Oriental Journal of Chemistry Vol. **26**(2), 607-611 (2010)

Kinetic and mechanistic studies of oxide film formation on zircaloy- 4 in lithium hydroxide using radio tracer ^{32}P

VIPLAV DUTH SHUKLA* and Ch. ANJANEYULU

Department of Chemistry, University College for Women, Osmania University,
Koti, Hyderabad - 500 095 (India).
*Department of Chemistry, BJR Govt. Degree College, Bazarghat, Nampally,
Hyderabad - 500 001 (India).

(Received: March 17, 2010; Accepted: April 20, 2010)

ABSTRACT

The kinetics of anodic oxidation of in 0.1M lithium hydroxide have been studied at a constant current density of 8 mA cm^{-2} and at room temperature. The conventional plots of formation voltage vs time and reciprocal capacitance vs time are found to be non-linear beyond a formation voltage of 180V. But with the addition of a millimole (mM)of sodium carbonate or sodium sulphates or sodium phosphate separately to 0.1M LiOH the conventional plots have became linear even upto breakdown voltage. This marked improvement in the kinetics can be attributed to the incorporation of anions (CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) into the oxide film. The phosphate ion incorporation was confirmed by radio-tracer studies using ^{32}P isotope. The uptake and distribution of $^{32}PO_4^{3-}$content in the film has suggested a mechanism for the growth of oxide film via interstitial movement of oxide ions. Migration of anion impurities from one layer to another layer in the oxide film has also been established by transferring the specimen from active to inactive solution of the electrolyte and vice versa and thinning subsequently. The amount of incorporation has been found to vary with experimental conditions. Radio-chemical experiments confirmed that the rate determining step is at the oxide /electrolyte interface.

Key words: Anodic oxide film, incorporation, anions, polarizing power, Radio-tracer technique.

INTRODUCTION

Thin oxide films are formed on Zirconium alloys when anodized in suitable electrolytes. Anodic oxide film is a subject of renewed interest both from a practical and theoretical point of view. Anodic oxide films formed on zirconium and its alloys are useful in the filed of electrical and electronic industry. Zirconium alloys due to their low cross section for thermal neutrons and because of their relatively good corrosion resistance against water and steam they are used in water cooled reactors. When the valve metals are anodized in some suitable electrolytes it was observed that small amounts of impurities mainly anions are incorporated into the oxide depending on the nature of electrolyte used. Sastry and Draper[1-3]] using radio-tracer technique studied the incorporation and depth distribution of sulphates ion into anodic films formed on zirconium in 0.05M H_2SO_4, 0.1M KOH + 0.005M Na_2SO_4 and 0.005M Na_2SO_4 the distribution of sulphate ions across the oxide formed in 0.05M Na_2SO_4 was found to be uniform in the inner layers and concentrated in the outer layers. They also studied the incorporation of chloride ion into ZrO_2 films using ^{36}Cl as marker.

Maraghini and Serra[4] used radio-active sulphate containing solutions to investigate the penetration of sulphate ions into the films formed by anodic oxidation of zirconium, large uptakes were found.

Rogers *et al*.[5] demonstrated the incorporation of anions containing carbon, sulphur and boron into anodic films formed on zirconium from the electrolytes containing those anions using ^{14}C, ^{35}S and an in-pile autoradiographic technique for boron. They found that the rate of incorporation increased with current density and the variation in rate was different for each anion. They showed that the sulphur moved in the film by growing films first labelled and then unlabelled H_2SO_4.

Shehata *et al.* [6] studied the incorporation of boron, phosphorous and sulphur into the anodic films on Be, Al and Zr using secondary photon profiling.

Leach and Panagopoulos[7] studied some effects of impurities present in the anodically formed oxide films on zirconium. They might be contaminated by ions from the chemical etching and anodizing solutions. They observed that the electrical field for anodization increased with increasing amount of the electrolyte oxy anion in the oxide. They interpreted the increase in the current efficiency as arising from the transfer of any anions across the oxide / solution interface such as SO_4^{2-}, PO_4^{3-} .

Kalyani and Sastry[8] studied the kinetics of anodic oxidation of zirconium in malonic acid and also in the presence of radio – active sodium propionate. The fall in the filed observed at 250 nm is explained from the radio tracer studies using ^{14}C and the mechanism was proposed.

