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Mechanism of anodic oxide film growth – Radiotracer techniques using ^{32}P

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ABSTRACT

The kinetics of anodic oxidation of zircaloy-4 have been studied in 0.1M L-ascorbic acid without and with addition of a millimole of sodium phosphate at a constant current density of $8 \text{ mA}\cdot\text{cm}^{-2}$ and at room temperature (300 K). The addition of phosphate ions found to improve the kinetics of film formation. This trend and mechanism of anodic oxide film growth is confirmed from radio-tracer techniques using labelled phosphate ions

Key words: Anodic oxide film, phosphate ions, migration, mechanism, radio-tracer studies.

INTRODUCTION

Zakhalov et al. [1] observed linear galvanostatic curves in the anodic oxidation of metals over a broad range of current density values ($0.1\text{--}10 \text{ mA}\cdot\text{cm}^{-2}$). They observed 100% current efficiency. During anodization they found different colours covering entire spectrum on the surface of the different formation voltages.

Bairachny and Gomofov [2] examined the effect of nature and composition of electrolyte on the properties of oxide films of niobium. They conducted anodic oxidation using a potentiostat under galvanostatic conditions at currents of 30–100 mA in 1-10% solutions of H_3PO_4 upto 100V. During oxidation in H_3PO_4 at $\text{pH} < 0.8$ (concentration < 10%), they found that PO_4^{3-} was introduced into the composition of the anodic oxide film. In this case, non-stoichiometric oxides

of variable composition are formed including oxides of variable composition are formed including oxides of Nb and P.

Young [3] observed that the Nb₂O₅ films are crystalline and the films recrystallize under the influence of applied field. Leach and Panagopoulos [4] studied the growth kinetics of anodization of zirconium in Na₃PO₄ 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 PO₄³⁻ into the growing oxide. Maraghini and Serra [5] used radio-active phosphate and sulphate containing solutions to investigate the incorporation of these anions into the films formed by anodic oxidation.

Randall et al. [6] 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 H₂SO₄ of comparable concentration. The two layer nature of anodic oxide film grown in H₃PO₄ was confirmed by Delloca and Young [7] by ellipsometric studies. Infrared transmission spectra of anodic films showed that anions such as phosphate, sulphate and carboxylate were incorporated [8].

Shoba et al [9] have studied the anodization of hafnium in phosphate baths using ³²P and confirmed the mechanism of film formation is via vacancy diffusion plus some exchange interstitial capture of oxide ions.

Amsel and Samuel [10] studied the ion transport mechanism for the growth of oxide films during the anodic oxidation of aluminium and tantalum. Tracer technique was used to determine the order of the atoms in the film. Randall et al [11] put forward that depth distribution of ³²PO₄³⁻ is conserved suggesting vacancy diffusion.

Raghunath Reddy [12] confirmed the incorporation of phosphate into the anodic oxide films formed on niobium in 0.05M picric acid + 0.001M Na₃PO₄ having radio-active isotope ³²P. Aparna [13] confirmed the incorporation of phosphate into the anodic oxide films formed on metals such as Zr-2, Ti and Ta in 0.1M picolinic acid / sodium methoxide + 0.001M Na₃PO₄ having radio-active isotope ³²P. Shukla [14] also confirmed the incorporation of phosphate into the anodic oxide films formed on Zr-4 and Nb in 0.1M sulphamic acid / lithium hydroxide + 0.001M Na₃PO₄ having radio-active isotope ³²P

In the present work, mechanism of anodic oxide film formation on zircaloy-4 in 0.1M L-ascorbic acid + 0.001M Na₃PO₄ having radio-active isotope ³²P are studied.

EXPERIMENTAL SECTION

All the experiments were carried out using 0.2 mm thick, annealed, rolled sheet of zircaloy-4 of more than 99.5% purity supplied by NFC, Hyderabad as a gift sample. The zircaloy-4 specimens used were cut with the aid of a punch giving working area of 1 cm² on either side and a tag of about 2 cm in length. Specimens were polished to mirror finish by using chemical polishing mixture which consists of concentrated acids- HNO₃, HF and H₂O in the definite volume ratio.

