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Research Article

COMPARISON OF THE KINETICS AND MECHANISM OF ANODISATION OF ZIRCALOY-2 AND NIOBIUM IN 0.1M (NH$_4$)$_2$SO$_4$ AND 0.1M(NH$_4$)$_2$SO$_4$ +0.001MK ^{125}I.

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Abstract

The kinetics and mechanism of anodic oxidation of Zircaloy-2 and niobium were studied at room temperature and at a constant current density of 8mAcm^{-2} in 0.1M (NH$_4$)$_2$SO$_4$ and also in 0.1M(NH$_4$)$_2$SO$_4$ +0.001MK ^{125}I. Thickness estimates were made from capacitance data. The formation rate , ionic current efficiency and differential field were higher when zircaloy-2 was anodized in 0.1M(NH$_4$)$_2$SO$_4$, than when niobium was anodized in the same electrolyte. Radiotracer studies using active KI gave insight to the mechanism of film formation.

Keywords: Kinetics 1,anodic oxidation 2,formation rate 3, ionic current efficiency 4, differential field 5, radiotracer studies 6.

Introduction

Valve metals when anodised in suitable electrolytes form thin insulating oxide films. The film grows to a thickness approximately proportional to the formation voltage impressed across it. The formation of the film is limited by a breakdown which occurs when a certain amount of thickness is reached. The kinetics and mechanism of the oxide films formed in different electrolytes have been studied earlier (1-5).Day and keil (6) studied the anodic oxidation of Nb in glacial acetic acid – sodium tetraborate solution over a potential range of 70 V. Kover and Musselin (7) have made a comparative study of anodic oxide films on Ti, Nb and Ta. In the present work , the kinetics and mechanism of the oxide films formed on Nb and Zr-2 were studied in 0.1M(NH$_4$)$_2$SO$_4$ and also in 0.1M(NH$_4$)$_2$SO$_4$ in the presence of a millimole of K ^{125}I.

Anodic oxidation plays a basic role in microcircuitory and in thin film formation. Zirconium alloys are of primary importance in nuclear technology. Anodic films of Nb are useful in the production of condensers and in microelectronics. In view of the apparent differences in the field strength required to grow films at a constant current density in different electrolytes, the kinetics and mechanism of anodic oxidation of Nb and Zr-2 were investigated in greater detail.

Materials and Methods

Zr-2 and Nb samples (0.125mm thick and about 99.7% purity) were supplied by N.F.C Hyderabad. Nb samples were polished in a mixture of HNO$_3$,HF and H$_2$ SO$_4$ in the volume ratio of 5 : 5 : 12.5, whilst samples of Zr-2 were polished in a mixture of HF, NNO$_3$ and distilled water in the ratio of 1:3:3.Specimens were cut with the help of a punch to get a working area of 1 cm^2 and a tag 2 cm long. The tags were heavily anodized in 0.1MH$_3$ PO$_4$ to about 270 V. For inactive anodisation a closed cell of 200ml capacity and a large Pt cathode of 30cm^2 area (to make the double layer capacitance as large as possible)l were used .Specimens were immersed vertically in solution from the heavily anodized tag. Radiotracer studies were made using active KI . ^{125}I was received from BARC as dilute solution with

1.8 m   ci /ml activity. 4 ml of 0.1M$(NH_4)_2SO_4$ with 0.1ml K^{125}I with a specific gravity of 4.5 mc i/m M was prepared. A specially designed cell of 20 ml capacity was used for radiotracer studies. The Pt cathode used was of "U" shape having 3 cm x1 cm dimensions with each side 1 cm^2 . Roughly parallel to the sides of the of "U" shape cathode the specimens were suspended vertically.

The thickness of anodic oxide films formed were calculated from capacitance measurements(8).The oxide film behaves as a dielectric and the system metal-metal oxide interface, oxide-oxide electrode interface-electrolyte can be considered as a parallel plate capacitor. The thickness of the film can be determined using capacitance measurements. The parallel plate capacitor can be schematically represented as metal/oxide/electrolyte.

