Journal of Nuclear Materials 466 (2015) 12–20

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Review

# A review on hydride precipitation in zirconium alloys

Jacob Bair [a], Mohsen Asle Zaeem [a, *], Michael Tonks [b]

[a] Missouri University of Science and Technology, 1400 N Bishop Ave., Rolla, MO 65409, USA
[b] Idaho National Laboratory, 2525 Fremont Ave., Idaho Falls, ID 83401, USA

ARTICLE INFO

*Article history:*
Received 29 January 2015
Received in revised form
30 June 2015
Accepted 8 July 2015
Available online 11 July 2015

ABSTRACT

Nucleation and formation of hydride precipitates in zirconium alloys have been an important factor in limiting the lifetime of nuclear fuel cladding for over 50 years. This review provides a concise summary of experimental and computational studies performed on hydride precipitation in zirconium alloys since the 1960's. Different computational models, including density functional theory, molecular dynamics, phase field, and finite element models applied to study hydride precipitation are reviewed, with specific consideration given to the phase field model, which has become a popular and powerful computational tool for modeling microstructure evolution. The strengths and weaknesses of these models are discussed in detail. An outline of potential future work in this area is discussed as well.

## 1. Introduction

Zirconium (Zr) and its alloys have been used in nuclear fuel claddings and pressure tubes for more than 50 years, because of their low neutron absorption, and good strength and corrosion resistance at high temperatures. Despite these desirable material properties, Zr alloys suffer from an important weakness. During operation in nuclear power plants and in the storage period after usage, the Zr claddings are constantly being water-cooled. Oxygen from the water bonds with the outer layer of the cladding to create Zr Oxides, releasing Hydrogen (H) atoms, some of which enter the cladding. When the H concentration surpasses the terminal solid solubility limit of the Zr, hydrides are formed which lead to embrittlement and fracture through delayed hydride cracking (DHC). Examples of hydride related failure have been outlined in detail in recent papers [1,2]. Because of these problems, significant research has been conducted over the past 60 years to better understand hydride formation and morphology. The objective of this paper is to provide a concise review of experimental research and computational modeling efforts completed to this point on the subject of Zr hydrides. A more exhaustive review on experimental works done to this point can be found in a book on hydrides by Puls [3].

This review paper is organized as follows: in Section 2 a review on the experimental studies of Zr hydrides from the past 60 years is discussed; in Section 3 computational research is discussed, starting from the atomic scale (Density Functional Theory and Molecular Dynamics) and working up to mesoscale models (Finite Element Models and Phase Field Models); in Section 4 some conclusions are drawn which include potential research topics which may improve our understating of hydride precipitation in Zr alloys.

## 2. Experimental study of zirconium hydrides

There are four known hydride phases in the Zr–H system: $ZrH_{0.5}$-$\zeta$, ZrH-$\gamma$, $ZrH_{1.5-1.7}$–$\delta$, and $ZrH_2$-$\varepsilon$. The recently discovered $\zeta$ phase is metastable and is believed to be a transitional phase between $\alpha$-Zr and $\delta$ or $\gamma$ hydrides [4]. Previous speculations on the potential existence of the fourth phase ($\zeta$ phase) can be found in Refs. [5,6] by Bailey and Carpenter. Zhao et al. [4] hypothesized that the new phase may play an important role in the stress-reorientation of hydrides. Several experimental studies have been performed to create an accurate phase diagram of the Zr–H system [7–15]. The $\zeta$ phase is not included in any phase diagram because it is metastable. Since the early 1960's, the stability or metastability of the $\gamma$ phase has been debated [15–21], and some early phase diagrams contained the $\gamma$ hydride phase. Most current works agree that the $\gamma$ hydride phase is indeed a metastable phase that is stable only under certain conditions [19–21]. The stability of $\gamma$ hydrides is discussed in detail in Section 2.2. Most experimental work has been done on the $\gamma$ and $\delta$ phases, which are most commonly credited with mechanical failures of claddings. In the following subsections important results of experimental studies related to Zr hydrides

---

* Corresponding author.
*E-mail address:* zaeem@mst.edu (M. Asle Zaeem).

http://dx.doi.org/10.1016/j.jnucmat.2015.07.014
0022-3115/© 2015 Elsevier B.V. All rights reserved.

and their effects on nuclear fuel rod claddings are discussed.

