**

Table-1 Anodization of zircaloy-4 in 0.1M NaOH + mM I^-

Electrolyte 0.1M	**Anodization rate, $V.s^{-1}$**	**Faradaic efficiency, η, (%)**	**Differential field, $F_D(MV.cm^{-1})$**
NaOH	**0.45**	**50**	**4.02**
NaOH+ mM I^-	**0.92**	**50.7**	**4.05**

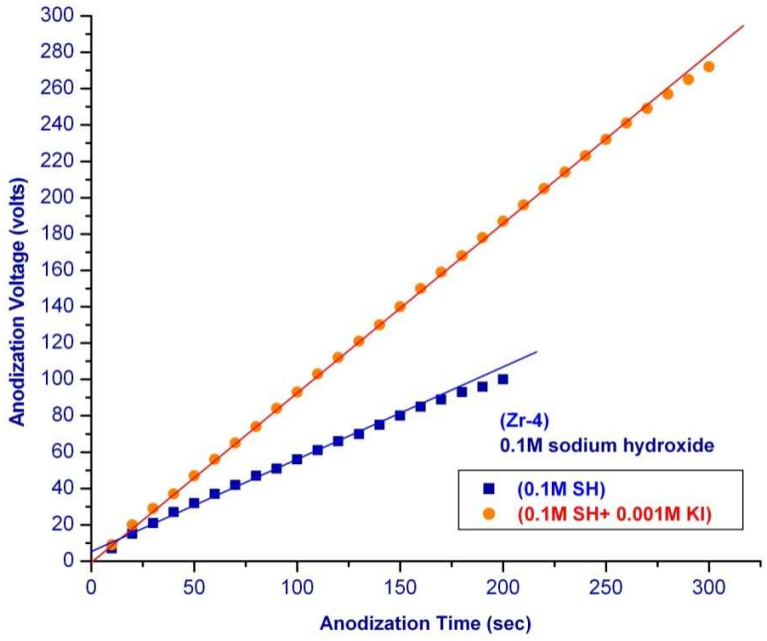

Fig a. Plot of anodization voltage as a function of anodization time in anion solution.

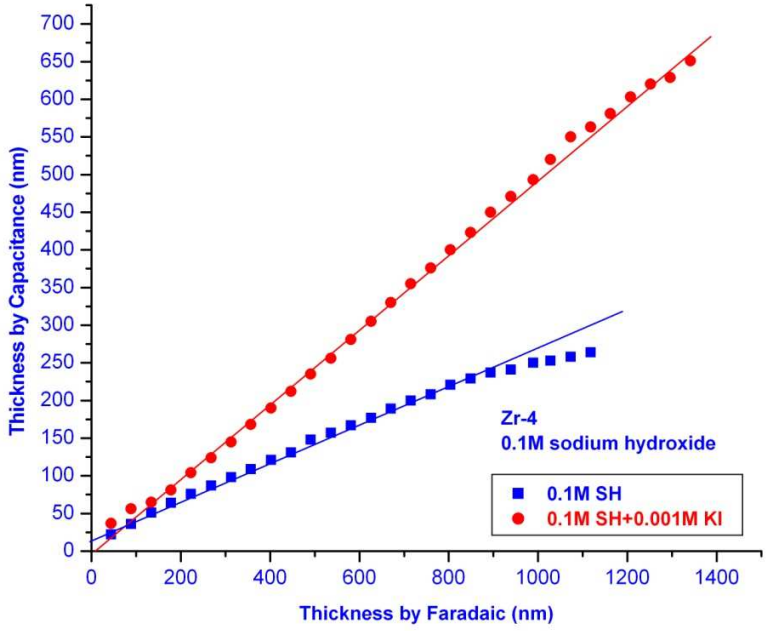

Fig b. Plot of thickness by capacitance as a function of faradaic in anion solution.

The increase in the kinetics when 0.001 I^- M of ions is added to 0.1 M sodium hydroxide can be explained by the firm incorporation of iodide ions into the layers of the oxide films. Added anions get incorporated between the ionic vacancy sites of the metal oxide films and reduce the height of the energy barrier of the movement of ions from one ionic site to another, thereby increasing the current. This incorporation increases the faradaic efficiency with much ionic current getting utilized for film formation, which implies better kinetic results.

