

Effect of Aquo-Methanolic Media on the Anodization of Zircaloy-4 in 0.1M Ammonium Oxalate

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Abstract- Anodization of zircaloy-4 in 0.1M ammonium oxalate has been carried out. Kinetics of anodic oxidation of zircaloy-4 has been studied at a constant current density of 8mA.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 were drawn. From these plots rate of formation; current efficiency and differential field were calculated. The addition of solvent (methanol) showed better kinetics results. For 25%, 50% and 75% aquo-methanolic media, the dielectric constant values are low leading to a marked improvement in the kinetics. In 80% methanol, 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.

Index Terms- Zircaloy-4, Anodization, Formation rate, Current efficiency, Differential field, Aquo-methanolic media.

I. INTRODUCTION

Zircaloy-4, which is a zirconium alloy containing Sn, Fe, Cr and O is mainly used in the Nuclear industry, especially in pressurized water reactors^{1,2} as fuel cladding integrity has to be ensured for its entire working life in the reactor core. Electrochemical oxidations of Zr-4 have been studied in electrolytes^{3,4}.

In this work, we focus on the oxidation of Zr-4 from an electrochemical stand point. The electrochemical experiments were performed at room temperature.

We have studied the electrochemical behavior of Zr-4 through constant current density i.e. 8mA.cm⁻² and at room temperature.

Thus specified experiments were performed and calculated to investigate the role of Zr-4 in 0.1M ammonium oxalate and the effect of solvent (methanol), formation rate, reciprocal capacitance vs. time, reciprocal capacitance vs. formation voltage and thickness vs. formation voltage were drawn. They were found to be optimum conditions for better kinetics and for better kinetic studies.

II. EXPERIMENTAL

Zr-4 was of 98% nominal purity supplied in the form of annealed sheet by NUCLEAR FUEL COMPLEX, HYDERABAD, as a gift sample was used. Thinning of this annealed sheet was done by DEFENCE METALLURGICAL

RESEARCH LAB, HYDERABAD. The chemical composition of Zr-4 was described in Table 1.

From the initial sheet, the foil samples used were cut with the aid of a punch into a flag shaped specimen of 1cm² working area on both side and 1 ½ cm long tag.

They were chemically polished. The chemical polishing mixture consisted of acids such as HF, HNO₃ and H₂O in a definite volume ratio 3: 3:1.

The samples were thoroughly cleaned in distilled H₂O, wiped with tissue papers, and exposed to dry before the experiment.

TABLE 1 Composition of the studied material.

Material	Weight	Composition (ppm)
Zircaloy-4	Cr	1100
	Fe	2200
	O	1200
	Sn	14400

Electrochemical Conditions : The counter electrode was a sheet of Platinum⁵ (2x3 cm, weight 3.000 gm). The working electrode was the Zr-4⁶ 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 ammonium oxalate and 25%, 50%, 75% aquo-methanolic media. All the experiments were carried out at constant current density range 8mA.cm⁻². The experimental procedure for the anodization is given elsewhere⁷. The kinetic results calculated are formation rate in Vs⁻¹, current efficiency (η) % and differential field (F_D) in MV cm⁻¹ from the conventional plots from the V vs. t, 1/C vs. t and 1/C vs. V.

III. RESULTS AND DISCUSSION

Effect of Substitution:

Anodization of Zr-4 was done in 0.1M ammonium oxalate. The formation rate, current efficiency and differential field were calculated. The effect of solvent i.e. Methanol on zircaloy-4 was studied in 0.1M ammonium oxalate to check whether there was enhancement of film formation^{8,9}.

Effect of Solvent:

Anodization of zircaloy-4 was performed in 0.1M ammonium oxalate and in aquo-methanolic media in 25%, 50%, 75%. There was an improvement in the kinetics as given in table 2.

The relevant plots are shown in figures 1 & 2. They were aid in the formation of good oxide films and acts as better

electrolytic capacitors¹⁰. These facts support the current results obtained in 0.1M ammonium oxalate. It can be explained on the basis of decrease in the dielectric constant of the medium (Table 3)

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 25% , 50% , and 75% aquo-methanolic media, the dielectric constant values are low leading to a marked improvement in the kinetics. The oxide film formed on the zircaloy-4 consists of two discrete layers in 0.1M ammonium oxalate were disappeared and made to a single layer in presence of methanol.

Figure 1: Plot of formation voltage as a function of time in aquo-methanolic solution

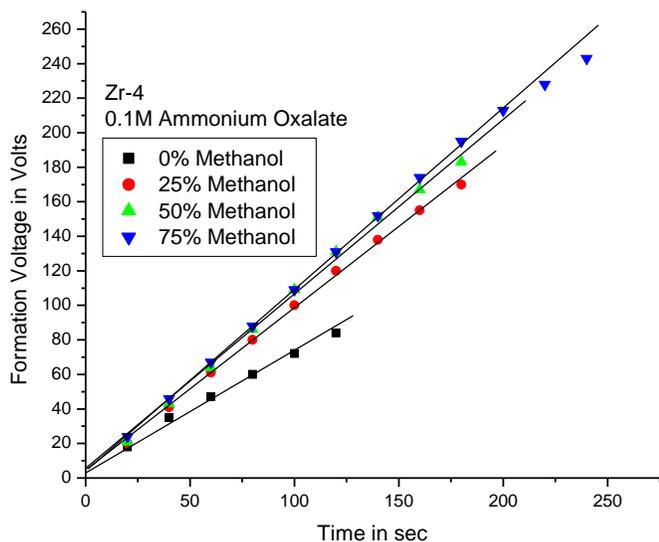


Figure: 2 Plot of reciprocal capacitance as a function of time in aquo-methanolic solution

