

Lab Report

Exact Crystal Structure of the γ -ZrD/ δ -ZrD system

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Abstract

Zirconium alloys have a strong affinity for hydrogen which leads to hydrogen pick-up during a corrosion reaction when exposed to water. The hydrogen is readily in solution at higher temperature but precipitates as Zirconium hydrides at ambient temperatures. At least three phases are known to exist at ambient temperature depending on hydrogen concentration and quenching rate. However, some controversy exist regarding the exact nature and stability of the γ -ZrH phase, which is closely related to the δ -ZrH phase through ordering of the hydrogen on tetrahedral sites in the matrix. In this report, we give short introduction to our experimental work at FRM II in September 2010. In this work, we use high-resolution neutron powder diffraction on deuterated samples to re-determine and verify the reported structures which essentially date back to the 1960s [1].

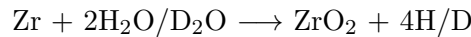
Keywords: γ -ZrD/ δ -ZrD, Zirconium, Hydrogen embrittlement

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1 Introduction

Zirconium (Zr) and its alloys are widely used in the nuclear industry as structural materials and as fuel rod cladding for nuclear fuel in fuel assemblies because of their excellent mechanical properties, low neutron absorptivity and high corrosion resistance. However, similar to other hydride forming alloys Zr alloys have a drawback, known as "Hydrogen Embrittlement" (HE) which mainly occurs at extended fuel burn-up [2]. At high temperatures Zr and its alloys have a considerable affinity for hydrogen/deuterium (H/D), which readily diffuses into hexagonal close packed (HCP) Zr phase, but has relative low solubility at ambient temperatures. During operation in a boiling or pressurized water reactor, the cladding material will undergo some aqueous corrosion



and some of the H/D released is absorbed into the Zr cladding material, while at the same time an oxide layer is formed at the surface. This eventually leads to the precipitation of hydrides once the solubility limit has been exceeded, which itself also depends also on mechanical stresses present. This is a potential issue when reactors are taken off-line and cooled to ambient temperature [3, 4, 5, 6, 7]. It is well known that the presence and orientation of these hydrides adversely affect the mechanical properties of the material, and the degradation of material properties depends on the concentration, distribution and morphology of the hydrides. The detrimental effect of hydride rich maximum when they are oriented normal to applied load (radial hydrides in the case of tubes under internal pressure)[8]. In principle, H can occupy interstitial tetrahedral and octahedral sites in HCP crystals (Fig.1), but for Zr hydrides, the reported crystal structures from diffraction measurements indicate that mainly the tetrahedral sites are occupied. Several types of hydrides have been observed, and their occurrence depends on the hydrogen concentration, specific composition, irradiation and thermo-mechanical history of the host-alloy [9]. The precipitation mechanism involves the simultaneous motion of hydrogen and the surrounding matrix atoms, and bear to this extent some resemblance to a martensitic transformation. Additionally, a stress induced transformation has often been invoked but until recently not yet experimentally verified. As with other hydride-metal systems, their presence leads to embrittlement, delayed hydride cracking (DHC) and hydride blistering; all of which reduce the lifetime of the component and are cause for considerable environmental concern in the storage of spent fuel rods [10]. From the literature, the tetragonal γ -ZrH phase has hydrogen ordered on alternating 110-planes, while in the face centered cubic (FCC) δ -ZrH hydrogen occupied the tetrahedral sites in a random way up to concentrations of H/Zr=1.66 when the stable ϵ -phase forms (Fig.2)[9]. The controversy surrounds the stability of the γ -ZrH phase [11]. Some reports

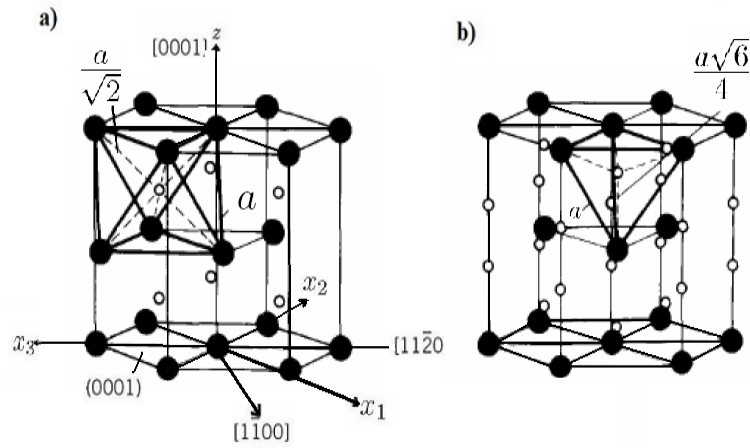


Figure 1: Crystallographic habit planes and directions of HCP α -Zr crystal, with interstitial preferred sites for H. a) octahedral sites ; b) tetrahedral sites.

