Incorporation and Depth Distribution of Sulphate Ions into Anodic Oxide Films Formed on Titanium in 0.1M KOH + 0.0005M $Na_2S^{35}O_4$.

Ch. ANJANEYULU AND K. S. SASTRY

Department of Chemistry, University College of Science, Osmania University, Hyderabad-500 007.

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THE kinetics of the anodic oxidation of titanium at a constant current density of 8 mA/cm2 and at room temperature in 0.1M KOH and 0.1M KOH + 0 0005M Na_2SO_4 were investigated with particular emphasis on the effects that the incorporated anion impurities might have. In 0.1M KOH a fall in the ionic current efficiency and an increase in the differential field are observed at a thickness of about 60nm(24V) but when a trace amount of sulphate ion (0.0005M) is present in 0.1M KOH the ionic current efficiency and differential field (calculated from capacitance measurements) are found to be constant even upto 60V, thus showing that the incorporated anions have a large effect upon the current efficiency and field of formation.

Radio-tracer studies using S^{35} in 0.1M KOH + 0.0005M Na_2SO_4 indicate the depth distribution of sulphate ion which is almost in the reverse order of uptake suggesting a mechanism of anodic film formation.

Anodization of titanium in concentrated and dilute KOH were studied previously by Faizullin and Baitalov[1], Peksheva[2,8] and recently by Kalyani *et al*[4,5]. Peksheva found that the oxide films formed in KOH solution were more dense than those formed in acid. Bogoyavlenski and Borodina[6] studied the penetration of sulphate ion from H_2SO_4 bath into the anodic oxide film of titanium using S^{35}.

In recent times Roch *et al*[7] used X-ray fluorescence technique to study the incorporation of sulphate and phosphate ion impurities into anodic films formed on titanium using H_3PO_4 and H_2SO_4 baths.

The effect of adding sulphate ion to 0.1M KOH upon the kinetics of anodization of zirconium at a constant current density of 4.1 mA/cm^2 was reported in our paper[8].

In the present work an attempt is made to understand a probable mechanism of anodic film formation on titanium in 0.1 M KOH and 0.1M KOH + 0.0005M Na_2SO_4 from the radiotracer studies using S^{35}.

EXPERIMENTAL

Titanium used was of 99.7% nominal purity. The method of preparation of specimens and procedure of chemical polishing of them were described in our earlier communication[4,5]. For inactive anodization a closed cell of 200ml capacity and a large platinum cathode of 20cm^2 area were used. For radioactive experiments a specially designed cell of 20ml capacity in which a platinum cathode of 'U' shape having 3 cm × 1 cm dimensions with each side one cm^2 was arranged at the bottom of the cell. The specimen was suspended vertically and roughly parallel to the sides of 'U' shape cathode.

The thicknesses of anodic films formed were calculated from capacitance measurements. A digital LCR meter (Type VLCR 6) supplied by Vasavi Electronics, Hyderabad was used to measure the capacitance. The constant current generator used was supplied by Instrument Techniques Pvt. Ltd., Hyderabad.

An end window G. M. Counter built by ECIL, Hyderabad with an automatic timer and counting system was used to measure the $S^{35}O_4^{--}$ content of the film. Thinning experiments were also made using 0.5μ diamond paste to examine the distribution of SO_4^{--} impurities in depth. The active electrolyte used was 0.1M KOH + 0.0005M $Na_2S^{35}O_4$. All experiments were carried out at a constant current density of 8mA/cm^2.

RESULTS AND DISCUSSION

Anodic films were formed on chemically polished titanium specimens in 0.1M KOH at a constant current density of 8mA/cm^2. The time taken for anodization and capacitance of the film formed were measured at an each interval of 10V

by interrupting the constant current circuit. The plots of formation voltage vs time and thickness vs formation voltage are given in Figures 1 and 2. The former plot was linear only upto 24V (the corresponding thickness was 60nm) and beyond that become non-linear. Below a thickness of 60nm the film grew at a differential field of 3.931 MV/cm and the current efficiency was 81%