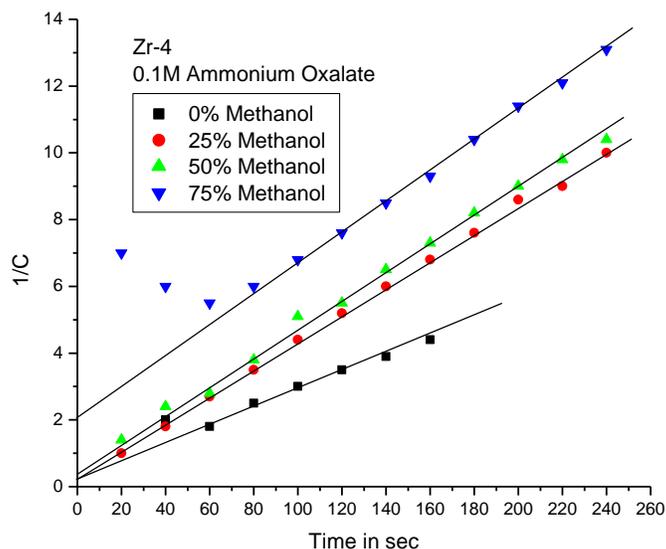


Table 2 Anodic films formed on Zircaloy-4 in 0.1M ammonium oxalate both aqueous and aquo-methanolic media.

Percentage of methanol	Formation rate dV/dt (V.s ⁻¹)	Current efficiency H, (%)	Differential field F _D (MV.cm ⁻¹)	BDV (V)
0.1M AO	0.66	26	5.68	84
0.1M AO+25% M	0.93	40	5.22	170
0.1M AO+50% M	0.99	42	5.29	183
0.1M AO+75% M	1.05	44	5.33	213

AO = ammonium oxalate, M = methanol

Table 3 Variation of dielectric constant as a function of solution composition

Methanol,%	Dielectric constant,ε
0	80
25	67.7
50	56.2
75	44.8
100	32.6

Vermilyea studied the formation of anodic films on tantalum in aqueous¹¹ and non-aqueous¹² solutions. He suggested that the composition of film depends on the solution in which it is formed.

Seregina et al¹³ studied the anodization of aluminium alloys in the solution of sulpho-salicylic acid (90/cc) and found that thick films are possible during anodization at room temperature. Nageshwar rao et al¹⁴ observed a change in the dielectric constant of oxide films by changing the medium from aqueous to glycolic.

D.Rama devi¹⁵ reported that anodization of niobium in non-aqueous electrolytes in 50% glycerol increasing kinetic results with increase in glycerol content in 0.1M K₂CrO₄.

Aparna¹⁶ 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.

Schmidt et al¹⁷ 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 al¹⁸ 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 al¹⁹ and Lavanya et al²⁰ 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 workers²¹.

V Jeevana Jyothi²² observed anodization of Zr-4 in 0.1M sodium methoxide the addition of solvent (ethylene glycol) showed better kinetic results.

Shukla²³ 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

IV. CONCLUSIONS

By changing the solvent medium from aqueous to glycolic, the kinetics of film formation on zircaloy-4 in 0.05M Ammonium oxalate 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 decreased in the dielectric constant of the solution with the increase in glycol content of the solution.

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REFERENCES

- [1] Williams C D, Atomic Energy of Canada Limited Report, AECL 1969, 3456.
- [2] Williams C D, *Reactor Technol.*, 1970, 13, 147.
- [3] Shobha Rani P, Anjaneyulu Ch and Sastry K.S, *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 J J, *Electrochim Acta*, 1975, 20, 663.
- [10] Lavanya A, Sarma C S N and Anjaneyulu Ch, *J Electrochem Soc India*, 2001, 50, 164.
- [11] DA Vermilyea. *Acta Met* 1953; 1:282
- [12] DA Vermilyea. *Acta Met* 1954; 2:482
- [13] IE Seregina, B Kopara and AV Thimoshenko, Deposited Doc. (Avail SPSTI), 1982; 10
- [14] B Nageshwar Rao, V Venkata Ramana and Ch Anjaneyulu. *J Electrochem Soc India* 1996; 45: 27
- [15] Rama devi D, Ph.D. Thesis, O.U.,(1995).
- [16] N.N.S.Aperna, Ph.D. Thesis, OU, 2009
- [17] HK Schmidt, R Capellodes and MI Vidal, *MT Vida, Lab. Invest. Components, Electron.S.A, Fr. Rev. Tech. Thomson C.S.F.*, 1982; 14, 657 (FR).
- [18] F Climent Montaliu, R Fart Capellodes & MI Vidal, *Plennels An. Quim. Ser B* 1983; 79-290
- [19] A Panasa Reedy, Ch Anjaneyulu and KS Sastry. *J Electrochem Soc India* 1990; 39-183.
- [20] Krishnaiah S, Ph.D. Thesis, Osmania University, 1993
- [21] Sastry K S, Ph.D. Thesis, Chelsea College, University of London, London, 1971
- [22] V Jeevana Jyothi and Ch.Anjaneyulu *Research Journal of Pharmaceutical, Biological and Chemical Sciences*
- [23] VD Shukla and Anjaneyulu Ch. *E-Journal Chem.* 2011; 8(1): 71-76
- [24] Lavanya A, Raghunath Reddy G and Anjaneyulu Ch, *Bull Electrochem*, 2004, 20(7), 305-308.
- [25] Wei Wei, Jan M.Macak, Nabeen, K.Shreshta and Patrick Schmuki. *J Electrochem Soc* 2009; 156:104-109.
- [26] Narayana M L, Ph.D. Thesis, Osmania University, 1980.
- [27] Nehru Prasad K, Ph.D. Thesis, Osmania University, 1992.
- [28] Nageshwar Rao B, Ph.D. Thesis, Osmania University, 1990.

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