### 2.1. Solubility and absorption of hydrogen in zirconium

Due to losses in ductility and other negative effects of hydrides, many experiments have been done to determine the Terminal Solid Solubility (TSS) of H in Zr [2,22–28]. The TSS is different for precipitation and dissolution of hydrides, so there are several papers that distinguish them by TSSP and TSSD, respectively. Solubility of H is important because hydrides can only precipitate after the solubility limit is surpassed. According to a review by Ells in 1968, the solubility of H drops drastically with temperature, from about 50 at% H at 500 °C to 0.7 at% H at 300 °C, and to around $10^{-4}$ at% H at 20 °C [29]. These values differ somewhat from those found by more recent studies, and the 50 at% H at 500 °C is most likely a typo in Ells' review paper, and is meant to be 5 at%. More recent studies still show a significant increase in solubility with temperature [24–30]. This increase in solubility shows the necessity of thoroughly understanding the TSSP and TSSD of H in Zr and its alloys. The results of previous experiments show that the TSSP changes very little due to alloying elements [22,23], applied stresses [25], and irradiation of the material [26]. However, Carpenter and Watters performed an *in situ* study of the dissolution of hydrides, and found that the TSSD may increase by irradiation [30]. Another work done by Cann and Atrens [28] shows that extrapolations of data found by others at high H concentrations is relatively accurate for lower H concentrations. Fig. 1 presents the results obtained by Une et al. [26] through Differential Scanning Calorimetry for TSS for precipitation and dissolution of hydrides in Zr. Their results compared very closely with experiments done through other methods, such as those in Refs. [24–30]. According to their equation, the solubility of H at 500 °C is around 5.6 at%, at 300 °C it is 1.5 at%, and at room temperature it is 0.01 at%.

Because of the importance of the amount of H in the system, there are some studies on determining the fraction of H absorbed into the Zr matrix during oxidation of the fuel claddings. The fraction of H absorbed by the claddings is related directly to the rate at which H concentration increases past the point of solid solubility. Couet et al. proposed a new technique for quantitatively determining H concentration in Zr alloys called cold neutron prompt gamma activation analysis [31]. They also recently showed that the ratio of H absorbed to total H generated in the corrosion reaction varies significantly with different alloying elements [32]. They found that Nb reduces H pickup while Cu increases it. It was also determined that coarser $ZrFe_2$ or $ZrCr_2$ precipitates reduce H pickup. In general, the fraction of absorbed H increases with exposure time. The results found by Couet et al. confirmed and expanded some previous studies [33–35]. These conclusions could become important in creating alloys which are more resistant to H pickup, resulting in less hydride formation and increasing the lifetime of claddings. For this reason, more research should be done to identify the factors that could reduce H absorption in the cladding materials; including the use of alloying elements or secondary precipitates that can potentially decrease H absorption. For example, finding the optimum amount of Nb and the optimum size of $Zr(Fe, Cr)_2$ precipitates that can provide the maximum protection against H absorption while maintaining sufficient mechanical properties, could be an important study which can help improving current cladding materials.

