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Incorporation of Anions into the Anodic Oxide Films Formed on Zircaloy-4: Kinetic and Mechanistic studies with Radiotracer Techniques.

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ABSTRACT

The kinetics of anodic oxidation of Zircaloy-4 in 0.1M sulphamic acid have been studied under galvanostatic conditions at a current density of 8mA.cm^{-2} and at room temperature (300K). The conventional plots of formation voltage vs. time and reciprocal capacitance vs. time were found to be non-linear. But with the addition of a millimole (mM) of sodium phosphate to 0.1M sulphamic acid, the conventional plots have become linear even upto break down voltage. This marked improvement in the kinetics can be attributed to the incorporation of phosphate ion into the oxide film. This was confirmed by radiotracer techniques using ^{32}P isotope. The uptake and distribution of $^{32}PO_4^{3-}$ content in the film has suggested a mechanism for the growth of oxide film via interstitial movement of oxide ions. Migration of anion impurities from one layer to another layer in the oxide film has also been established by transferring the specimen from active to inactive solution of the electrolyte and vice versa and thinning subsequently

Keywords: Anodic oxidation, galvanostatic conditions, sulphamic acid, radiotracer techniques, interstitial movement, thinning.

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INTRODUCTION

Anodization is a subject of renewed interest both from a practical and theoretical point of view. Anodic oxide films formed on zirconium and its alloys are useful in the electrical and electronic components, corrosion protection and for decorative purposes. Zirconium alloys due to their low cross-section for thermal neutrons and because of their relatively good corrosion against water and steam, they are used in water cooled reactors. Several other applications have been reviewed by Aladjem [1].

When the valve metals are anodized in some suitable electrolytes it was observed that small amounts of impurities mainly anions are incorporated into the oxide depending on the nature of electrolyte used. This was supported by Guntherschultz and betz [2].

Sastry and Draper [3-4] using radio-tracer technique studied the incorporation and depth distribution of sulphate ion into anodic films formed on zirconium in 0.05M H_2SO_4, 0.1M KOH + 0.005M Na_2SO_4 and 0.05M Na_2SO_4 the distribution of sulphate ions across the oxide formed in 0.05M Na_2SO_4 was found to be uniform in the inner layers and concentrated in the outer layers. They also studied the incorporation of chloride ion into ZrO_2 films using ^{36}Cl as marker.

Zakhalov et al [5] observed linear galvanostatic curves in the anodic oxidation of metals over a broad range of current density values (0.1-10 $mA.cm^{-2}$). They observed 100% current efficiency. During anodization they found different colours covering entire spectrum on the surface of the different voltages. Young [6] observed that Nb_2O_5 films are crystalline and the films recrystallize under the influence of applied field. Leach and Panagopoulas [7] studied the growth kinetics of anodization of zirconium in Na_3PO_4 and NaOH solutions. They showed that the anodization rate, current efficiency and electric field were found to be higher in the phosphate than in the hydroxide for the same growth current. This behaviour was attributed to the incorporation of PO_4^{3-} into the growing oxide. Maraghini and Serra [8] used radioactive phosphate and sulphate containing solutions to investigate the incorporation of these anions into the films formed by anodic oxidation.

Randall et al [9] showed that the large amounts of phosphate were incorporated uniformly in the outer layer which decreased the permittivity and ionic conductivity of the oxide compared to films formed in dilute sulphuric acid of comparable concentration. The two layer nature of anodic oxide film grown in H_3PO_4 was confirmed by Delloca and Young [10] by ellipsometric studies. Infrared transmission spectra of anodic films showed that anions such as phosphate, sulphate and carboxylate were incorporated [11].

Shoba et al [12] have studied the anodization of hafnium in phosphate baths using ^{32}P and confirmed the mechanism of film formation is via vacancy diffusion plus some exchange interstitial capture of oxide ions.

Amsel and Samuel [13] studied the ion transport mechanism for the growth of oxide films during the anodic oxidation of Aluminium and Tantalam. Tracer technique was used to determine the order of the atoms in the film. Randall et al [14] put forward that depth distribution of $^{32}PO_4^{3-}$ is conserved suggesting vacancy diffusion.

