



Anodic Oxidation of Zr-Nb in 0.1M Sodium bisulphite: Scanned Electron Micrograph Studies

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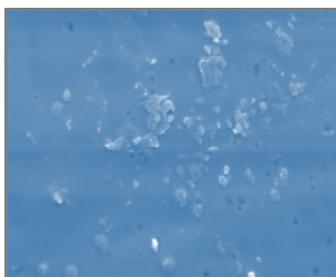
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ABSTRACT

The Kinetic studies were done on the films formed on Zr-Nb in 0.1M sodium bisulphite at a constant current density of 8mA.cm^{-2} and at 273K. 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 different aquo-glycolic media, the dielectric constant values are low leading to the marked improvement in the kinetics as Aquo-organic solutions aid in the formation of good oxide films and act as better electrolytic capacitors. The surface morphology of the anodic films was also studied by Scanning Electron Micrographs (SEM).

Graphical Abstract



SEM formed in 0.1M Sodium bisulphite
(aqueous media)

Keywords: Anodization, formation rate, Current efficiency, Differential field, Zr-Nb, Sodium bisulphate.

INTRODUCTION

Zirconium based alloys are used as the structural material in the water- cooled thermal reactors [1, 2]. Zr-Nb, due to their low cross-section for thermal neutrons and because of their relatively good corrosion resistance against water and steam, has been used in water cooled reactors. Zirconium and its alloys are of primary importance in nuclear technology. Anodization of Zirconium alloys have been studied in some electrolytes [3-6]. Vermilyea studied the formation of anodic films on tantalum in aqueous [7] and non-aqueous [8] solutions. He suggested that the composition of film depends on

the solution in which it is formed. Seregina *et al.*, [9] studied the anodization of aluminium alloys in the solution of sulpho-salicylic acid (90 g cc⁻¹) and found that thick films are possible during anodization at room temperature. Nageshwar Rao *et al.*, [10] observed a change in the dielectric constant of oxide films by changing the medium from aqueous to glycolic.

Aparna [11] also observed the same trend of increasing kinetic results with increase in glycol content in 0.1M Picolinic acid and sodium methoxide for Zr-2 and Ti. Vermilyea [8] 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 Koyama [12] 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 *et al.*, [13] 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 NH₄F.

Schmidt *et al.*, [14] observed that the layers of TiO₂ obtained in non-aqueous electrolytes are much adherent and uniform than those realized in aqueous media. Climent Montoliu *et al.* [15] studied the anodization of titanium in acid, alkali and neutral baths (aqueous and aquo-glycolic) and suggested from the structure and dielectric properties, that the anodic coatings formed in non-aqueous media acts as better dielectric capacitors.

Panasa Reddy *et al.*, [16] and Lavanya *et al.*, [17] also studied in trisodium citrate, 0.1M KOH(aquo-glycolic) respectively and found that the breakdown voltage was higher when anodized in ethylene glycol medium. This was also supported by other workers [18]. Shukla [19] carried out the study of effect of aquo-glycolic media on Anodization of zircaloy-4 in 0.1M sulphamic acid and found that the addition of solvent improved the kinetic results.

In the present work, the kinetics of anodic oxidation of Zr-Nb in aqueous solutions of 0.1M Sodium bisulphite and aquo-glycolic media in various proportions (v/v) of water-ethylene glycol mixtures ranging from 0% to 80% ethylene glycol are studied. Scanning electron microscopic studies was also carried out to observe the changes in the surface morphology of the anodic films formed.

MATERIALS AND METHODS

Zr-Nb was of 98% nominal purity, supplied in the form of annealed rolled sheet with 0.2 mm thickness, gifted by Nuclear Fuel complex, Hyderabad as gift samples. A typical composition of nuclear-grade zirconium alloys is more than 95 weight percent zirconium and less than 2% of tin, niobium, iron, chromium, nickel and other metals, which are added to improve mechanical properties and corrosion resistance.