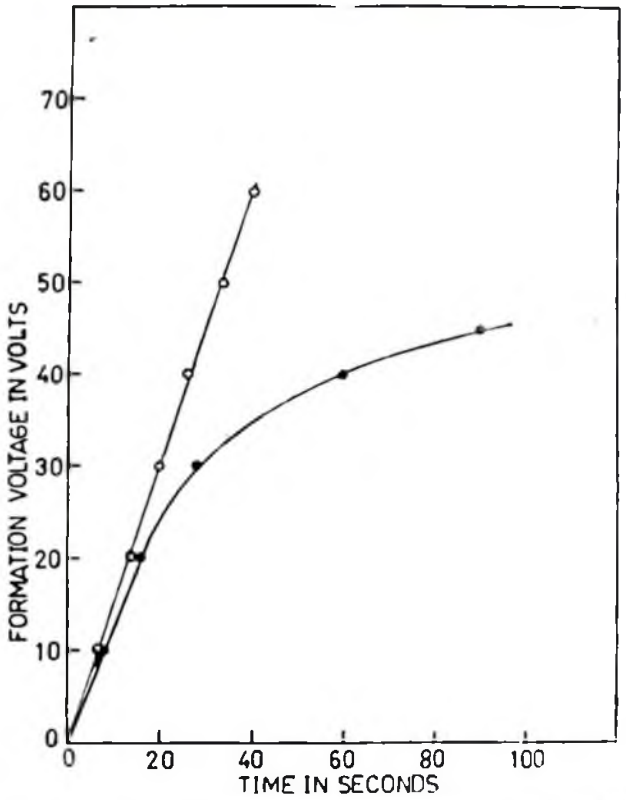


Fig. 1 Formation voltage vs time for films formed in 0.1M KOH (closed circles) and 0.1M KOH + 0.0005M Na_2SO_4 at a constant current densito of 8 mA/cm2.

When 0.0005M Na_2SO_4 was added to 0.1M KOH a significant effect was observed on the kinetics of anodic oxidation. The plots of formation voltage vs time and thickness vs formation voltage became linear even beyong 24V of formation voltage and upto 60V as shown in figures 1 and 2. The current efficiency and differential field were found to be 87.4% and 4.375 MV/cm respectively.

Therefore a trace amount of sulphate ion present in 0.1M KOH exerts a considerable influence upon the field and current efficiency; they became constant independent of thickness and the changes observed in its absence were no longer seen.

Radio-Tracer measurements using S^{35} and thinning experiments: A solution was made up containing 0.1M KOH + 0.0005M $Na_2S^{35}O_4$ with a specific activity of about 20 mC/mM. Anodic films were formed successively at intervals of 10V to 60V and their activity measured. In Figure 3 curve 'a' is the uptake of SO_4^{--}/cm² plotted vs thickness. The points refer to a single sample in the cell for further oxidation after each count.

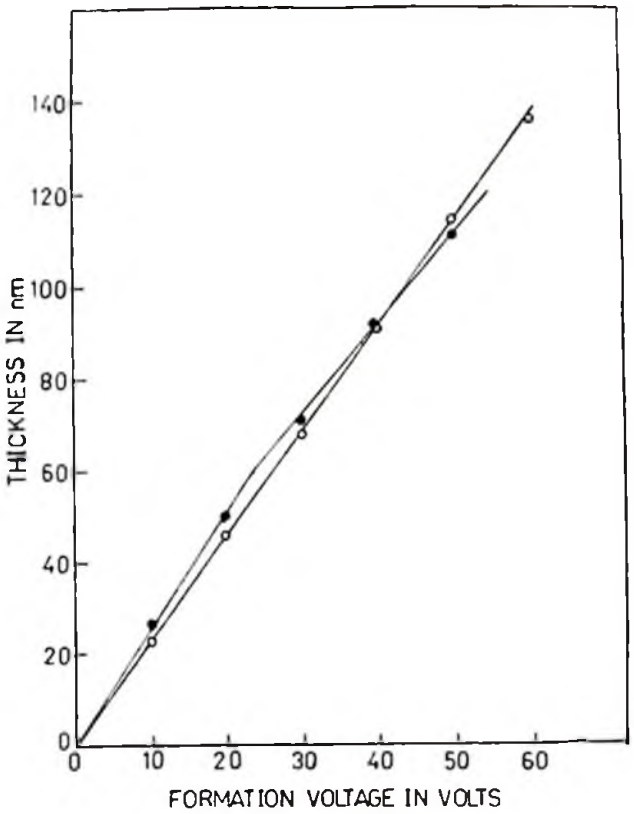


Fig. 2 Thickness vs formation voltage for films formed in 0.1M KOH (closed circles) and 0.1M KOH + 0.0005M Na_2SO_4 at a constant current density of 8 mA/cm².

