Direct Observation of Hydrogenation and Dehydrogenation of a Zirconium Alloy

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Abstract

The hydrogenation and dehydrogenation behaviors of a zirconium alloy were *in-situ* studied by scanning electron microscopy and transmission electron microscopy. The zirconium alloy can absorb hydrogen to form Zr hydride which is enhanced by the relaxation of inner stress in the alloy. The hydrogen is generated from an ion/electron beam stimulated decomposition of an organometallic precursor, trimethyl (methylcyclopentadienyl) platinum (IV), in a scanning electron microscope and focused ion beam system. The formed δ -type zirconium hydride that has a face centered cubic structure was observed to grow as preferentially oriented platelets in the zirconium alloy matrix. [The platelets have a common crystallographic relationship of \$\[010\]_a//\[1-10\]_\delta\$, \$\(001\)_a//\(111\)_\delta\$](#) . The dehydrogenation of the zirconium hydride was *in-situ* investigated in a transmission electron microscope by [heating the materials](#). It was found that the δ -ZrH_{1.5-1.66} hydride transformed into ζ -ZrH_{0.25} at 450 °C even at a longer heating time. The experiment demonstrates a new way for *in-situ* study of hydrogenation behaviors of other hydrogen storage alloys.

Keywords: Zirconium alloy; Hydride platelet; Dehydrogenation; Stress relaxation; *In-situ* observation.

1 Introduction

Metal hydrides are one option under consideration for hydrogen storage in solid state for alternative energy applications. Zirconium [1-3] and its alloys [4-6] are important H storage materials owing to their high storage capacity of H [3] and strong stability of Zr hydrides [7, 8]. The main requirements of a H storage material are very low absorption pressure at room temperature and a high H storage capacity. Shi *et al.* [3] reported their ability to attain the theoretical maximum H storage capacity ($H/Zr = 2$) when exposing Zr films to H with relative low contamination and a hydrogen pressure of ~ 2 Pa and a substrate temperature of 120°C for 10 min. Tritium-zirconium targets have also been prepared by absorbing gaseous tritium in thin Zr metal foils. It was found that maximal absorption of tritium could be obtained by holding the Zr thin foil at about 600°C for a few minutes, followed by cooling to room temperature [1].

In addition, the Zr-H reaction is concerned for the fuel cycles in fusion reaction [8, 9]. Zr and its alloys have also been used as the fuel cladding and structural materials in nuclear reactors due to their low thermal neutron absorption cross sections, good mechanical performance and corrosion resistance.

In nuclear reactors, the performance of Zr fuel cladding is susceptible to degradation partly due to H pickup that induces the precipitation of brittle Zr hydride [10]. If a loss-of-coolant accident occurs in a reactor, free H_2 gas would be produced by the reaction between the hot Zr alloy cladding material on the surface of fuel rods and the water vapor. Part of the H would be absorbed by the metallic Zr alloy [11] resulting in the hydrogenation of the Zr alloy, as the solubility of H in Zr is below 10 wt. ppm at room temperature [12]. Three types of Zr hydrides have been reported and presented in the Zr-H phase diagram [11], the γ -, and ϵ -type face centered tetragonal (fct) phases [13, 14], [and the \$\delta\$ -type face centered cubic \(fcc\) phase](#) [15]. [The \$\delta\$ -type hydride is stable at room temperature \(RT\) and is](#)

[considered to be a potential for hydrogen storage in solid phase.](#) Recently, Zhao *et al.* [16] reported a new Zr hydride namely ζ -type hydride formed at RT in a cathodic hydrogen charged Zircaloy-4 sample. The ζ -type hydride belongs to the trigonal system with space group P3m1 and it is fully coherent with the Zr matrix [16]. The hydrogenation of the Zr alloys was reported to experience a phase transformation with a volume expansion of 12.3% for $\alpha \rightarrow \gamma$ and 17.2% for $\alpha \rightarrow \delta$ [13]. The hydrogenation or deuteration of Zr alloys in the reactors resulting in problems such as embrittlement and strength degradation of the alloys [9]. [Therefore, there has been great interest](#) in the study of the hydrogenation behaviors of the alloys.