Adams *et al.*, [15, 16] and Willis *et al.*, [17] used chemically polished specimens which gave higher values of current efficiency at higher current densities. A laboratory scale undivided cell was assembled with a 100 ml glass beaker, fitted with a PVC cover having slots to introduce the anode and cathode. The platinum cathode had a 20 cm² superficial area to make the double layer capacitance as large as possible. For radio-active experiments a specially designed cell of 20 ml capacity in which a platinum cathode of "U" shape having 3 cm x 1 cm dimensions is arranged at the bottom of the cell. The zircaloy-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 (P) Ltd was used to measure the capacitance. The constant current generator used was supplied by Powertronics, Hyderabad.

An end window G.M. counter built by Nucleonix Pvt Ltd, Hyderabad, with an automatic digital timer and counting system was used to measure the radio-active phosphate content of the film. Thinning experiments were also made using 0.5 μ diamond paste to examine the depth distribution of phosphate ion impurities. All the reagents used were Analar grade and the solutions were prepared using double distilled water.

RESULTS AND DISCUSSION

The chemically polished zircaloy-4 specimens were anodized separately in 0.1M L-ascorbic acid at a constant current density of 8 mA.cm⁻² and at room temperature (300 K). 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, reciprocal capacitance vs. time and reciprocal capacitance vs. formation voltage were shown in Figs - 1, 2, and 3.

However a marked improvement in the kinetics of film formation with uniformity upto 240V is found with the addition of a millimole of Na₃PO₄ to 0.1M L-ascorbic 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 (PO₄³⁻) into the anodic film.

TABLE-1: Anodic films formed on Zircaloy-4 in 0.1M L-Ascorbic Acid (AA)

| Electrolyte | Formation rate, dv/dt (V.sec ⁻¹) | Current efficiency, η (%) | Differential field, F_D (MV.cm ⁻¹) |
|---|---|-----------------------------------|---|
| 0.1M AA | 1.52 | 60.0 | 5.385 |
| 0.1M AA + 0.001M PO ₄ ⁻³ | 2.23 | 70.1 | 7.118 |