The equation for A/C capacitance is given by

$$C = \varepsilon A/4 \quad D.9X10^{11} \text{ in farads}$$

Where

ε =dielectric constant of the medium i.e. oxide

A=Area I cm^2

D = Thickness of the dielectric medium in cm units.

The reciprocal capacitance can be a measure of thickness. The electrical double layer capacity(C_{edl}) at the oxide- electrolyte interface must be high in comparison to the capacity of the oxide .The resultant capacitance (C_r) of combined capacitances in series is given by ,

$$1/C_r = 1/C_{oxide} + 1/C_{edl}$$

Where C_{edl} is very large, the measured resultant capacitance, C_r approximates closely to that of C_{oxide} to within usually + or - 1%.

In the present work ,the capacitance of the electrode was measured in series with a subsidiary electrode of Platinum mesh. The capacitance of the subsidiary electrode was constant and much larger than that of the valve electrode. So the measured capacitance is considered as equal to that of latter. The charge on the solution side of the oxide is effectively equivalent to the normal electrical double layer, which is relatively large and probably virtually constant. Hence the capacitance actually measured is effectively that of the valve electrode itself.

The ^{125}I content of the film was measured with an end window G.M counter. Anodic films formed on samples of

Nb and Zr-2 in 0.1M$(NH_4)_2SO_4$ in the presence of a mill mole of ^{125}I$^-$ were thinned by abrasion with a tissue paper impregnated with 0.5µ diamond paste. Uniform layers of oxide films could be removed and this could be judged from interference colours. The thickness remaining was estimated from capacitance data and activity was measured with G.M counter.

Results and Discussion

Zircaloy-2 and niobium samples were anodized in 0.1M$(NH_4)_2SO_4$, separately at a constant current density of 8 m A/cm^2 and at room temperature. The variation of formation voltage vs. time was measured. The plots of formation voltage vs. time are shown in Fig.1 and Fig.2 for Zr-2 & Nb respectively. The plots were found to be linear up to breakdown voltage in case of Zr-2 and formation rate (dV/dT) was constant 1.69 v sec^{-1} and independent of thickness up to a formation voltage of 100 volts. Whilst plot of Nb consisted of two linear portions intersecting at 30 volts. The formation rate was initially 1.33 v sec^{-1} and beyond 30 volts it fell to 0.5 v sec^{-1} .

The plots of reciprocal capacitance vs. time for Zr-2 and Nb (Fig.3 & Fig.4 respectively) were found to be linear. The linear plots of reciprocal capacitance vs. Time (Fig-3 and Fig.4 for Zr-2 and Nb respectively) show that field strength required to maintain a constant ionic current through the film is independent of the thickness .There are two methods of evaluating field strength across the oxide.

1.An integral field defined as V/D.
2.Differential field by (d V / d D)$_{W,a,q}$

Where V = oxide over potential formation voltage(for thick films)

D = thickness
w = The height of the energy barrier
a = half jump distance associated with 'W'
q = charge on mobile ion or vacancy

If the current efficiency is not 100% , the total current passed is made up of an ionic current (which is responsible for the growth of the oxide) , electronic current (which liberates oxygen) and leakage current (down the cracks and other imperfections across the film). For a chemically polished specimen , the leakage current may be considered to be negligible and the current efficiency is given by,

$$\eta = \frac{D \text{ (experimental)}}{D \text{ (calculated)}}$$

Current efficiency is calculated from the rate of film formation. As the rate of film formation increases the current efficiency increases.

