Formate Ions in Anodic Oxide Films Formed on Zirconium in Duplex Baths

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Duplex experiments have been carried out by transferring zirconium samples from 0.1 M KOH to 0.1 M HCOONa and vice versa. These studies using radio tracer carbon as $H^{14}COONa$ indicated that the distribution of formate ion is almost in the reverse order of the uptake suggesting that the mechanism of anodic oxidation is via interstitial movement of oxygen ions, throughout the film. The radio-tracer and electrochemical studies show that the films do not remain as completely discrete layers and that changes take place within the first film laid down during the formation of further film.

The films formed anodically on zirconium are not pure oxides. It has been shown that small amounts of anion impurities are incorporated into the oxides when tantalum, titanium, zirconium or aluminium are anodized in suitable electrolytes.

The incorporation of anions into anodic films is greatest with pore-forming electrolytes and least for barrier-type electrolytes. It was confirmed by several workers [1-3] using aluminium as anodizing metal. Maraghini and Serra [4] found large quantities of uptake of phosphate and sulphate ions into the films on zirconium during anodization.Rogers et al.[5] demonstrated the incorporation of anions containing carbon, sulphur and boron into anodic films formed on zirconium. They found that the rate of incorporation increased with the current density and variation in rate was different for each ion. Using radio tracer technique, Sastry and Draper[6-8] studied the incorporation and depth distribution of sulphate ion into anodic film formed on zirconium. Anjaneyulu and Sastry[9] studied the incorporation and depth distribution of formate ion into anodic films formed on zirconium and titanium in 0.1 M HCOONa using radio-tracer technique.

Narayana[10] has carried out duplex experiments by transferring zirconium specimens from oxalic acid to sodium sulphate.

Wilkins[11] reported a preliminary examination of the effects of transferring zirconium from 1% KOH to 0.2 N H_2SO_4 and vice versa. However, his transfer experiments were confined to lower voltages.

In the present work, duplex experiments have been carried out by transferring the zirconium specimens from 0.1 M KOH to 0.1 M HCOONa and vice versa to investigate whether the pre formed film has got any effect on the second electrolyte. Incorporation and depth distribution of formate ion into the oxide film and a probable mechanism of anodic film formation on zirconium were also investigated using ^{14}C as marker.

EXPERIMENTAL

Specimens were pressed out from 0.125 mm thick van Arkel zirconium (supplied by Imperial Metal Industries Limited). The surfaces were chemically polished in 1 part HF, 3 parts HNO_3 and 3 parts water, rinsed in concentrated HNO_3 and finally cleaned several times in distilled water. After chemical polishing the tags were anodized in 0.05 M Na_2CO_3 to about 400 volts leaving a working area of about 1 cm^2 on either side.

The cells used for active and inactive anodization and the counting procedure using an end window G.M. Counter were described by Anjaneyulu and Sastry[9]. The active eletrolyte used was 0.1 M $H^{14}COONa$. Thinning experiments were also carried out using 0.5 μ diamond paste to examine the depth distribution of formate ion into the oxide film. All experiments were carried out at a constant current density of 8 mA/cm^2 . The thickness of anodic films formed were estimated from their capacitance data. To measure the capacitance a digital LCR meter (type VLCR 6) built by Vasavi electronics, Hydrabad was used. The constant current generator used was a stabilized power supply unit, built by Gargya Research Instruments, New Delhi.

RESULTS AND DISCUSSION

Anodization of Zirconium - Duplex Experiments

Anodic films were formed on separate samples in 0.1 M HCOONa upto the formation voltage of 60, 100 and 140 V and each was then further anodized in 0.1 M KOH upto a voltage of 260 V at a constant current density of 8 mA/cm^2 .

In these transfers, further growth began at lower voltages and considerable decrease in thickness

as observed in all cases. An instantaneous change ver in the kinetics of formation was approached s is usually observed in the new electrolyte KOH). Plots of thickness vs formation voltage or these transfers are shown in Figure 1. An ncrease in differential field of formation was bserved in all cases after film formation to a hickness of 340 nm. Details are given in Table-1.