X-ray diffraction (XRD)

Analysis of the X-ray diffraction pattern of non-anodized reveals the presence of cubic phase and anodized zirconia (ZrO_2) is also cubic phase **(Figures c, d & e).** The X-ray diffraction patterns from the (as-received) non-anodized Zr-4 and anodized zirconia are displayed in **Figures- c, d & e.** In order to clarify the zirconia phase diffraction patterns were obtained by the glancing angle XRD method. The result showed the presence of cubic zirconic phases in the anodic film. The XRD results show that the phase compositions are c- ZrO_2. The anodized zirconia in electrolyte was examined by XRD. The phase identification of samples is summarized in **Table-2.** XRD patterns of anodized zirconia formed in 0.1M sodium hydroxide. According to **Figures c, d & e** the main phases of the non-anodized and anodized oxide films are cubic zirconia. Sharp XRD peaks were observed for non-anodized and anodized zirconia. Non-anodized was shown to be a cubic and anodized zirconia ZrO_2. The very small peaks were due to the ordered arrangement of the cations [21]

The crystallite size estimated from the line width of intense line employing Scherrer equation was found to be 22nm (non-anodized), 58nm (NaOH) and 18nm (NaOH + KI) ZrO_2 only for 100% sharp peaks, one in non-anodized and the other in the oxidized zirconia are shown in **Tables- 3, 4 & 5.** The dislocation density and strain for 100% sharp peaks, values (non-anodized) and zirconia are shown in **Tables- 3, 4 & 5.**

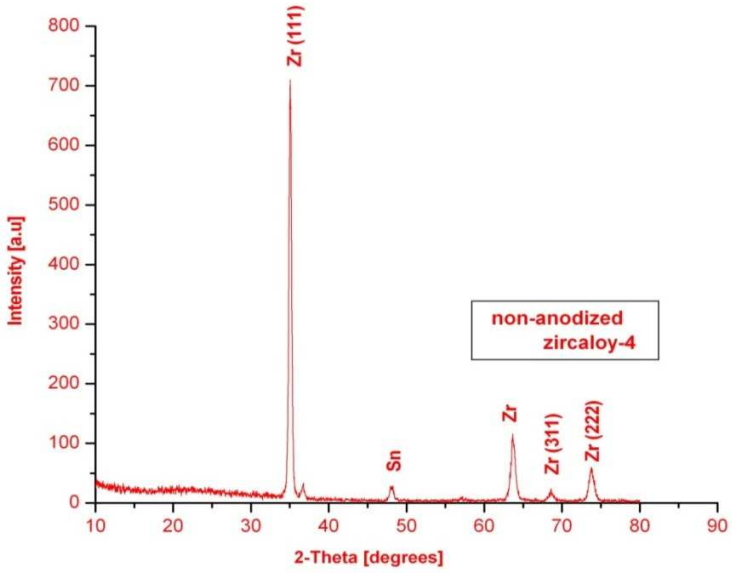

Fig c. X- ray diffraction pattern of non-anodized material.

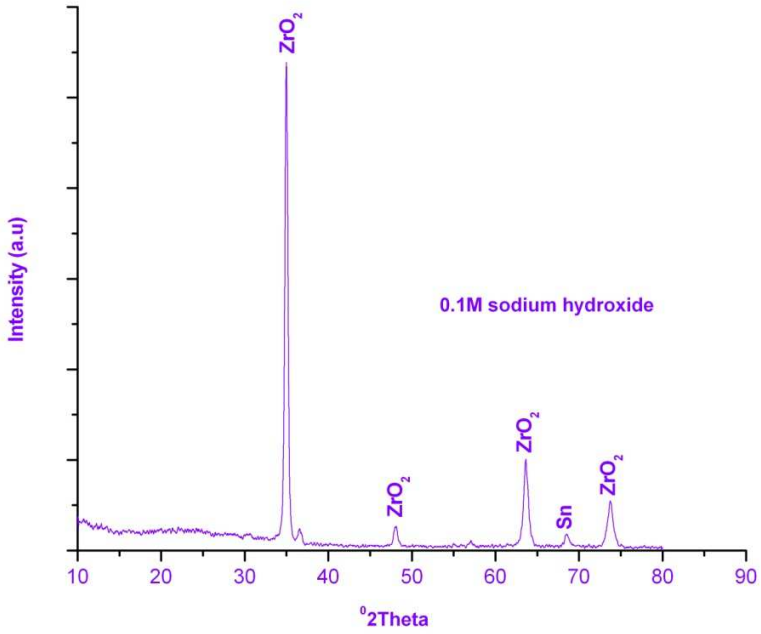

Fig d. X-ray diffraction pattern of anodized (0.1M sodium hydroxide) zirconia.

