



The preparation of Zr-deuteride and phase stability studies of the Zr-D system



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HIGHLIGHTS

- Controversial γ phase observed both *in-situ* and *ex-situ* after heat treatments.
- γ -ZrD is observed at room temperature after 5 h of heat treatment at 286 °C.
- Presence of $\alpha + \delta \leftrightarrow \gamma$ at 255 °C was not observed.
- It was observed that there is a $\delta \rightarrow \gamma$ transformation present around 150 °C.

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ABSTRACT

Deuteride phases in the zirconium-deuterium system in the temperature range 25–286 °C have been studied *in-situ* by high resolution neutron diffraction. The study primarily focused on observations of $\delta \rightarrow \gamma$ transformation at 180 °C, and the peritectoid reaction $\alpha + \delta \leftrightarrow \gamma$ at 255 °C in commercial grade Zr powder that was deuterated to a deuterium/Zr ratio of one to one. A detailed description of the zirconium deuteride preparation route by high temperature gas loading is also described. The lattice parameters of α -Zr, δ -ZrD_x and ϵ -ZrD_x were determined by whole pattern crystal structure analysis, using Rietveld and Pawley refinements, and are in good agreement with values reported in the literature. The controversial γ -hydride phase was observed both *in-situ* and *ex-situ* in deuterated Zr powder after a heat treatment at 286 °C and slow cooling.

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1. Introduction

Because of their good mechanical properties at high temperature and high pressure, their excellent corrosion resistance at moderate temperatures and low thermal neutron absorption cross section, zirconium (Zr) alloys are frequently used as a structural material in the nuclear industry [1–4]. As illustrated in Fig. 1a, Zr-alloys are primarily used for fuel rod cladding to hold the fuel pellets inside the reactor core. The Zr alloy fuel rods are surrounded by a liquid that acts as both a coolant and neutron moderator.

Depending on the type of nuclear power plant, either light (H₂O) or heavy water (D₂O) is used as a moderator. In ambient conditions, Zr reacts with oxygen and forms a thin (of the order tens of nm) passive oxide layer, which makes the alloy more corrosion resistant. However, during reactor operation the environment inside the reactor core becomes harsher (250–350 °C, 7–15 MPa) and Zr-alloys undergo corrosion, which produces free hydrogen (H)/deuterium (D). Some of the H/D atoms released through corrosion are absorbed into the cladding material. Some absorbed hydrogen may fill various faults in an area containing defects [5,6] and may become nucleation sites for hydrides [7]. Some of the hydrogen might be absorbed by Zr and may lead to the precipitation of hydrides once the solubility limit is exceeded [6,8]. Since Zr-hydride phases have a relatively large volume compared with the metallic

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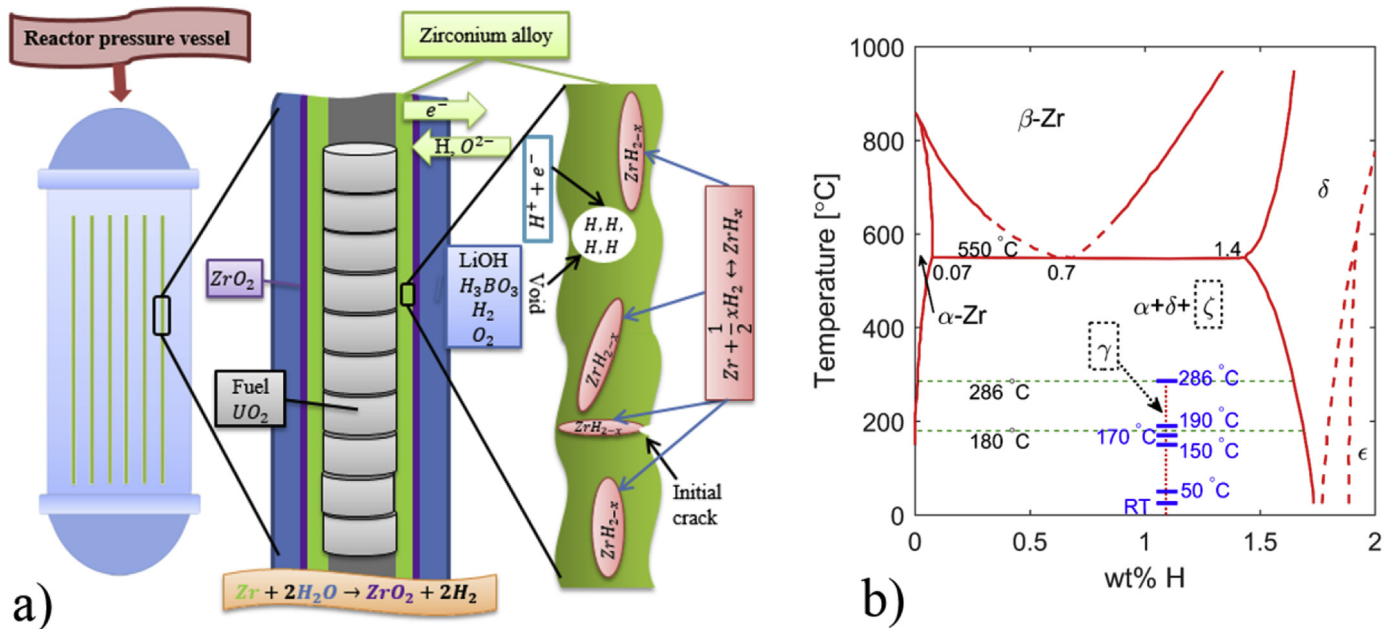