Raghunath Reddy [15] studied the incorporation of phosphate ions during anodic oxidation of Nb in 0.05M picric acid. Several others [16-17] also supported these studies and explained the mechanism of film formation.

In the Present work, kinetic and mechanistic aspects of anodic oxide film formation on Zircaloy-4 in 0.1M sulphamic acid + 0.001M Na_3PO_4 having radioactive phosphate ^{32}P are studied.

EXPERIMENTAL

All the experiments were carried out using 0.2 mm thick, annealed sheet of Zircaloy-4 of more than 99.5% purity supplied by NFC, Hyderabad as a gift sample. The Zr-4 specimens used were cut with the aid of punch giving working area of 1cm^2 on either side and a tag of about 2 cms in length. The Zr-4 specimens were polished to mirror finish by using chemical polishing mixture. The composition of the polishing mixture is 1:3:3 by volume of HF, HNO_3 and H_2O.

Adams et al., [18-19] and Willis et al [20] used chemically polished specimens which gave higher values of current efficiency at higher current densities. A laboratory scale undivided cell was assembled with a 100ml glass beaker, fitted with a PVC cover having slots to introduce the anode and cathode. The platinum cathode had a 20cm^2 superficial area to make the double layer capacitance as large as possible. For radioactive experiments a specially designed cell of 20 ml capacity in which a platinum cathode of “U” shape having 3cm x 1cm dimensions is arranged at the bottom of the cell. The Zr-4 specimen is suspended inside the “U” shape cathode.

The thickness of anodic films formed was calculated from capacitance measurements. A digital LCR meter type VLCR-17 supplied by Vasavi electronics Pvt. Ltd. Was used to measure the capacitance. The constant current generator used was supplied by Powertronics, Hyderabad.

Radio-Tracer Measurements and Thinning experiments

An end-window G.M. Counter, built by Nucleonix Pvt. Ltd, Hyd, with an automatic timer and counting system was used to measure the radioactive phosphate content of the film. Thinning experiments were carried out using 0.5µ diamond paste to examine the depth distribution of phosphate ion impurities.

All electrolytes used were made from analytical grade material and all solutions were prepared with doubly distilled water and stored in closed bottles

RESULTS AND DISCUSSIONS.

The chemically polished Zircaloy-4 specimens were anodized separately in 0.1M sulphamic acid at a constant current density of 8mA.cm^{-2} and at room temperature (300K). The time taken for anodization and the capacitance of the film formed were measured at an interval of 20V by interrupting the constant current circuit. The plots of formation voltage vs. time and reciprocal capacitance vs. time were shown in Figs-1 and 2.

However a marked improvement in the kinetics of film formation with uniformity upto 240V is found with the addition of a millimole of Na_3PO_4 to 0.1 M sulphamic acid.

The Kinetic results, formation rate, current efficiency and differential field obtained are given in Table-1. The improvement observed in the kinetics is attributed to the incorporation of anion impurities (PO_4^{3-}) into the anodic film.

