SHORT COMMUNICATION

Anodic oxidation of zirconium: Effect of fluoride contamination on oxide structure and transport processes

N. KHALIL*

Department of Chemistry, University of Alexandria, Egypt

J. S. L. LEACH[†]

Department of Metallurgy and Materials Science, University of Nottingham, Nottingham, Great Britain

1. Introduction

Leach *et al.* [1] developed a model to account for the variation in pickup, in the oxide, of anions from solution during anodic oxidation of metals. The effects of F⁻ pickup upon subsequent anodic oxide growth are reported. The early work of Young [2] studied the effect on adhesion and this, together with effects on electrical parameters, has been the subject of more recent work [3–5].

Anodic ZrO_2 is crystalline [6–8], unlike many other anodic oxides which are glassy. It has been shown that, for ZrO_2 growth in a series of electrolytes, not only phosphorus and sulphur, but a variety of other electrolyte species may be incorporated and this is more likely from acid than from alkaline electrolytes [9]. Many authors have noted the effects of incorporation on oxide properties, particularly those related to mechanical, electrical, chemical and structural parameters. For example, the effects of incorporation have been seen to affect internal growth stresses [10–12], plasticity [13, 14], growth electric field [15, 16], structure/crystallinity [17, 18] and transport processes [19].

Many of these oxide properties are important in maintaining well defined protective barrier films. XPS has contributed to the information about the influence of anodizing conditions, of substrate surface and of electrolyte which lead to incorporation of foreign ions in anodic oxides and their effects on oxide properties.

The work presented here combines data on the metal transport number, t_m, and diffraction measurements to elucidate the effect of F⁻ on the growth behaviour of the anodic oxides of zirconium.

2. Experimental details

The zirconium used was approximately 99.9% pure 0.1 mm sheet. The chemical etchant was a $HF + HNO_3 + H_2O$ mixture at 25 °C, the composition being 5:45:50 vol% electropolishing was carried out using perchloric acid-methanol mixture (1:4) (kept below −30 °C) at a current density of 0.25 A cm⁻² for 30S.

All samples were anodized in 0.044 M ammonium hydrogen tetraborate. Small additions of fluoride to the electrolyte were made from a stock $NH_4F.HF$ solution. All anodization was carried out at 25 °C. The X-ray photoelectron spectroscopy (XPS) machine used was a Vacuum Generators ESCA with an aluminium anode producing AlK_α X-rays ($h\nu = 1486.6\,eV$). Depth profiles using XPS could be assessed using an in situ Ar^+ ion etching facility (4 keV, 20 μA) progressively to remove quantities of material from the sample surface. The etching rate from ZrO_2 was typically 2–4 nm min⁻¹.

α-spectrometry has been used [20] to measure metal transport numbers, t_m. The isotope Rn^{222} of the noble gas radon was used as the inert marker. This emits α-particles (5.486 MeV) which lose energy at a predictable rate on passing through matter. By measuring the loss of energy of the α-particles, the mass of
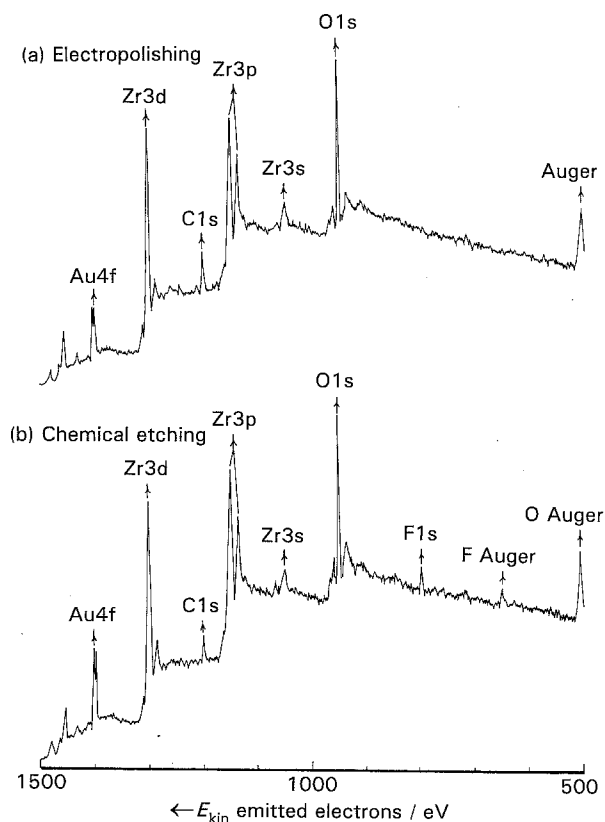