Even though many experiments have been performed on the study of the H pickup and H diffusion behaviors in a Zr matrix, there are only a few *in-situ* experiments reported in the literature [10-12]. The H diffusion in Zircaloy-4 was investigated by means of *in-situ* neutron radiography experiments [11]. The activation energy of H diffusion in Zircaloy-4 was determined as 55.4 kJ/mol. Colas *et al.* [12] reported that the Zr hydrides would be re-orientated under an external stress [load as observed by an *in-situ*](#) synchrotron radiation method. It was suggested that a threshold stress for hydride re-orientation is between 75 and 80 MPa for Zircaloy. A stress induced transformation from δ -type hydride to γ -type hydride via ordering of the H atoms was suggested by Steuwer *et al.* [10] who performed an *in-situ* uniaxial mechanical tensioning experiment on hydride-containing Zircaloy-2 and Zircaloy-4 specimens using energy-dispersive synchrotron X-ray diffraction. Kuroda *et al.* [17] described that the hydrogenation could be the dominant factor affecting the strength degradation of [Zircaloy claddings. The induced](#) degradation depends on the distribution and orientation states of the hydride precipitates. Transmission electron microscope (TEM) coupled with an ion accelerator was utilized by Shinohara *et al.* [18] to perform an *in-situ* investigation on the growth process of Zr hydrides in Zircaloy-4. In their study, the growth

processes of Zr hydrides accompanying the formation of dislocations were observed in the intergranular and intragranular grain of the Zircaloy during the hydrogen ion implantation [18]. Although those reported experiments have given us information on [hydrogenation](#) of different Zr alloys, the direct observation of Zr hydride precipitation during hydrogenation still remains unknown.

A lot of work has been done on the desorption behavior of Zr hydrides [7, 13, 19-21] by experimental techniques of thermal desorption spectroscopy (TDS) [20], differential scanning calorimeter (DSC) [22], *in-situ* X-ray diffraction [13, 23], thermogravimetric analysis (TGA) [24], and also by theoretical method based on the density functional theory (DFT) [25]. Nevertheless, the stability of various hydride phases is still debated, as such studies are working on bulk samples on the macroscopic scale. The stability of the hydrides is strongly correlated to the multiple kinds of material properties and defect status of the Zr matrix [10, 22-27]. Recent studies indicate that the stability and occurrence of the Zr hydrides is a complex phenomenon, where the stress in the matrix [10, 26], matrix yield strength [23], alloying additions [25], β -Zr distribution [23, 27] and ion irradiation [22] all have pronounced effects on the desorption kinetics of Zr hydrides. It has been demonstrated that nanoscale systems exhibit significant thermodynamic deviation from the bulk [28]. Therefore, it is necessary to estimate the desorption kinetics of the Zr hydride [without the influence of the crystalline Zr matrix](#).

In the present study, we introduce a new methodology, based on a focused ion beam (FIB) system, for an *in-situ* study of hydrogenation behavior of a Zr alloy during the H uptake process. The TEM sample preparation called flash polishing was employed to obtain the individual platelet for better characterizing the desorption kinetics of Zr hydride. The desorption kinetics of Zr hydride are investigated by the [combination of electron energy-loss spectrometer](#) (EELS) and selected area electron diffraction (SAED) in TEM.