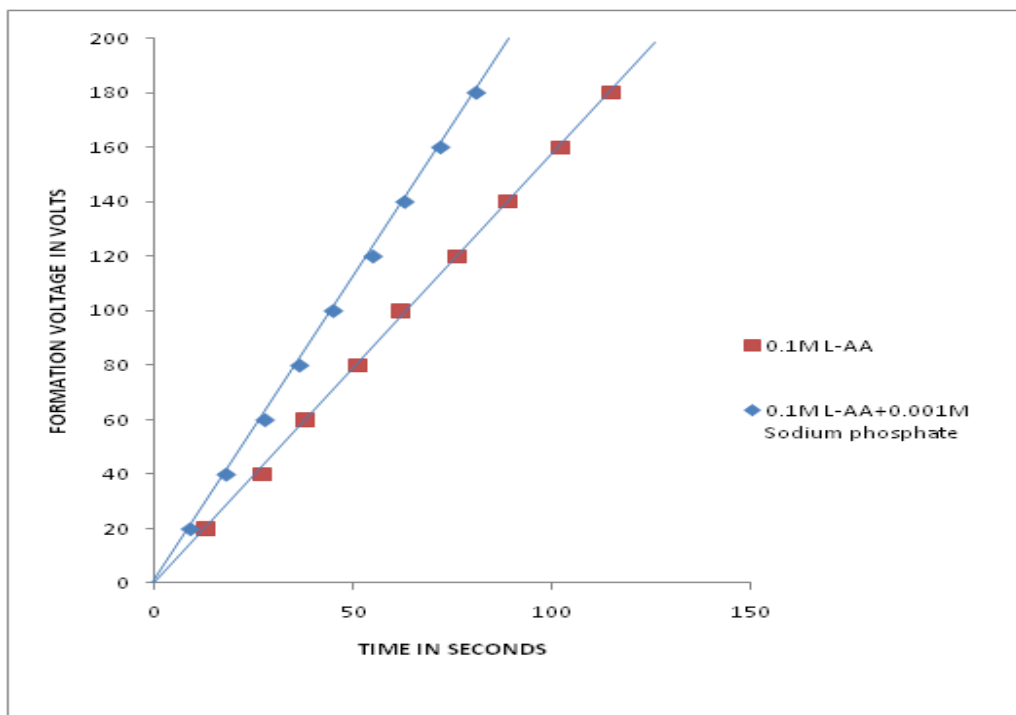


Fig-1: Formation voltage vs. time plot (zircaloy-4)

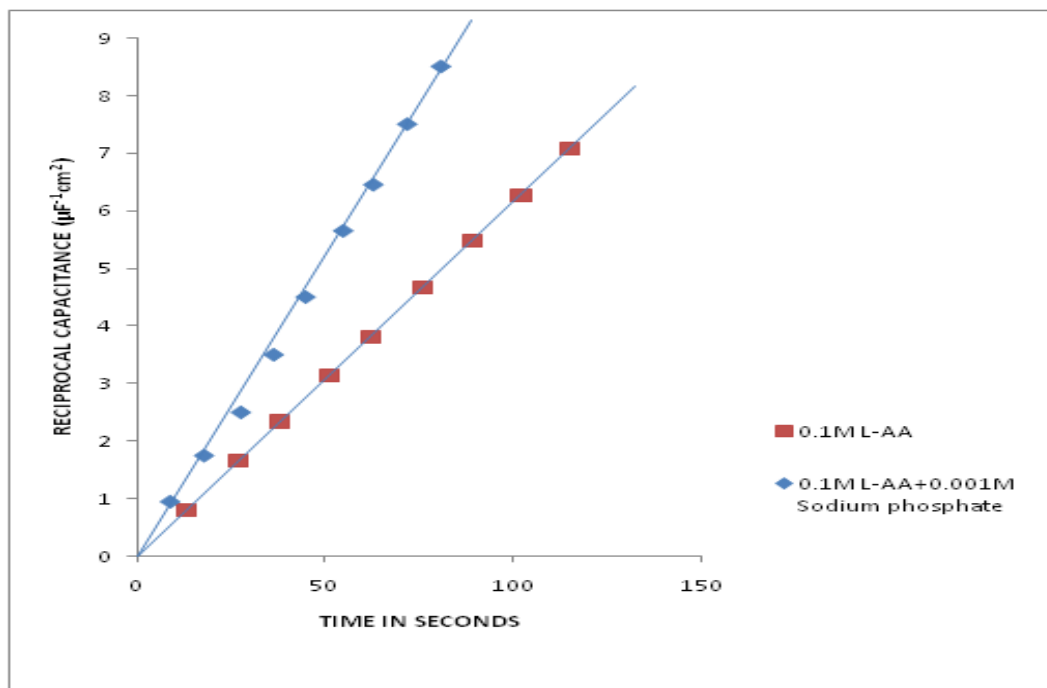


Fig-2: Reciprocal capacitance vs. time plot (Zircaloy-4)