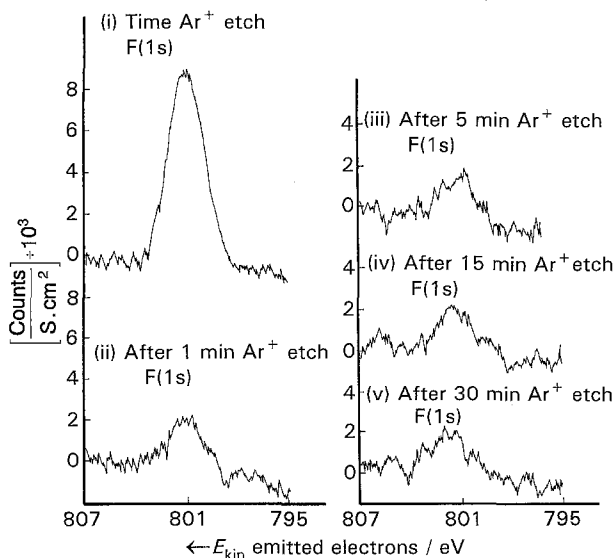Fig. 1. Overall XP spectra of the initial oxide films on zirconium after (a) electropolishing and (b) chemical etching.

Fig. 2. F(1 s) depth profiles through the thickness of 50 V anodic ZrO_2 films growth at $6\,mA\,cm^{-2}$.

material above the radon layer can be determined. In order to determine the transport number the total thickness of the oxide (dielectric constant = 21) was measured by capacitance measurements using a Wayne–Kerr Universal Bridge (B221); the measurements were made at a frequency of 400 Hz. A correction of 8 nm was added to the calculated oxide thickness to account for the hydrated layer formed on the surface of the specimen due to absorption of water [19].

