Electrolytic hydrogen penetration through the native oxide on zirconium: Part I

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In previous neutron reflectometry experiments, we observed the ingress of hydrogen (or deuterium) atoms through native oxide films on titanium under cathodic polarization [1,2]. Neutron reflectometry (NR) was successfully used to monitor and quantify the ingress of hydrogen through the oxide film and into the underlying metal. The oxide film on titanium acts as a barrier to hydrogen ingress in the metal, but if it is defective, hydrogen atoms may pass through the defects and into the underlying metal [1]. Under strong cathodic polarization, it is possible to transform the oxide into one that is not a good barrier to solid-state hydrogen ingress [3,4]. Like Ti, Zr has an affinity for hydrogen, and can be similarly embrittled and cracked by hydride accumulation within the metal. This is a particular concern for nuclear reactor core components employing Zr, in which it is imperative that we avoid hydrogen (deuterium) absorption leading to cracking. In the present work, we intend to quantify hydrogen penetration through the native (air-formed) oxide on the Zr surface, a layer that is composed of ZrO2, about 5 nm thick, to determine the threshold potential required for hydrogen absorption, if one does exist as it does for Ti.

During the course of this beam time, we initially used NR to characterize the quality of the Zirconium thin films substrates prepared by sputtering machine at CNBC on Silicon wafers. For this experiment we only used one sample (#1) for our in-situ electrochemical NR measurements. For this sample the NRs were measured in air, through silicone and while mounted on the electrochemical cell (EC). Figure 1, shows the experimental NR data (red points) from this sample measured in empty electrochemical cell together with the fitted curve (black curve) and least square fitted parameters (inset table). The inset SLD profile shows a ~50A native ZrO2 film on Zr thin film metal. The successfully in-home prepared high quality Zr films allowed performing in-situ NR experiments.

Figure 2 shows the overlay of the NR curves recorded from sample #1 at different electrode polarizations together with the NR data obtained at single pH=3. These measurements were performed in 0.2 M H2O/K2SO4 solution as electrolyte and H2SO4 was used to adjust pH. The comparison between the NR curves measured at different electrode polarizations showed that, almost all of the NR curves could be superimposed with no significant changes except the measurement at Eoc. If these observations are true then, we can conclude that the hydrogen ingress started at -400V and remained unchanged during the course of the potential application. This early result is somehow unexpected as the breakthrough voltage for hydrogen ingress into the Zirconium metal was/is expected to appear at lower cathodic voltages. Other dramatic changes were seen when the pH of the solution was reduced to 3 and 2 respectively.

Figure 3 displays the overlay of the SLD profiles from the NR data where the most dramatic changes were observed. The important regions in these SLD profiles are the regions from 50 to 500Å and 500 to 550Å along the z axis. These regions carry the information about the SLDs and thicknesses of the Zr metal and ZrO2 respectively. As seen, when pH was decreased to 3 and 2, the SLDs of both Zr metal and ZrO2 decreased. This lower SLD values could be due to the hydrogen ingress into both metal and native oxide layer. Interestingly, this process was reversible and the SLDs were recovered when potential was set at Eoc from -1.6V however, these observations should be repeated to confirm.

References

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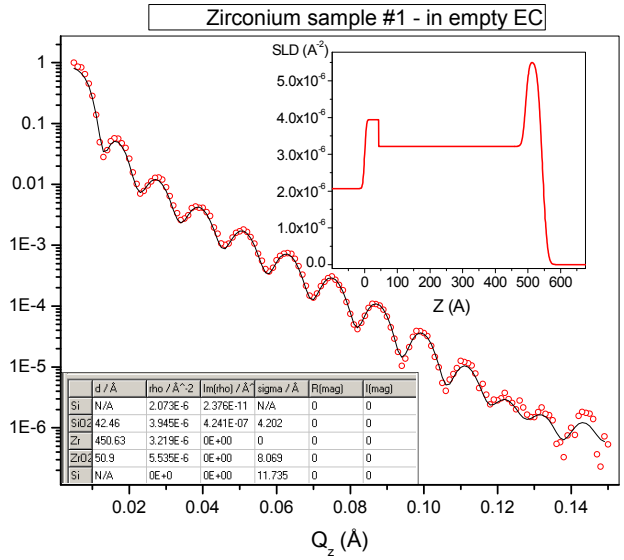

Figure 1 NR of Zirconium film sample #1 prepared on Silicon wafer by sputtering technique (red points). Inset table shows the parameter used by Parrat32 to fit (black curve) experimental data points. The inset graph is the SLD profile as a function of thickness of the layers (z). The z = 0 is the location of the first interface (Si/SiO2) seen by neutron beam.

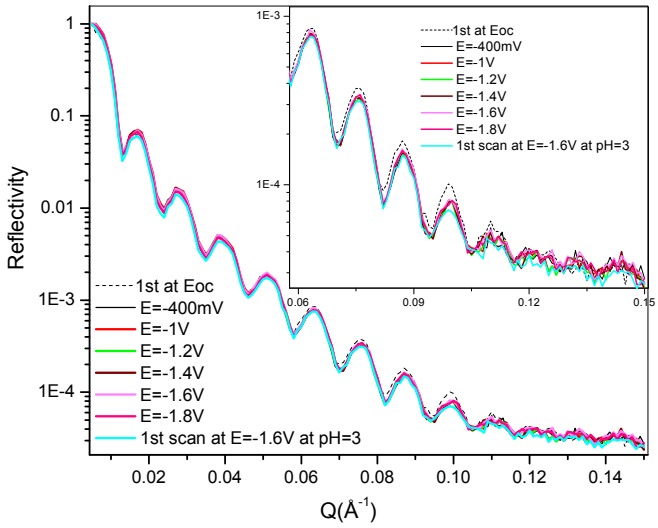

Figure 2 Overlay of the NR data obtained from the Zr sample #1 measured in different applied potentials. The inset graph shows the zoomed Q region in which the curves are not perfectly superimposed. As seen, except the NR data measured at Eoc (dotted curve) and at pH=3 (cyan curve) the other experimental data points at different electrode voltages do not show significant differences and can be superimposed. This experiment was performed in 0.2M potassium sulfate in H_2O.

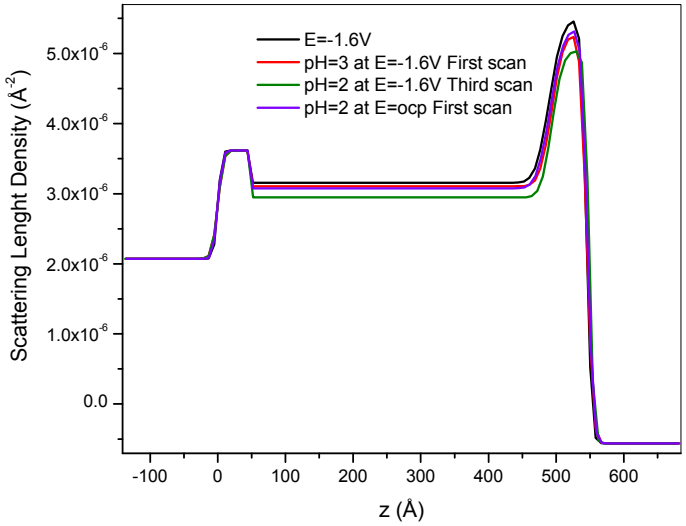

Figure 3 The overlay of the SLD profiles obtained at different experimental stages in H2O/K2SO4H electrolyte.