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Kinetic and mechanistic studies of anodic oxide film formation on Niobium

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Abstract

The kinetics of anodic oxidation of niobium 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 $mA.cm^{-2}$ 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 studies using labeled phosphate ions. The conclusion of the results obtained is migration of anion impurity and accumulation of active phosphate in the inner layers of the oxide film formed.

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 niobium 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 formation voltages.

Bairachny and Gomozov [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 P^H<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 Nb_2O_5 films are crystalline and the films recrystallized under the influence of applied field. Leach and Panagopoulas [4] 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 [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 H_2SO_4 of comparable concentration. The two layer nature of anodic oxide film grown in H_3PO_4 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].

Raghunath Reddy [9] confirmed the incorporation of phosphate into the anodic oxide films formed on niobium in 0.05M picric acid + 0.001M Na_3PO_4 having radio-active isotope ^{32}P. Aparna [10] 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 Na_3PO_4 having radio-active isotope ^{32}P. Shukla [11] 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_3PO_4 having radio-active isotope ^{32}P.

In the present work, kinetic and mechanistic aspects of anodic oxide film formation on niobium in 0.1M L-ascorbic acid + 0.001M Na_3PO_4 having radio-active isotope ^{32}P are studied.

Materials and Methods

All the experiments were carried out using 0.2 mm thick, annealed, rolled sheet of niobium of more than 99.5% purity supplied by NFC, Hyderabad as a gift sample. Main impurities were C, N, Ni, Fe and Ta. The niobium foil samples used were cut with the aid of a punch giving working area of 1 cm^2 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. HNO_3, HF and H_2SO_4 in the definite volume ratio.

Adams et al., [12, 13] and Willis et al., [14] 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 cm^2 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 niobium 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 Discussions

The chemically polished niobium 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 Na_3PO_4 to 0.1M L-ascorbic acid.

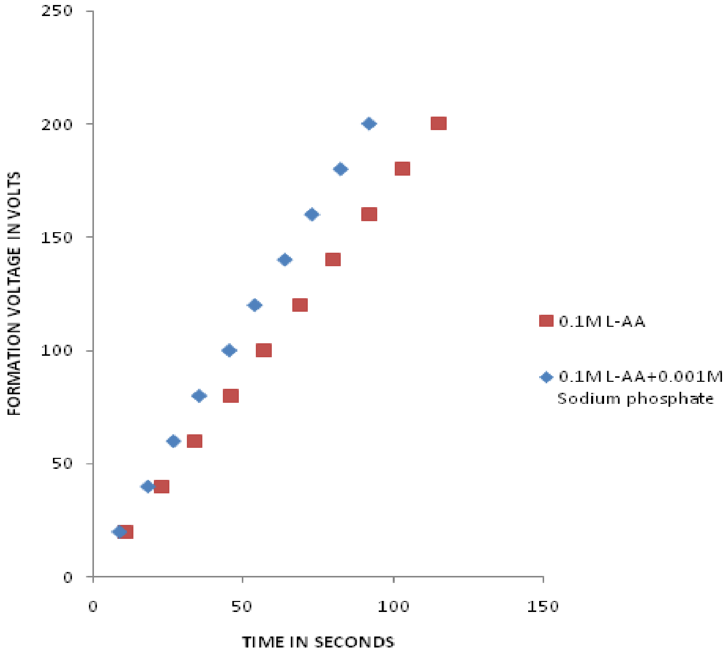

Fig-1: Formation voltage vs. time plot (niobium)