Figure 1: Plot of formation voltage as a function of time on Zr-4

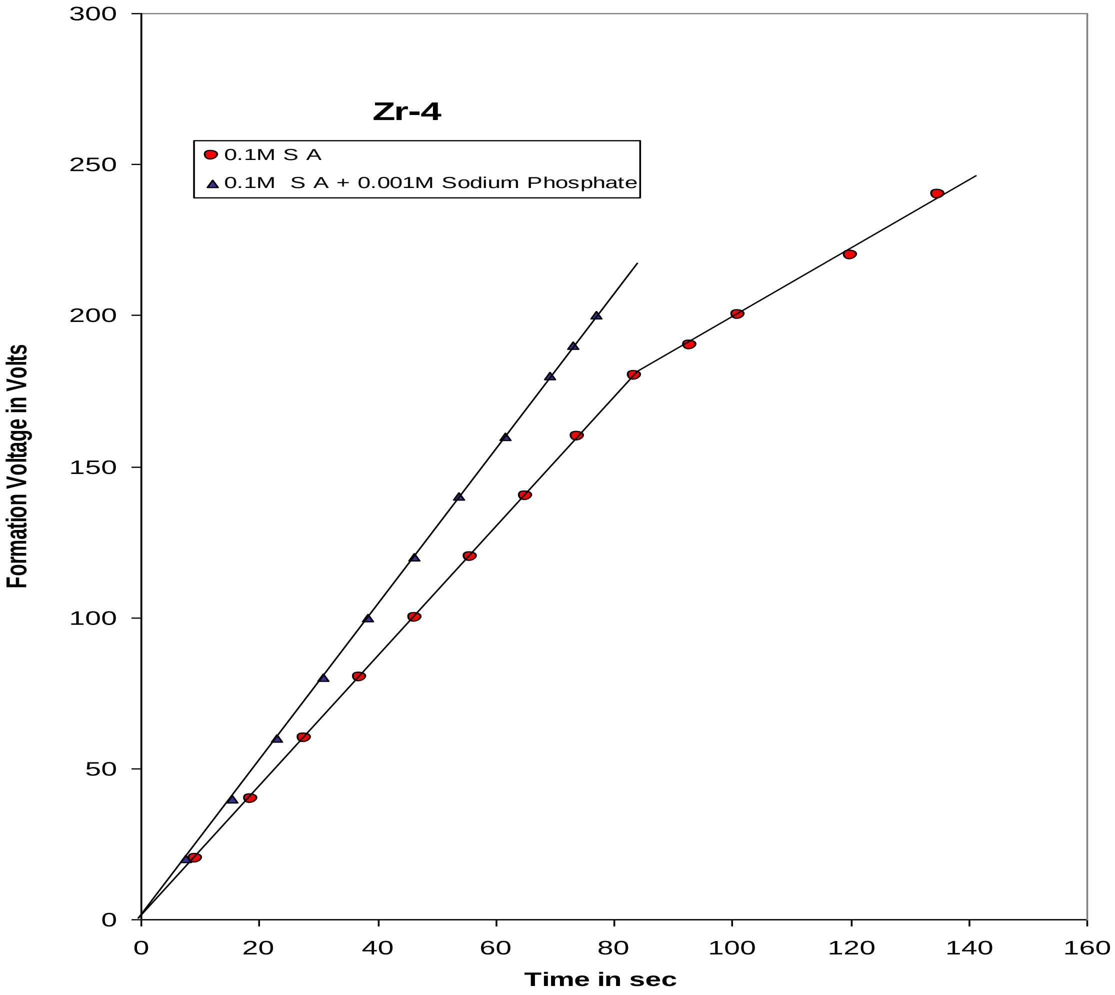


Figure 2: Plot of reciprocal capacitance($\mu F^{-1} cm^{2}$) as a function of time on Zr-4