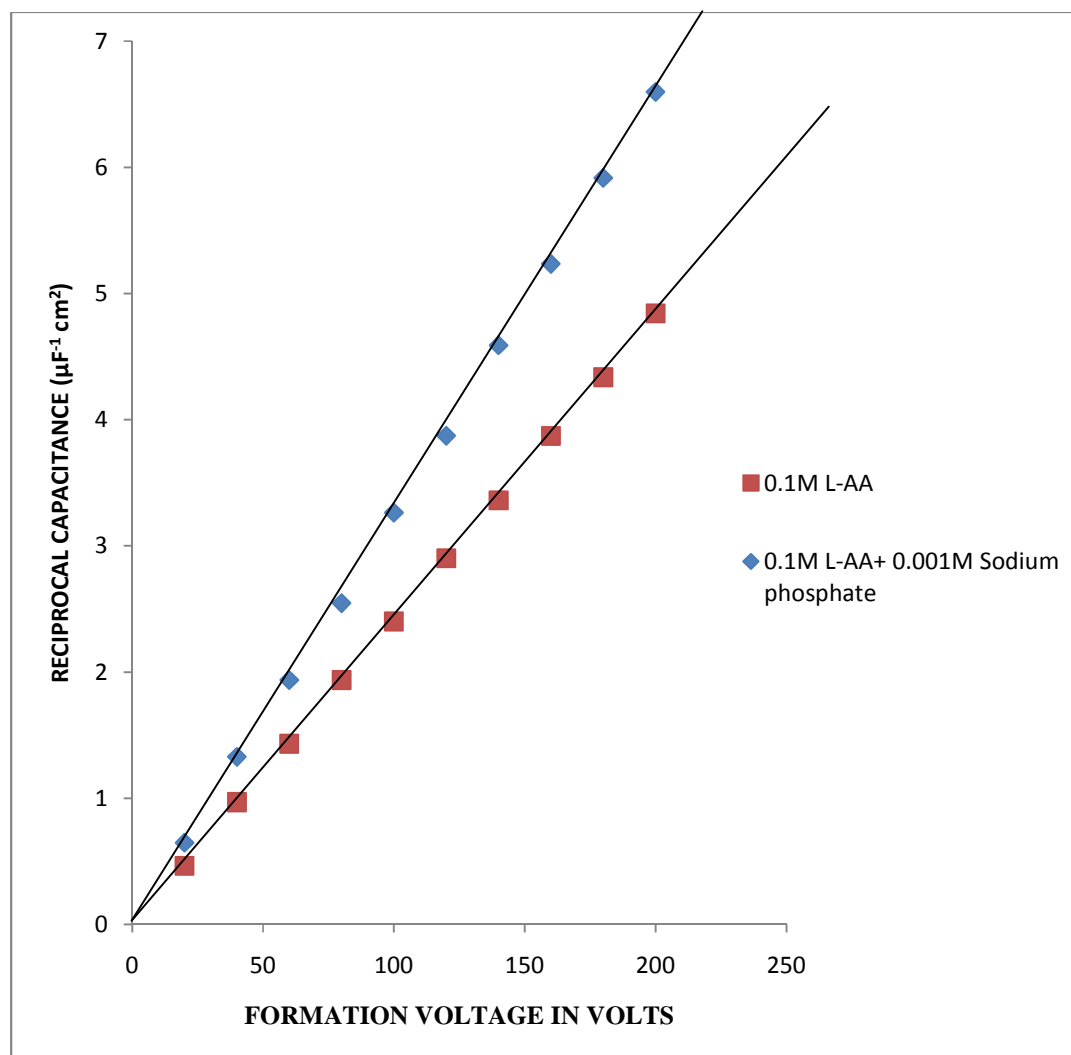


Fig-3: Reciprocal capacitance vs. formation voltage plot (zircaloy-4)

Radio-tracer studies mechanism:

For the confirmation of incorporation of phosphate into the anodic oxide films formed on zircaloy-4 in 0.1M L-ascorbic acid + 0.001M Na_3PO_4 an active solution of 8 ml volume containing 2 drops of radio-active $\text{Na}_3^{32}\text{PO}_4$ was taken in the specially designed cell as described in the experimental part. Specific activity of the solution was $0.25 \mu\text{Ci} / \text{mM}$. From the counts measured at regular intervals of 40V the weight of the phosphate ion uptake was estimated and shown in the Fig - 4 (curve a). The uptake is found to be uniform upto 240V. From the thinning experiments using 0.5μ diamond paste the distribution curve is also plotted and shown in the Fig - 4 (curve b). From the nature of the uptake and distribution curves the mechanism of anodic film formation on zircaloy-4 in 0.1M L-ascorbic acid + 0.001M Na_3PO_4 may be via vacancy diffusion mechanism (i.e.) the distribution followed almost same path of uptake confirming the growth of the film is due to vacancy diffusion of metal ions.

