Experimental report

14/05/2024

Proposal: 1-04-253 **Council:** 4/2023

Title: Absorption of hydrogen into copper-coated titanium under active corrosion in a sulphide solution

Research area: Materials

This proposal is a new proposal

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Samples: copper-coated titanium
aqueous solution for electrichemical cell

Instrument	Requested days	Allocated days	From	To
SUPERADAM	4	2	23/09/2023	25/09/2023

Abstract:

The generally accepted safest method for disposal of spend nuclear fuel is in deep geological repositories. No final repository is yet in operation. The Swedish and Finnish KBS-3 method employs a multibarrier approach to shield the spent fuel from future generations. The chosen corrosion barrier is a 5 cm thick copper (Cu) canister made from oxygen free, phosphorous doped copper. In the long-term perspective, sulphide (SH-) is the most significant corrosive agent for Cu canister. Under anaerobic conditions, SH- will corrode Cu to produce copper(I)sulphide as well as hydrogen gas. In sufficiently high concentrations, H may negatively affect the mechanical properties of the metal via embrittlement or stress corrosion cracking. To complement the large body of work in this field, NR will be employed with in-situ electrochemical measurements to study the absorption of hydrogen in thin copper-coated titanium films under active corrosion in a SH- solution. If successful, the proposed experiments will provide critical evidence for exceedingly small H absorption in the Cu matrix. This will lay to rest controversies around the detrimental influence of H in these materials.

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Neutron reflectometry and *in-situ* electrochemistry experiments have been carried out at the SuperADAM instrument. Silicon wafers were coated with a 4 nm base layer of titanium and subsequently with a 50 nm layer of copper. A sample cell dedicated for NR measurements was developed for *in situ* EIS and corrosion potential monitoring, with a sufficient solution volume to not influence the corrosion process. The titanium layer effectively functioned both as an adhesion layer to the silicon as well as a hydrogen sink and absorption indicator. The 0.1 M NaCl solution was deaerated by Ar sparging before and during the experiment. In order to corrode the copper surface and simultaneously study hydrogen transport and absorption through sulphide corrosion, controlled additions of sulphide solution were added to the test cell. This allowed for a precise control of the growth of the corrosion film and ultimately the theoretically possible hydrogen absorption through the copper into the underlying titanium. Preliminary results are presented in Figure 1 below, showing first the reflectivity of the bare copper surface, and the reflectivity after two additions of sulphide solution to the test cell. After the first addition, most prominently, an increase in the surface roughness of the copper–solution interface was observed. This is expected and corresponds to the formation of a copper sulphide film. A similar effect was observed after the second addition of sulphide solution. After preliminary fits to the data, no appreciable change in the titanium layer which would suggest an absorption of hydrogen could be observed.

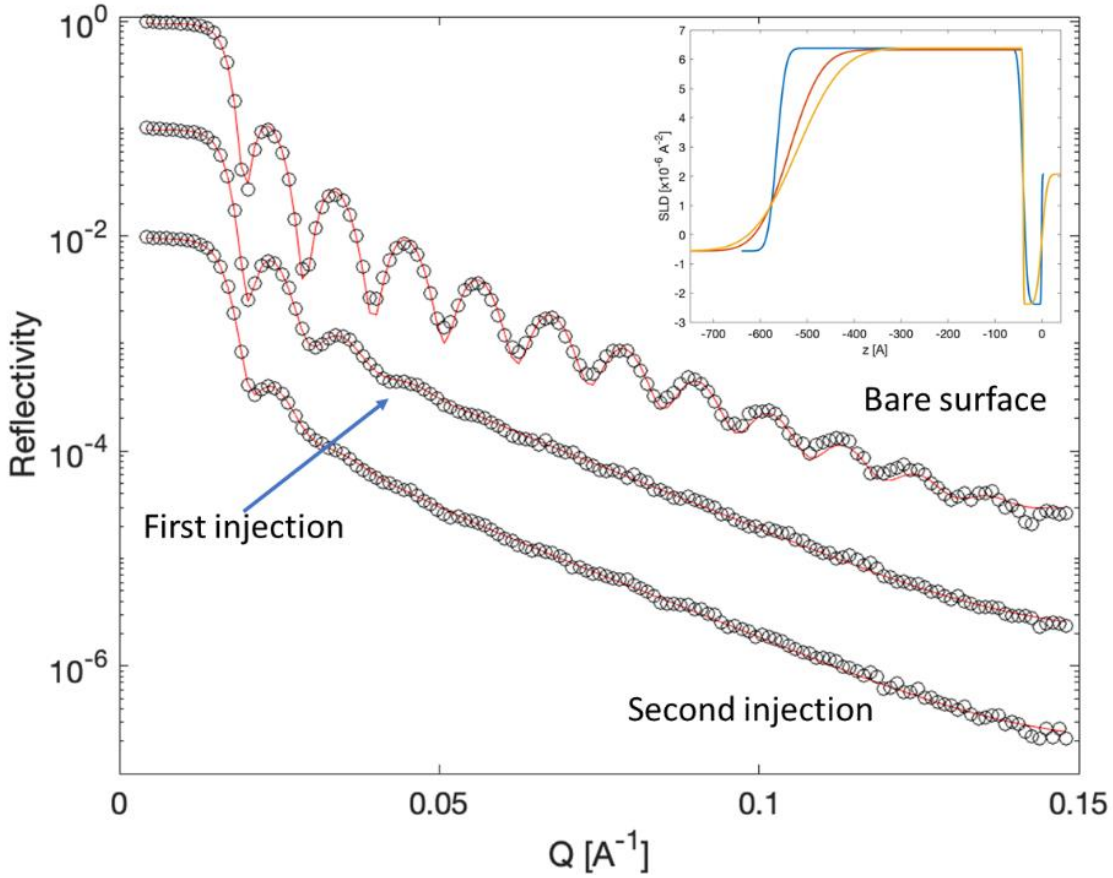

Figure 1 Measured reflectivity and associated fits as a function of applied sulphide solution. The curves have been offset vertically for clarity. The inset depicts SLD-profiles, which show no changes in the sld of the Ti, and therefore no H concentration accumulating in the Ti layer. The data can be modelled by a single roughness parameter at the surface of the Cu layer and a change in the Cu thickness. This is expected due to the formation of Cu_2S on the surface.