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Foreign Anions are Enhanced on Thin Films upto the Breakdown Voltage Investigated Which is Applied to Multidisciplinary Science

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ABSTRACT: Zircaloy-4 studied by galvanostatic technique at constant current density 8mA.cm^{-2} in an aqueous solution of weakly organic acid electrolyte oxalic acid dihydrate and to investigate the foreign anions i.e., in basic salts of sodium carbonates and sulphates in different concentrations for zircaloy-4 samples. Foreign anions in an electrolyte 0.1M OAD, enhanced the quality of anodic polarized coloured smooth oxide films. The purpose of this scientific investigation of foreign anions is to identify the thickness over the surface of the samples. The formation of coloured oxide layer on zircaloy-4 is attributed of zirconia on the surface of the anodic oxide in the basic salt sodium carbonate and sodium sulphate solution. When the sulphate ions incorporated in the aqueous electrolyte increases the ionic conductivity of the aqueous electrolyte solution which enhances the uniformity of current distribution on zirconia. Ionic conductivity of OAD solution contains $(2\text{H}^+ + \text{C}_2\text{O}_4^{2-})$. This ionic conductivity for an anodic polarization process occurs which acts as a component that actually acts as an insulator. This process is often used to modify the surface properties of Zircaloy-4, such as increasing its corrosion resistance or altering its surface morphology. This information gives to study and calculate, the kinetic parameters of the samples at constant current density. Increase of the voltage per each ten seconds of time upto the break down voltage anodization rate increased. Increasing the anodization voltage increases the thickness of capacitance in nanometer and thickness of faradaic in nanometer marginally. There exists a breakdown voltage with sparks which could be applied on the sample. The OAD does not act as an insulator instead it facilitates the formation of an insulating ceramic oxide which is zirconium dioxide layer on the surface of zircaloy-4. The BDV role is important at the anodic polarized zirconia which are used as capacitors and dielectrics.

KEYWORDS: Zircaloy-4, Foreign Anion's, Breakdown Voltage's. Application's.

I. INTRODUCTION

Zirconium based alloys are used as structural material in water-cooled thermal reactors [1, 2]. Zirconium alloys are used in nuclear power plants for example as fuel cladding [3].

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. Zirconia nanoparticles are one of the nanomaterials applied in the synthesis of refractories, foundry sand, and ceramics[4].

II. EXPERIMENTAL SAMPLES

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 Metallurgical 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 scientific research 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.

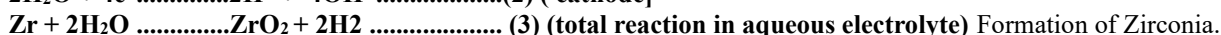
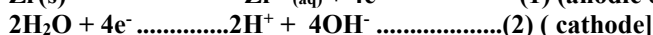
1. Electrochemical conditions

The counter electrode was a sheet of Platinum (2x3 cm, weight 3.000 gm). The working electrode was the Zr-4 sample. For anodizing, a double walled glass cell 100mL capacity was used. The experiments were performed in an electrolyte, 0.1M OAD at 8mA.cm⁻². All experiments were carried out at a constant current density of 8 mA.cm⁻². The authors investigated the growth kinetics and growth morphology of 0.1M OAD in millimolar concentrations of carbonates and sulphates of sodium. The present scientific research work is devoted to a study foreign anions which are incorporated into zirconia films. The experimental procedure for the anodic polarization by faraday 1st law is given elsewhere [5]. 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.

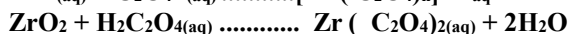
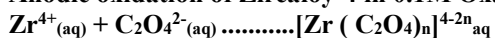
III. RESULTS AND DISCUSSION

1. Anodic oxidation of Zircaloy-4

The authors investigated the growth kinetics and growth morphology of 0.1M OAD in millimolar concentrations of carbonates and sulphates of sodium salts. The present scientific research work is devoted to a study foreign anions which are incorporated into zirconia films. Anodic polarization by galvanostatic process involves zirconium of the zircaloy-4 as anode where oxidation occurs, the zirconium in the alloy is oxidized then releasing Zr⁴⁺ ions into the solution. The below oxidation process is fundamental reaction.



Anodic oxidation of Zircaloy-4 in 0.1M Oxalic Acid Dihydrate



When oxalate anions are incorporated into the oxide film and alters the growth kinetics. The film growth process involves the movement of oxygen ions from the oxalate anions of the electrolyte OAD into the zircaloy-4. The platinum electrode is the cathode where reduction occurs. In an aqueous solution of 2H⁺ ions from the OAD, the reaction is the reduction of water to form hydrogen gas. Here platinum is an inert electrode that means does not participate in the reaction itself but it facilitates the electron transfer.

