

## Mechanism of anodic oxide film formation on zircaloy-2, zircaloy-4, titanium and niobium (Radio tracer technique)

V. JEEVANA JYOTHI<sup>1</sup>, N.N.S. APARNA<sup>2</sup> and CH. ANJANEYULU<sup>2</sup>

<sup>1</sup>Department of Chemistry R.B.V.R.R. Women's College, Nazrayanguda, Hyderabad (India).

<sup>2</sup>Department of Chemistry, University College for Women,  
Osmania University, Hyderabad - 500 007 (India).

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### ABSTRACT

The kinetics of anodic oxidation of zircaloy-2, zircaloy-4, titanium and niobium have been studied in 0.1M sodium methoxide without and with addition of a millimole of sodium phosphate at a constant current density of 8mA.cm<sup>-2</sup> 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 technique using labeled phosphate ions. The conclusion of the results obtained is migration of anion impurity and accumulation of active phosphate in the layers of the oxide film formed.

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

### INTRODUCTION

Zakhalov *et al.*<sup>1</sup> observed linear galvanostatic curves in the anodic oxidations of niobium over a broad range of current density values (0.1-10 mA.cm<sup>-2</sup>). They observed 100% current efficiency. During anodization they found different colors covering entire spectrum on the surface of the different formation voltages.

Bairachnyu and Gomozov<sup>2</sup> 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 30-100mA in 1-10% solutions of H<sub>3</sub>PO<sub>4</sub> upto 100V. During oxidation in H<sub>3</sub>PO<sub>4</sub> P<sup>H</sup><0.8 (concentration ,10%), they found that PO<sub>4</sub><sup>3-</sup> was introduced into the composition of the anodic oxide film. In this case, nonstoichiometric oxides of variable composition are formed including oxides of variable composition are formed including oxides of Nb and Phosphorous.

Young<sup>3</sup> observed that the Nb<sub>2</sub>O<sub>5</sub> films are crystalline and the films recrystallize under the influence of applied field. Leach and Panagopoulos<sup>4</sup> studied the growth kinetics of anodization of zirconium in Na<sub>3</sub>PO<sub>4</sub> 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 behavior was attributed to the incorporation of PO<sub>4</sub><sup>3-</sup> into the growing oxide. Maraghini and Serra<sup>5</sup> used radio – active phosphate and sulphate containing solutions to investigate the incorporation of these anions into the films formed by anodic oxidation.

Randall<sup>6</sup> *et al.* 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 H<sub>2</sub>SO<sub>4</sub> of comparable concentration. The two layer nature of anodic oxide film grown in H<sub>3</sub>PO<sub>4</sub> was confirmed by Delloca and Young<sup>7</sup>. By

ellipsometric studies. Infrared transmission spectra of anodic films showed that anions such as phosphate, sulphate and carboxylate were incorporated<sup>9</sup>.

Raghunath Reddy<sup>9</sup> Confirmed the incorporation of phosphate into the anodic oxide films formed on niobium in 0.05M picric acid + 0.001M Na<sub>3</sub>PO<sub>4</sub> having radio – active isotope <sup>32</sup>P. Anjaneyulu<sup>10</sup> Studied the mechanism of anodic film formation on Ti and Zr by using Na<sub>2</sub><sup>35</sup>PO<sub>4</sub> and H<sup>14</sup>COONa. Shukla<sup>11</sup> 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 Na<sub>3</sub>PO<sub>4</sub> having radio – active isotope <sup>32</sup>P.

In the present work, an attempt is made to study the mechanism of anodic oxide film formation on zircaloy-2, zircaloy-4, titanium and niobium in 0.1M sodium methoxide + 0.001M having radio – active isotope <sup>32</sup>P are studied.

#### MATERIAL AND METHODS

All the experiments were carried out using 0.2 mm thick, annealed, rolled sheet of zircaloy-2, zircaloy-4, titanium and niobium of more than 99.5% purity supplied by NFC, Hyderabad as a gift sample. The specimens used were cut with the aid of a punch giving working area of 1 cm<sup>2</sup> on the 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. HNO<sub>3</sub>, HF and H<sub>2</sub>SO<sub>4</sub> in the definite volume ratio.

