

Effect of Solvent and Temperature on the Anodic Oxide Films Formed on Nb in 0.1 M EDTA (Sodium Salt): Scanned Electron Micrograph Studies

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Abstract: Anodization of Nb in 0.1 M EDTA (Sodium salt) has been carried out. Kinetics of anodic oxidation of Nb has been studied at a constant current density of 8 mA cm^{-2} and at room temperature. The plots of formation voltage *vs.* time, reciprocal capacitance *vs.* time and reciprocal capacitance *vs.* formation voltage were drawn. From these plots, formation rate, current efficiency and differential field were calculated. The Addition of solvent (Ethylene glycol) showed better kinetic results. For 20, 40, 60 and 80% aquo-glycolic media, the dielectric constant values are low leading to the marked improvement in the kinetics. The surface morphology of the anodic films was also studied by scanning electron micrographs (SEM). Kinetics was also studied at different temperatures ranging from 273 K to 333 K at a constant current density of 8 mA cm^{-2} . It was observed that kinetic results were found to be increasing linearly with the decrease in temperature

Keywords: Anodization, Formation rate, Current efficiency, Differential field, Nb, EDTA (Sodium salt), Temperature

Introduction

Metals such as niobium, zirconium and its alloys, tantalum, titanium *etc.*, can be anodized to give thin, uniform and relatively flaw free oxide films, which are stable chemically and mechanically. Anodic oxide films formed on Niobium are useful in the field of electrical and electronic components (capacitors, resistors, diodes, photoelectric devices *etc.*), corrosion protection and for decorative purposes. Several other applications have been investigated by others¹⁻⁵.

In the present work, the kinetics of anodic oxidation of niobium in aqueous solution of 0.1 M EDTA (Sodium salt) and aquo-glycolic media in various proportions (v/v) of water-ethylene glycol mixtures ranging from 0 to 80% ethylene glycol were studied. Scanning electron microscopic studies was also carried out to observe the changes in the surface morphology of the anodic films formed. An attempt was also made to study the kinetics at various temperatures ranging from 273 K to 333 K at a constant current density of 8 mA cm^{-2} .

Experimental

Niobium was of 99.5% purity, supplied in the form of annealed sheet by NFC, Hyderabad as gift samples. In the present work, the foil samples used were cut with the aid of a punch into flag shaped specimens of 1 cm² working area on both side and 2 cm long tag. The chemical polishing mixture for niobium is 5:5:1.5 by volume 53% HNO₃, 49% HF and 98% H₂SO₄. For anodizing, a closed shell of 200 mL capacity was used. The cathode used was a platinum foil of 20 cm² superficial area to make double layer capacitance as large as possible. Electrolytes used were 0.1 M EDTA (Sodium salt) in 20, 40, 60 and 80% aquo-glycolic mixtures, the solvent being ethylene glycol. The temperatures used in the current study were ranging from 273 K to 333 K. All the experiments were carried out at a constant current density of 8 mA. Cm⁻². The experimental procedure for the anodization is given elsewhere⁶. The kinetic results calculated are formation rate in Vs⁻¹, current efficiency (η) % and differential fields of formation (FD) in MV cm⁻¹ from the conventional plots V vs. t, 1/C vs. t and 1/C vs. V.

The surface morphology of the anodic film was examined using scanning electron microscope (SEM). The SEM's were taken at IICT, CSIR and Hyderabad. The surface was thoroughly rinsed with distilled water and dried under infrared lamp and cleaned gently with fine tissue paper. The surface was coated with gold, palladium conducting material using evaporation technique and signal processed secondary electron images were taken from scanning electron microscope model SEM Hitachi- S520 at 10 KV, Hitachi instruments made in Japan (Oxford link ISIS- 300 UK)

Results and Discussion

Solvent effect and SEM studies

Anodization of niobium in 0.1 M EDTA (Sodium salt) was performed by mixing various proportions of ethylene glycol to the aqueous solution (20, 40, 60 and 80%). There was an improvement in the kinetics as given in Table 1. The relevant plots are shown in Figure 1 and Figure 2. Aquo-organic solutions aid in the formation of good oxide films and act as better electrolytic capacitors⁷. These facts support the current results obtained in aquo-organic mixtures of 0.1 M EDTA (sodium salt). It can be explained on the basis of decrease in the dielectric constant of the medium as shown in Table 2.