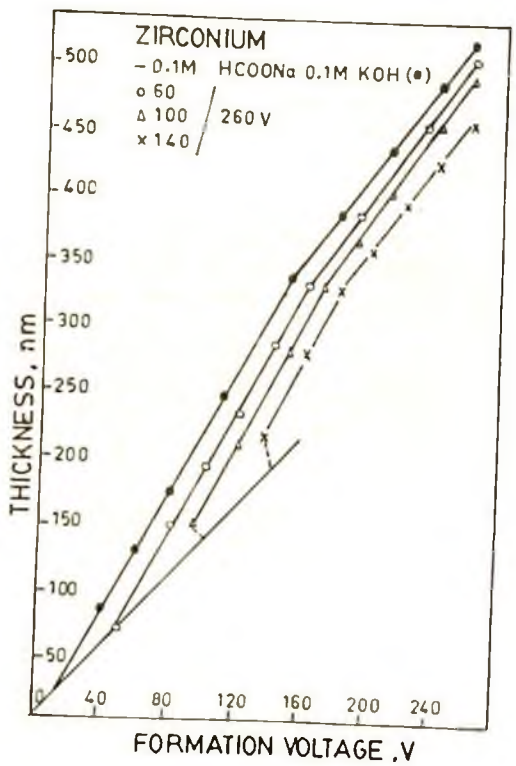


Fig.1 Thickness of film on anodizing zirconium in sodium formate upto 60 V, 100 V & 140 V and further anodized in 0.1 KOH solution upto 260 V

In the second series of duplex experiments anodic films were formed on separate samples in 0.1 M KOH upto 60, 100 and 120 V and further anodized successively in .1 M $H^{14}COONa$ (specific activity of 0.143 MC/mM). Further growth in 0.1 M HCOONa began at the same voltages as shown above. The plots of thickness vs formation voltage are shown in Figure 2. After the transfer, the kinetics of anodic film formation are found to be similar to that of HCOONa/KOH transfer. The

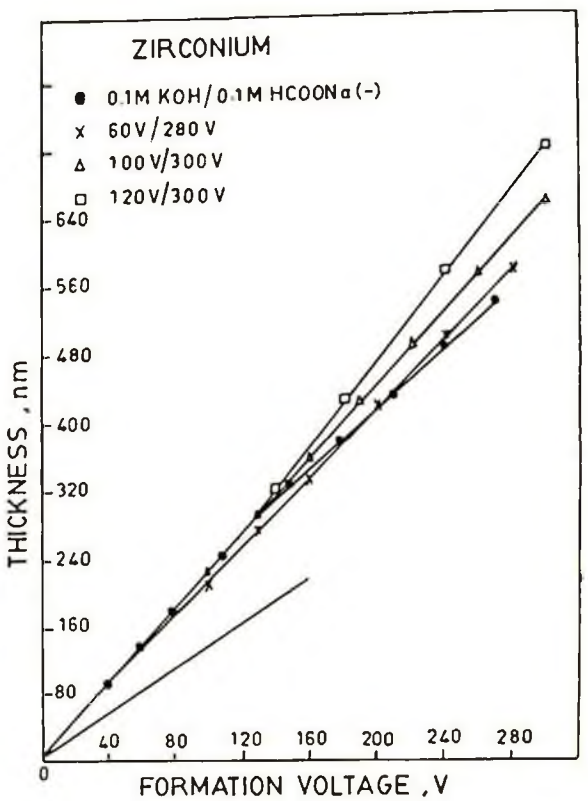


Fig.2 Thickness of films on anodizing zirconium in 0.1 KOH upto 60 V, 100 V & 120 V and further anodized in 0.1 M H COONa

details of initial differential field of formation are given in Table 2.

The plots of formate ion content of the film vs thickness are shown in Figure 3. Curves I, II and III are for samples anodized in 0.1 M H $H^{14}COONa$ after an initial anodizing in 0.1 M KOH upto the formation voltages of 60, 100 and 120 V respectively.