2 Experimental methods

2.1 Material preparation

The as-received Zr alloy, consisting of Zr, Sn, Nb, Fe, Cr elements, was provided by Nuclear Power Institute of China [29, 30]. The Zr-Sn-Nb-Fe-Cr plate was prepared by the following procedures: (a) forge an ingot with composition of 1.0 wt.%Sn, 0.3 wt.%Nb, 0.3 wt.%Fe, 0.1 wt.%Cr and 98.3 wt.%Zr, in the temperature range of 900-1100 °C; (b) quench the melting billet at 1000-1050 °C; (c) cold roll the billet into plate at 600-700 °C; (d) finally anneal the plate at 560-600 °C. The final chemical composition of alloy measured by energy dispersive spectroscopy (EDS) in a TEM is 1.6 wt.%Sn, 0.6 wt.%Nb, 0.2 wt.%Fe, 0.1 wt.%Cr, and 97.5 wt.%Zr.

2.2 *In-situ* observation of Zr alloy hydrogenation

The hydrogenation of the Zr alloy was observed in a FIB system through a lamella thinning process. A thin lamella with a thickness around 1 μm was cut from the bulk Zr alloy by the lift-out method [31]. Then, the lamella was glued onto a half TEM grid at its two ends by platinum deposition to reduce the lamella deformation caused by the stress relaxation. In order to observe the Zr alloy hydrogenation process, a designed thinning procedure with two steps was applied to the lamella. A series of SEM images taken while the lamella was undergoing the Ga ion beam thinning [are](#) displayed in Figure 1. Firstly, the ion beam thinning was performed on [the right half of the thin lamella](#) denoted by the rectangle frame. As shown in Figure 1(a) to Fig. 1(c), the thickness of thin lamella decreases with the increase of ion thinning time. The SEM image of original lamella before it was further thinned down [is](#) shown in Figure 1(a). Many platelet features appear in the thinning area (Fig. 1(b)), and the platelet features become much clearer in Fig. 1(c). Those platelets seem to be

preferentially precipitated in the Zr matrix. Secondly, [ion beam](#) thinning was performed [on the left half of](#) the thin lamella. With continuous ion milling, the platelet features change [from unnoticeable in the Fig. 1\(d\) to remarkable in Fig. 1\(e\)-\(f\)](#) when it was further thinned down to about 100 nm.

Bright-field (BF) images taken from the Zr alloy [are shown in Fig. 2, the thin lamella with a thickness around 200 nm is compared to that taken from exactly the same area after it had been further thinned down to 100 nm by the ion beam \(Fig. 2\(a\) and \(b\), respectively\).](#) Before final thinning was applied, only dislocation lines were observed in the alloy [\(indicated by arrows in Fig. 2\(a\)\)](#). After final thinning, a large number of platelets denoted by arrows were observed to form in the Zr alloy with preferential orientations. The lengths of the platelets are nonuniform and ranging from ~ 100 nm to ~ 500 nm which are in agreement with those observed during hydrogenation in SEM.

2.3 Thin lamella preparation for *in-situ* dehydrogenation investigation in TEM

Thin lamella for *in-situ* dehydrogenation investigation through heating in a TEM was prepared using the procedure mentioned above followed by a flash electrochemical polishing procedure that was initially developed to remove the surface radiation damage layer introduced by Ga FIB [32]. In the present study, the flash polishing was designed to dissolve/thin the Zr matrix leaving the Zr hydride platelets in the dissolved Zr matrix. The etchant is 4 vol.% perchloric acid mixed with 96 vol.% methanol. The flash polishing was performed at - 40 °C and operated at an applied voltage of 12 V for 0.03 s.

2.4 Electron microscopy characterizations

A FEI Helios 650 Nanolab workstation was used for the study of *in-situ* hydrogenation and the microstructure changes of the alloy during the H uptake process. To further study the

microstructure and analyze the phases of the hydrogenated alloy, a JEOL JEM 2010F TEM running at 200 kV was used. Selected area electron diffraction (SAED), high resolution TEM (HRTEM) and BF imaging were performed in TEM mode. Scanning transmission electron microscopy (STEM) BF and annular dark field (ADF) images were also acquired from the specimens using a JEOL JEM2100F with a CEOS hexapole probe corrector working at 200 kV in STEM mode.