2. Oxidation of Kinetic studies:

Anodic oxide films were carried on zircaloy-4 in 0.1M oxalic acid dihydrate having in millimolar concentration of salts of sodium carbonates, sulphates at a constant current density 8mA.cm⁻² to determine the effect of carbonate and sulphate ions on the kinetics of anodic polarization of coloured oxide films. The conventional plots were drawn in **Figure 1 and Figure 2**, and it was observed that in the plots of anodization voltage vs. anodization time, thickness by capacitance vs. thickness by faradaic were found to be linear for zircaloy-4. The formation rate and faradaic efficiency were found to be increased with 0.001M sodium carbonate and 0.001M sodium sulphate but the differential field was increased with sodium carbonate (due to the incorporation of carbonate ions) and decreased with sodium sulphate due to the poor incorporation of sulphate ions than sodium carbonate. When compared with oxalic acid dihydrate the incorporation of sulphate ions is better improved. The results are summarized in the **Table- 1**.

Table-1 Anodic films formed on zircaloy-4 in 0.1M oxalic acid dihydrate.

Electrolyte	Anodization rate, V.sec ⁻¹	Faradaic efficiency, η (%)	Differential field, F_D (MV.cm ⁻¹)
0.1M OAD	0.77	58.53	5.452
0.1MOAD+ 0.001M SC	0.77	60	5.746
0.1MOAD+ 0.001M SS	0.8	78.6	5.725

3. Mobility of Ions during the Anodic oxidation of Zircaloy-4 in 0.1M OAD + 0.001mM salts of Sodium Carbonate, Sulphates:

During the anodization, if metal ions move, new layers of oxide will be formed on the outside of the existing layer, i.e., oxide/electrolyte interface. If oxide ions move, fresh layers should be produced on the inside of the existing layers i.e., oxide/ interface. If both metal and oxygen (oxide) foreign anions move, fresh layers of oxide will be formed at both the interfaces.

4. Incorporation of Foreign Anions in Anodic Oxide Films:

Anodic oxidation of Zircaloy-4 in 0.1M + OAD +0.001mM Sodium Carbonates:

The use of sodium carbonates in the electrolyte OAD was due to the need to increase the ionic conductivity of the electrolyte OAD. The use of doubly charged carbonate ions which acts as foreign anions allows for enhancement of films. The more efficient charge transfer occurred when compared with doubly charged oxalate dianions which are enhanced for the uniformity of current distribution. The capacitance increased in nanometers and the faradaic efficiency increased in nanometers [Table 1]. Sastry and Draper[6,7,8] using radio-tracer technique studied the incorporation and depth distribution of sulphate ion into anodic films formed on zirconium in 0.05M H₂SO₄, 0.1M KOH + 0.005M Na₂SO₄ and 0.05M Na₂SO₄ the distribution of sulphate ions across the oxide formed in 0.05M Na₂SO₄ was found to be uniform in the inner layers and concentrated in the outer layers.

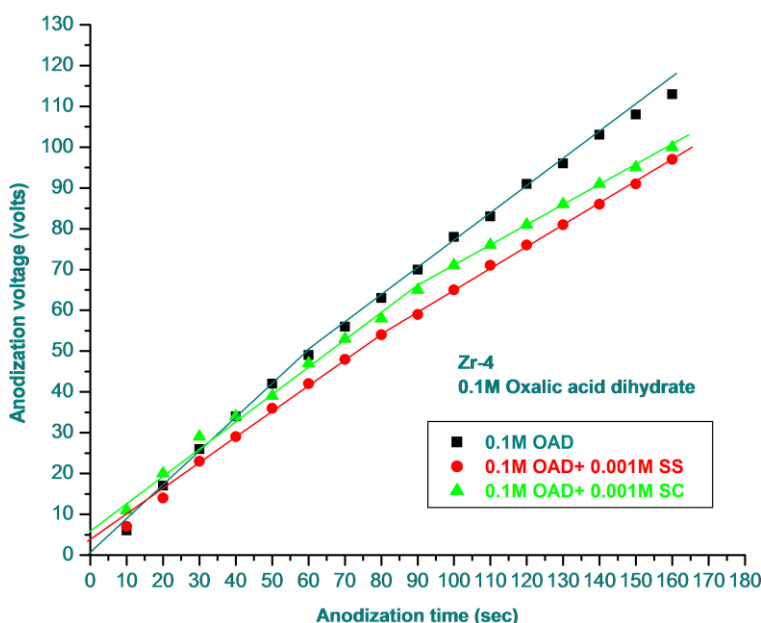


Figure 1: Plot of Anodization of Voltage vs. Anodization Time per each 10 seconds.