TABLE 1

FILMS FORMED TO 260 V IN 0.1 M HCOONa/0.1 M KOH

Formation voltage in HCOONa, V	After transfer and on passage of charge, fall in V in HCOONa	After transfer fall in D_{HCOONa} nm	Differential field MV/cm	
			Below 340 nm	About 340 nm
60	10 V	23	4.806	4.990
100	5 V	29	5.490	6.040
140	5 V	46	5.125	6.040

TABLE 2

TRANSFER FROM 0.1 M KOH TO 0.1 M HCOONa

Formation voltage in 0.1 M KOH, V	Initial differential field in 0.1 M HCOONa, MV/cm
0	6.750
60	4.795
100	4.429
120	4.027

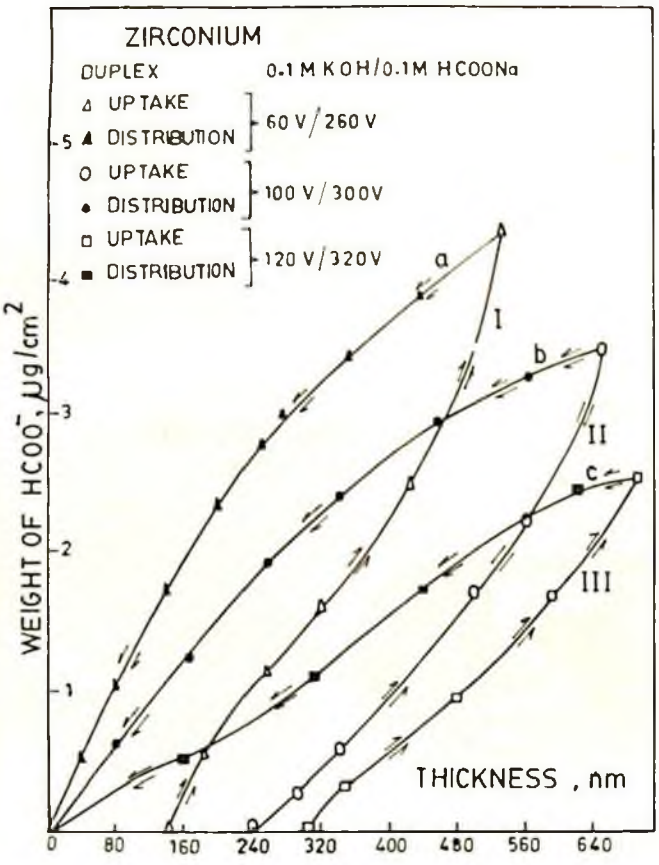


Fig.3 Distribution of formate ions in the film during duplex experiments

Thinning experiments were carried out using 0.5µ diamond paste for films formed upto 300 V in active 0.1 M $H^{14}COONa$ electrolyte. In Figure 3 curves a,b and c show the formate ion distribution/cm² in depth across the film for the three samples.

In the H COONa to KOH transfers, the thickness vs formation voltage plots are made up of two straight lines formed in KOH. It is also observed that irrespective of the thickness laid down in HCOONa, a sudden change in differential field is noticed when the total thickness (in HCOONa as well as in KOH) reaches the critical thickness of 340 nm. This coincides with the thickness at which the change over in the differential field is observed in KOH alone. From this it can be concluded that the kinetics of film formation on zirconium in 0.1 M KOH depend on the pre-formed film in HCOONa in such a manner that at a total thickness of 340 nm the maximum ratio of cubic to monoclinic is always maintained i.e. 0.515[6,7] whether formed in KOH alone or in duplex experiments.

As in HCOONa alone[12], the thickness vs formation voltage plots are linear for film formed upto 100 and 120 V in 0.1 M KOH and further anodized in 0.1 M HCOONa.

In the transfer of zirconium samples from 0.1 M KOH to 0.1 M $H^{14}COONa$ electrolyte, radio-tracer studies indicated that the distribution of formate ion is almost in the reverse order of the uptake. As suggested with the zirconium[7,9], it is concluded that the mechanism of anodic oxidation is via interstitial movement of oxygen ions throughout the film. The radio tracer and electrochemical studies suggest that the films do not remain as completely discreate layers and changes takes place within the first film laid down during the formation of further film.

