Anodic Oxide Film Growth on Zirconium Observed with In Situ Neutron Reflectometry

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We are using in situ neutron reflectometry to study and compare the structure, composition, and reactivity of passive oxide films on titanium and zirconium alloys in aqueous solutions [1-4].

Electrochemical experiments [5] have shown that oxide film stability during anodization of zirconium alloys is critically influenced by the type of anions in the supporting electrolyte. In chloride or perchlorate solutions, oxide film growth seems to occur via solid-state ion transport. This leads to accumulation of stresses and the eventual rupture of the oxide film, followed by a rapid and severe corrosion process at potentials just above 1 V/SCE. In sulphate solutions, however, oxide film growth does not lead to breakdown and corrosion of the Zr, even with many volts of anodic polarization applied. We hypothesize that oxide film growth on Zr in sulphate solution is assisted by a solution phase ion transport mechanism, possibly involving the complexation of zirconium ions by sulphate, and that in this mode of film growth less stress build-up occurs because zirconium ions are transported away from the metal/oxide interface. Subsequently, zirconium oxide precipitates at the oxide/solution interface without the introduction of significant stress in the film. Electrochemical evidence supporting this hypothesis includes the observation that anodization charge measurements indicate a thicker oxide film than do electrochemical impedance experiments [5] (which may not "see" precipitated deposit layers) and the fact that we have seen no catastrophic film failures in sulphate-containing solutions, even under electrochemical conditions much more aggressive than those under which failure occurred in perchlorate- or chloride-containing solutions.

Neutron reflectometry provides an independent and absolute measure of film thickness, and may also be able to distinguish layers of oxide grown by solid-state ion transport from precipitated deposits, if the two layers have different densities or compositions. This presentation describes our use of in situ neutron reflectometry to try to resolve this discrepancy in oxide layer thickness and find further evidence to help explain the anion effects in oxide film growth on Zr.

References:

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