Table 1. Anodic films formed on niobium in 0.1 M EDTA (Sodium salt) both aqueous and aquo-glycolic-media

Electrolyte	Formation rate, dV/dt, V.s ⁻¹	Current efficiency, η , %	Differential field, F _D (MV.cm ⁻¹)
0.1 M EDTA(sodium salt)	1.98	72.0	5.465
0.1 M EDTA(sodium salt) + 20% EG	2.32	85.1	5.407
0.1 M EDTA(sodium salt) + 40% EG	2.44	90.2	5.358
0.1 M EDTA(sodium salt) + 60% EG	2.53	94.3	5.321
0.1 M EDTA(sodium salt) + 80% EG	2.60	97.2	5.295

EDTA-Ethylene diamine tetra acetic acid EG-Ethylene glycol

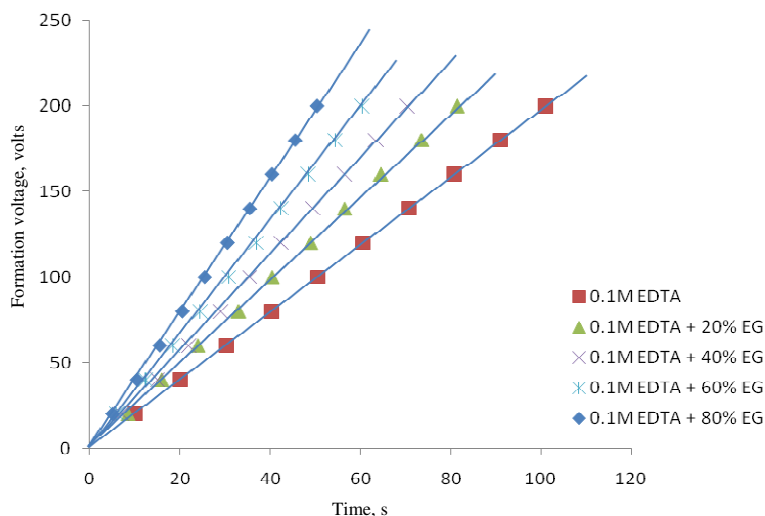


Figure 1. Plot of formation voltage as a function of time in aquo-glycolic solution

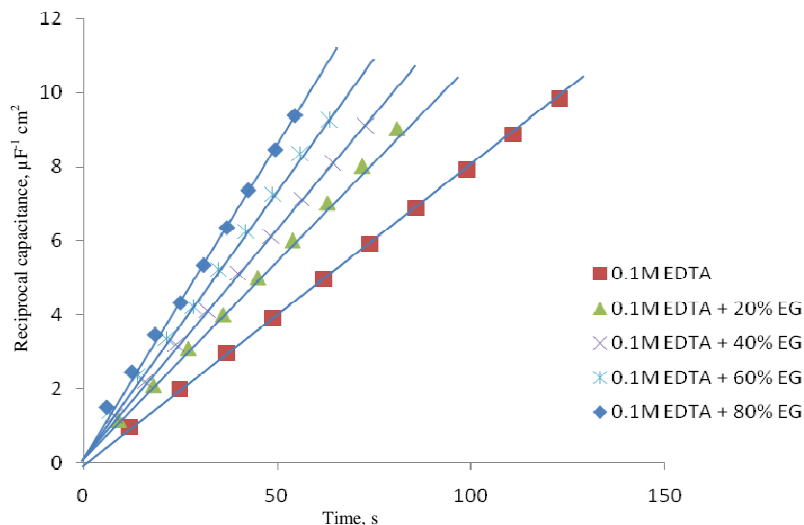


Figure 2. Plot of reciprocal capacitance as a function of time in aquo-glycolic solution

Table 2. Variation of dielectric constant as a function of time in aquo-glycolic solution

EG, %	0	20	40	60	80	100
Dielectric constant	80.0	72.8	69.2	57.8	43.2	37.7

In solutions of low dielectric constant there is less chance of ion-dipole interactions (solvent-ion interactions) which do not interfere in the oxide film formation. However the ions in the high dielectric constant solutions interact with oxide ions responsible for oxide film formation due to high solvation with water molecules. In such solutions, the kinetics is poor. The kinetics are better in low dielectric constant solutions for 20, 40, 60 and 80% aquo-glycolic media, the dielectric constant values are low leading to a marked improvement in the kinetics.