Now, the foil samples used were cut with the aid of a punch into flag-shaped specimens of 1cm² working area on both sides and 2 cm long tag. The chemical polishing mixture consisted of acids such as HNO₃, H₂O and HF in a definite volume ratio of 3:3:1. Electrolytes used were 0.1M sodium bisulphite in 20%, 40%, 60% and 80% aquo-glycolic mixtures, the solvent being ethylene-glycol. For anodizing, a closed shell of 200 mL capacity was used. The cathode used was a platinum foil of 20cm² superficial area to make double layer capacitance as large as possible.

All the experiments were carried out at a constant current density of 8 mA.cm⁻². The experimental procedure for the anodization is given elsewhere [20]. The kinetic results calculated are formation rate in Vs⁻¹, current efficiency (η) % and differential fields of formation (F_D) in MV cm⁻¹ from the conventional plots V vs. t, 1/C vs. t and 1/C vs. V. The Kinetics of film formation was studied at different concentrations of added solvent i.e ethylene glycol to the main electrolyte (Sodium bisulphite)

The surface morphology of the anodic film was examined using Scanning Electron Microscope (SEM). The SEM's were taken at ICT-CSIR, 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

Anodization of Zr-Nb was done in 0.1M Sodium bisulphite. The formation rate, current efficiency and differential field were calculated. The effect of solvent on Zr-Nb was studied in 0.1M Sodium bisulphite to check whether there was enhancement in kinetics of film formation [21, 22].

Effect of Solvent: Anodization of Zr-Nb in 0.1M Sodium bisulphite 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 figures 1 and 2. Aquo-organic solutions aid in the formation of good oxide films and act as better electrolytic capacitors [23]. These facts support the current results obtained in aquo-organic mixtures of 0.1M Sodium bisulphite. It can be explained on the basis of decrease in the dielectric constant of the medium (Table 2).

Table 1. Anodic films formed on Zr-Nb in 0.1M Sodium Bisulphite (SB) both aqueous and aquo-glycolic media

Electrolyte	Formation Rate, dV/dt ($V.s^{-1}$)	Current efficiency, η (%)	Differential field, F_D ($MV.cm^{-1}$)
0.1M SB	2.00	68.0	5.810
0.1M SB + 20% EG	2.12	81.0	5.741
0.1M SB + 40% EG	2.19	87.4	5.620
0.1M SB + 60% EG	2.30	93.5	5.540
0.1M SB+ 80% EG	2.40	97.5	5.495

SB- Sodium bisulphate, EG-Ethylene glycol

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

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

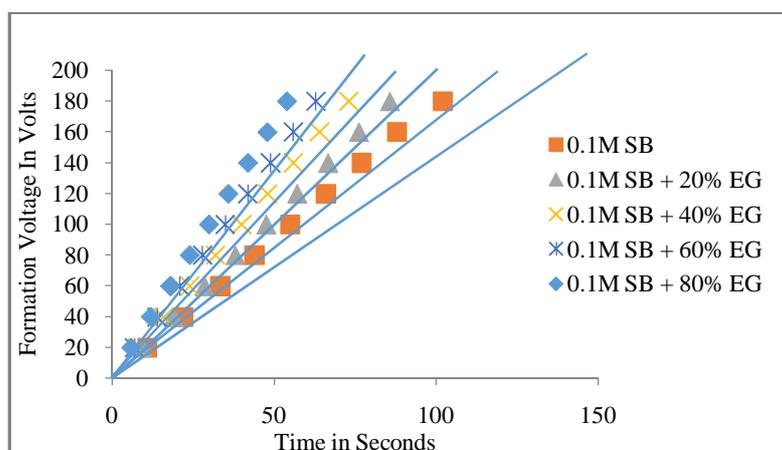


Figure 1. Plot of formation voltage as a function of time in aquo-glycolic solution.

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.

