

## Impedance Spectroscopy Investigation of Thick Anodic Oxide Films Grown on Zirconium and Zirconium Alloys

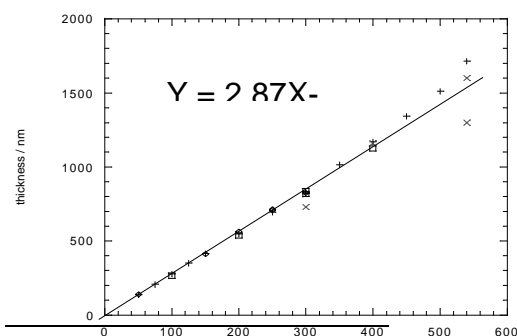
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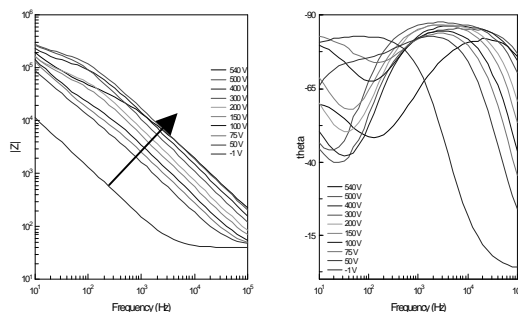
Zirconium and its alloys are of considerable interest to the nuclear power industry, where zirconium alloys are being used in light water reactors as fuel cladding and box material. For this application, an important aim is to increase the fuel burn up by reducing the oxidation rate of zirconium and its alloys. We have investigated anodization as a possible accelerated test method by which the corrosion process could be investigated [1-3]. The main objectives of this investigation were: (i) to study the effect of the electrolyte during the anodic oxide growth, and (ii) attempt to find a kinetic transition that is observed in the autoclave experiments. The growth of the anodic oxide layer was performed in three different medium: an acid (0.5M H<sub>2</sub>SO<sub>4</sub>), a basic (0.1M NaOH) and a near neutral (0.1M (NH<sub>4</sub>)<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) electrolytic solutions. The electric properties of the films were characterized by impedance spectroscopy (fig. 1). Their thickness was followed at high frequency during the growth and the results have been correlated with the direct SEM post-anodization observations of rod cross sections. NaOH is described in the literature as a medium that leads to a contamination-free zirconium oxide film [2]. However, we have observed a breakdown at 300V in this medium. The experiments in H<sub>2</sub>SO<sub>4</sub> indicate that whatever sample composition and insulation mode, the breakdown occurs at voltages below 200V. In (NH<sub>4</sub>)<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, anodization was successfully performed up to 600V (fig. 2). The SEM observation of the zirconium rod (Zr-99.8%) anodized at 540V showed a dense oxide film that had dispersion in thickness between 1.3 μm and 1.6 μm. No cracks are observed in the oxide film contrary to the zirconium wire (Zr-99.2%). The remarkable behaviour of Zr rod in (NH<sub>4</sub>)<sub>2</sub>B<sub>4</sub>O<sub>7</sub> is attributed to a different breakdown mode, linked to the electrolytic solution composition. In the two former media, the breakdown is very intense and localized. It leads to a short circuiting between the solution and the metal. Whereas in the latter medium, it is diffuse, given rise to electrical discharges throughout the sample which increases in intensity with the applied bias.

**Figure 1.** Bode representation of the impedance spectra obtained at different potentials for the anodic oxide film grown in 0.1 M (NH<sub>4</sub>)<sub>2</sub>B<sub>4</sub>O<sub>7</sub> electrolyte on zirconium with a scan rate of 100 mV/s.



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**Figure 2.** Variation of the anodic oxide film thickness with increasing voltage. IS measurements (+, x, φ) and SEM observations (x) on zirconium rod during anodisation in 0.05 M (NH<sub>4</sub>)<sub>2</sub>B<sub>4</sub>O<sub>7</sub> with the scan rate



of 100 mV/s for + and x, and 25 mV/s for φ.

## References

1. T. Pauporté, D. Veys, J. Schefold, D. Lincot, A. Ambard. Formation of thick anodic oxide layers on zirconium and zirconium alloys. in 201st Meeting of the electrochemical society. Slope 2.87 nm.V<sup>-1</sup> : J. Electrochem.
2. M.A.A. Rahim, A.A.A.R., M.W. Khalil, J. Appl. Electrochem., 1996. 26: p. 1037-1043.
3. G.A. McRae, M.A.M., J. Electrochem. Soc., 2002. 149(4): p. B123-B129.