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Barrier oxide chemistry and hydrogen pick-up mechanisms in zirconium alloys

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ABSTRACT

The chemistry of barrier oxide layers formed on zirconium alloys was investigated using atom probe tomography (APT). Grain boundary segregation of Fe and Ni was observed. The $Zr(Fe, Cr)_2$ particles maintain a constant Zr:Fe:Cr ratio through the oxide until they reach an oxygen content of approximately 50 at%, when Fe depletion occurs. Enrichment of hydrogen along oxide crystallite boundaries was observed, which is interpreted as a sign of ingress being localized to grain boundaries. TEM revealed porosity networks around particles and oxide grain boundaries. It is proposed that pores are local reduction sites where H_2 evolves on transition metal sites.

1. Introduction

Zirconium alloys have been used as fuel cladding in water moderated nuclear reactors for over half a century owing to a combination of desirable properties in the aggressive environment in the core. Two of the limiting factors for cladding lifetime are oxidation and hydrogen pick-up. These degradation phenomena have been extensively studied over the years and a good understanding of the corrosion behavior under various autoclave and reactor conditions has developed [1,2].

The oxidation kinetics of the alloys in the Zircaloy family conforms to a cyclic pattern, where a protective nanocrystalline barrier oxide film of approximately 1–3 μm builds up and slows down growth, followed by a "transition", an increase in oxidation rate when the protective oxide breaks down [1,3]. The past decades has seen significant improvements in the corrosion resistance of the fuel cladding through subtle changes the chemistry and heat treatment of the alloys, and their operational lifetime has nearly been doubled. This has lead to other degradation mechanisms than oxidation being limiting for the performance, such as hydrogen pick-up and irradiation growth. The hydrogen pick-up fraction (HPUF), defined as the ratio between the hydrogen absorbed in the metal and the hydrogen released by the corrosion process, varies depending on the alloy composition and reactor environment, and is usually in the range of 10–20% but can be as high as 80% for Zircaloy-2 [4,5].

The corrosion reaction of Zr in water is an electrochemical process that is governed by a set of redox reactions. In the anodic half-cell reaction, Zr metal is consumed and electrons are released according to

$$Zr + 2H_2O \rightarrow ZrO_2 + 4H^+ + 4e^- \quad (1)$$

Zr fuel cladding does not suffer crevice, pitting or grain boundary corrosion, so the spatial location of the anodic reaction occurs relatively homogeneously along the metal-oxide interface, generating oxygen vacancies that move through the oxide scale. The exception is the transition in corrosion rate, when the protective oxide breaks down locally, allowing water to penetrate the depth of the scale [6]. Charge neutrality dictates that a cathodic reaction also needs to take place, usually taken to be [1]

$$4H^+ + 4e^- \rightarrow 4H \quad (2)$$

Atomic hydrogen can recombine to form gaseous H_2 that dissolves in the reactor coolant. Spatial separation of anodic and cathodic reactions requires the facilitation of an electronic or ionic current. This is difficult to reconcile with the fact that the oxide scale is a wide band gap insulator [7]. However, as the hydrogen pick-up fraction of Zr alloys typically spans from 10 to 50%, a majority of the hydrogen released from the overall corrosion reaction makes its way to the coolant water in the reactor. Recent studies suggest

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Table 1
Nominal compositions of the investigated materials. Concentrations are given in weight% with Zr as balance.

	Zircaloy-2		Zr-2.5Nb
	LK2	LK3	
Sn	1.46	1.32	–
Nb	–	–	2.5
Fe	0.12	0.17	0.11
Cr	0.10	0.10	–
Ni	0.05	0.05	–

Table 2
Autoclave data and corresponding oxide thicknesses for the analyzed Zircaloy-2 materials in this study. Data provided by manufacturer Sandvik Materials Technology.

Alloy	Temperature (°C)	Time (days)	Oxide thickness (μm)
LK2	400	3	1.3
	400	6	2.3
	415	30	8.8
LK3	400	3	1.0
	400	15	1.8
	415	60	9.0

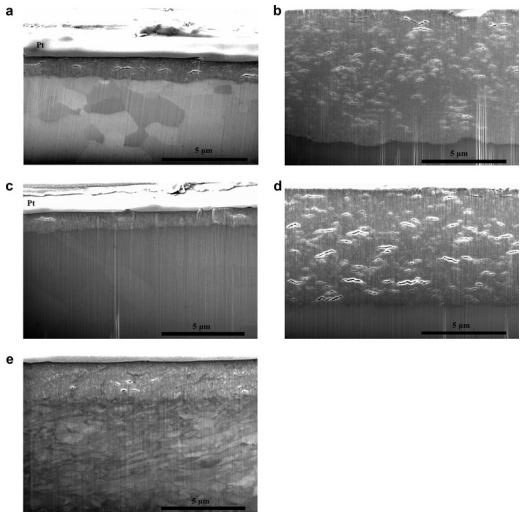

Fig. 1. Secondary electron SEM micrographs of cross-sections from (a) Zircaloy-2 LK2 with a 1 μm oxide thickness, (b) Zircaloy-2 LK2 with a 9 μm oxide thickness, (c) Zircaloy-2 LK3 with a 1 μm oxide thickness, (d) Zircaloy-2 LK3 with a 9 μm oxide thickness and (e) Zr-2.5Nb with a 2.8 μm oxide thickness.