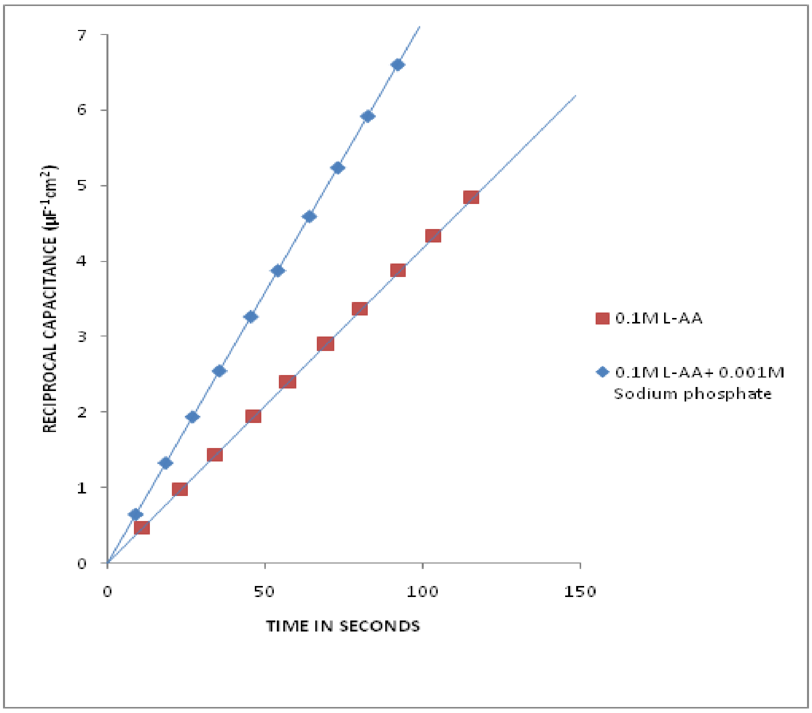

Fig-2: Reciprocal capacitance vs. time plot (niobium)

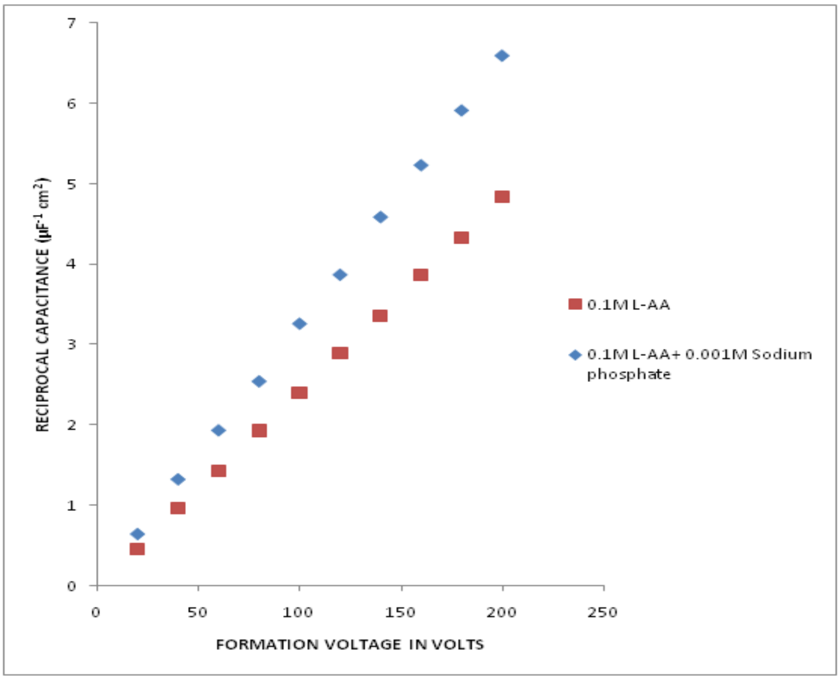

Fig-3: Reciprocal capacitance vs. formation voltage plot (niobium)

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.

Table-1: Anodic films formed on Niobium 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	1.74	61.0	5.648
0.1M AA + 0.001M PO_4^{-3}	2.10	68.0	6.111

Radio-tracer studies mechanism:

For the confirmation of incorporation of phosphate into the anodic oxide films formed on niobium in 0.1M L-ascorbic acid + 0.001M Na_3PO_4 an active solution of 8 ml volume containing 2 drops of radio-active $Na_3{}^{32}PO_4$ was taken in the specially designed cell as described in the experimental part. Specific activity of the solution was 0.25 μC_i / 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 niobium in 0.1M L-ascorbic acid + 0.001M Na_3PO_4 may be via mixed mechanism (i.e.) the distribution has not followed either in the reverse order or in the same path of uptake indicating a mixed mechanism of film formation.