In the present work an attempt is made to study the effect of carbonate, sulphate and phosphate on the kinetics of anodization of zircaloy-4 in 0.1M LiOH. The results are found to be interesting, from radio-tracer studies anion incorporation into the oxide film is conformed, and also proposed a mechanism of anodic oxidation of zircaloy-4 from the incorporation and depth distribution of phosphate ions in the anodic films formed in 0.1M LiOH + 0.001M $Na_3\,{}^{32}PO\text{-}_4$ solution.

EXPERIMENTAL

All experiments were carried out using 0.2 mm thick annealed, rolled sheet of zircaloy-4 supplied by “Nuclear Fuel Complex” Hyderabad as a gift sample. Zircaloy -4 is a an alloy of zirconium and tin with 98 % and 1.44% respectively. Fe and Cr are also present as impurities with 0.23% and 0.07% respectively. The specimens consist of a working area of 1 cm^2 on either side and a tag of 2 cm in length. Specimens were polished to mirror finish by using chemical polishing mixture which consists of concentrated acids of HF, HNO_3 and H_2O in the definite volume ratio. Adams *et al.* [9-10] and Wills *et al*.[11] used chemically polished specimens which gave higher values of current efficiency at higher current densities. For anodization a closed cell of 100 ml Pyrex glass beaker is used. The cathode is a platinum mesh having 20 cm^2 superficial area to make the double layer capacitance as large as possible. For radio-tracer studies, a specially designed cell of 20 ml capacity in which a platinum cathode of “U” shape having 3 × 1 cm dimensions was arranged at the bottom of the cell. Zr-4 specimen was suspended vertically and parallel to the sides of the cathode.

The constant current generator used was stabilized power supply unit built by Powertronics Pvt. Ltd., Hyderabad. The unit employed had a provision to supply constant current from 0-100mA. The capacitance measurements were made with a digital LCR meter, supplied by Vasavi Electronics Pvt. Ltd., Hyderabad. The current passed was measured accurately on a digital milli-ammeter. The potential directly across the cell was measured by a digital voltmeter. The thickness of anodic films formed were estimated from capacitance measurements for this the constant current was interrupted at regular voltage increments (20V) by reversing the DPDT switch. An interval of about 30 seconds was allowed to lapse prior to reading a capacitance data.

To measure the phosphate content of the film an end window G.M. Counter built by Nucleonix Pvt. Ltd., Hyderabad with an automatic digital timer and counting system was used. The films were thinned by abression with a tissue paper impregnated with 0.5µ diamond paste to examine the distribution of anion impurities in depth. All the reagents used were analar grade and the solutions were prepared with double distilled water.

RESULTS AND DISCUSSION

Zircaloy-4 specimen were anodized in 0.1M LiOH, 0.1M LiOH + 0.001M Na_3PO_4 ; 0.1M LiOH + 0.001M Na_2SO_4 and 0.1M LiOH + 0.001M Na_2CO_3. The conventional plots were found to be non-linear in 0.1M LiOH beyond a formation voltage of 180V, whilst the plots are linear when a millimole of CO_3^{2-}, SO_4^{2-} and PO_4^{3-} are added separately to 0.1 M LiOH the non-linearity completely disappeared (Fig.1 & 2) and a significant improvement is observed in the kinetics. The kinetic results are shown in the Table 1.

It is observed that, addition of a trace amount of carbonate, sulphate and phosphate ion to 0.1M LiOH exerts a considerable influence upon the filed and current efficiency. They became constant independent of thickness and the changes observed in their absence were no longer seen. The improvement observed in the kinetics is attributed to the incorporation of anion impurity CO_3^{2-}, SO_4^{2-},

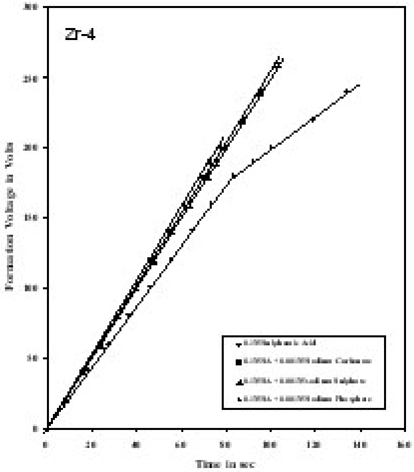

Fig. 1:

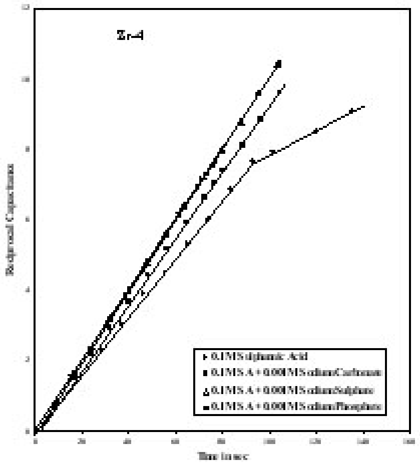

Fig. 2:

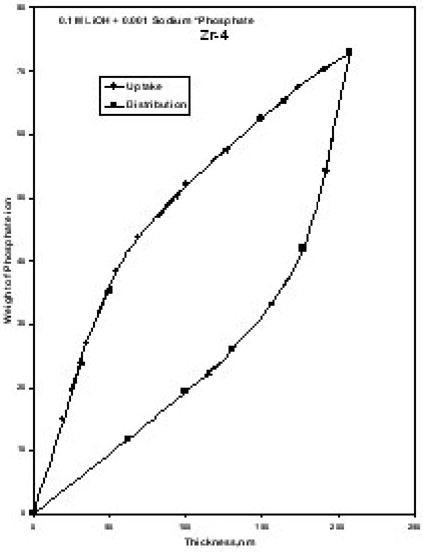

Fig. 3:

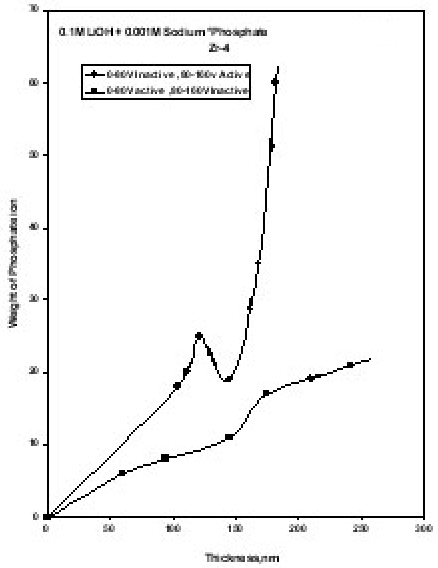

Fig. 4:

PO_4^{3-} into the anodic film. Further it is observed that the improvement in the kinetics with PO_4^{3-} is much greater than with CO_3^{2-} and SO_4^{2-}. This can be explained on the basis of polarizing power of anions. More the polarizing power, more will be the dissociation of water molecule which facilitates easy liberation of O^{2-} ions. These ions then freely go to the metal surface and combine with metal ions to form the film on the metal surface.

Radio-Tracer Studies - Mechanism

In order to understand the incorporation of anion impurity into the oxide film radio-tracer studies were carried out on Zr-4 upto 160V using ^{32}P isotope. 8 ml solution of 0.1M LiOH + 0.001M Na_3PO_4 containing 2 drops radio-active $Na_3{}^{32}PO_4$ is taken in the specially designed cell as described in the experimental part. Specific activity of the solution is 2.5 x 10^{-4} mCi/Mm. From the measurement of counts at regular intervals of 20V the weight of PO_4^{3-} ion uptake is estimated and plotted against thickness as shown in Fig. 3. From the uptake curve it is known that when a trace amount of PO_4^{3-} (0.001M) is present in 0.1M LiOH a little amount of PO_4^{3-} is incorporated below 100 nm (15 µg / cm^2) and above this thickness the rate of uptake is found to increase rapidly with thickness.

Thinning experiments were carried out using 0.5µ diamond paste, distribution curve also plotted as shown in Fig. 3.

Below 100 nm, the amount of PO_4^{3-} uptake is so small as to make the type of distribution uncertain and it is considered that the order of distribution is conserved. Hence the mechanism is via vacancy diffusion of oxide ions. Above 100 nm the depth distribution of PO_4^{3-} is almost in the reverse order of uptake. It is suggested that the fall in ionic current efficiency above 100 nm may be due to recrystallization as suggested with zirconium and this results in an increase of grain boundaries and the mechanism of anodic film formation may thus appear to be via interstitial movement[12] as the depth distribution of PO_4^{3-} is almost reversed.

Table 1: Anodic films formed on Zircaloy-4 in 0.1M LiOH

Electrolyte	Formation rate V.sec^{-1}	Current efficiency η,%	Differential field MV.cm^{-1}
0.1M LiOH	1.01	50.70	4.46
0.1M LiOH+ 0.001M Na_2CO_3	1.13	51.18	5.02
0.1M LiOH+ 0.001M Na_2SO_4	1.34	51.04	5.88
0.1M LiOH + 0.001M Na_3PO_4	1.60	60.84	5.88

As has been discussed, when ever a trace amount of PO_4^{3-} (0.001M) is present in the film, the current efficiency remain constant even above 100 nm, that is to say that the barrier to electron flow is maintained. When no PO_4^{3-} is present in film formed in LiOH, electron movement becomes appreciably easier 13-16 and thus the ionic current efficiency in latter part of anodization falls almost continuously above 100 nm.