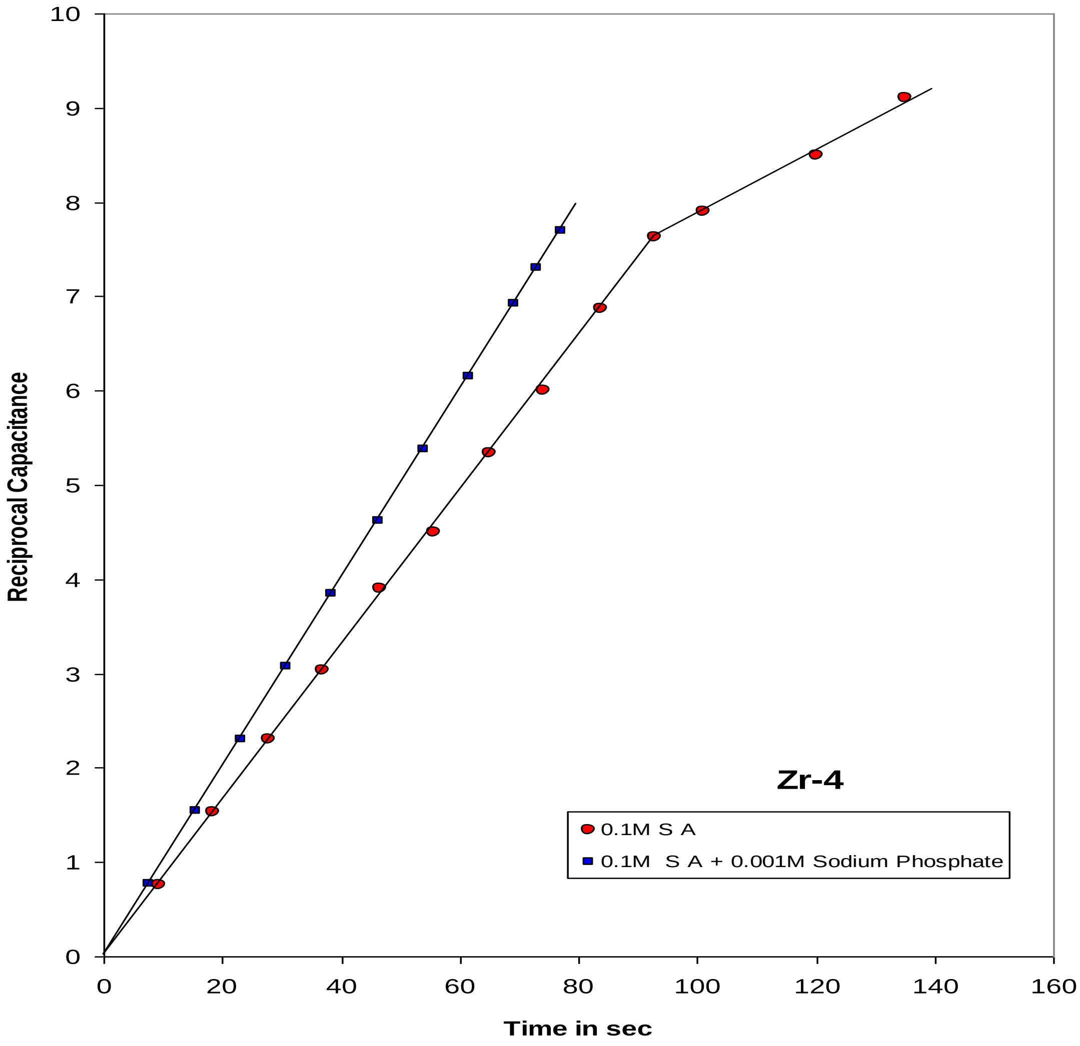


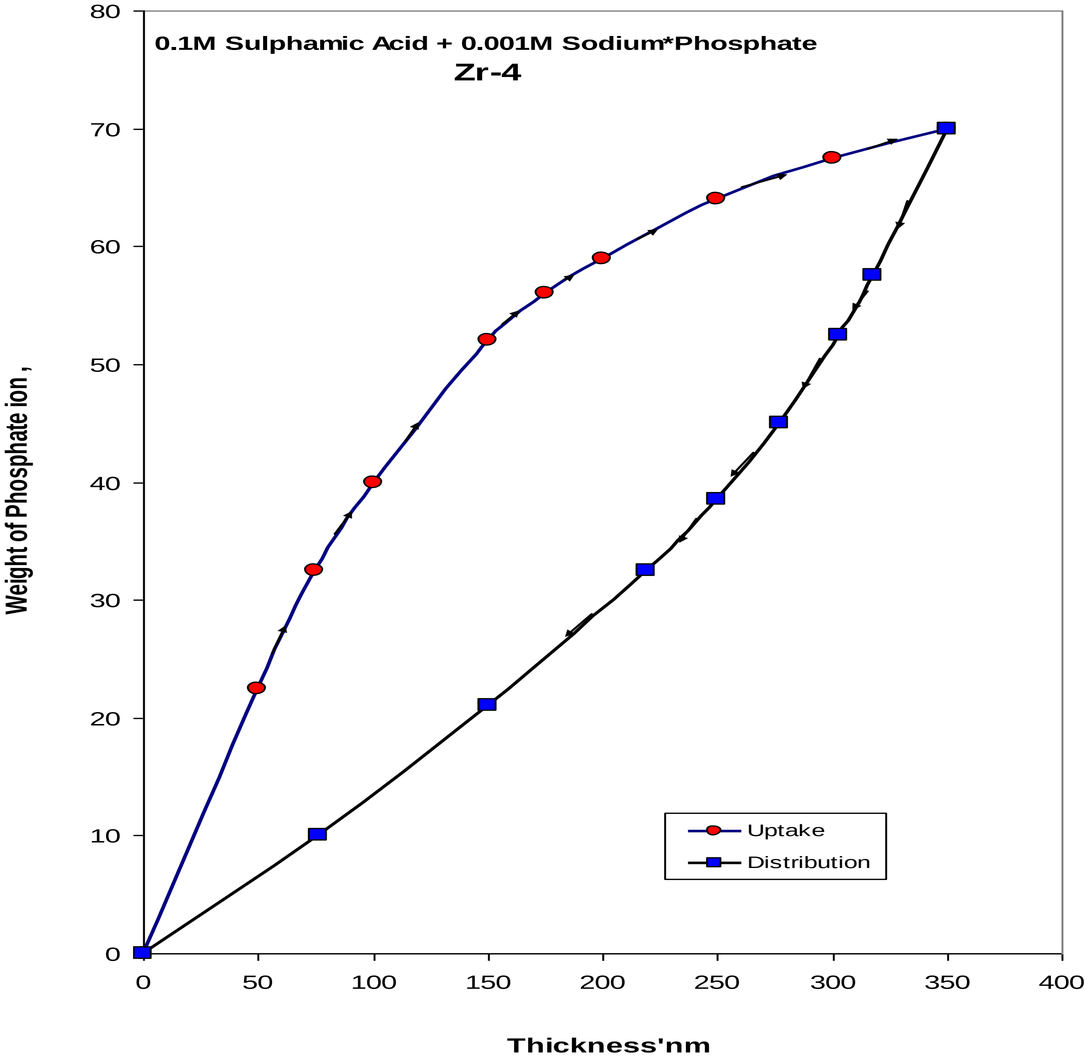
Table-1: Anodic films formed on Zircaloy-4 in 0.1M Sulphamic Acid (SA)

