RESEARCH ARTICLE

KINETICS OF ANODIC OXIDATION OF ZIRCALOY-4 IN 0.1M SODIUM CARBONATE IN BOTH AQUEOUS AND GLYCOLIC MEDIA

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A B S T R A C T

Kinetics of anodic oxidation of Zircaly-4 have been studied at a constant current density of 8 mA/cm^2 and at room temperature. Thickness estimates were made from capacitance data. The plots of formation voltage vs time, reciprocal capacitance vs time, reciprocal capacitance vs. formation voltage and thickness vs formation voltage are liner upto a formation voltage of 130 V (120mm) in aqueous medium whilst in25%, 50% and 75% glycolic media they were liner upto 165 V (230 nm), 220 V (230 nm) and 270 V (260 nm) respectively. The rate of formation the differential field of formation and the current efficiency in aqueous, 25%, 50% and 75% glycolic media were found to be 6.66 MV/cm, 79.92%; and 6.54 MV/cm, 91.23%, 6.45 MV/cm, 94.38%,respectively.

INTRODUCTION

It is well known that when valve metals such as zirconium, its alloys are anodically polarized, interference – coloured oxide films are formed. Smooth and mechanically perfect anodic films can act as dielectrics in capacitors. The phenomenon of anodic oxidation plays a basic role in micro-circuitry. Mclean 1

The kinetics of anodic oxidation of titanium have been studied in various electrolytes in both aqueous and glycolic media by Dyer and Leach[1], Muzushima[2], Masashi Koyama[3,4], Tazima and Mori[5], Cheseldine[6], and Anjaneyulu[7].

Dyer and Leach[1] studied the anodic oxidation of titanium in 3% ammonium tetra hydrogen borate and 0.1M Na$_2$CO$_3$ + 0.1 M NaHCO$_3$ at various constant current densities. They found that the density values of the oxide during the initial stages of film formation were lower than the generally reported values and it was attributed to the formation of amorphous films during the initial growth.

Muzushima[2] studied the formation of anodic films on titanium in 10% ammonium borate in glycolic medium at constant current densities ranging from 12.5 mA/dm^2 to 200 mA/dm^2 and at various temperatures and found that the rate of thickness per volt (A/V) was found to decrease with increase in temperature. Tazima and Mori[5] studied the oxide film formation on titanium in saturated ammonium borate at a constant current density of 100 mA/cm^2 and at 25°C and found that the capacitance of the films formed on titanium in borate solution was about 40 times that of the anodic Al$_2$O$_3$ films.

In the present work an attempt is made to study the kinetics of anodic oxidation of titanium in aqueous and glycolic solutions of 0.1 M Sodium Carbonate.

MATERIALS AND METHODS

The specimens used were cut with the aid of a punch from 0.1 mm thick annealed, rolled sheet of zircaloy-4 of 97.9% purity. Main impurities reported were tin, iron and chromium. The specimen has 1cm^2 working area on either side and a tag of about 2 cm long. The specimens were chemically polished in a mixture of 2 parts HNO$_3$, 1 part HF, and 4 parts H$_2$O, rinsed in concentrated HNO$_3$ and finally cleaned several times in distilled water. The tags were heavily anodized in 0.1M propionic acid up to 200 volts. A small portion of the film towards the terminal end of the tag was filed for the purpose of electrical contact. Anodization was carried out at a constant current density of 8mA/cm^2 and at room temperature in a closed cell of 200 ml capacity. The specimens were suspended from the heavily anodized tag, the minimum of it being immersed in the electrolyte. The platinum cathode had a 20 cm^2 superficial area to make the double layer capacitance as large as possible. The constant current generator used was a stabilized power supply unit (built by Physitech, Hyderabad). A digital LCR meter (Type VLCR 6, built by Physitech, Hyderabad) was used at 1KHz to measure the capacitance data and thickness of the dielectric were calculated from these values assuming the oxide forms a parallel plate capacitor with a dielectric constant of 47[12].

RESULTS AND DISCUSSION

Anodic films were formed on separate samples in aqueous, 25%, 50% and 75% glycolic solutions of 0.1 M Sodium Carbonate at a constant current density of 8mA/cm^2. The current was interrupted at regular voltage increments to measure the capacitance.

The plots of formation voltage vs time, reciprocal capacitance vs time, reciprocal capacitance vs formation voltage, and

thickness vs formation voltage were drawn in each of the experiments. In aqueous medium the plots were linear upto a formation voltage of 130 V (120mm) whilst in 25%,50% and 95% glycolic media they were liner up to 165 V (230 nm) ,220 V (230 nm) and 270 V (260 nm) respectively. The details are given in Fig. 1 & 2. The rate of formation, the differential field of formation, and the current efficiency were found to be more in 75% glycolic medium that in 50%, 25% and aqueous media. The results are summarised in the table I.

Table 1 Anodic films formed on Zircaloy-4 in 0.1M Sodium Carbonate

Percentage of glycol	Formation rate, V.sec^{-1}	Current efficiency, η, %	Differential field, MV.cm^{-1}
0	2.00	66.40	6.75
25	2.38	79.92	6.66
50	2.67	91.23	6.54
75	2.72	94.38	6.45

The linearity of the plots up to the voltages mentioned above in different media suggest that the growth of the film is uniform and the rate of formation, differential field of formation and current efficiency are independent of the thickness of the oxide film.