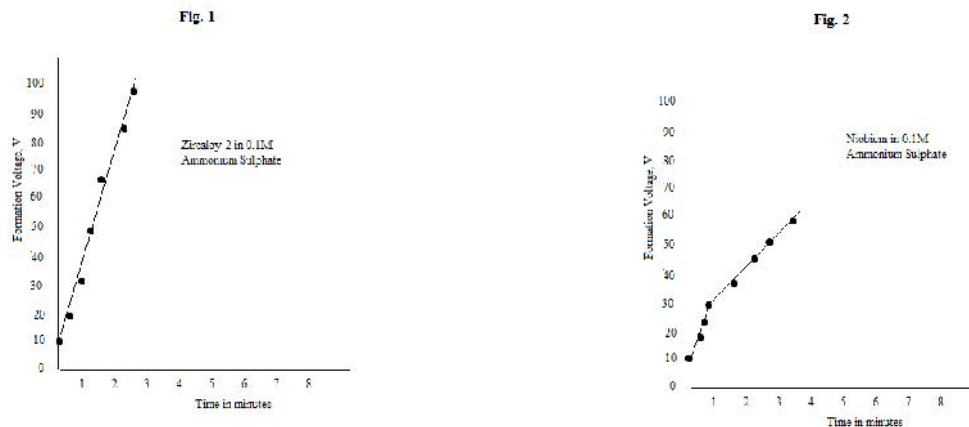**Fig.1 and Fig.2**. The plots of formation voltage vs. time of Zr-2 & Nb

Fig.3 & Fig.4 The plots of reciprocal capacitance vs. time for Zr-2 and Nb
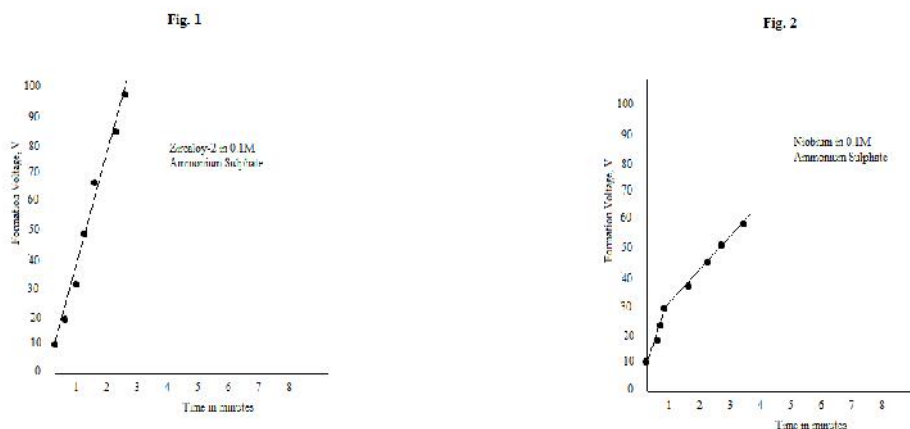

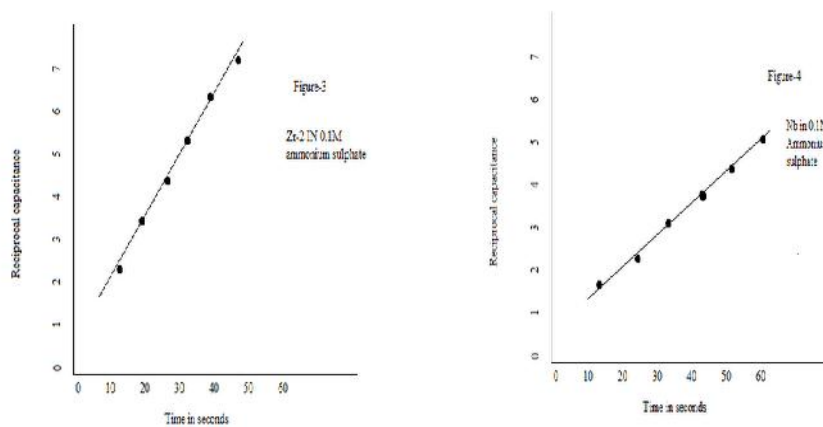**Fig-3 and Fig.4** The linear plots of reciprocal capacitance vs. Time (for Zr-2 and Nb r

179

Table-1 Anodisation parameters:

Metal	electrolyte	Formation rate (v/sec)	Current efficiency %	Differential field
Zircaloy-2	$0.1M(NH_4)_2SO_4$	1.69	80	4.2
Niobium	$0.1M(NH_4)_2SO_4$	1.33	65	3.9