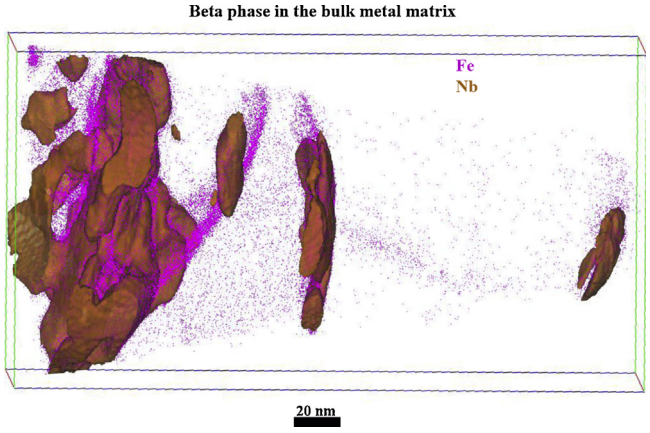

Fig. 2. Distribution of β-phase (brown surfaces) and Fe (purple dots) in the bulk metal of the Zr-2.5Nb material. The size of the box is $260 \times 120 \times 120\,nm^3$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

that the instantaneous hydrogen pick-up fraction in some zirconium alloys is inversely proportional to the oxidation rate [8,9], and has a maximum prior to the breakdown of the protective oxide known as transition. This implies that the cathodic reaction site will be shifted from the metal—which leads to hydrogen pick-up—to the oxide during an oxidation cycle. The locations of the cathodic reactions have proven very difficult to determine and there is no consensus as to where reduction occurs. By cathodic polarization in a dilute $CuSO_4$ solution, Cox et al. were able to show Cu deposits, signifying reduction sites, only at faults in the oxide, such as cracks and pores [10]. This suggests a localized hydrogen pick-up process, where the local mechanical properties of the barrier oxide play a critical role [11].

Alloying elements in Zr are known to greatly influence the hydrogen pick-up properties of the material. Recent atom probe tomography (APT) studies have highlighted some redistribution of alloying elements in the suboxide that is often found at the metal-oxide interface, and in the deforming metal [12] ahead of the advancing oxide front [13,14]. However, the barrier oxide layer, that is likely to be limiting for oxidation and hydrogen pick-up, has not yet been extensively studied with APT. As the oxygen partial pressure drops between the coolant or porous outer oxide and the Zr metal, gradual oxidation of precipitates and redistribution of alloying elements is expected across this layer. This study aims to elucidate the chemical profile of the barrier layer, and discuss its implications for the mechanisms of oxidation and hydrogen pick-up in zirconium alloys.

2. Experimental method

Three different zirconium alloys have been investigated in this study (see Table 1). The main focus is Zircaloy-2 fuel cladding that is used primarily in BWRs (boiling water reactors). Two different Westinghouse designated Zircaloy-2 materials were used; the older LK2 alloy and the more modern LK3 type [15]. A CANDU pressure tube material (Zr-2.5Nb) was also investigated. In order to simulate BWR conditions, the Zircaloy-2 alloys were oxidized in 400 °C and 415 °C steam at a pressure of 10.3 MPa. Oxidation times were chosen so that oxide scales of approximate thicknesses 1, 2 and 9 μm would be formed, see Table 2. For more details on the oxide growth kinetics, see reference [16]. The Zr-2.5Nb material consisted of elongated α-Zr grains in a network of thin Nb-enriched β-Zr lamellae. The pressure tubes were corroded in a D_2O autoclave operated at 335 °C, yielding an average oxide thickness of 2.8 μm. The in-reactor oxidation and hydrogen pick-up properties of the material have been investigated previously [17].

Transmission electron microscopy (TEM) specimen were prepared using a FEI Versa 3D combined focused ion beam scanning electron microscope (FIB-SEM) through a lift-out technique commonly used for producing site-specific samples with large electron transparent areas. Micrographs were obtained with conventional bright field imaging in TEM mode (BF TEM). The microscope used was a FEI Tecnai T20, with a LaB_6 crystal electron source.

Atom probe samples were produced using a conventional in situ lift-out procedure onto pre-fabricated Si flat-top microtips in a FIB-SEM [18]. Needle-shaped specimens were prepared using annular milling with Ga^+ ions at 30 kV and successively decreasing currents, followed by a cleaning step at 5 kV. Atom probe analysis was performed with an Imago LEAP 3000X HR system, using laser pulsing with green light ($\lambda = 532$ nm). The laser was pulsed at 200 kHz using a 0.5 nJ pulse energy. The pressure in the analysis chamber was approximately 10^{-9} Pa and the temperature of the tips was held at 40 or 70 K, where no notable difference in data quality was