Electrolyte	Formation rate, dV/dt ($V.s^{-1}$)	Current efficiency, η (%)	Differential field, F_D ($MV.cm^{-1}$)
0.1M SA	2.15	80.23	6.00
0.1M SA + 0.001M PO_4^{3-}	2.60	97.50	5.96

Radio-tracer studies mechanism

For the confirmation of incorporation of phosphate into the anodic oxide films formed on Zircaloy-4 in 0.1M sulphamic acid + 0.001M Na_3PO_4, an active solution of 8ml volume containing 2 drops of radioactive $Na_3{}^{32}PO_4$ was taken in the specially designed cell as described in the experimental part. Specific activity of the solution was 0.25μCi/mM. From the counts measured at regular intervals of 40 V the weight of the phosphate ion uptake was estimated and shown in the fig-3 (uptake curve). The uptake is found to be uniform upto 240V. From the thinning experiments using o.5 μ diamond paste the distribution curve is also plotted and shown in the Fig-3 (distribution curve). From the nature of the uptake and distribution curves the mechanism of anodic film formation on Zr-4 in 0.1M sulphamic acid + 0.001M Na_3PO_4 may be in the reverse order via interstitial movement of oxide ions. The uptake and distribution curves followed reverse order as shown in Fig-3.

Figure 3: Uptake and distribution of $^{32}PO_4^{3-}$ vs. Thickness 0.1M Sulphamic acid + 0.001M **Na_3PO_4**
(Weight of phosphate ion in micrograms per centimetre)