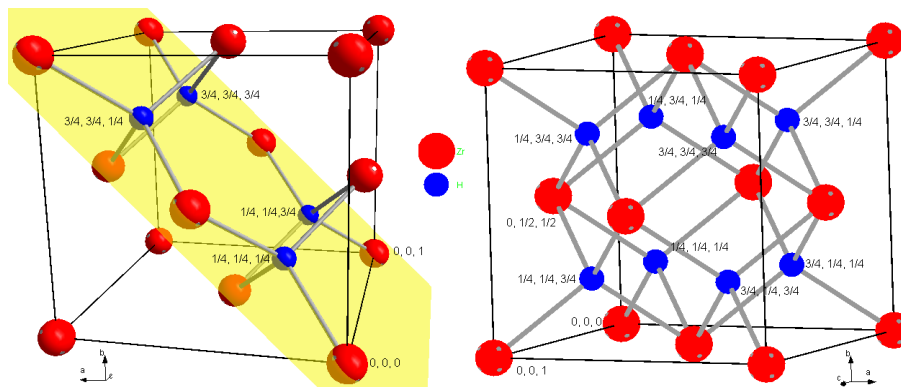


Figure 2: Possible hydride precipitation sites in γ - and δ -hydride phases. a) γ -ZrH phase an ordered tetragonal sites on 110 planes ; b) δ -ZrH_{x \approx 1.66} phase with randomly occupied tetrahedral sites.

suggest that this phase is the stable room temperature phase, with a δ -to- γ transition at 180 °C [12], while other quote the δ -phase as being the stable room temperature phase with no such transition [11]. Additionally, the exact structure of γ -ZrH also not clear. Many reporters suggest that γ phase is tetragonal phase with P42/n space group, but Kolesnikov et al.[13] reported that the structure of γ -ZrH is orthorhombic which belong to space group Cccm. Most reports agree that γ -ZrH occurs after rapid quenching (>10 °C/s), while δ -ZrH is often found after annealing. Thus, there is a need to clarify the exact structure of hydride, stability and their transformation behavior for better understand the effect of hydride faces in zirconium alloys.

In this report, we will give short introduction to our experimental work at Forschungsneutronenquelle Heinz Maier-Leibnitz(FRM II) in September, 2010 which focused on these issue described above. The result presented here are just friction of studies and it is not final, the analysis work is still going on. The final result will be disseminated in the standard peer-reviewed academic journals after whole analysis is complete.

2 Material and method

Why neutron diffraction?

Nowadays neutron and X-ray diffraction are used extensively for investigate the material property, since these diffraction techniques enables us to measure the absolute atomic spacings in the crystal. This is a particular use of Bragg's law, which states that diffraction can happen on a crystalline arrangement of atoms bombarded by a beam of X-rays or neutrons only if Bragg's conditions are fulfilled. Among these test methods, neutron diffraction always be used to establish the structure of light materials than a synchrotron radiation, since some light materials have a higher cross section for neutron interaction than higher atomic weight materials. The main advantage of neutron diffraction over synchrotron diffraction is that the neutron diffraction is very effective if there are 1H or 2H (i.e. Deuterium, D) present. This means that the presence and position of hydrogen in a crystal structure and its thermal motions can be determined far more precisely with neutrons. Synchrotron X-ray diffraction experiments [14] on hydrided Zirconium alloys deformed in-situ with very low strain rates show a crystallographic phase change (Fig.3). However, hard synchrotron X-rays are only sensitive to the Zirconium in the hydride phases. We expect that with deuterated Zirconium alloys we will obtain a larger signal to noise ratio at low concentrations of deuterium (up to 1000ppm weight) with a high resolution neutron diffraction facility like SPODI (Structure Powder Diffractometer) at FRM II. The data from SPODI will allow much better structure refinement, and the determination of the exact location of the deuterium atoms in the hydrides.