Adams<sup>12-13</sup> *et al* and Willis<sup>14</sup> *et al.* used chemically polished specimens which give 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 20 cm<sup>2</sup> superficial area to make the double layer capacitance as large as possible. For radio – active experiments a specially designed cell of 20ml 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 specimens are 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 Power tronics, 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 0.5µ 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 DISCUSSIONS

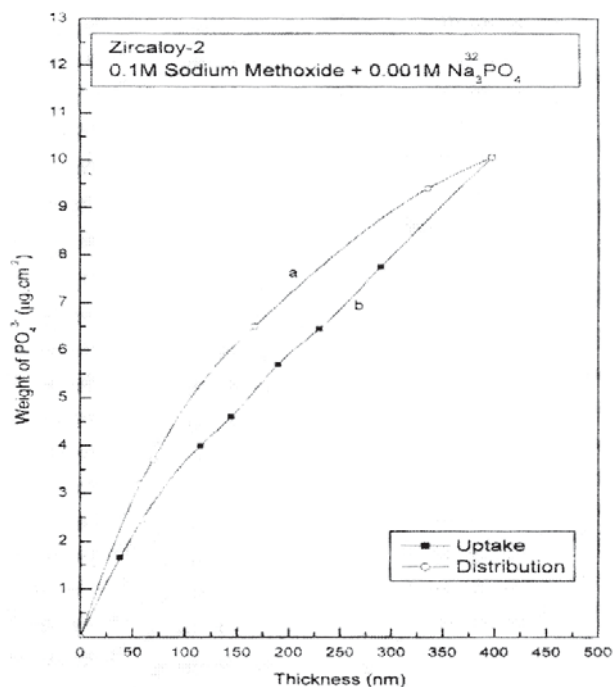
The chemically polished zircaloy-2 zircaloy-4, titanium and niobium specimens were anodized separately in 0.1M sodium methoxide at a constant current density of 8mA.cm<sup>-2</sup> and at room temperature (300 K). the time taken for anodization and the capacitance of the film formed were measured at an interval of 20V by interrupting the constant current circuit. The plots of formation voltage vs. time reciprocal capacitance vs. time were found to be linear upto the breakdown voltage. The differential field across oxide and the current efficiency were calculated from these plots.

However a marked improvement in the kinetics of film formation with uniformity up to 240V is found with the addition of a millimole of Na<sub>3</sub>PO<sub>4</sub> to 0.1M sodium methoxide.

The kinetic results, formation rate, current efficiency and differential field obtained for zircaloy-2, zircaloy-4, titanium and niobium are given in tables – 1,2,3,4. the improvement observed in the kinetics is attributed to the incorporation of anion impurities (PO<sub>4</sub><sup>-3</sup>) into the anodic film.

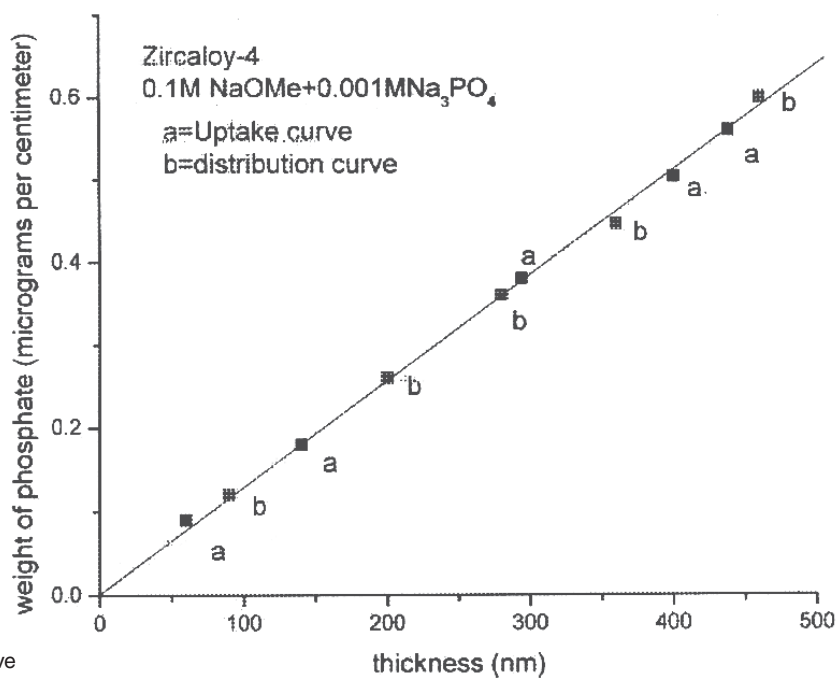
#### Radio – tracer studies mechanism

For the confirmation of incorporation of phosphate into the anodic oxide films formed on zircaloy-2, zircaloy-4, titanium and niobium in 0.1M sodium methoxide + 0.001M Na<sub>3</sub><sup>32</sup>PO<sub>4</sub> an active solution of 8ml volume containing 2 drops of radio –