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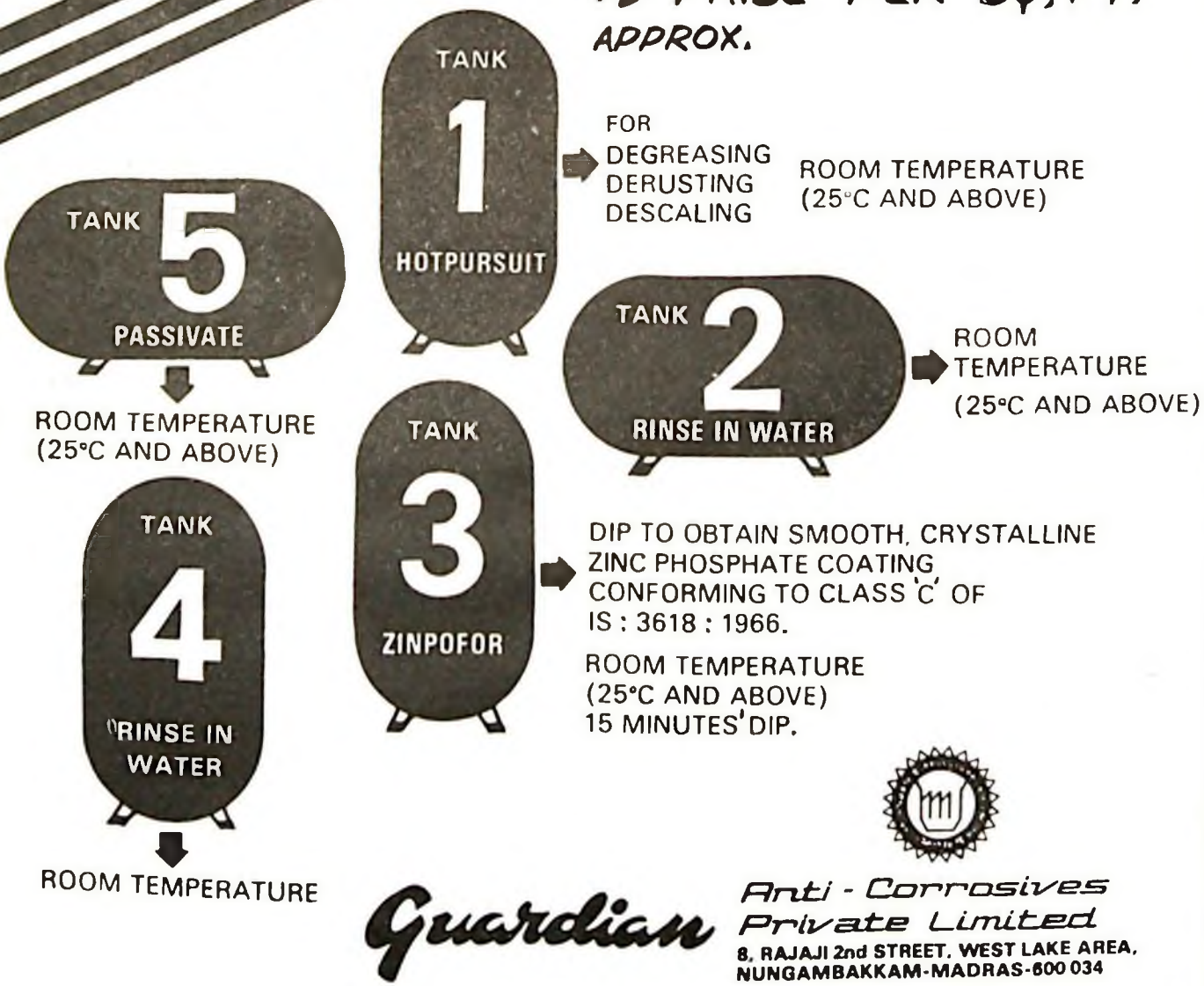
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