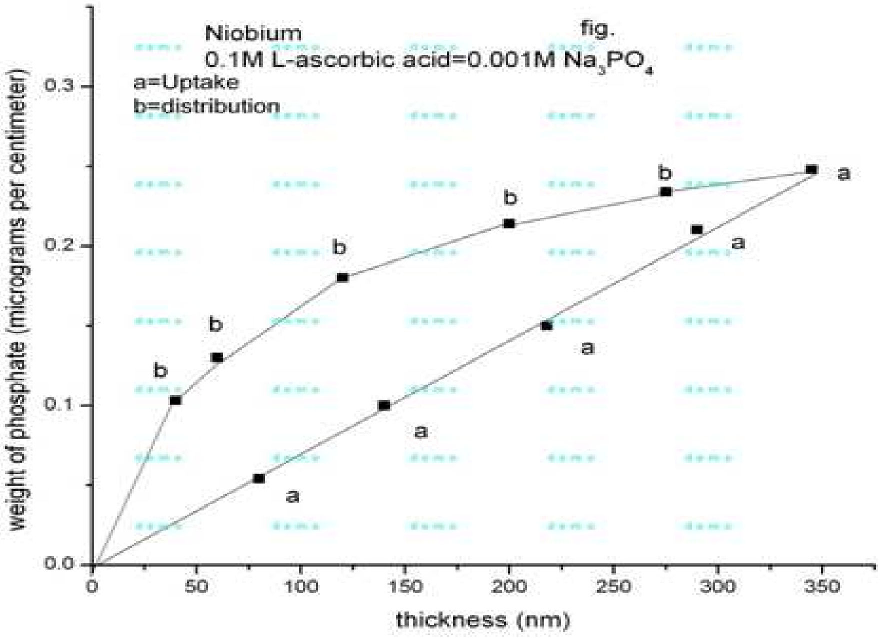

Fig-4: Uptake and distribution of PO_4^{3-} vs. thickness 0.1M L-ascorbic acid + 0.001M Na_3PO_4 (a) Uptake curve (b) Distribution curve upto 240V

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 L-ascorbic acid + 0.001M Na_3PO_4 and the remaining part of the film was formed in the active solution. The conditions and distribution curves are shown in Fig-5.

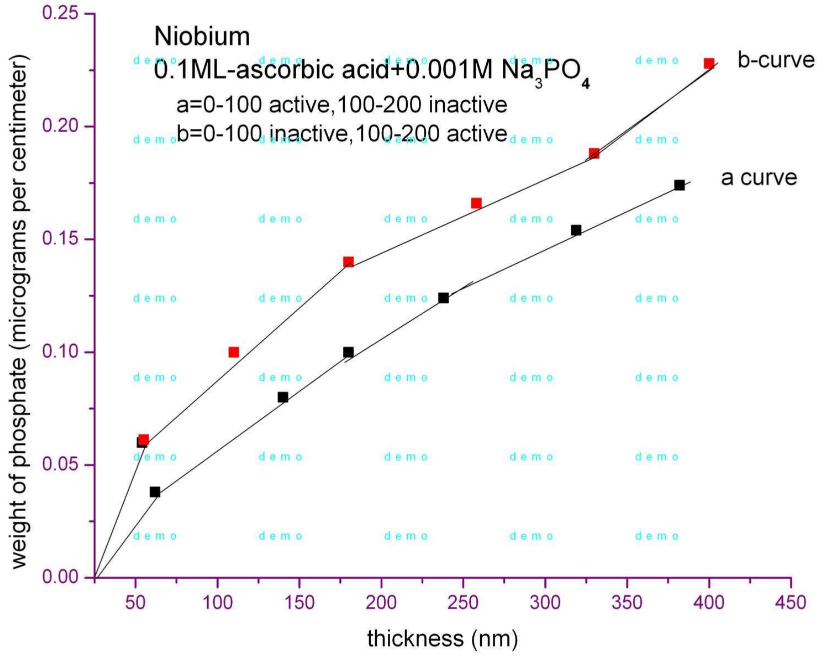

Fig-5: Distribution curves for the film formed partly in active and partly in inactive 0.1M L-ascorbic acid + 0.001M Na_3PO_4

(a) 0-100 active, 100-200 inactive
(b) 0-100 inactive, 100-200 active

Conclusion

A marked influence and improvement in the kinetics of anodic oxide film formation on Nb in 0.1M L-ascorbic acid has been observed with the addition of 1 mM of phosphate ions. Radio-tracer studies 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 mixed mechanism of film formation. Transfer of specimen from active to inactive and vice-versa in 0.1M L-ascorbic acid + 0.001M Na_3PO_4 solution confirmed the migration of anions in the oxide film.

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