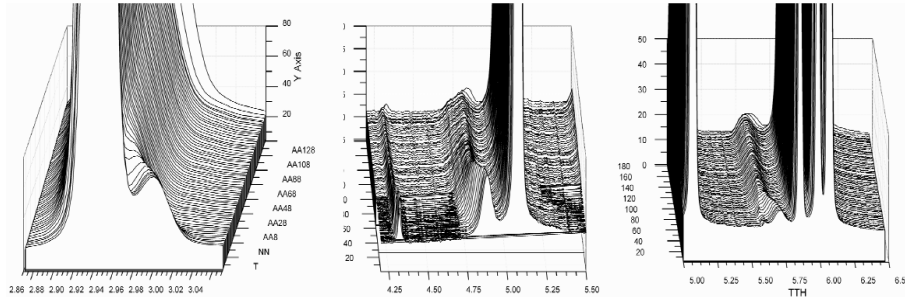


Figure 3: The discrepancy in the evolution of the hydride peaks (small peaks) compared to the matrix peaks (large peaks) during in-situ tensile loading suggest a phase change in the hydride phase, which could be explained by a (stress-induced) ordering transition from δ -to- γ ZrH [14]

Material

The powder sample which is used in experiment was prepared in strict order: First, the sample baked three days at 300 °C (after baking $P=5 \times 10^{10}$ mbar). Then, the sample exposed to a volume with a given amount of deuterium, when the volume had reached a low pressure (deuterium absorbed in the sample), the volume was refilled. This cycle repeated until the desired amount of absorbed deuterium acquired. During whole sample preparation process the powder was handled in glove box with argon to avoid any sort of contamination. Additionally, the hydrided, cold worked Zircaloy-2 and Zircaloy-4 samples, as well as commercially pure zirconium were tested both in furnace and outside the furnace. These alloys have a typical composition (in wt.%) of 1.31.6 Sn, 0.070.2 Fe, 0.050.16 Cr, 0.030.08 Ni and 0.13 other elements for Zircaloy-2, and without the nickel and increased iron content for Zircaloy-4. The H/D charge of these samples are 300, 400 and 500 ppm.

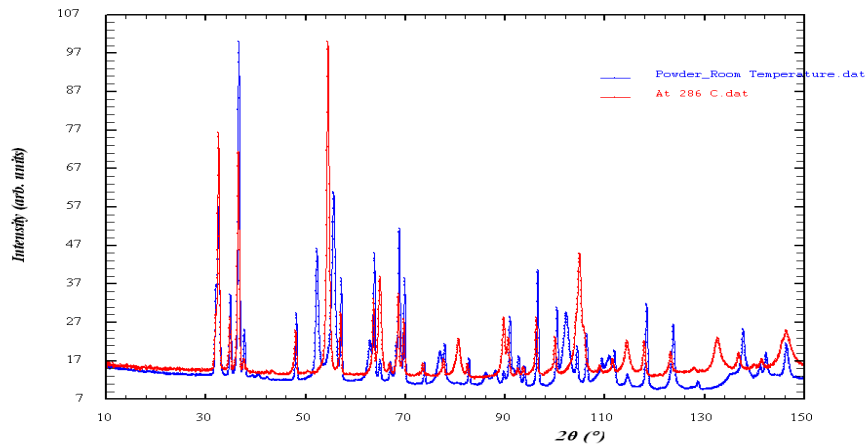
Experimental design

The thermal, high-resolution structure powder diffractometer at FRM II was used for investigation, since data from this world leading equipment have a high accuracy and suitable for Rietveld analysis. In SPODI, detector array consists of 80 ^3He position sensitive detector tubes with fixed collimators of 10° horizontal divergence located in front of each detector. The multidetector of SPODI spans an angular range of $2\Theta = 160^\circ$. As each detector covers 2° the data collection is performed via stepwise positioning of the detector array to obtain a diffraction pattern of desired step width $\Delta(2\Theta)$. For example, a typical step width of $\Delta(2\Theta)=0.05^\circ$ requires the number of steps $N = 2/\Delta(2\Theta) = 40$ [15]. In our work, we used 40 steps with 300000 counting and several overlaps for each test. During whole experiment the wave length

