Chem Sci Trans., 2013, **2(3)**, 1070-1073
DOI:10.7598/cst2013.437

Chemical Science Transactions
ISSN/E-ISSN: 2278-3458/2278-3318

RESEARCH ARTICLE

Growth Kinetics of Zr-4 in Sodium Bisulphite: Solvent Studies

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Received 11 November 2012 / Accepted 15 December 2012

Abstract: Anodization of zircaloy-4 in 0.1 M sodium bisulphite has been carried out. Kinetics of anodic oxidation of zircaloy-4 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.

Keywords: Anodization, Formation rate, Current efficiency, Differential field, Zircaloy-4

Introduction

Zirconium based alloys are used as structural material in the water cooled thermal reactors[1,2]. Zr-4 is an alloy of 98% pure zirconium with other trace impurities. Zr-4 due to their low cross-section for thermal neutrons and because of their relatively good corrosion resistance against water and steam, used in water cooled reactors. Anodization of zirconium alloys have been studied in some electrolytes[3-6].

In the present work, the kinetics of anodic oxidation of Zr-4 in aqueous solutions of 0.1 M 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.

Experimental

Zircaloy-4 was of 98% nominal purity, supplied in the form of annealed sheet by Nuclear Fuel complex, Hyderabad as gift samples. The chemical composition of zircaloy-4: 0.07 wt.% chromium; 0.23 wt.% iron; 1.44 wt.% tin and balance is zirconium.

In the present work, the foil samples used were cut with the aid of a punch into flag-shaped specimens of 1 cm^2 working area on both side and 2 cm long tag. The chemical polishing mixture consisted of acids such as HNO_3, HF and water in a definite volume ratio of 3:3:1.

For anodizing, a closed shell of 200 mL capacity was used. The cathode used was a platinum foil of 20 cm^2 superficial area to make double layer capacitance as large as possible. Electrolytes used were 0.1 M sodium bisulphite in 20, 40, 60 and 80 aquo-glycolic mixtures, the solvent being ethylene-glycol.

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[7]. 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.

Results and Discussion

Anodization of zircaloy-4 was done in 0.1 M sodium bisulphite. The formation rate, current efficiency and differential field were calculated. The effect of solvent on zircaloy-4 was studied in 0.1 M Sodium bisulphite to check whether there was enhancement in kinetics of film formation[8,9].

Effect of solvent

Anodization of zircaloy-4 in 0.1 M 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 & 2. Aquo-organic solutions aid in the formation of good oxide films and act as better electrolytic capacitors[10]. These facts support the current results obtained in aquo-organic mixtures of 0.1 M sodium bisulphite. It can be explained on the basis of decrease in the dielectric constant of the medium (Table 2).

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 are 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.

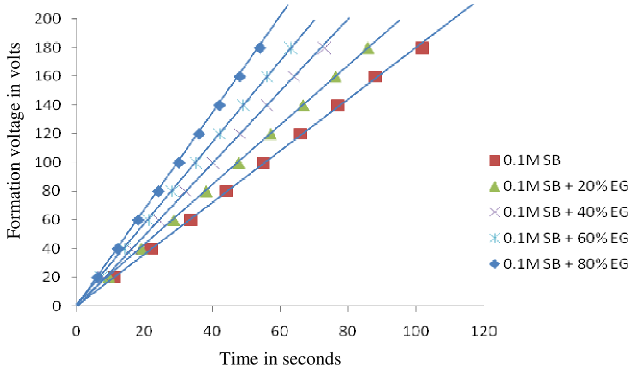

Figure 1. Plot of formation voltage as a function of time in aquo-glycolic solution

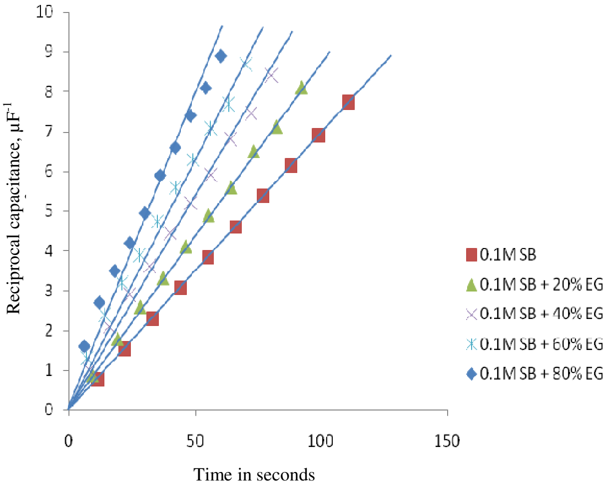

Figure 2. Plot of reciprocal capacitance as a function of time in aquo-glycolic solution

Table 1. Effect of solvent on the anodization of zircaloy-4 in 0.1 M sodium bisulphite

Electrolyte	Formation Rate, dV/dt, V.s^{-1}	Current efficiency, η, %	Differential field, F_D, MV.cm^{-1}
0.1 M 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 bisulphite 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

Vermilyea studied the formation of anodic films on tantalum in aqueous[11] and non-aqueous[12] solutions. He suggested that the composition of film depends on the solution in which it is formed.

Nageshwar rao *et al.*[13] observed a change in the dielectric constant of oxide films by changing the medium from aqueous to glycolic.Vermilyea[12] 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[14] 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.*[15] 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.*[16] observed that the layers of TiO_2 obtained in non-aqueous electrolytes are much adherent and uniform than those realized in aqueous media. Climent Montoliu *et al.*[1] 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.*[18] and Lavanya *et al.*[19] 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 workers[20]. Shukla[21] 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.

Conclusion

By changing the solvent medium from aqueous to glycolic, the kinetics of film formation on zircaloy-4 in 0.1 M 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.

Acknowledgement

The authors are grateful to Prof. Rafiq Mohiuddin, Head, Department of Chemistry, University College for Women, Osmania University. The authors are also grateful to Prof. K. S. S. Sastry for helpful discussions throughout this work. One of the authors (VJJ) wishes to thank Dr. M Surekha Reddy, Head, Department of Chemistry, RBVRR Women's College. The authors are also thankful to Nuclear Fuel Complex, Hyderabad for generous help in providing Zr-4 and Nb samples.

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