Fig. 1. a) Illustration of nuclear fuel cladding and hydrogen related degradation; b) binary Zr-H phase diagram after Ref. [1]. Blue horizontal lines crossing the γ -ZrH phase line represent measurements carried out in this study. Both γ and ζ phases are poorly established and are indicated with dashed rectangle. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Zr phase, the formation of hydrides introduces internal stresses in the material [9,10]. The local stress redistribution and plastic deformation induced by the growth of hydrides may contribute to the degradation of the material [11] and delayed hydride cracking [12–15]. Thus, the precipitation and growth of hydrides is a potential issue during extended fuel burn-up, and when reactors are taken off-line and cooled to ambient temperature.

It is known that the presence and orientation of hydrides degrades the mechanical properties of the material, with the degree of degradation depending on the concentration, distribution and morphology of the hydrides [13,16]. The detrimental effect of hydrides reaches a maximum when they are oriented normal to the applied load (radial hydrides in the case of tubes under internal pressure) [13]. Furthermore, different hydride phases exist in needle or plate like morphology depending on hydrogen concentration and environment [17,18]. In service, hydrides with different crystallographic structure and morphology might transform between each other under the influence of the surrounding environment (e.g., temperature and loading) [17,19], and react to external applied stress differently [20,21]. Therefore, to extend the life span of Zr-alloys and avoid failure, it is necessary to identify the nature of Zr hydrides and their exact structure.

Since the binary phase diagram of the Zr-D system is principally the same as the Zr-H system (Fig. 1b) [22,23] (D and H are chemically similar and there is no isotopic effect on phase boundaries), knowledge about Zr deuteride and Zr hydride can be used interchangeably for the purpose of phase transformation studies. However, deuterium has a higher coherent neutron scattering amplitude than hydrogen [22,24], which allows a better signal/noise ratio in neutron diffraction experiments. Therefore, deuterium is used in this work. Here D is used for hydrogen, and the term deuteride represents both hydride and deuteride.

At ambient pressure and temperature below 868 °C, Zr has a hexagonal close-packed (HCP) structure known as α -Zr, which is of Mg structure type with $P6_3/mmc$ space group symmetry. The unit cell constants of α -Zr are $a = 3.2316 \text{ \AA}$ and $c = 5.1475 \text{ \AA}$, and the c/a ratio is 1.593, which is slightly below the ideal value 1.633 of perfect

HCP but very close to the value of Ti $c/a = 1.587$ [1–3,25–27]. There are two atoms in each primitive unit cell, one at 000 and the other at $\frac{1}{3}\frac{2}{3}\frac{1}{2}$ or at $\frac{2}{3}\frac{1}{3}\frac{1}{2}$ [28]. At higher temperatures ($>868 \text{ °C}$), α -Zr allotropically transforms into the body-centred cubic (BCC) phase while the pressure is still low. This cubic phase is known as β -Zr phase, which is of W structure type with $Im\bar{3}m$ space group symmetry and a lattice constant $a = 3.6090$ [1,25–27] (see Fig. 1b). Under increased pressure while at room/low temperatures the HCP phase transforms into another hexagonal structure called ω -Zr phase ($c/a = 0.622$) [26,27,29]. In contrast to α -Zr, the ω -Zr phase has three atoms instead of two [26,27,29].

The HCP structure of α -Zr consists of both tetrahedral and octahedral sites, and D is expected to diffuse and occupy these sites. However, according to experimental evidence, D tends to occupy tetrahedral sites [1–3,26,27]. According to most of the published literature [1–4,17,18,25–27], there exist at least four different deuteride phases (named δ -, ϵ -, γ - and ζ -deuteride) at ambient temperature under atmospheric pressure (Figs. 1b and 2) depending on crystal structure, hydrogen concentration and quenching rate. The δ -deuteride (δ -ZrD $_x$) has a face centred cubic (FCC) structure with randomly positioned deuterium at eight tetrahedral sites with concentration ranges from $x = D/Zr = 1.5$ –1.7. The ϵ -deuteride (ϵ -ZrD $_x$) has a face centred tetragonal (FCT) structure with concentrations of $x = 1.74$ –2 (Fig. 2). Both δ - and ϵ -deuteride are accepted as stable phases. Experimental evidence from the literature indicates that there is at least one more tetragonal phase existing in the Zr-D system with a Zr to D ratio of 1:1, which is denoted γ -deuteride (γ -ZrD) (Fig. 2). However, controversy surrounds the stability and structure of the γ -ZrD phase. Some researchers suggest that γ -ZrD is the stable room temperature phase [30–33] with a δ to γ transition at 180 °C [31] or transforms by a peritectoid reaction $\alpha + \delta \leftrightarrow \gamma$ below $\approx 255 \text{ °C}$ [30], while others claim it is a metastable phase [13,34–38]. Additionally, several studies [1–4,22,39] propose that the γ -phase is a tetragonal phase with the $P4_2/n$ space group (Fig. 2), but Kolesnikov et al. [40] reported that the structure of the γ -ZrD is orthorhombic, belonging to the space group $Cccm$. Many research findings report that the γ -ZrD

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