Scanning electron micrographs

Figure 3 and Figure 4 are the scanning electron micrographs of anodic films formed on niobium in aqueous and aquo-glycolic solutions of 0.1 M EDTA (Sodium salt) upto 200V.

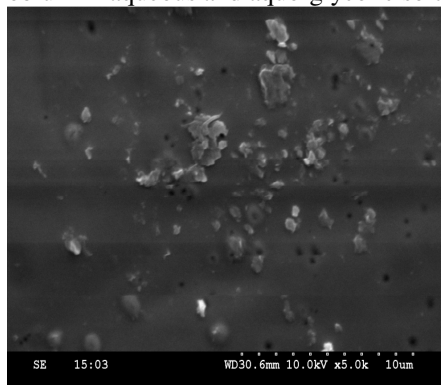


Figure 3. SEM of the film formed up to 220 V in 0.1 M EDTA (Sodium salt) (aqueous medium) at room temperature (Magnification of the micrograph is X 5000)



Figure 4. SEM of the film formed upto 220 V in 0.1 M EDTA (Sodium salt) (glycolic medium) at room temperature (Magnification of the micrograph is X 5000)

When compared, the roughness and non-uniformity of the surface are decreased when electrolytic medium is changed from aqueous to aquo-glycolic medium (Figure 4) is observed to be smoother than the film formed in aqueous medium (Figure 3)

Vermilyea⁸ studied the formation of anodic films on tantalum in aqueous and non-aqueous⁹ solutions. He suggested that the composition of film depends on the solution in which it is formed. Nageshwarrao *et al.*,¹⁰ observed a change in the dielectric constant of oxide films by changing the medium from aqueous to glycolic. Vermilyea⁹ reported that the optical thickness was smaller in the non-aqueous solutions and the increase in weight for a given charge passed could be as much as twice that expected. Moshashi Koyama¹¹ carried out anodization of titanium in non-aqueous media and confirmed that the oxide film consists of double layers and suitable for electrolytic capacitors.

Wei Wei *et al.*,¹² reported the growth of layers by anodization of tantalum in a non-aqueous electrolyte consisting of an optimized glycerol/ethylene glycol mixture with the addition of NH_4F . Schmidt *et al.*,¹³ observed that the layers of TiO_2 obtained in non-aqueous electrolytes are much adherent and uniform than those realized in aqueous media. Lavanya¹⁴ studied Anodization of zirconium-niobium-copper (ZNC) alloy in 0.1 M mandelic acid and suggested that the effect of solvent (ethylene glycol) and added anionic impurities (sulphates, phosphates and carbonates) showed better kinetic results

Panasa Reddy *et al.*,¹⁵ and Lavanya *et al.*,¹⁶ also studied in trisodium citrate, 0.1 M KOH (aquo-glycolic) respectively and found that the breakdown voltage was higher when anodized in ethylene glycol medium. This was also supported by other worker¹⁷. Shukla¹⁸ carried out the study of effect of aquo-glycolic media on anodization of zircaloy-4 in 0.1 M sulphamic acid and found that the addition of solvent improved the kinetic results.

Effect of temperature

Anodizations were carried out on niobium at various temperatures ranging from 273 K to 333 K and at a constant current density of 8 mA.cm^{-2} in 0.1 M EDTA (Sodium salt).

The conventional plots were drawn as shown in the Figure 5 and Figure 6. From these plots, the kinetic results were calculated. It was observed that the formation rate, current efficiency, differential field and break down voltage were found to be increasing linearly with the decrease in temperature as shown in Table 3. The decrease in the field, formation rate and Breakdown voltage with the increase in temperature may be attributed to the decrease in the incorporation of anions into the film and may also be due to the dissolution of the film with the increase in temperature. Colton and Wood¹⁹ reported that the BDV was decreased with increase in temperature in the case of titanium oxide films and explained the observation on the basis of dissolution of the film. Bhaskarreddy *et al.*,²⁰ observed the similar trend of decreasing kinetic results with increase in temperature in 0.1 M potassium tartrate. The same results were observed by other workers²¹⁻²⁶.