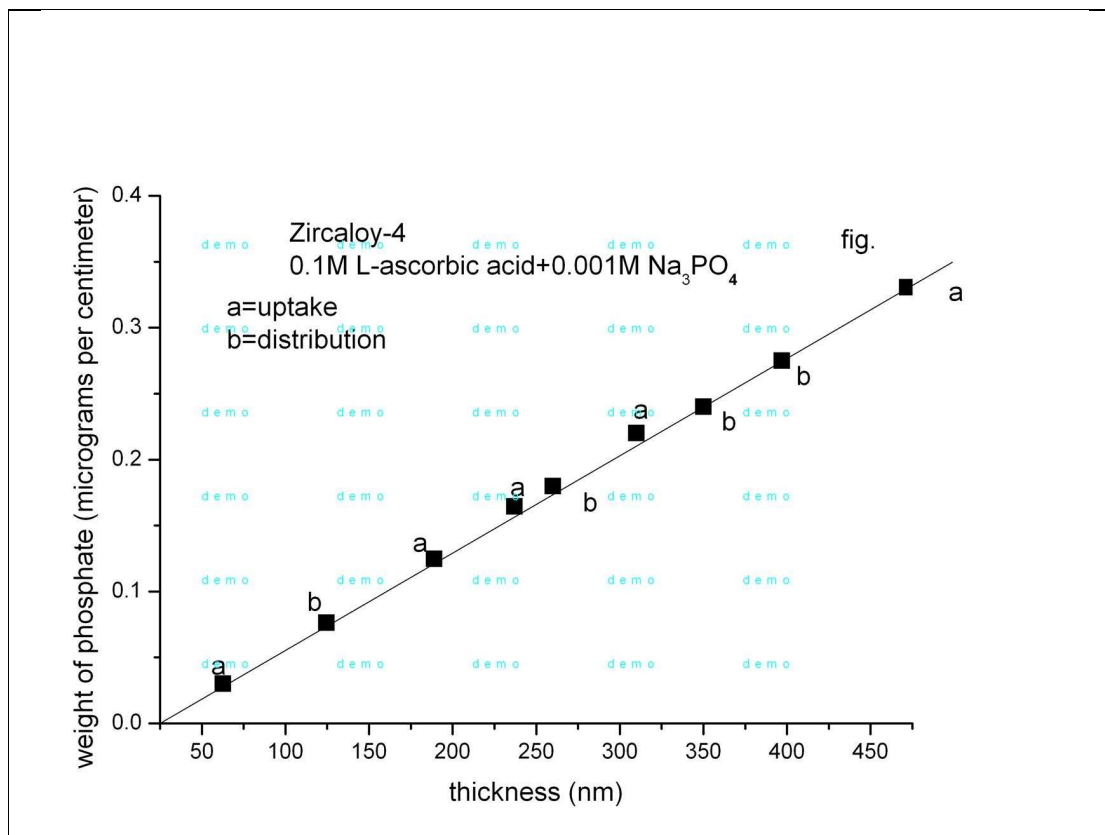


Fig-4: Uptake and distribution of PO_4^{3-} vs. thickness 0.1M L-ascorbic acid + 0.001M Na_3PO_4

- (a) Uptake curve
- (b) Distribution curve upto 240V

CONCLUSION

A marked influence and improvement in the kinetics of anodic oxide film formation on zircaloy-4 in 0.1M L-ascorbic acid has been observed with the addition of 1 mM of phosphate ions. Radio-tracer techniques confirmed the implantation and migration of phosphate ions in the oxide film. The mechanism of the growth of the oxide film is found to be via vacancy diffusion of metal ions i.e. the distribution followed almost same path of uptake.

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