EELS tests were carried out on a JEOL JEM3100R5 TEM operated at 300 kV. The microscope was equipped with a cold-field emission gun, double Cs-Correctors and a Gatan 965 Quantum imaging filter. All the EELS collections were performed in STEM mode using a 30 μm condenser aperture, a 20 mm camera length, a 5 mm spectrometer entrance aperture and at a dispersion of 0.05 eV per channel. This configuration corresponds to a convergence semi-angle of 22 mrad, a Gatan DF detection semi-angle of 41.5 mrad and energy resolution of 1 eV. Dual-EELS spectra with both low-loss region (-5 - 95 eV) and high-loss region (500 - 600 eV) were recorded at the same time. The exposure time of 0.5 s and 3 s was used to record the low-loss region and high-loss region spectra, respectively. EELS line scan and mapping were acquired with a dwell time of 0.5 s at a step size of 0.5 nm and pixel size of 2 nm $\times$ 2 nm, respectively.

The TEM lamella with denuded orientated platelets were mounted onto a Gatan 652 double-tilt heating holder for *in-situ* dehydrogenation study up to 700 °C at an interval of 50 °C with a temperature ramping rate 20 °C/min.

3 Results and discussions

3.1 Identification of phase and composition of the platelet

HRTEM images and SAED patterns taken from the α -Zr alloy matrix and a platelet are shown in Figure 3. The intergrowth of the α -Zr alloy matrix and a hydride platelet is shown

in Figure 3(a). The SAED pattern in Fig. 3(b) is a composite one consisting of the [010] from the α -Zr alloy matrix and the [1-10] zone axis of the δ -type Zr hydride consistent with commonly acceptable statements that the δ -type Zr hydride is [the](#) most predominant phase at room temperature [15]. The enlarged HRTEM images from the Zr alloy matrix and the δ -type Zr hydride are separately shown in Fig. 3(c) and 3(d). The above analysis confirms that those two phases have an epitaxial relationship of $[010]_{\alpha\text{-Zr}}//[1-10]_{\delta\text{-ZrH}}$, $(001)_{\alpha\text{-Zr}}/(111)_{\delta\text{-ZrH}}$, which is in good agreement with the previous studies [12, 18, 33-35].

STEM-BF image of a Zr hydride platelet embedded in the Zr matrix is shown in Figure 4(a). EELS spectra collected from both of platelet and Zr matrix were shown in Fig. 4(b). Two EELS spectra were collected from the points labeled as A and B in Fig. 4(a), which correspond to the areas of Zr matrix and hydride platelet. Those two spectra were normalized to the energy loss peak height at 42 eV. The peaks labeled as 1 and 2 in the two spectra collected from the positions A and B, have energies of 16.9 eV and 19.2 eV, respectively, which are in excellent agreement with the reported plasmon peak energies for the α -Zr and the δ -type hydride [16, 36]. An EELS line scan along the line labeled in Fig. 4(a) was also performed and the EELS spectra collected are shown in Fig. 4(c). Two points marked by arrows in the line profile indicate the region that has not been hydrogenated. The EELS line scan indicates that the hydride was not fully hydrogenated due to the appearance of the α -Zr inside the hydride platelet. The EELS map collected from the rectangle area denoted in Fig. 4(a) are shown in Fig. 4(d) and colored by red and green corresponding to the energy loss peaks of 16.9 eV and 19.2 eV in the EELS spectra of Zr matrix and δ -hydride.