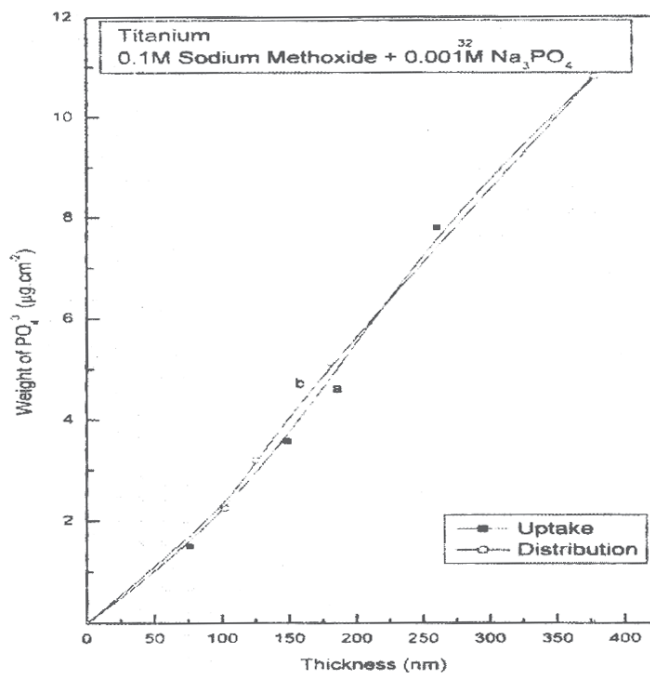
- a) Uptake curve
- b) Distribution curve upto 2

**Fig. 1: Uptake and distribution of  $\text{PO}_4^{3-}$  vs. thickness 0.1M sodium methoxide + 0.001M  $\text{Na}_3^{32}\text{PO}_4$  (Zircaloy-2)**



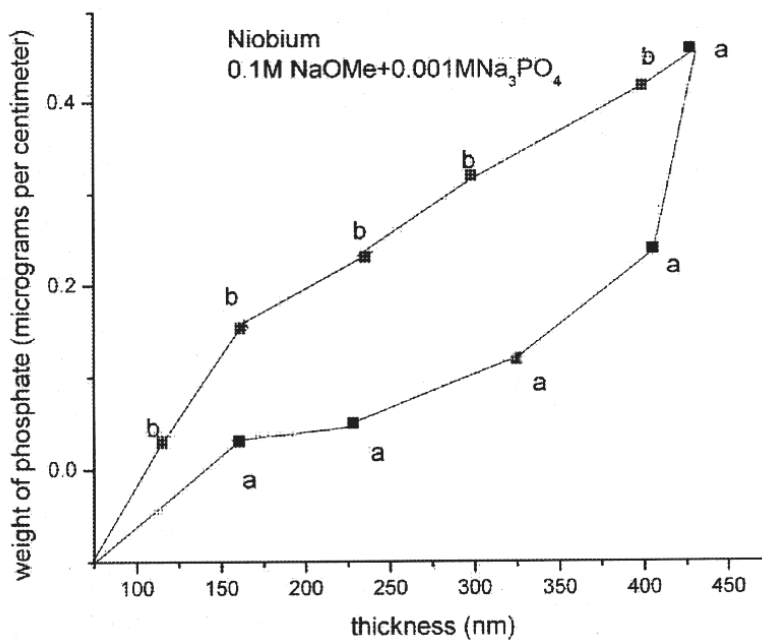
- a) Uptake curve
- b) Distribution curve upto 240V)

**Fig. 2: Uptake and distribution of  $\text{PO}_4^{3-}$  vs. thickness 0.1M sodium methoxide + 0.001M  $\text{Na}_3^{32}\text{PO}_4$  (Zircaloy-4)**



- a) Uptake curve
- b) Distribution curve up

Fig. 3: Uptake and distribution of  $PO_4^{3-}$  vs. thickness 0.1M sodium methoxide + 0.001M  $Na_3^{32}PO_4$  (Titanium)



- a) Uptake curve
- b) Distribution curve upto 240v

Fig. 4: Uptake and distribution of  $PO_4^{3-}$  vs. thickness 0.1M sodium methoxide + 0.001M  $Na_3^{32}PO_4$  (Titanium)

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  $0.25\mu\text{Ci}/\text{mM}$ .