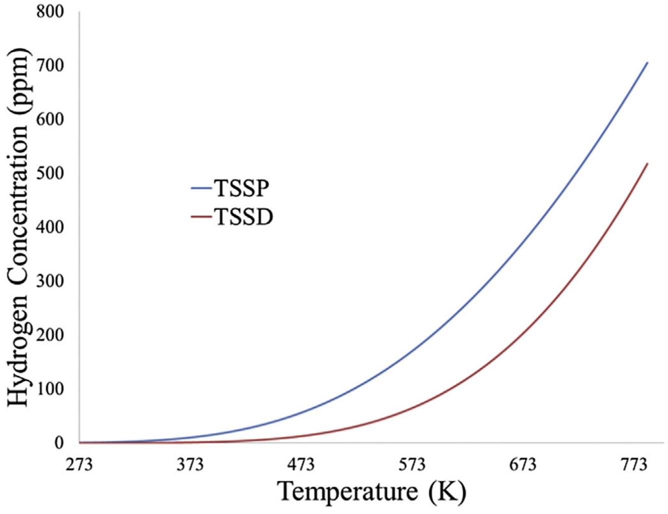

**Fig. 1.** Terminal solid solubility (TSS) of H in Zr by Une et al. [26]. They found very little differentiation between their studies and other experimental work in finding the terminal solubility of H in Zr.

### 2.2. Hydride crystallography

It has been shown by experiments that the four phases of Zr Hydrides have different crystal structures. $\delta$ hydride and $\varepsilon$ hydride are stable Face-Centered Cubic (FCC) and Face-Centered Tetragonal (FCT) phases, respectively [4]. $\gamma$ hydrides are FCT and $\zeta$ hydrides are trigonal. The majority of experimental studies done to date have been on $\delta$ and $\gamma$ phases, since they are the phases most liable for embrittlement and fracture of materials. Although they differ in crystallography, both the $\delta$ and $\gamma$ phases grow in similar directions within the Zr matrix. The direction of growth has been determined to be $[11\bar{2}0]$, but conflicting data has been collected on the habit planes. These hydride phases grow in the form of plates, and the broad side of the plate which is parallel to the crystallographic plane in $\alpha$ Zr is called the habit plane. Weatherly [36] found that $\gamma$ hydrides form as acicular plates having $\{10\bar{1}0\}$ or $\{10\bar{1}L\}$ habit planes, where $L \approx 7$. Westlake [37] found that the preferred habit plane of an unspecified phase of hydride (probably $\delta$ from the sample preparation) is $\{10\bar{1}7\}$ in Zircaloy 2 and 4, and it is $\{10\bar{1}0\}$ in pure Zr. Other possible $\delta$ hydride habit planes reported in the literature are $\{10\bar{1}2\}$, $\{11\bar{2}1\}$, and $\{11\bar{2}2\}$ [38], $\{10\bar{1}1\}$ [39], and the basal plane [40–45]. Singh et al. noted that temperature may have an important effect on which planes are the habit planes [41]. These discrepancies are briefly discussed by Kim et al. [46], speculating that DHC growth patterns and notch directions indicate that the $\{10\bar{1}7\}$ plane is the most probable habit plane.

The fraction of $\delta$ and $\gamma$ hydrides is related to the H concentration and cooling rate of the Zr. A higher H concentration and/or a slower cooling rate will lead to production of more $\delta$ hydrides, and the opposite will lead to more $\gamma$ hydrides [47–49]. The possibility of formation of each of these two hydride phases has also been linked to oxygen concentration by Cann et al. [50], who stated that higher amounts of oxygen impurity led to higher $\delta$ fractions, and low oxygen impurity favors $\gamma$ hydrides. They also found that the hydrogenation technique, grain size, and prior heat treatments had no effect on the phase of the hydrides formed. Studies by several other researchers have indicated that $\gamma$ hydrides may be a stable phase at temperatures below 250 °C [15–18], and a work by Root et al., in 2003 show that $\delta$ to $\gamma$ phase transformation can occur very slowly at low temperatures [16]. However, in 2004, Lanzani and Ruch found that $\gamma$ is a metastable phase at least in low purity Zr, and no $\delta$ to $\gamma$ transformation could be obtained [20]. In a recent paper on the effects of yield strength on hydride phase stability, Tulk et al. [19] referenced several other studies that found $\gamma$ to be a stable phase, but they realized that after heating to the H dissolution temperature, no $\delta$ to $\gamma$ phase transformation could be observed