3.2 Mechanism of Zr hydride formation enhanced by stress relaxation

As having been mentioned above, two basic requirements for the Zr hydrogenation are needed, the generation of local stresses and the introduction of H. According to Colas *et al.*

[12] and Steuwer *et al.* [10], the hydrogenation behavior of Zr and its alloys would be strongly correlated to the local stresses [34]. In the present study, two kinds of milling procedures have been employed to do the final ion milling on the thin lamella. For the first case, the whole thin lamella was ion milled to a final thickness around 100 nm, which is called the conventional ion milling. After ion beam thinning, the side-view and top-view images of the thin lamella are shown in Fig. 5(a) and 5(b), respectively. Obvious deformation can be observed from the top-view image, and the formation of many platelets can be observed from the side view image. The other kind of final ion beam thinning procedure called gradient ion milling was adopted, as shown in Fig. 5(c)-(d). In this case, the denoted areas 'A' to 'D' in Fig. 5(c) continuously decrease in gradient from a original thickness of 1 [μm](#). Each labeled area has a typical width of 2 [μm](#). Only the area 'D' was thinned down to around 100 nm. After the ion beam thinning, no clear deformation and no platelets were observed in the lamella. It can be concluded that the stress relaxation accompanied by the lamella deformation generated during the conventional FIB milling processing provides the driving force for the Zr hydrogenation. Carr *et al.* [37] reported that the longitudinal macroscopic stress still exists in the Zircaloy-4 alloy after it had been heat treated at 475 °C for 30 min with only 40% reduction from that before heat treatment. A partial reduction of residual stresses after heat treatment at 530 °C for 1 hour was also found in Zr-2.5Nb alloy by Root *et al.* [38]. Therefore, it is believed that the Zr alloy studied here still contains some internal residual stresses even after it has been finally annealed at 600 °C.

In general, platinum deposition is employed as an irradiation protective coating or to glue a thin lamella to a manipulation tip or a grid during TEM sample preparation [31]. The platinum deposition can be conducted via either an electron beam or ion beam induced deposition methods. In any case, the organometallic gas precursor was firstly flowed and adsorbed onto the sample surface. Then, the decomposition of precursor would be

stimulated by either electron or ion beam, resulting in localized deposition of various [materials](#) [39]. Typical gas precursor used for the deposition of platinum is trimethyl (methylcyclopentadienyl) platinum (IV) [39, 40], which was also used in the Helios 650 FIB system. Wnuk *et al.* [40] demonstrated that electron irradiation stimulated desorption of organometallic precursor. Desorption of precursor was accompanied by the evaporation of methane and H molecules from the adsorbate layer and the loss of C-H groups. The electron stimulated reactions of adsorbed gas precursor can be expressed as [40]:

Hydrogen has been detected by the mass spectrometer as gas phase product during the electron/ion beam irradiation [39]. In the present study, the H source for the Zr hydrogenation [is generated by](#) electron/ion beam irradiation of the organometallic precursor. The free hydrogen gases can be consecutively produced immediately after the electron or ion beam focused on the area [which is](#) covered by the adsorbed organometallic precursor.

3.3 *In-situ* investigation of dehydrogenation of the Zr hydride

BF images with corresponding SAED patterns (shown in Fig. 6 (d)-(f)) taken from the hydride platelet at the temperatures of RT, 450 °C and 700 °C are shown in Figure 6(a)-(c). The hydride platelet remains a needle-like morphology without significant transformation during [the heating up](#) to 700 °C. Before heating, the hydride platelet has a fcc structure corresponding to δ -type $\text{ZrH}_{1.5-1.66}$ phase, which is confirmed by the indexed pattern in Fig. 6(d) having a zone axis of [110]. A subtle difference was observed between the SAED patterns taken at RT and 450 °C. The angle between crystal planes of $(1\bar{1}1)$ and $(1\bar{1}\bar{1})$ is measured as 70.5° at RT and changes to 66.9° at 450 °C, indicating that a phase

transformation [has occurred](#).

