

## Investigation of $\delta$ -ZrH<sub>1.66</sub>/ $\alpha$ -Zr interface in Zr-Based Cladding Materials with Aberration-Corrected Scanning Transmission Microscopy

S. Rajasekhara, P. G. Kotula, D. G. Enos, B. L. Doyle, B. G. Clark

Sandia National Laboratories, Albuquerque, New Mexico – 87185, USA

Zirconium (Zr) -based alloys are employed as cladding tubes for nuclear fuel due to their substantially lower neutron absorption cross-section per unit strength relative to other commercially available structural materials [1]. During service, Zr-based claddings absorb hydrogen due to waterside corrosion and radiolysis [2] and hydrogen in excess of solid-solution solubility in zirconium precipitates out as circumferential Zr-hydrides [3]. Circumferential hydrides, although brittle, do not adversely impact the mechanical properties of the cladding. However, when used fuel assemblies are exposed to the high temperature excursions associated with drying, the circumferential hydrides dissolve and re-precipitate as radially oriented hydrides due to hoop stress in the cladding wall. Oriented radially, the brittle hydrides can significantly reduce the fracture toughness of the cladding [4]. This is a cause for concern since claddings are considered to be the last line of defense against accidental material release and therefore required to maintain their structural integrity not only during storage, but also during transportation to their final destination. In order to mitigate hydride formation, it is therefore crucial to understand hydrogen uptake in Zr-based cladding materials. Despite extensive work on this aspect of cladding degradation [5], insights into the hydrogen uptake during the initial period of hydrogen/Zr-cladding interaction is still limited. While laboratory based experiments are non-ideal representatives of a reactor environment, we have examined the hydrogen absorption efficiency of Zircaloy – 2 (Zr-2) and a relatively new Zirlo™ cladding alloy (Fig. 1A). These alloys were electrolytically charged and the resulting microstructure and hydrogen uptake were investigated with aberration-corrected scanning transmission electron microscopy (AC-STEM) and elastic recoil detection (ERD), respectively.

The hydrogen profiles in these alloys, obtained from ERD, suggest a larger hydrogen ingress in Zr-2 (Fig. 1B). Equivalent thickness measurements, obtained by analysis of these profiles [6] assuming  $\delta$ -ZrH<sub>1.66</sub> formation, confirmed this observation ( $d_{\text{eq}(Zr-2)} \sim 1.3 \mu\text{m}$ ,  $d_{\text{eq}(Zirlo)} \sim 0.2 \mu\text{m}$ ). Microstructure analysis showed a non-uniform hydride formation in Zr-2 with a maximum hydride thickness of approximately 2  $\mu\text{m}$  (Fig. 1C), and a hydride/Zr-matrix interface (Fig. 1D) with a  $\langle 111 \rangle_{\delta\text{-ZrH}_{1.6}} // \langle 0001 \rangle_{\alpha\text{-Zr}}$  orientation relationship (Fig. 1E) that is consistent with previous literature [5].

In contrast, Zirlo™ microstructure reveals a minimal hydride formation ( $\sim 0.2 \mu\text{m}$ ) (Fig. 2A). Although the hydride phase (Fig. 2B) could be easily characterized as  $\delta$ -ZrH<sub>1.66</sub> (Fig. 2C), its interface with the Zr-matrix exhibited a complex diffraction signature (Fig. 2D). Analysis of this diffraction pattern (Fig. 2E) suggested the expected hydride and Zr-matrix phase, and an additional set of spots that was consistent with body centered cubic Zr-Nb phase. Although further work is required to fully understand the presence of Zr-Nb phase, it appeared that the hydride phase followed  $\langle 111 \rangle_{\delta\text{-ZrH}_{1.6}} // \langle 0001 \rangle_{\alpha\text{-Zr}}$  and  $\langle 111 \rangle_{\delta\text{-ZrH}_{1.6}} // \langle 011 \rangle_{Zr\text{-Nb}}$  orientation relationships with both phases, respectively. Hydrogen ingress at shorter hydrogen charging durations (100 and 300 s) were also analyzed, and will be presented [7].