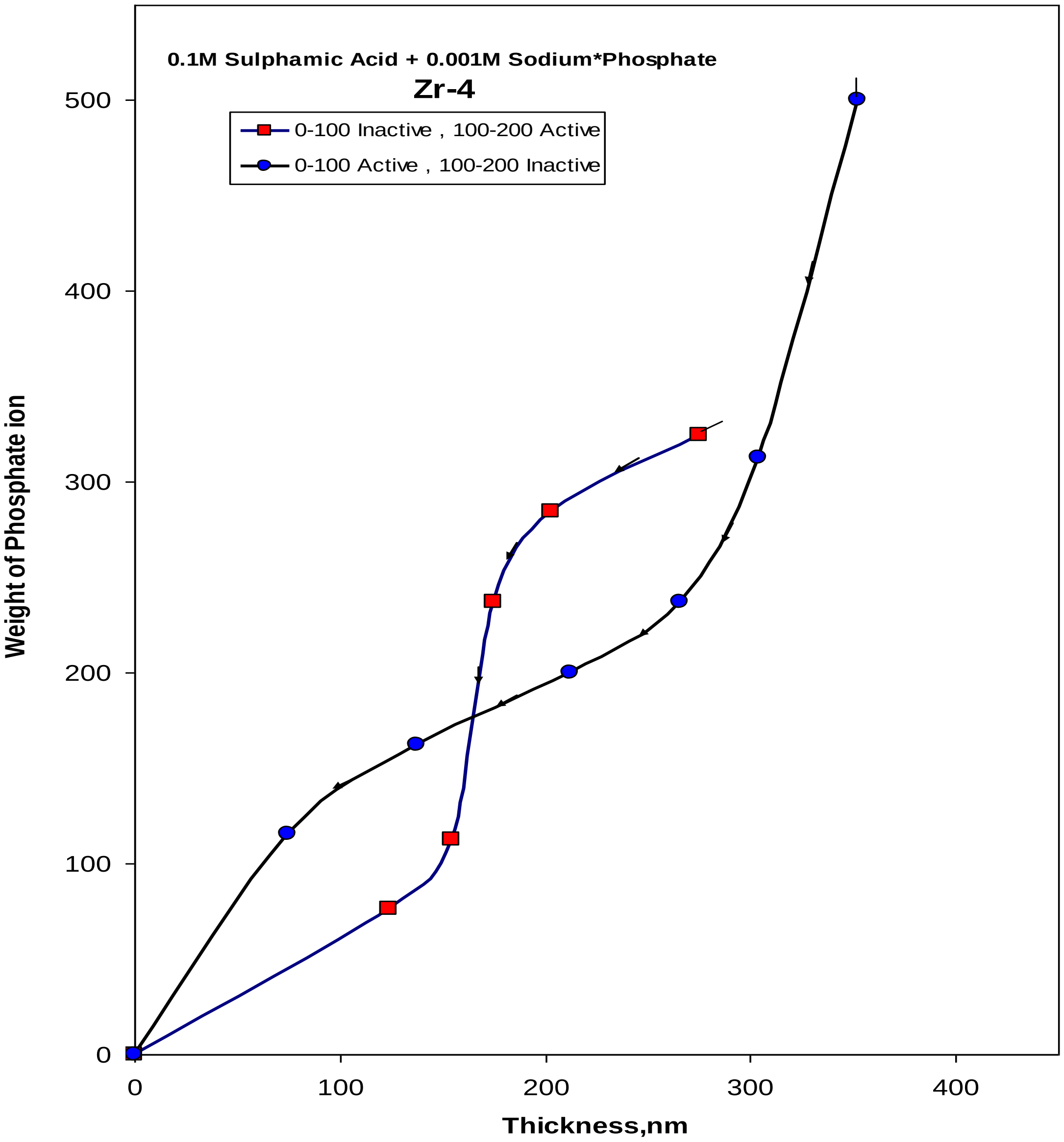


Migration of anion impurities:

In order to understand the migration of anion impurities into the different layers of oxide films, active-inactive and vice-versa transformations were carried out upto 200V for which part of the film was formed in the normal inactive solution of 0.1M sulphamic acid + 0.001M Na_3PO_4 and the remaining part of the film was formed in the active solution. The conditions distribution curves are shown in Fig-4.

Figure 4: Distribution curves for the film formed partly in active and partly in the inactive 0.1M sulphamic acid + 0.001M Na_3PO_4

(Weight of phosphate ion in micrograms per centimetre)



CONCLUSION

A marked influence and improvement in the kinetics of anodic oxide film formation on Zr-4 in 0.1M sulphamic acid has been observed with the addition of 1mM of phosphate ions. Radiotracer studies confirmed the implantation and migration of phosphate ions in the oxide film. From the nature of uptake and distribution curves, the mechanism of the growth of the anodic oxide film formation on Zr-4 in 0.1M sulphamic acid + 0.001M Na_3PO_4 is found to be reverse order via interstitial movement of oxide ions.

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