Fig 5 and 6. The uptake and distribution of iodide vs. thickness of anodic film for the anodisation of Nb and Zr-2
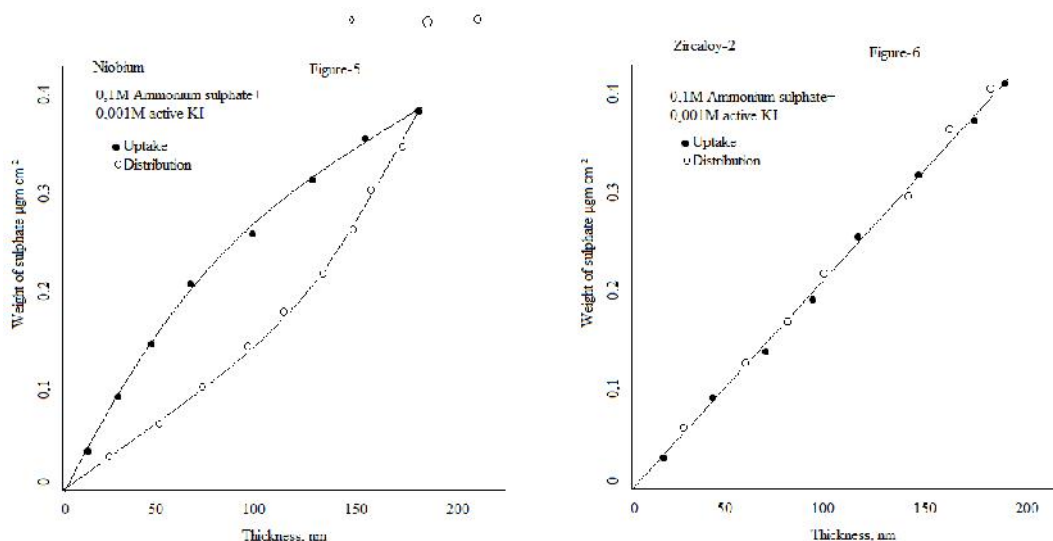
The values of formation rate (dV/dT), current efficiency and differential field are summarized in Table-1.

Radiotracer studies were done using active KI to know the mechanism of film formation .Anodic films were formed on separate samples o f Zr-2 and Nb *in* $0.1M(NH_4)_2SO_4$ in the presence of a mill mole of K ^{125}I at intervals of 20 v and their activity measured. The uptake and distribution of iodide vs. thickness of anodic film for the anodisation of Nb and Zr-2 are shown in figures 5 and 6 respectively.

Conclusion

It is interesting to note that when the anodisation of Zr-2 was carried in $0.1M(NH_4)_2SO_4$, the formation rate , ionic current efficiency and differential field were more than when Nb was anodized in $0.1M(NH_4)_2SO_4$ .The variation in formation rate, current efficiency and differential field may be attributed to the amount of anion incorporation (10) which might be more in the case when Zr-2 was anodized in $0.1M(NH_4)_2SO_4$.

When Nb was anodized in $0.1M(NH_4)_2SO_4$ +0.001M k^{125} I (fig.5) the distribution of iodide ions was found to be in the reverse order of uptake. The thickness and Uptake of I $^-$ was measured at different stages. It can be seen that as the outer layers are removed I$^-$ content decreases steeply. Thus the distribution of iodide ions across the oxide is found to be concentrated in the outer layers . The distribution in the inner layers is approximately uniform and in the reverse order of the uptake of I$^-$ /V/CM^2 Hence the mechanism for the oxide film formation is via interstitial movement of metal ions(11) for the anodisation of Nb. Whilst in fig.6 for the anodisation of Zr-2 the distribution of iodide ions was found to be conserved. Hence the mechanism suggested is via vacancy diffusion of oxide ions(12,13).As the anion movement is predominant during the growth of the oxide film , it can be suggested that the new oxide layers are formed at the oxide/ electrolyte interface (14,15).

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Biography

The author Dr. P.Shobharani has completed her MSc.(with four gold medals – 1990) , PhD (CSIR - 1995) , Post Doctoral Research (CSIR - 2000) , CSIR Research scientist , Pool Officer (2004) from Osmania University , India . She was a C.S.I.R fellow for a period of 14 years and has more than 18 years of research and teaching experience with 17 research papers published in national and international journals. Area of research is physico – organic chemistry.