### Zircaloy – 2

From the counts measured at regular intervals of 40V the weight of the phosphate ion uptake was estimated and shown in the fig – 1 (curve a). the uptake is found to be uniform upto 240V. from the thinning experiments using  $0.5\mu$ . diamond paste the distribution curve is also plotted and shown in fig -1 (curve b). from the nature of the uptake and distribution curves the mechanism of anodic film formation on Zircaloy-2 in 0.1M sodium methoxide +  $0.001\text{M Na}_3^{32}\text{PO}_4$  is via

interstitial movement of oxygen ions through out the film the same mechanism of oxide film formation was given by Raghunath Reddy 15 for Zr-4 in 0.1M  $\text{KOH}+0.001\text{M Na}_3^{32}\text{PO}_4$

### Zircaloy-4, Titanium and Niobium

From the counts measured at regular intervals of 40V the weight of the phosphate ion uptake was estimated for zircaloy – 4 titanium and niobium and shown in the fig – 2,3,4 (curve a). respectively. The uptake is found to be uniform upto 240V. from the thinning experiments using  $0.5\mu$ . diamond paste the distribution curve is also plotted and shown in fig -2,3,4 (curve b) for zircaloy – 4 titanium and niobium respectively. From the nature

**Table 1: Anodic films formed on Zircaloy-2 in 0.1M sodium methoxide (SM)**

Electrolyte	Formation rate, dv/dt (V.Sec <sup>-1</sup> )	Current efficiency $\eta$ (%)	Differential field, FD(MV.cm <sup>-1</sup> )
0.1M SM	1.30	56.5	5.08
0.1M SM+0.001M $\text{PO}_4^{-3}$	1.35	57.3	5.26

**Table 2: Anodic films formed on Zircaloy-4 in 0.1M sodium methoxide (SM)**

Electrolyte	Formation rate, dv/dt (V.Sec <sup>-1</sup> )	Current efficiency $\eta$ (%)	Differential field, FD(MV.cm <sup>-1</sup> )
0.1M SM	1.58	64.3	5.310
0.1M SM+0.001M $\text{PO}_4^{-3}$	1.81	84.0	4.821

**Table 3: Anodic films formed on Titanium in 0.1M sodium methoxide (SM)**

Electrolyte	Formation rate, dv/dt (V.Sec <sup>-1</sup> )	Current efficiency $\eta$ (%)	Differential field, FD(MV.cm <sup>-1</sup> )
0.1M SM	1.20	39.0	7.12
0.1M SM+0.001M $\text{PO}_4^{-3}$	1.45	64.5	3.36

**Table 4: Anodic films formed on Niobium in 0.1M sodium methoxide (SM)**

Electrolyte	Formation rate, dv/dt (V.Sec <sup>-1</sup> )	Current efficiency $\eta$ (%)	Differential field, FD(MV.cm <sup>-1</sup> )
0.1M SM	1.71	66.0	5.061
0.1M SM+0.001M $\text{PO}_4^{-3}$	2.05	75	5.409

of the uptake and distribution curves the mechanism of anodic film formation on Zircaloy – 4 titanium and niobium in 0.1M sodium methoxide+0.001M  $\text{Na}_3^{32}\text{PO}_4$  is found to be in the same order of uptake confirming the vacancy diffusion of metal ions. The same mechanism results were obtained by Shobha 16 for HF.

### CONCLUSION

A marked influence and improvement in the kinetics of anodic oxide film formation on Zr-2,Zr-4, Ti and Nb in 0.1M sodium methoxide have been observed with the addition of 1mM 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 interstitial movement of oxygen ions through out the film for Zircaloy - 2 . for Zircaloy – 4. titanium and niobium the mechanism is found to be in the same order of uptake confirming the vacancy diffusion of metal ions.

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