

Hydride formation in cladding materials studied via in-situ environmental heating transmission electron microscopy

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The mechanical properties of Zr-based nuclear cladding alloys are inherently affected by the presence of Zr hydrides, which are known to embrittle the cladding if oriented along radial directions. Radially oriented hydrides can be precipitated by a reorientation process when the cladding tubes cool under stress from temperatures at which pre-existing hydrides dissolve into the host matrix [1]. This is of particular concern for fuel assemblies in long term dry storage, where the cladding must maintain its strength and ductility over potentially hundreds of years. The aforementioned precipitation mechanism is highly dependent on the underlying host microstructure, comprised of grains, precipitates and line defects. In order to develop mesoscale models capable of predicting the structural integrity of nuclear cladding materials during dry storage, a detailed knowledge of the hydride precipitation mechanisms as a function of alloy composition, microstructure, cladding texture, and cooling rates is needed. To date, past studies have employed ex-situ characterization techniques such as optical and transmission electron microscopy (TEM) [2], electron backscatter diffraction [3], and synchrotron X-ray diffraction [4] to examine hydride precipitation in cladding materials. These ex-situ studies have suggested hydrogen uptake and hydride formation depend on (i) hydrogen content [4], (ii) modes of cladding material fabrication [5], (iii) heat treatment procedure [6], and (iv) the presence or absence of stress in the cladding material [7]. However, there remain questions regarding the details of the hydride precipitation mechanisms at the nanoscale that may only be addressed by observing hydride formation in-situ.

In this work, hydride formation in ZirloTM cladding material was studied using an environmental in-situ heating TEM stage developed by Protochips, Inc. The stage tip holds a gas cell comprised of two Si-based chips with 5 nm thick SiN_x viewing windows, one of which is patterned with a resistive heater, enabling in-situ observation of microstructure evolution during exposure to temperatures up to 1200 °C and pressures up to 1 atm. The ZirloTM sample was first prepared using focused ion beam lift out, and then carbon tacked onto the heater-coated SiN_x window of the gas cell. During in-situ observation, hydrogen was introduced and maintained at a pressure of 327 Torr (approximately 0.5 atm, absolute pressure). The temperature was then increased at a rate of 1 °C/s to approximately 400 °C, and held for 90 minutes. Figures 1A and 1B show a comparison of the microstructure of the ZirloTM observed prior to the experiment with that observed in the later stages of annealing. In this comparison, the disappearance of microstructural features (arrow 1) and the formation of a new grain (arrow 2) are evident. The region around the new grain is examined at a higher magnification (Fig. 1C) and the analysis of diffraction information acquired from the new grain (Fig. 1D) indicates a superimposition of two patterns, one of the parent α -Zr matrix and the other of a face-centered tetragonal phase,

consistent with the formation of either ϵ -ZrH_x ($x > 1.8$) or γ -ZrH. Although further work is required to fully explore the hydride precipitation mechanism, these results show that in-situ environmental heating TEM can be applied to study this mechanism at the nanoscale in order to verify and validate predictive material models. Experimental results will be discussed in the context of mesoscale models being developed in parallel, which address reorientation of hydrides and the influence of hydrides on the mechanical properties of Zr-based claddings.

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Figure 1: A) and B) Overview of images before the start of in-situ experiment, and after 72 minutes at 400 °C in H₂ atmosphere, C) zoomed-in image of the region of interest around arrow 2 in B), and D) shows the superimposition of two diffraction patterns obtained from the circled dark grain shown in C), one of the parent α -Zr phase (diffraction spots of weaker intensity) and the other is consistent with a face centered tetragonal hydride phase.