The initial increment in the uptake of PO_4^{3-} / V / cm^2 is found to depend on pH of the electrolyte used.

Migration of anions in the oxide film

To establish the anion migration in the oxide film layers, active-inactive and vice-versa transformations were carried out upto 160V with a change over at 80V in 0.1 M LiOH+0.001M $Na_3PO_{4.}$ The conditions for the various active-inactive transformations and the distribution curves are shown in Fig. 4.

The result obtained with the other metals Ti, Zr and Hf in the electrolyte solution containing anion impurities containing ^{35}S, ^{14}C, ^{125}I and ^{32}P are supporting the result of the present work[17-21].

CONCLUSION

Improvement in the kinetics of anodic oxide film formation on zircaloy-4 in 0.1M LiOH was found to depend on the polarizing power of the added anion carbonate or sulphate or phosphate ion. From the radiotracer studies using ^{32}P the mechanism of oxide film formation was found to be via interstitial movement of oxide ions. Transfer of specimen from active to inactive and vice versa in 0.1M LiOH+0.001M Na_3PO_4 solution confirmed the migration of anions in the oxide film.

ACKNOWLEDGEMENTS

The authors wish to thank Prof. Zubaida Azeem, Principal and Prof. Rafiq Mohiuddin, Head, Department of Chemistry, Osmania University College for Women for their keen interest and encouragement. The authors are also grateful to the NFC, Hyderabad for generous help in providing zircaloy-4 and the DMRL, Hyderabad for thinning down the zircaloy-4 samples to the required specifications. The authors are also thankful to the CCMB, Hyderabad for their generous help in providing ^{32}P isotope. One of the authors (VDS) expresses his gratitude to Dr.B.Rajender, Principal, B.J.R. Govt. Degree College, Nampally, Hyderabad for his encouragement.

REFERENCES

1. Sastry K S, *Ph.D., Thesis,* London (1971).
2. Sastry K S, *J.Electrochem Soc.India,* **22:** 161 (1973)
3. Sastry K S and Draper P H G, *J.Electrochem Soc. India* **24**: 121 (1975).
4. Maraghini M and Serra N, La Ricerea, *Scientifica,* **27**: 2468 (1957); **29:** 2201 (1959).
5. Rogers G T, Draper P H G and Wood S S, *Electrochim Soc.*, **13**: 251 (1968).
6. Shehata M T, Good-Zamin C J, Kelley and Roger, *Proc. Electrochem Soc.*, **78**: 428 (1978).
7. Leach J S and Panagopoulos C N, *Proc. Intl Cong Met Corros,* **1**: 89-95 (1984)
8. Kalyani G and Sastry K S, *Z Phys Chem,* **271**: 1021 (1990).
9. Adams G B, P Van Rysellberghe and Moraghini M, *J.Electrochem Soc.,* **1102:** 502 (1955).
10. Adams G B, Lee T S, Dragonov S M and Van Rysselberghe P, *J Electrochim Soc.,* **105**: 660 (1958).
11. Willms Jr G C, Adams G M and Van Rysselberghe P, *Electrochim Acta,* **9**: 79 (1964).
12. Amsel G and Samuel D, *J.Phys Chem Solids*, **23:** 1707 (1962); *Anal Chem,* **39:** 1689 (1967).
13. Young L*, Anodic Oxide Films*, *Academic Press London (*1961).
14. Adams G B, Van Rysselberghe P and Moraghini M, *J.Electrochem Soc.*, **102**: 502 (1955).
15. Whitton J L, *J.Electrochem Soc.*, **155**: 58 (1968).
16. Vermilyea D A, *J. Appl Phys,* **27**: 963 (1956).
17. Anjaneyulu Ch and Sastry K S, *J. Electrochem Soc. India,* **30**: 27 (1981)
18. Anjaneyulu Ch and Sastry K S, *Trans SAEST,* **16**: 25 (1981)
19. Nageshwar Rao B, *Ph.D., Thesis*, O U, 1990
20. Shobha T, Sarma C S N, Sastry K S and Anjaneyulu Ch, *Bull Electrochem*, **17**: 519 (2001)
21. Raghunath Reddy G, Anjeneyulu Ch, *Bulletin of Electrochem*., **19**: 471-475 (2003).