3. Results and discussion

Typical overall XP spectra of the surface layers after electropolishing and chemical etching are shown in Fig. 1. The most prominent peaks are those of zirconium and oxygen but carbon is also seen. For chemically etched specimens, fluoride is detected. XPS has shown that in the residual surface film left after etching, the concentration of F^- ions is typically 3 at %.
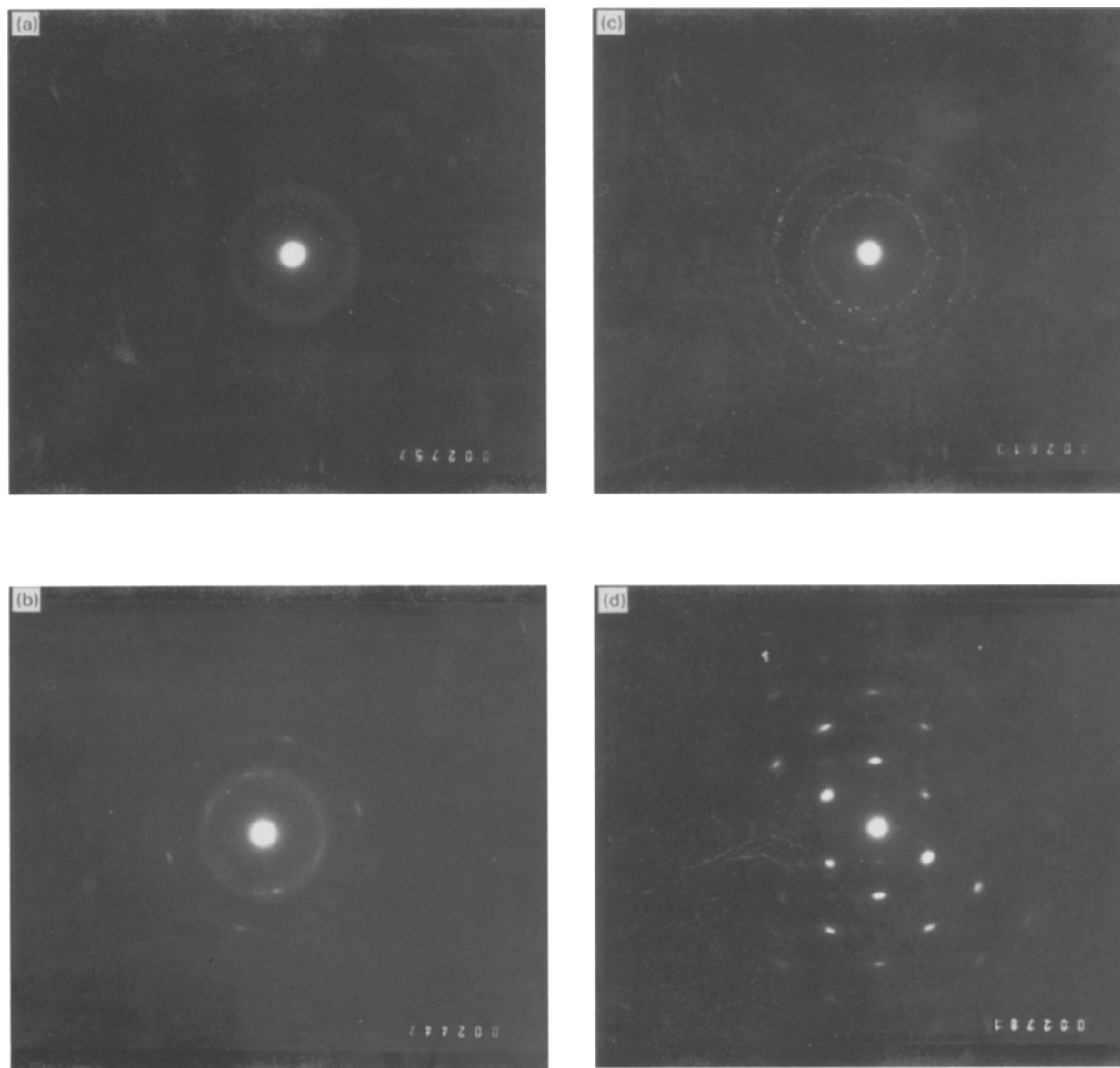

Fig. 3. Transmission electron diffraction patterns produced from ZrO_2 films stripped from chemically etched (a–c) and electropolished (d) Zr surfaces.
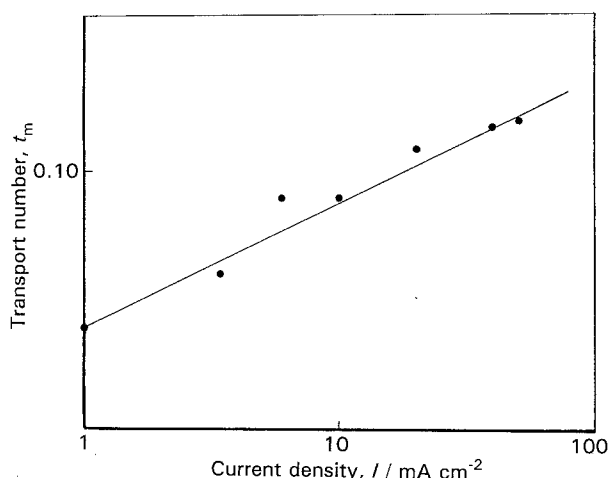
Fig. 4. Metal transport number as a function of current density for a 100 V ZrO_2 film formed in borate solution in presence and absence of F^- ions.

The electrolyte is the most important source of impurity ions during the growth of anodic oxides. Significant quantities of impurity may be incorporated during anodization. When fluoride ions in the form of ammonium fluoride were added in sufficient concentration to the anodizing electrolyte ($NH_4HB_4O_7$), the rate of voltage rise (dV/dt) decreased due to breakdown of the oxide film [21]. The anodizing rate before breakdown is the same as in fluoride-free ammonium borate electrolyte and the breakdown potential increases with current density. XPS and argon sputtering shown in Fig. 2 prove that fluoride anions are built into the oxide film. Progressive removal of ZrO_2 layers with Ar^+ ion etching F(1s) profiles were obtained. Composition profiles in these measurements were based on estimated F (1s) peak heights. F^- pickup was measured quantitatively by Leach et al. [12].

