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Effect of Aquo-Glycerolic Media and Added Anions on the Anodization of Zircaloy-4 in 0.1M sodium hydroxide

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ABSTRACT

Anodization of zircaloy-4 in 0.1 M sodium hydroxide 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. Thickness estimates were made from capacitance data. The plots of formation voltage vs. time, 1/C vs. Time [or] Thickness by capacitance vs. Thickness by Faradaic, and Formation voltage vs. Thickness by capacitance were drawn and rate of formation, current efficiency and differential field were calculated. The addition of solvent (glycerol) showed better kinetic results in aquo-glycerolic media. For 25%, 50% and 75% aquo-glycerolic media, the dielectric constant values are low leading to a marked improvement in the kinetics .In 80% glycerol, though the dielectric constant value of solution is less, the kinetics was slow which may be attributed to the fact that the electrolyte becomes highly non-polar. Improvement in the kinetics of oxide film formation was observed by the addition of millimolar concentration of anions (SO_4^{2-}, CO_3^{2-} ,). The presence of carbonate ions improved the kinetics of anodization to better extent.

Keywords: Zircaloy-4, Anodization, Formation rate, Current efficiency, Aquo-glycerolic media, Anion impurities.

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INTRODUCTION

Zirconium based alloys are used as structural material in water-cooled thermal reactors [1,2]. Zircaloy-4 is a alloy of 98% pure zirconium with other trace impurities. Zircaloy-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 [3-5].

In the present work, we report the results of our studies on the anodization of zircaloy-4 in 0.1 M sodium hydroxide and the effect of solvent (glycerol) and also the effect of added anion impurities (sulphates and carbonates). We have calculated the formation rate, current efficiency and differential field of formation of zircaloy-4.

EXPERIMENTAL

Zircaloy-4 was of 98% nominal purity, supplied in the form of annealed sheet by Nuclear Fuel Complex, Hyderabad as gift samples. Thinning of this annealed sheet was done by DEFENCE METALLERGICAL RESEARCH LAB, HYDERABAD. 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 1 ½ cm long tag .The chemical polishing mixture consisted of acids such as HNO3, HF and water in a definite volume ratio of 3:3:1.

ELECTROCHEMICAL CONDITIONS

The counter electrode was a sheet of Platinum [6], (2x3 cm, weight 3.000 gm). The working electrode was the Zr-4 [7] sample. For anodizing, a double walled glass cell 100mL capacity was used.The experiments were performed in aqueous media in an electrolyte, 0.1 M sodium hydroxide in 25%, 50% and 75% aquo-glycerolic mixtures, the solvent being glycerol and the added anionic impurities were SO_4^{-2} and CO_3^{-2} in 0.001 M concentration

All experiments were carried out at a constant current density of 8 mA.cm^{-2}. The experimental procedure for the anodization is given elsewhere [8]. 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, D_c vs. D_F and V vs. D_c .

RESULTS AND DISCUSSION

Anodization of zircaloy-4 was done in various electrolytes (acidic, basic and neutral). The formation rate, the current efficiency and the differential fields were calculated.
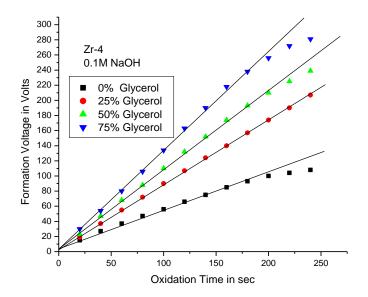
Effect of substitution

The kinetics of zircaloy-4 anodization in 0.1 M sodium hydroxide was better. The effect of solvent and added anionic impurities was studied in 0.1 M sodium hydroxide to check whether there was enhancement in the kinetics of film formation [9,10].