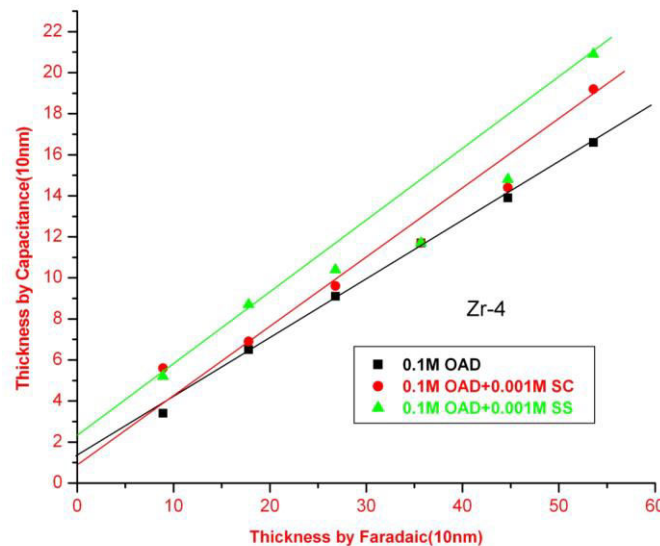


Figure 2: Plot of Capacitance vs. Faradaic to measure the thickness of oxide films.

Anodic oxidation of Zircaloy-4 in 0.1M + OAD +0.001mM Sodium Sulphates

The use of sodium sulphate in the electrolyte OAD was due to the need to increase the ionic conductivity of the electrolyte OAD. The use of doubly charged sulphates anions which acts as foreign anions allows for enhancement of films. The more efficient charge transfer occurred when compared with doubly charged oxalate dianions. The capacitance and the faradaic efficiency increased [Table 1].

5. Breakdown phenomenon of Anodic Oxide Films by Visible Sparks

Zirconia ceramics have several advantages over other ceramic materials due to the transformation toughening mechanisms operating in their microstructure that can give to components made out of them, very interesting mechanical properties[9].

The breakdown voltage is recognized in the anodization voltage- anodization time graph (figure one) by a significant increase of voltage per each ten seconds time. Later light sparks i have seen in a cell which is a breakdown voltage and no increase of voltage seen in the cell voltage. The rate of voltage increased in different concentrations in a cell [Table one]. The zirconia films conductivity increases and oxygen evolution begins within or on the oxide layer.

The formation of anodic oxide film is normally limited by a breakdown which occurs when a certain range of thickness is reached or when certain potential is reached is the breakdown voltage. We detected the breakdown voltage as a visible spark.

The breakdown voltage is one of the key parameter describes the dielectric breakdown concept or breakdown voltage concept. This BDV measures the dielectric breakdown potential of the zirconia film plays crucial role for applications such as capacitors and dielectrics.

The breakdown voltage occurred because of the conduction of avalanching in the bulk of anodic film. The foreign anions of the electrolytes provide electrons which are injected into the films during polarization. Due to high field strength, the electrons acquire very high energy cause release of secondary electrons by impact of ionization, foreign anions enhance in the multiplication of avalanches which leads to breakdown voltage of the oxide film.

IV. CONCLUSION

The anodic polarization technique facilitates the fabrication of an colour coated oxide layer on films with increased deposition foreign anions for anodization rate. It is noted that at the corners, edges and centre of the oxide films thickness is significantly higher in sodium sulphate than OAD and in foreign anions of carbonates in OAD. This information useful to investigate kinetic parameters of zircaloy-4. The presence of foreign anions in the electrolyte oxalic acid dihydrate enhances the quality of the parameters. Sodium Sulphates are environmentally friendly electrolyte which does not occur corrosion for long years also. The formation of kinetics of the oxide films on zircaloy-4 due to the super active role of incorporation of foreign anions such as sulphates and carbonates of salts sodium in the oxide film growth of anodic polarization mechanism. Oxide films are applicable for ceramics. Anodic oxide films formed in suitable conditions have versatile applications as resistors, dielectrics, reflectors, rectifiers, semiconductors and photoanodes etc.

V. ACKNOWLEDGEMENT

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