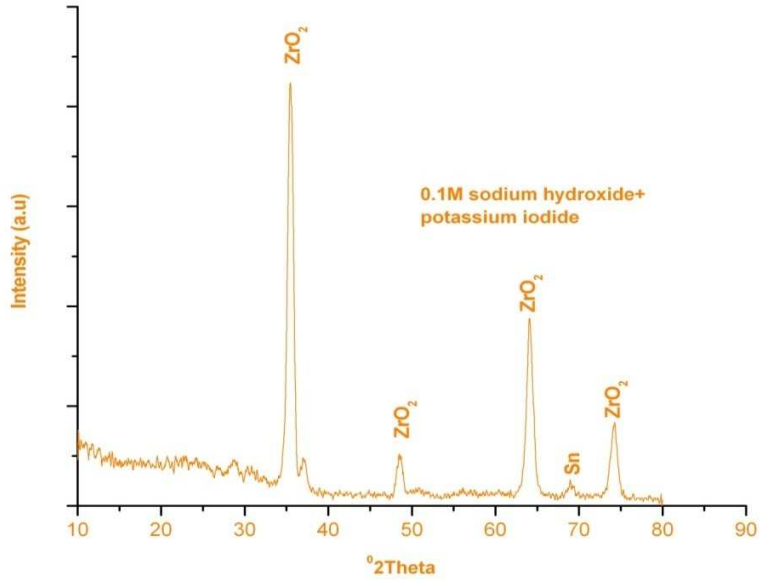

Fig e. X- ray diffraction pattern of anodized (0.1M sodium hydroxide + potassium iodide) zirconia.

Table 2: Phases identified determined by XRD

Material	Phase
Non-anodized Zr-4	Cubic
ZrO_2	Cubic

The data refer to JCPDF file, PDF # 882329 (non-anodized Zr-4), I have taken zirconium as standard values. JCPDF file, PDF# 0899069 I have taken ZrO_2 as standard values.

Table- 3: Non-anodized zircaloy-4: crystallite size, dislocation density and strain calculated values.

°2θ	FWHM	Crystallite size (nm)	δ x 10^{-3}(nm)$^{-2}$	ε x10^{-2}
35.0374	0.0787	22	2.0	1.8
36.6816	0.3149	55		
68.5570	0.3149	63		
73.7685	0.7680	27		

Table 4: Anodized zirconia (0.1M sodium hydroxide) crystallite size, dislocation density and strain calculated values.

°2θ	FWHM	Crystallite size (nm)	δ x 10^{-4}(nm)$^{-2}$	ε x10^{-2}
34.9823	0.2952	58	2.9	7.0
48.0638	0.3936	46		
63.6216	0.3149	62		
73.7492	0.4320	48		

Table 5: Anodized zirconia (0.1M sodium hydroxide + potassium iodide) crystallite size, dislocation density and strain calculated values.

°2θ	FWHM	Crystallite size (nm)	δ x 10^{-3}(nm)$^{-2}$	ε x10^{-1}
28.6440	0.9446	18	3.0	2.2
35.4400	0.2362	73		
48.5699	0.9446	19		
64.0659	0.2755	71		
74.2158	0.8640	24		

Conclusion:

The anodic polarization of zircaloy-4, the kinetics (Faradaic efficiency) is better in 0.1 M sodium hydroxide and added iodide ions. For the anodized zirconia it can be concluded that the oxide film formed on the alloy consists of two discrete layers in 0.1M sodium hydroxide and they made a single layer in the presence of added anion. The materials were characterized by XRD technique and composed as cubic phase. From XRD, the crystallite sizes were found to be 22 nm and 18 nm for the non-anodized and anodic polarized zirconia for 100%. After anodic polarization the thickness of the crystallite sizes are not stable due to the incorporation of anions. The dislocation density and (strain

is increased in NaOH and then decreased due to the addition of iodide ions) is increased in zirconia due to the addition of iodide ions.

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