Effect of solvent

Anodization of zircaloy-4 in 0.1 M sodium hydroxide was performed by mixing various proportions of glycerol to the aqueous solution (25%, 50% and 75%). There was an improvement in the kinetics as given in Table 1. The relevant plots are shown in Figures 1&2. Aquo-Inorganic solutions aid in the formation of good oxide films and act as better electrolytic capacitors [11]. These facts support the current results obtained in aquo-Inorganic mixtures of 0.1 M sodium hydroxide. It can be explained on the basis of decrease in the dielectric constant of the medium (Table 2).
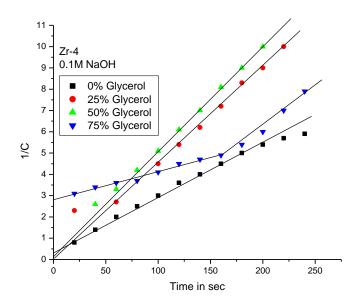
In solutions of low dielectric constant there is less chance of ion-dipole interactions (solvent–ion interactions), which do not interfere in the oxide film formation. However, the ions in the high dielectric constant solutions, interact with oxide ions responsible for oxide film formation due to high salvation with water molecules. In such solutions, the kinetics are poor. The kinetics are better in low dielectric constant solutions. For 25%, 50% and 75% aquo-glycerolic media, the dielectric constant values are low leading to a marked improvement in the kinetics [12]. The oxide film formed on the zircaloy-4 consists of two discrete layers in 0.1 M sodium hydroxide were disappeared and made to a single layer in presence of glycerol .

Fig- 1. Plot of formation voltage as a function of time in aquo-glycerolic solution

Fig 2. Plot of reciprocal capacitance as a function of time in aquo-glycerolic solution

TABLE-1: Effect of solvent on the anodization of zircaloy-4 in 0.1M sodium hydroxide.

Electrolyte	Formation Rate, V.s-1	η, %	F_D in, MV.cm^{-1}
0.1 M SH	0.48	24	4.47
0.1 M SH + 25 % G	0.85	45.6	4.16
0.1 M SH + 50 % G	1.03	47.8	4.81
0.1 M SH + 75 % G	1.3	13	2.36

SH = sodium hydroxide, G= glycerol, η = current efficiency; F_D = differential field of formation.

TABLE-2: Variation of dielectric constant as a function of solution composition

G, %	Dielectric constant, ε
0	80
25	71.4
50	64
75	52.3

G=glycerol

A further increase in the percentage of glycerol 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 glycerol. At high glycerol concentrations, the mobility of the oxide ions (Which form the oxide film) decreases. Hence, in 80% glycerol solution, the kinetics are slow. Though the dielectric constant value of the >80% glycerol solution is less, there is still

poor film formation. 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.

Effect of added anion impurities

Experiments were carried out in 0.1 M sodium hydroxide + 0.001 M SO_4^{2-}, CO_3^{2-} anions to check the effect of the added anions. The addition of sulphates and carbonates resulted in improvement of the kinetics. The presence of carbonate ions improved the kinetics of anodization to better extent. It is observed that the oxide film formed on the alloy consisting of two discrete layers in 0.1M sodium hydroxide appear as a single layer in presence of added anion impurity. The results are given in Table 3 and the plots are shown in Figures 3&4.

Table-3: Effect of added anion impurities

Electrolyte	Formation rate, $V.s^{-1}$	η, %	F_D, $MV.cm^{-1}$
0.1 M SH	0.45	25	40.25
0.1 M SH +0.001 M SO_4^{2-}	0.53	27.7	42.81
0.1 M SH +0.001M CO_3^{2-}	0.7	36.1	43.37

SH = sodium hydroxide; η = current efficiency; F_D = differential field of formation.

The increase in the kinetics when 0.001 M of CO_3^{2-} is added to 0.1 M sodium hydroxide can be explained by the firm incorporation of carbonate ions into the layers of the oxide films [13]. Added anions get incorporated between the ionic vacancy sites of the metal oxide films and reduce the height of the energy barrier of the movement of ions from one ionic site to another, thereby increasing the current. This incorporation increases the current efficiency with much ionic current getting utilized for film formation, which implies better kinetic results.

On the other hand, by the addition of and SO_4^{2-} and CO_3^{2-} there is a little improvement in the kinetics, which implies that certain anions have favorable high influence on the kinetics of oxide film formation. Such ions that are capable of interstitial occupation in the film lattice increase the kinetics.

Fig-3: Plot of fomation voltage as a function of time in anion impurity solution
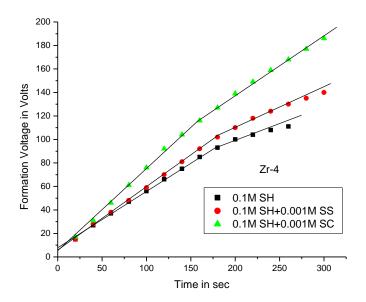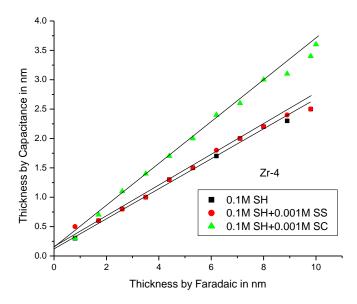

Fig -4: Plot of Thickness by capacitance as a function of Faradaic in anion impurity solution

SS=Sodium Sulphate, SC=Sodium Carbonate

Vermilyea studied the formation of anodic films on tantalum in aqueous [14] and non-aqueous [15] solutions. He suggested that the composition of film depends on the solution in which it is formed.