The influence of F^- contamination on crystal structure is demonstrated in Fig. 3a–c. On chemically etched material, glassy oxide is formed in very thin anodic zirconium oxide films (Fig. 3a). The development of microcrystals in ZrO_2 films is shown in Fig. 3b–c. However, Fig. 3d shows how, on electropolished metal, the macrocrystalline material is produced almost immediately.

Figure 4 shows the affect of fluoride contamination on metal transport number, at different applied current densities using α-spectrometry. There is a real increase in metal transport number, with applied current density. However, no effect of fluoride on metal transport number is observed at all investigated applied current densities, despite the recorded evidence of oxide contamination with fluorides shown

in Fig. 2 and its effect on structure demonstrated in Fig. 3. The residual F^- in anodic films of ZrO_2 appears to promote amorphous or microcrystalline, rather than macrocrystalline, oxide over the initial part of growth (20 V) where [F] is highest. This corresponds with observations by Leach et al. [12]. The effects of contaminants have been shown to include change in electrical parameters, mechanical properties as well as structure and crystallinity. Leach et al. attributed these changes in variations in ionic transport numbers as a result of film contamination with fluorides.

4. Conclusion

Evidence produced by XPS confirms previous work concerning contamination of anodic oxides both from substrates after pre-treatment and from electrolyte. The incorporated F^- in ZrO_2 appears to promote amorphous or microcrystalline, rather than macrocrystalline oxides. However, the observed change in structure in the presence of residual F^- cannot be interpreted in terms of an expected shift in the ionic transport numbers.

References

[1]   L. C. Archibald and J. S. L. Leach, Electrochim. Acta 22 (1977) (21).
[2]   L. Young, Trans. Farad. Soc. 55 (1959) 841.
[3]   B. Maurel, D. Dieumegard and G. Amsel, J. Electrochem. Soc. 199 (1972) 1715.
[4]   J. K. Barrandon, PhD Thesis, Orsey University, Paris (1970).
[5]   J. Siejka, J. P. Nadai and G. Amsel, J. Electrochem. Soc. 118 (1971) 727.
[6]   A. Charlesby, Acta Metall. 1 (1953) 340.
[7]   B. Cox, J. Electrochem. Soc. 177 (1970) 654.
[8]   R. A. Ploc and M. A. Miller, J. Nucl. Mats. 64 (1977) 71.
[9]   J. C. Banter, J. Electrochem. Soc. 114 (1967) 508.
[10] L. C. Archibald and J. S. L. Leach, Electrochim. Acta 22 (1977) 15.
[11] J. S. L. Leach and B. R. Pearson, Proceedings of the 7 International Congress of Metal Corrosion, Rio de Janeiro (1978) p. 151.
[12] J. S. L. Leach, C. Panagopoulos and B. R. Pearson, Rev. Coatings Corros. 6 (1984) 1.
[13] D. H. Brandhurst and J. S. L. Leach, J. Electrochem. Soc. 113 (1966) 1289.
[14] J. S. L. Leach and P. Neufeld, Corr. Sci. 9 (1969) 225.
[15] N. J. M. Wilkins, J. Electrochem. Soc. 109 (1962) 998.
[16] P. H. G. Draper, Electrochim. Acta 8 (1963) 847.
[17] G. T. Rogers, P. H. G. Draper and S. S. Wood, ibid. 13 (1968) 2151.
[18] K. Shimizu, G. E. Thompson and G. C. Wood, Thin Solid Films 85 (1981) 53.
[19] N. Khalil and J. S. L. Leach, Electrochim. Acta 33 (1988) 1721.
[20] N. Khalil and J. S. L. Leach, Ibid. 31 (1986) 1279.
[21] N. Khalil and J. S. L. Leach, Electrochim. Acta, in press.