253
doi:10.1017/S1431927615002068 Paper No. 0127
Microsc. Microanal. 21 (Suppl 3), 2015

In-situ TEM Study of the Initial Oxidation Behavior of Zry-4

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This research investigates the early stages of oxidation in Zircaloy-4 (Zry-4) using a Protochips environmental cell in a transmission electron microscope (TEM). The oxidation behavior was studied using bright field TEM to monitor the sample in an oxygen rich elevated temperature environment. Precession diffraction was used to identify the phases present in the sample before and after the in situ experiment. Following oxidation, the samples were then cross-sectioned to determine oxidation depth into the base metal.

Zircaloy-4 is a zirconium-based alloy often used as nuclear fuel rod cladding because of its good corrosion resistance and low neutron cross-section[1,2]. However, despite Zry-4s good corrosion resistance, corrosion is still a limiting factor in fuel rod lifespan. This limits the burn up which can be achieved, especially as harsher environments, which increase corrosion, are being used to help increase burn up and decrease waste. In addition, for some proposed Generation IV reactors, which place high demands on cladding materials due to extreme conditions, Zirconium-based alloys are under consideration[3–5]. Extensive past work using ex-situ autoclave and reactor corroded samples has resulted in the long term corrosion behavior of Zry-4 being well characterized[4,6,7]. Thus, the long-term oxidation behavior is well understood, but the knowledge of the initial corrosion behavior is still lacking. The initial oxidation response is important, as the effects of microstructural features such as grain boundaries can be significant, and this knowledge will allow for better alloy design to resist corrosion.

Using a Protochips™ in-situ gas cell holder, in which gas pressure and gas mixture as well as temperature can be controlled, we have oxidized FIB prepared samples of Zry-4 to study the initial oxidation response of this alloy. Focused Ion Beam (FIB) samples were prepared from the bulk Zry-4 sample to contain a random assortment of grain boundaries. These samples were placed onto Protochips E-Chips for use in the gas cell holder. As shown in figure 1, precession diffraction was used to characterize both the phases present in the pristine sample, as well as the boundary orientations. After characterization of the pristine sample, oxidation experiments are conducted at elevated temperature in an oxygen rich gas environment while the sample is observed using conventional TEM. Following oxidation, precession diffraction is again used to characterize the phases and orientations present in the sample. Finally, the sample is removed from the E-Chip and cross-sectioned to determine the depth of oxidation and study the oxide microstructure formed as seen in figure 2.

In summary, in-situ TEM was used to study the initial corrosion behavior of Zry-4. We have observed the oxidation process initiating, and have cross-sectioned these samples to study the initial oxide structure. Precession diffraction shows that both tetragonal and monoclinic ZrO_2 are present in the oxidized samples, although when cross-sectioned the sample show less tetragonal ZrO_2 than the plan view imaging. The oxide formed has many small grains, as is expected for the oxide in this system[8].

References:

[1] C.L. Whitmarsh, Review of Zircaloy-2 and Zircaloy-4 Properties Relevant to N.S. Savannah Reactor Design, 1962.
[2] B. Cox, J. Nucl. Mater. **336** (2005), p. 331.
[3] DOE-NERAC, A Technology Roadmap for Generation IV Nuclear Energy Systems, 2002.
[4] A.T. Motta et al, J. Nucl. Mater. **371** (2007), p. 61.
[5] E.A. Marquis et al, Mater. Today **12** (2009), p. 30.
[6] A. Yilmazbayhan et al, J. Nucl. Mater. **349** (2006), p. 265.
[7] D. Fruchart, P. Convert, G. Lelievre, **347** (2002), p 288.
[8] This research is funded by the Department of Energy's Nuclear Energy University Program (NEUP). The authors would like to thank Arthur Motta of Penn State University for providing the Zircaloy samples.

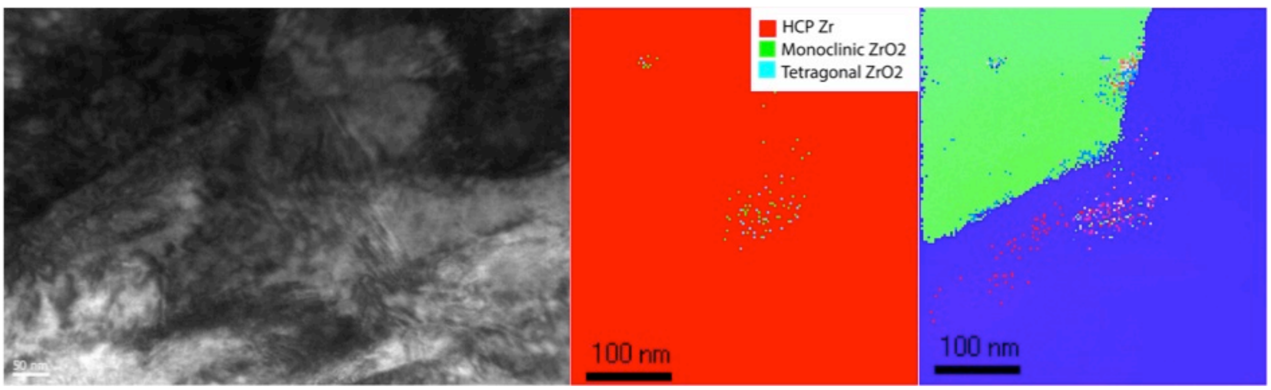

Figure 1. Initial sample condition prior to oxidation. TEM image on left shows area from which precession diffraction was used to create a phase map (center) and orientation map (right).

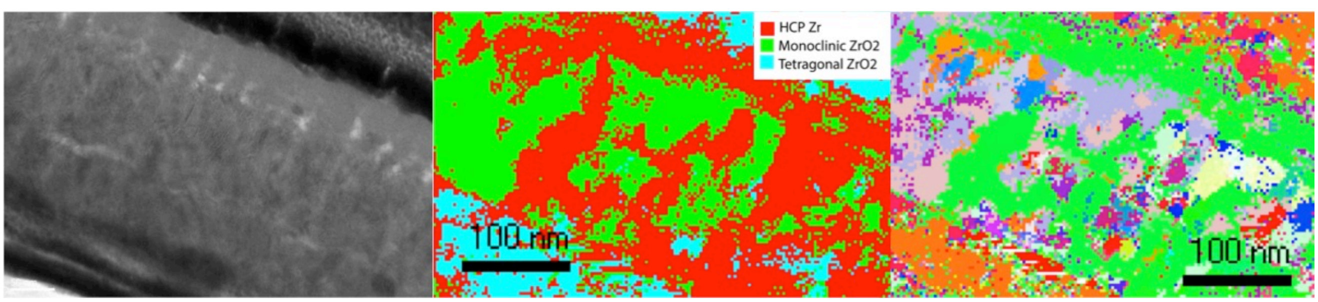

Figure 2. Cross section of TEM sample after oxidation. On left, TEM image showing the precession diffraction area, phase map in center showing sample oxidation, and orientation map on right showing many small oxide grains.

https://doi.org/10.1017/S1431927615002068 Published online by Cambridge University Press