Masashi Koyama[3] studied the formation of anodic films on titanium in non-aqueous solutions (mono or polyhydric alcohols, organic acids, or liquid ethers) of borax, ammonium borate, ammonium phosphate, ammonium citrate and found that the film was composed of double layers and suitable for electrolytic capacitor. He has also found[4] that the current efficiency was less (67-68%) in aqueous solutions than in non-aqueous solution. Cheseldine[6] observed that during the anodization of titanium in aqueous and non-aqueous solutions of HCOOH, HF, H_3PO_4, and Et_3N the limiting voltages went upto 60-70 V in aqueous solutions whilst in the absence of water it increased to 260V.

Anjaneyulu[7] studied the kinetics of anodic oxidation of titanium in 0.04 M KNO_3 by changing the glycol content of the aqueous solutions from 0 to 100%. He observed that with titanium an increase in the glycol content in the solution increased the maximum formation voltage that could be reached, formation rate (dv/dt) and differential field.

Narayana[13] studied the kinetics of anodic oxidation of zirconium in aqueous and glycolic solutions of 0.05 M oxalic acid at 4 mA/cm^2 and at room temperature. He found that the sudden decrease in rate of formation observed at about 120V in aqueous medium and the non-uniformity in surface interference colours at this formation voltage disappeared when films were formed in alcoholic medium. The rate of formation, the differential field of formation, and the current efficiency were more with glycol and glycol water mixture than in water.
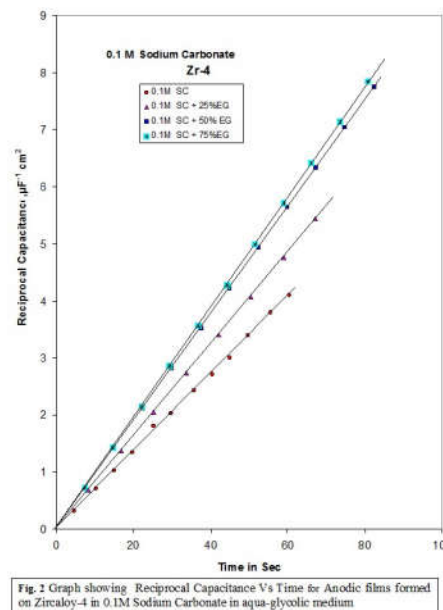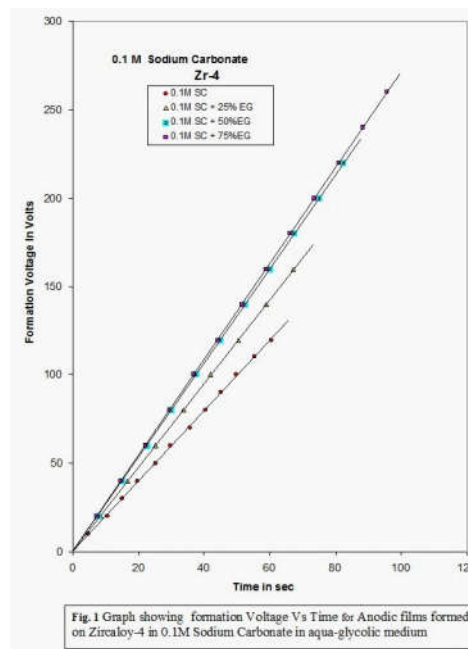
Vermilyea studied the formation of anodic films on tantalum in aqueous[8] and non-aqueous solutions[9] and suggested that the composition of a film depends on the solution in which it was formed. Charlesby[10] studied the formation of anodic films on zirconium in citric acid, ammonium borate and boric acid solutions and found that they possessed similar colours and capacity values but were 10% thinner than the films formed in sulphuric acid.

Table 2 Variation of dielectric constant as a function of solution composition

EG	% Dielectric constant
0	78.1
25	73.8
50	69.2
75	57.8

EG= ethylene glycol

A further increase in the percentage of ethylene glycol to 80% results in non-uniformity in the film formation, which may be attributed to the fact that the electrolyte becomes highly non-polar due to the addition of more ethylene glycol. At high ethylene glycol concentrations, the mobility of the oxide ions (Which form the oxide film) decreases. Hence, in 80% ethylene glycol solution, the kinetics are slow. Though the dielectric constant value of the >80% ethylene glycol solution is less, there is still poor film formation Table-2. This can be explained on the basis of the highly non-polar nature of the medium, which plays a major role in the anodization process.

Fig. 1 Graph showing formation Voltage Vs Time for Anodic films formed on Zircaloy-4 in 0.1M Sodium Carbonate in aqua-glycolic medium

Fig. 2 Graph showing Reciprocal Capacitance Vs Time for Anodic films formed on Zircaloy-4 in 0.1M Sodium Carbonate in aqua-glycolic medium

The increase in the peak voltage, formation rate, differential field of formation and the current efficiency with the increase in the glycol content of the solution may be attributed to the decrease in the dielectric constant of the solution with increase in the glycol content of the solution.

CONCLUSION

For the anodization of zircaloy-4, the kinetics (formation rate, current efficiency) are better in 0.1 M Sodium Carbonate with aquo-glycolic media. Use of aquoglycolic media with up to 75% ethylene glycol showed improvement in the kinetics.

Acknowledgements

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