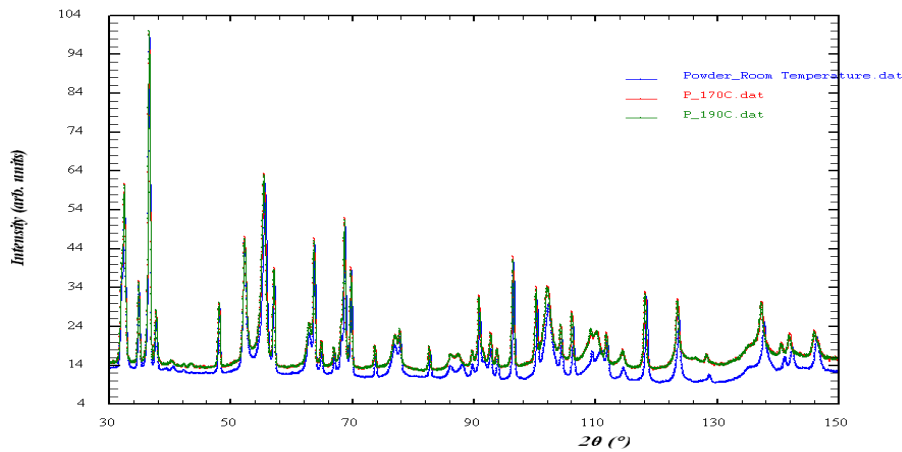
of the neutron kept as constant ($\lambda=1.548211 \text{ \AA}$). The powder and solid samples tested both in room temperature and elevated temperature for the seek of investigate the stability of the phases, in particular any transition around $180 \text{ }^\circ\text{C}$ and $286 \text{ }^\circ\text{C}$. For find out the correct transition (γ to δ) temperature between $180 \text{ }^\circ\text{C}$ and $250 \text{ }^\circ\text{C}$ we made more measurement in these temperature ranges. For reduce the texture effect we had measured sold sample in both normal and transverse direction separately.

3 Data analysis and result

The Fig.4a and Fig.4b shows the comparison of neutron diffraction profile



(a) Room temperature VS $286 \text{ }^\circ\text{C}$.



(b) Room temperature VS $170 \text{ }^\circ\text{C}$ and $190 \text{ }^\circ\text{C}$

Figure 4: Neutron diffraction pattern of the deuterated Zr powder measured at room temperature, 286 ° , 170 ° and 190 ° .

of deuterated Zr powder sample at room temperature with 286 °C and 150 °C, respectively. Thanks to the high resolution of SPODI, the data are very promising. From figure it is clearly seen that there are significant changes between 286 °C but not neither 150 °C nor 190 °C. The data from solid samples were also showed us very interesting and potential results as well. We had seen some changes and difference on these samples both on normal and transverse direction.

The neutron diffraction data were treated using the structure analysis software Topas-Acadamic, Matlab and FullProf. Since it is quite known that the Zr-H system at least consist of three phases, the data treatment started with assume there are three phases α , δ and γ are present. The matrix phase α and hydride phase δ were fitted with space group P63/mmc (No.194) with cell parameters $a=3.2276 \text{ \AA}$, $c=5.1516 \text{ \AA}$ and Fm-3m (No.225) with cell parameters $a=4.768 \text{ \AA}$, respectively. Since there are controversy exist about structure of γ , we used both assumption in our analysis. For tetragonal structure assumption we used space group P42/n (No.86) with cell parameters $a=4.586 \text{ \AA}$, $c=4.948 \text{ \AA}$ and for orthorhombic assumption we used Cccm (No.66) with cell parameters $a=4.549 \text{ \AA}$, $b=4.618$, $c=4.965 \text{ \AA}$. The pre-result of Rietveld analysis showed that the tetragonal structure of γ fits quite well than octahedral structure. The calculated lattice parameters of both α and δ -phase are close to other reporter [14]. Here it is worth to mention that the hydrogen-rich ϵ (ZrH_2) with a space group I4/mmm (No.139) with a lattice parameters $a=4.9689 \text{ \AA}$, $c=4.4497 \text{ \AA}$ was not observed in this annealed powder sample. However, it is bit early to make a conclusion about all these question we had introduced in introduction. They require some more experimental evidence.

4 Conclusion

As seen, the experiment was very successful and the results will going to verify the structure of ZrH, transition temperature between hydride phases and their stability for the first time using modern, high-resolution neutron powder diffraction techniques. We expect to be able to determine accurately the location of the deuterium in the respective deuterides. However, it will be quite helpful if we able to do some more experiments.

Acknowledgment

We are grateful to FRM II for gave us a chance to make our experiment. We also thankful to Christina Bjerken for her support and encouragement.

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