Thinning experiments were carried out using 0.5μ diamond paste for the films formed successively at intervals of 10V to 60V in 0.1M KOH + 0.0005M $Na_2S^{35}O_4$. In Figure 3 the distribution of SO_4^{--}/cm² vs thickness is plotted (curve b).

Below 60nm, the amount of SO_4^{--} uptake is so small as to make the type of distribution is uncertain and it is considered that the order of distribution is conserved. Hence the mechanism for the oxide film formation in KOH suggested is via interstitial movement of metal ions[9]. Above 60nm the depth distribution of SO_4^{--} is almost the reverse order of uptake. It is suggested that the fall in ionic current efficiency in KOH at 60nm may be due to some sort of recrystallization as suggested with zirconium[11] and there may be an increase of grain boundaries and the mechanism of anodic film

formation may appear to be via interstitial movement as the depth distribution of SO_4^{--} is almost reversed.

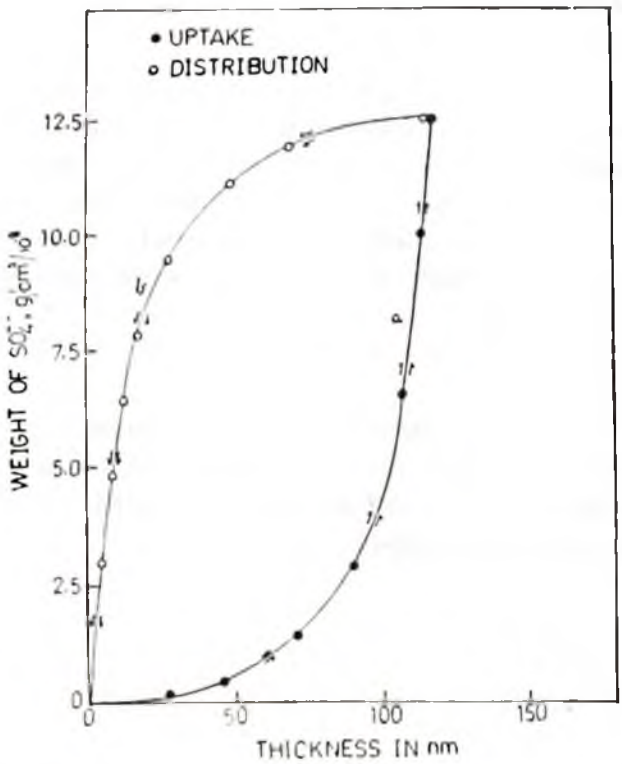


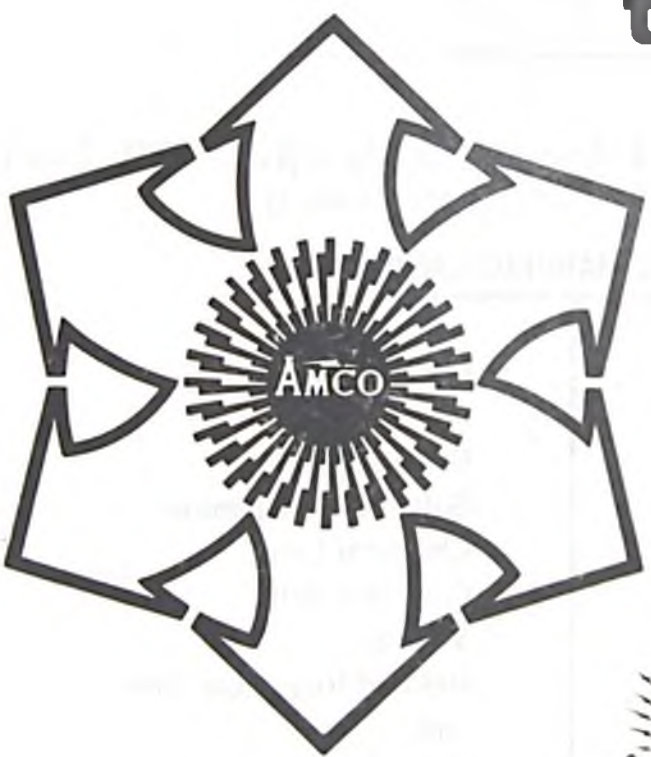
Fig. 3 Weight of sulphate ions/cm^2 in oxide films vs thickness for anodization in 0.1M KOH + 0.0005M Na_2SO_4.

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