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Added Anions to Zirconia as a Ceramic Material

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Abstract: Anodic polarization 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. Anodic polarized coloured zirconia film was observed by the addition of millimolar concentration of anions (Cl^-). By the addition of chloride ions to the oxalic acid dihydrate was better improvement in the anodization rate, faradaic efficiency field strength zirconia ceramic is recorded for exhibiting enhanced mechanical properties for manufacture of medical devices as well as biocompatability and have biological properties also. In future research needed to validate zirconia ceramic applications
Keywords: Added anions to zirconia, Faradiac efficiency, zirconia ceramic material

I. INTRODUCTION

Transformation- toughened zirconia is prone to be a successful alternative in the different clinical situations compared to other all-ceramic systems [1].

Paertially-stabilised zirconia ceramics are increasingly utilised in hard-wearing and high temperature applications,due to the material's exceptional thermochemical properties. Abrasives, enamels, insulation, protective coatings, refractories.

Zirconia ceramics have several advantages over other ceramic materials due to the transformation toughning mechanisms operating in their microstructure that can give to components made out of them, very intresting mechanical properties[2].

Zirconia nanoparticles are one of the nanomaterials applied in the synthesis of refractories, foundrysand, and ceramics[3]. Zircaloy-4, although not yet in use as a reactor material because of its newness, has been recommended as the pressure-tube material in the design of the CANDU reactor. Considerable experimental work pertinent to reactor applications is being performed at various locations on zirconium-basealloys[4].

Sastry and Draper [5] 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. 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[6] 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. Zirconium phosphate is used in the ion-exchange medium in kidney dialysis machines. Zirconium alloys are corrosion resistant and biocompatible, and therefore can be used for body implants. Archibald and Leach [7] observed that fluoride ions in the surface preparation or in found that by a suitable choice of surface preparation, anodizing electrolytes and growth rate, anodic oxide film could be grown on the surface of zirconium, having tensile, compressive or effectivelyzerostress

In the current research work, the report of the results of studies on the anodic polarization of zircaloy-4 in subsequent anodizing of zirconium have a profound effect upon the stresses in the zirconium oxide anodic layer. The 0.1M oxalic acid dihydrate at 8mA.cm^{-2} and the effect of added anions (chlorides). I have calculated the anodization rate, faradaic efficiency and field strength of anodic polarized zirconia.In future research needed to validate zirconia ceramic applications

II. 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 current 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.

A. *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 oxalic acid dihydrate and added anions (chlorides) in 0.001M concentration.

All experiments were carried out at a constant current density of 8 $mA.cm^{-2}$. The experimental procedure for the anodic polarization by faraday 1st law is given elsewhere [8]. The kinetic results calculated are formation rate in Vs^{-}, faradaic efficiency (η) % from the conventional plots V vs. t, D_c vs. D_F.

III. 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.

A. *Effect of Substitution*

The kinetics of zircaloy-4 anodized in 0.1M oxalic acid dihydrate. The effect of added anions was studied in 0.1 M oxalic acid dihydrate to check whether there was enhancement in the kinetics of film formation.

B. *Effect of Added Anions*

Experiments were carried out in 0.1 M oxalic acid dihydrate + 0.001 M (Cl^{-}) anions to check the effect of the added anions. The addition of chloride 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 oxalic acid dihydrate appear as a single layer in presence of added anions. The results are given in Table 1 and the plots are shown in Figures 1&2.

Table 1 Anodized oxide 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 NH_4Cl^{-}	0.82	62.6	5.899

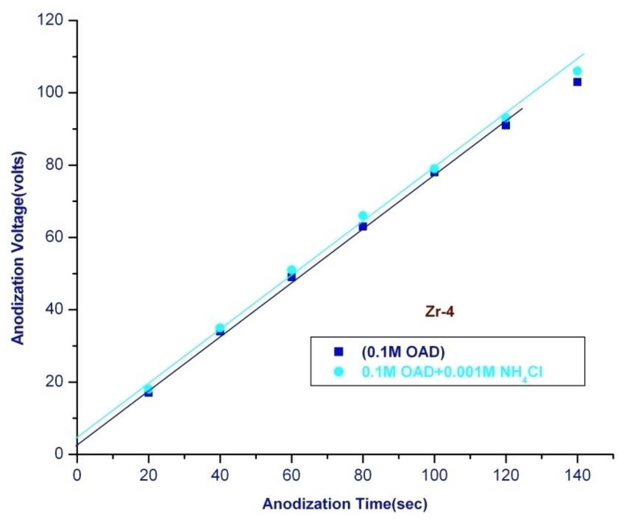

Fig 1. Plot of anodization voltage as a function of anodization time in anion solution.

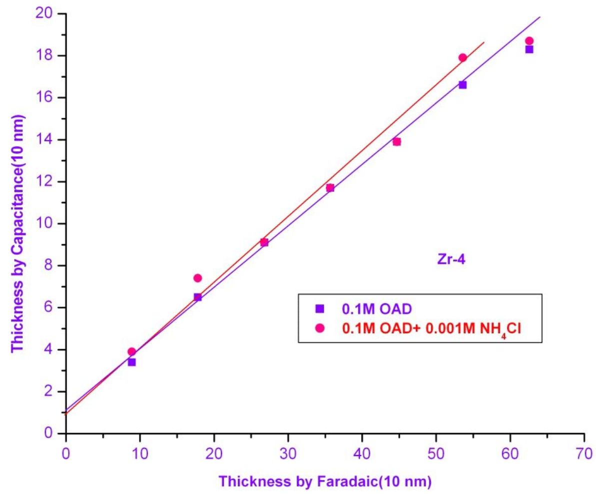

Fig 2. Plot of thickness by capacitance as a function of faradaic in anion solution

The increase in the kinetics when 0.001 Cl^{-} M of ions is added to 0.1 M oxalic acid dihydrate can be explained by the firm incorporation of chloride 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.

IV. CONCLUSION

The kinetics of zircaloty-4 is better in 0.1 M oxalic acid dihydrate and added chloride ions. Kinetics of anodic polarized coloured zirconia film was observed by the addition of millimolar concentration of anions (Cl^{-}). For the anodized zirconia it can be concluded that the oxide film formed on the alloy consists of two discrete layers in 0.1M oxalic acid dihydrate and they made a single layer in the presence of added chloride. Zirconia ceramic is recorded for exhibiting enhanced mechanical properties for manufacture of medical devices as well as biocompatability and have biological properties also. In future research needed to validate zirconia ceramic applications**.**

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