The decomposition of Zr hydrides with the increase of temperature has been reported in the Zr-H system [7, 13, 19-21]. The known phases of ζ -, γ -, δ -, ϵ -type hydrides and pure α -, β -Zr are considered as candidate phases when indexing the new formed phase at 450 °C. After carefully comparing the SAED pattern in Fig. 6(e) with the SAED patterns simulated with the crystal structure parameters of α -Zr and ζ -ZrH_{0.25-0.5}, it is reasonable to index the SAED pattern in Fig. 6(e) as ζ -ZrH_{0.25-0.5} structure with a zone axis of $[12\bar{1}]$. The SAED pattern in Fig. 6(f) [is the same](#) as that in Fig. 6(e), indicating that the ζ -ZrH_{0.25-0.5} is thermally stable up to 700 °C. To further verify the phase structure of hydride at 700 °C, three SAED patterns were taken along different viewing directions by tilting the specimen and shown in Fig. 7(a)-(c). They are in excellent agreement with the zone axis of $[1\ 2\ -1]$, $[-1\ 3\ -1]$ and $[3\ 5\ -1]$ of ζ -hydride, respectively. In addition, polycrystalline rings observed in the SAED patterns should be arising from the nano-size ZrO_x phases in the dissolved matrix and can be indexed as (002) and (021) of monoclinic ZrO_x.

Low-loss and high-loss EELS spectra collected from the area marked in Fig. 6(a) at different temperature during the *in-situ* heating from RT to 700 °C are shown in Figure 8(a)-(b). The intensity of all low-loss EELS spectra has been normalized to the energy loss peak at 42 eV, which is attributed to an excitation of the Zr 4*p* level electrons [41]. In the present study, we will focus on the energy loss peak ranging from 15 eV to 20 eV. [Only](#) one peak is observed at 19.3 eV for those spectra collected from RT to 425 °C, indicating that the hydride platelet is the δ -ZrH_{1.5-1.66} and is thermally stable below 425 °C. The energy loss peak in the spectrum collected at 450 °C started to shift towards to 18.3 eV, which belongs to the metastable γ -ZrH phase [14, 16, 23]. With the temperature increasing to 475 °C, the energy loss peak shifts to 17.3 eV that is ascribed to the energy loss of Zr element in the chemical states of ζ -ZrH_{0.25-0.5} [16]. The EELS spectra remain [the same](#) during the following

heating up to 700 °C. In Fig. 8(b), no obvious energy loss peak of [oxygen](#) was found around 532 eV in the EELS high-loss region spectra, indicating that Zr hydride is free of oxidation during the decomposition. The above *in-situ* EELS results demonstrate that the δ -ZrH_{1.5-1.66} is thermally stable below 450 °C, and afterwards, it would be decomposed to ζ -ZrH_{0.25-0.5} which stably exists up to 700 °C. The stability of the ζ - and δ -type hydrides concluded from the EELS analysis is consistent with our *in-situ* SAED study.

As mentioned above, the Zr hydride phase transformation from δ -ZrH_{1.5-1.66} to ζ -ZrH_{0.25-0.5} was confirmed to occur at 450 °C. The results on the transformation temperature and decomposition [products](#) are contrary to those found in the literatures [7, 10, 13, 19-21, 23, 26]. The reason for the stability of the hydrides in the present work differing from those in the literatures might be due to the effect from the Zr matrix, such as stress state, defect structure and yield strength. Moreover, our [results confirm](#) that the ζ -ZrH_{0.25-0.5} is stable up to 700 °C even [though \$\alpha\$ -Zr](#) has been recognized as the final [decomposition product](#) [13, 21]. The existence of the ζ -ZrH_{0.25-0.5} at 700 °C suggests that it has been stabilized by the dissolved ZrO_x matrix. [The main reason might be attribute to the stress state of Zr crystalline matrix which could enhance hydrogen reordering and phase transformation from \$\zeta\$ -ZrH_{0.25-0.5} to \$\alpha\$ -Zr in a bulk sample.](#)

