Neutron reflectometry as *in situ* probe of thin film composition and layer structure for investigating corrosion and hydrogen absorption in titanium

J.J. Noël[1], Z. Tun[2], and D.W. Shoesmith[1]

jjnoel@uwo.ca

[1]*Department of Chemistry, The University of Western Ontario*
London, ON Canada N6A 5B7
[2]*Canadian Neutron Beam Centre, National Research Council of Canada, Chalk River, ON Canada, K0J 1J0*

Titanium readily absorbs hydrogen into its lattice in solid solution, and precipitates crystals of a separate hydride (TiH_x) phase once the local concentration of dissolved hydrogen atoms reaches or exceeds the solubility limit. The presence of a hydride phase in Ti tends to make the material more brittle, leading eventually to brittle fracture under tensile stress, in the form of hydrogen-induced cracking (HIC). Adsorbed hydrogen atoms can be generated on Ti surfaces by cathodic polarization or as a by-product of the corrosion reaction, under certain conditions, and these hydrogen atoms in some circumstances, can be a source of absorbed hydrogen in the material. Fortunately, Ti surfaces exposed to air or aqueous environments tend to be covered by an extremely adherent and highly insoluble TiO_2 film that acts as a very good barrier to both corrosion and hydrogen absorption.

This presentation describes the use of in situ neutron reflectometry measurements to follow the growth of the protective oxide film on Ti under anodic polarization in 0.27 M NaCl solution and the subsequent defeat of this oxide barrier under cathodic polarization, leading to hydrogen ingress and mechanical failure. In neutron reflectometry, a ribbon beam of monochromatic thermal neutrons is elastically scattered from the flat surfaces (outermost or buried) within a sample. The intensity of elastic scattering (i.e., reflectivity) and its variation with the scattering vector (a function of incidence angle) allow the determination of the composition and thickness of any surface layers, in situ and non-destructively, with a resolution of about 1 at.% and 0.5 nm, to a maximum thickness of about 300 nm. Neutrons are also uniquely sensitive to hydrogen and readily differentiate between hydrogen (^1H) and deuterium (^2H).

Our experiments demonstrated the incorporation of OH species from water during the anodic growth of the oxide film on Ti, the validity of the anodization and Pilling-Bedworth ratios for Ti measured by other means, and tracked the progress of electrochemically introduced absorbed hydrogen as it penetrated the oxide film and entered and eventually destroyed a thin Ti film on Si substrate.