

Passive Oxide Film Growth on Ti and Zr Studied by In
Situ Neutron Reflectometry
J.J. Noël, Z. Tun*, and D.W. Shoesmith
University of Western Ontario
London, ON, Canada, N6A 5B7
*NRC, Chalk River Laboratories, Chalk River, ON,
Canada, K0J 1J0

The effectiveness of an oxide film as a corrosion barrier depends, in part, on the degree to which it is cracked, discontinuous, or defective. The presence of such damage in an oxide film can be strongly influenced by the way in which the film is grown, yet oxide film growth on metals is not well understood. After the formation of the first thin layer of oxide on a metal surface, the metal is physically separated from the oxidant species in the surrounding environment. For oxidation to proceed, metal ions, oxidant species, or both must be transported through the oxide already present at the metal/environment interface. The two leading theories of how this happens are the field-assisted ion transport (FAIT) [1] model and the point defect model (PDM) [2].

In this presentation, the results of in situ neutron reflectometry measurements made on oxide films on Ti and Zr while they were being grown under electrochemical control will be presented and discussed. Neutron reflectometry provides a non-destructive means to determine materials composition and layer thicknesses in the range 0.5 - 300 nm. Thus, we were able to measure the Pilling Bedworth ($\mathfrak{R}_{PB}$) and anodization (α) ratios of Ti and Zr directly. The value of $\mathfrak{R}_{PB}$ on Zr was 1.52 at polarizations up to 2 V (SCE), consistent with the value calculated from crystal lattice parameters for bulk zirconia. At an applied potential of 3 V (SCE), this ratio increased to 1.63, indicating a less dense film. On Ti, $\mathfrak{R}_{PB}$ had a value of 1.72, which corresponds to the rutile phase. The anodization ratios were found to be $34 \text{ \AA}\cdot\text{V}^{-1}$ for Zr, and $25 \text{ \AA}\cdot\text{V}^{-1}$ for Ti, both of which agree with the literature values. The anodic oxide on Ti was found to be a two-layer structure, composed of a TiO_2 inner layer and a hydrated outer layer, whereas the oxide on Zr consisted of a single, homogeneous layer.

Electrochemical impedance spectroscopy performed simultaneously with neutron reflectometry has allowed us to determine the apparent dielectric constant of the thin passive film in situ, as a function of applied potential. On Zr, polarization positive of 1 V (SCE) results in dramatic changes in the apparent dielectric constant, specific resistivity, and protectiveness of the oxide film. These changes seem to correspond to crystallization and breakdown of the protective oxide, which lead to rapid and severe corrosive attack.

Ongoing neutron reflectometry experiments are using an isotopically labeled Ti layer to track movements of atoms during anodic film growth on Ti in an effort to determine the atomistic mechanism of oxide film growth.

- [1] L. Young, "Anodic Oxide Films", Academic Press, London, 1961.
- [2] D.D. MacDonald, *J. Electrochem.Soc.*, **139**(1992)3434-3449.