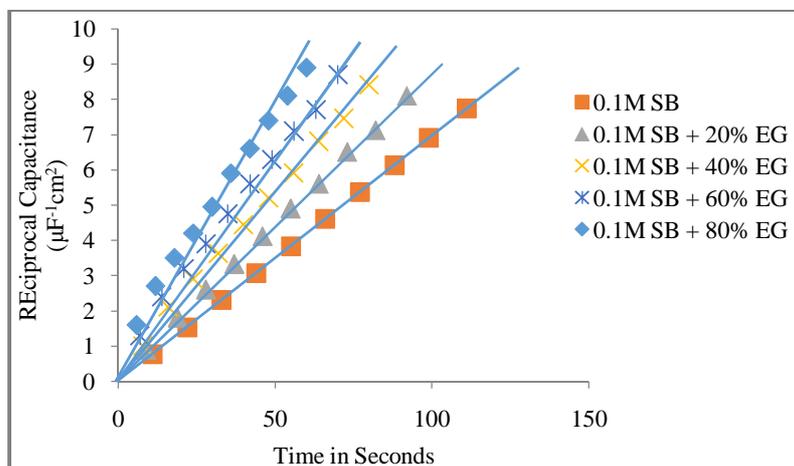


Figure 2. Plot of reciprocal capacitance as a function of time in aquo-glycolic solution.

Scanning Electron Micrographs: Figure 3 and 4 are the Scanning Electron Micrographs of anodic films formed on Zr-Nb in aqueous and aquo-glycolic solutions of 0.1M Sodium bisulphite upto 200V.

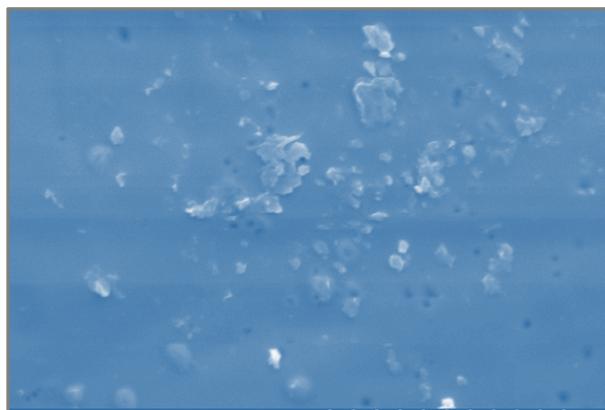


Figure 3. SEM of the film formed upto 220V in 0.1M Sodium bisulphite (aqueous medium) at room temperature (Magnification of the micrograph is X 5000).

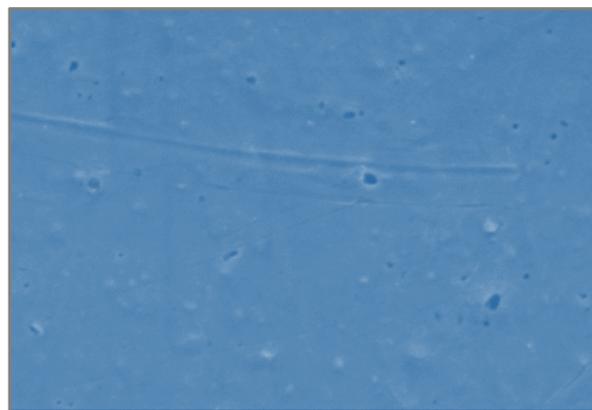


Figure 4. SEM of the film formed upto 220V in 0.1M Sodium bisulphite (glycolic medium) at room temperature (Magnification of the micrograph is X 5000).

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).

APPLICATION

These have wide range of applications such as preparation of Capacitors, Diodes, Semiconductors, Resistors, Photo chemical devices, As a base for selective electroplating, painting and decorative

purposes, Nuclear technology (nuclear fuel storage and water- cooled nuclear reactors), Electrolytic condensers, Insulators, Good corrosion resistant.

CONCLUSION

By changing the solvent medium from aqueous to glycolic, the kinetics of film formation on Zr-Nb in 0.1M sodium bisulphite 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.

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