Seregina et al [16] studied the anodization of aluminium alloys in the solution of sulpho-salicylic acid (90g/cc) and found that thick films are possible during anodization at room temperature.

Nageshwar rao et al [17] observed a change in the dielectric constant of oxide films by changing the medium from aqueous to glycolic.

Aparna [18] also observed the same trend of increasing kinetic results with increase in glycol content in 0.1Mpicolinic acid and sodium methoxide for Zr-2 and Ti.

Vermilyea [15] 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 [19] 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 [20] 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 [21]   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 [22] studied the anodization of titanium in acids, 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 [23] and Lavanya et al[24] also studied in tri sodium 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 [25].

Rama devi et al [26] carried out Anodization of Niobium in 0.1M potassium chromate, in aquo-glycerol media showed better kinetic results.

Shukla[27] 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.

CONCLUSION

For the anodization of zircaloy-4, the kinetics (formation rate, current efficiency) are better in 0.1 M sodium hydroxide with aquo-glycerolic media and added anion impurities. Use of aquo-glycerolic media with up to 75% glycerol showed improvement in the kinetics.

Addition of carbonate anions in 0.001 M concentration showed improvement in the kinetics. For the anodization of zircaloy-4 it can be concluded that the oxide film formed on the alloy consists of two discrete layers in 0.1 M sodium hydroxide and they are made to a single layer in presence of glycerol and added anion impurity.

ACKNOWLEDGMENT

REFERENCES

[1] Williams CD. Atomic Energy of Canada Limited Report, AECL 1969; 3456.
[2] Williams CD. Reactor Technol 1970; 13: 147.
[3] Shobha Rani P, Anjaneyulu Ch and Sastry KS. J Electrochem Soc India 2000; 49(3):129.
[4] Lavanya A and Anjaneyulu Ch. Bull Electrochem 2004; 20(4): 153.
[5] Lavanya A, Raghunath G and Anjaneyulu Ch. Bull Electrochem 2004; 20(7):305.
[6] Ashok Kumar V, Raghunath G and Anjaneyulu Ch. Bull Electrochem 2005; 21(1): 17.
[7] Lavanya and Anjaneyulu Ch. Bull Electrochem 2002; 18:317.
[8] Arifuku F, Iwakura C, Yoneyama H and Tamura H, Denki Kagaski. 1978; 46:19.
[9] Randal JJ. Electrochim Acta 1975; 20: 663.
[10] Lavanya A, Sarna CSN and Anjaneyulu Ch. J Electrochem Soc India 2001; 50: 164.
[11] Lavanya A, Raghunath Reddy G and Anjaneyulu Ch. Bull Electrochem 2004; 20(7):305-308.
[12] Ashok Kumar V, Raghunath Reddy G and Anjaneyulu Ch. Bull Electrochem 2005; 21: 17-21.
[13] Rama devi D. Ph.D. Thesis O.U.1995.
[14] Wei Wei, Jan M.Macak, Nabeen, K Shreshta and Patrick Schmuki. J Electrochem Soc 2009; 156:104-109.
[15] F Climent Montaliu, R Fart Capelllodes & MI Vidal. Plennels An Quim Ser B 1983; 79-290.
[16] A Panasa Reedy, Ch Anjaneyulu and KS Sastry. J Electrochem Soc India 1990; 39-183.
[17] HK Schmidt, R Capellodes and MI Vidal, MT Vida, Lab. Invest Components, Electron SA, Fr Rev Tech Thomson CSF 1982; 14: 657 (FR).
[18] Sastry KS. Ph D Thesis. Chelsea College, University of London, London, 1971.
[19] Narayana ML. Ph D. Thesis, Osmania University, 1980.
[20] Nehru Prasad K, Ph.D. Thesis, Osmania University, 1992.
[21] Nageshwar Rao B, Ph.D. Thesis, Osmania University, 1990.
[22] Krishnaiah S, Ph.D. Thesis, Osmania University, 1993.
[23] VD Shukla and Anjaneyulu Ch. E-Journal Chem. 2011; 8(1): 71-76.