4 Conclusions

In summary, we have reported the direct observation of the hydrogenation and dehydrogenation of the Zr hydride platelet in a Zr alloy. The reaction of the Zr alloy with H generated by the decomposition of the organometallic precursor induces the precipitation of Zr hydrides. The formed δ -type Zr hydrides have a fcc structure and exist as preferentially oriented platelets with a common crystallographic relationship of $[010]_a//[1-10]_\delta$, $(001)_a/(111)_\delta$ with respect to the Zr matrix. The stress is confirmed as a crucial factor

enhancing the formation of Zr hydride. The δ -type hydride is thermally stable up to 450 °C. Then, it desorbs H atoms and undergoes a phase transition to the ζ -type hydride, which is stable up to 700 °C [for this sample configuration \(i.e. thin, FIB milled, flash polished\)](#). The presented methodology may also be applied to the studies of hydrogenation behaviors of other metallic alloys for H storage like palladium.

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Figure Captions

Fig. 1. A series of SEM images captured during the final milling of the lamella prepared by FIB technique. From (a) to (f), the thickness of thin lamella decreases to a finally thickness of nearly 100 nm. The thin lamella was ion milling by two steps: ion milling on the right side ((a) ~ (c)) and then on the left side ((d) ~ (f)) of the lamella. Many platelets denoted by arrows appear in the area where the ion beam was targeting on.

Fig. 2. STEM-BF images taken from the same area of the Zr alloy with a grain boundary shown in the center (a) before and (b) after the final ion milling procedure.

Fig. 3. (a) HRTEM images and (b) SAED patterns taken from the α -Zr matrix and the δ -type Zr hydride. The magnified HRTEM images for Zr matrix and Zr hydride captured from the denoted areas in (a) were shown in (c) and (d), respectively.

Fig. 4. (Color online) (a) BF image of one Zr hydride platelet with positions A and B marked from which EEL spectra were taken. (b) EELS spectra collected from A and B corresponding to the areas of the Zr matrix and the Zr hydride platelet, respectively. The labeled peaks 1 and 2 in (b) reveal the chemical state of the element of Zr in pure Zr and the δ -type Zr hydride. (c) The EELS line scan collected along the line labeled in (a) is plotted from top to bottom. The specific EELS spectra of the Zr matrix and the δ -type Zr hydride are shown at the bottom. Two points marked by arrows in the line profile indicate the region that has not been hydrogenated. (d) Element map collected using EELS from the rectangle area denoted in (a) are colored by red and green corresponding to the energy loss peaks of 16.9 eV and 19.2 eV in the EELS spectra representing the Zr matrix and the δ -hydride.

Fig. 5. (a) and (c) side views and (b) and (d) top views of the final thin lamella prepared by two kinds of final ion milling procedures: ((a) ~ (b)) conventional ion milling; ((c) ~

(d)) gradient ion milling: only the selected area indicated by the rectangle frame is final milled down to around 100 nm.

Fig. 6. BF images ((a) - (c)) and SAED patterns ((d) - (f)) from one Zr hydride platelet taken at temperatures of RT, 450 °C and 700 °C. The SAED pattern in (d) is indexed as the δ -type Zr hydride along its [110] zone axis. The SAED patterns in (e) and (f) are indexed as the ζ -type Zr hydride along its [12-1] zone axis. The polycrystalline rings shown in all the SAED patterns ((d) - (f)) are ascribed to Zr oxides in the dissolved matrix.

Fig. 7. SAED patterns taken from the hydride platelet that has been heated to 700 °C along three different zone axes via tilting the platelet which are indexed as [12-1], [-13-1] and [35-1] zone axes of the ζ -type Zr hydride shown in (a), (b) and (c), respectively.

Fig. 8. (Color online) The low-loss (a) and high-loss (b) regions of EELS spectra collected from the denoted area in Fig. 6(a) at different temperatures during the *in-situ* heating from RT to 700 °C. Three energy loss peaks of 17.3 eV, 18.3 eV and 19.3 eV, corresponding to the ζ -hydride, γ -hydride and δ -hydride, are labeled in (a) with dash lines. The dash line labeled in (b) reveals the energy loss peak of oxygen element.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.