References:

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- [7] Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

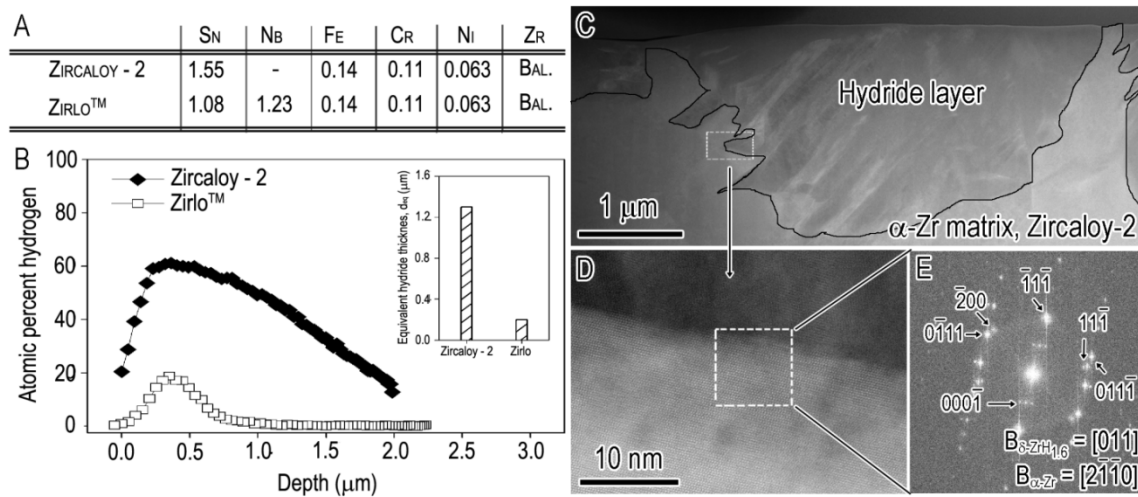


Figure 1: (A) Typical composition of Zircaloy – 2 (Zr-2) and Zirlo™, (B) Hydrogen profile acquired from ERD analysis of Zr-2 and Zirlo™ with equivalent hydride thicknesses shown in the inset, (C) STEM image of Zr-2 that shows an uneven hydride layer, (D) and (E) Atomic resolution image of the interface acquired from the boxed region in (B), and diffraction pattern acquired from the interface gives the orientation relationship  $\langle 111 \rangle_{\delta-ZrH_{1.6}} // \langle 0001 \rangle_{\alpha-Zr}$ .

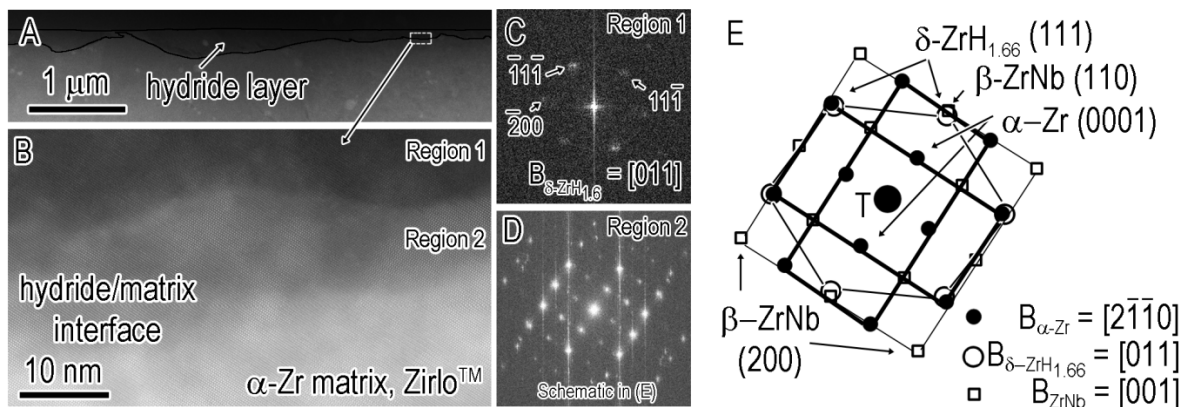


Figure 2: (A) Overview image of Zirlo™ charged to 1000 s that exhibits ~ 0.2 μm of hydride, (B) Atomic resolution image of the hydride interface, (C) and (D) are the diffraction patterns from the hydride layer and the interface, and (E) analysis of diffraction pattern shown in (D).