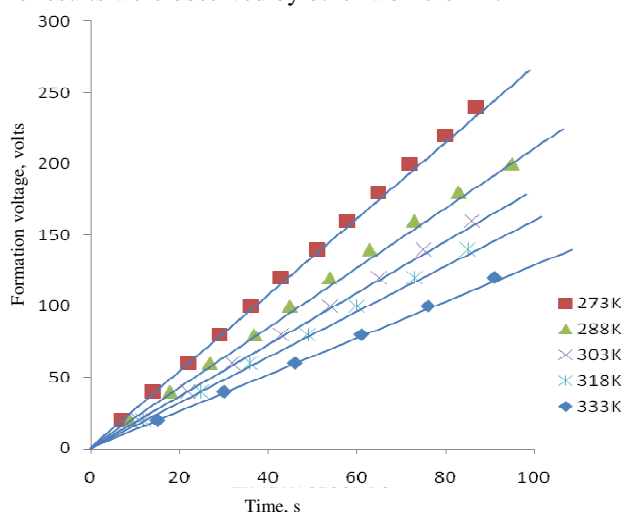


Figure 5. Plot of formation voltage as a function of time at different temperatures

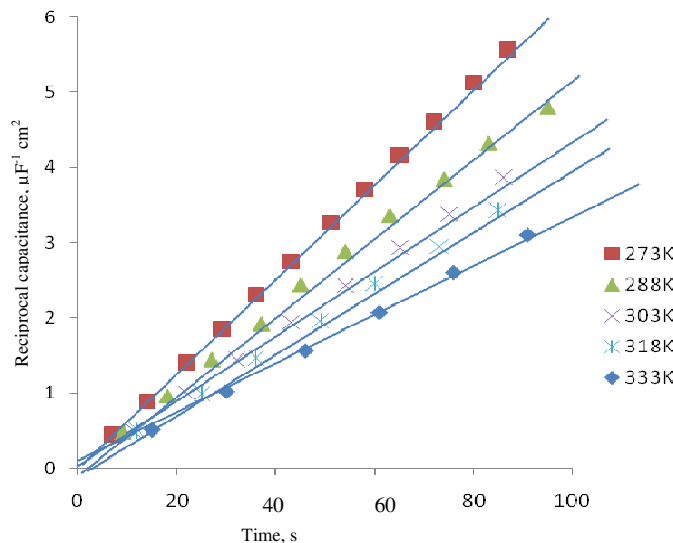


Figure 6. Plot of reciprocal capacitance as a function of time at different temperatures

Table 3. Anodic films formed on niobium in 0.1 M EDTA (Sodium salt) at different temperatures

Temperature, T, K	Formation rate, dV/dt, V.s ⁻¹	Current efficiency, η , %	Differential field, F_D (MV.cm ⁻¹)	Break down voltage (V_B), Volts
273	2.65	91.0	5.830	229
288	2.15	66.0	5.710	212
303	1.78	61.0	5.648	197
318	1.54	57.8	5.441	167
333	1.32	46.2	5.210	139

Conclusion

By changing the solvent medium from aqueous to glycolic, the kinetics of film formation on niobium in 0.1 M EDTA (Sodium salt) have been studied and it is observed that the peak voltage, formation rate, current efficiency are increased but differential field of formation decreased with the glycol content of solution. This can be attributed to the decrease in the dielectric constant of the solution with the increase in glycol content of the solution.

It was also observed that the kinetics were good at low temperatures. It was observed that the formation rate, current efficiency, differential field and break down voltage were found to be increasing linearly with the decrease in temperature. The decrease in the field, formation rate and breakdown voltage with the increase in temperature may be attributed to the decrease in the incorporation of anions into the film and may also be due to the dissolution of the film with the increase in temperature.

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