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Hydrogen in Zircaloy-4: effects of the neutron irradiation on the hydride formation

Pablo Vizcaíno · Abraham D. Banchik ·
José P. Abriata

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Abstract X-ray diffraction patterns of neutron irradiated Zircaloy-4 samples were obtained at the Brazilian Synchrotron Light Laboratory (LNLS) to study the effects of the fast neutron fluxes and post-irradiation thermal treatments on the zirconium hydride evolution. The high intensity and resolution of the synchrotron beam allowed to detect the $(111)_\delta$ and $(220)_\delta$ diffraction peaks of the $ZrH_{1.5+x}$ ($0 \leq x \leq 0.16$) δ-phase in unirradiated Zircaloy-4 samples having a hydrogen concentration as low as 0.2 at.% (20 wppm). Then, irradiated samples, that were taken from the Zircaly-4 core components of the argentine HWPR Atucha I Nuclear Power Plant (CNA-1) were studied with that radiation to detect the diffraction peaks of $ZrH_{1.5+x}$ δ-phase particles precipitated in samples having hydrogen isotope concentration lower than 2 at.% (220 wppm). A significant increment of the $(111)_\delta$ and $(220)_\delta$ peak areas were observed at room temperature after post-irradiation thermal treatments at 600 °C during 4 h. These results indicate that *after the annealing* a hydrogen concentration between 35 to 70 wppm, which were apparently *absent* in the irradiated samples has *precipitated* at room temperature as zirconium hydrides. That amount was estimated from a $(220)_\delta$ peak area versus the bulk H concentration regression line, made with unirradiated samples. These results get support to a hydrogen trapping hypothesis proposed in previous works. In addition, it has been shown that the zirconium hydride that precipitate in the irradiated samples have the equilibrium δ-$ZrH_{1.5+x}$ cubic crystalline structure.

Introduction

In recent works the temperature of Terminal Solid Solubility in dissolution, TSSd; and the dissolution enthalpy, ΔH_{solvus}, of the hydrogen isotopes in neutron irradiated Zircaloy-4 samples taken from the vertical 6 m long fuel channels of the reactor core of the argentine HWPR Atucha I Nuclear Power Plant (CNA-1) were determined by differential scanning calorimetry, DSC, [1, 2]. Calorimetric curves of samples having a bulk [H+D] higher than the $c_{\alpha:\delta}$ solubility limit at the reactor operating temperature T_{op} have shown TSSd values much lower than the equilibrium TSS. After different post irradiation annealing the TSSd values of the irradiated samples monotonously grow toward the unirradiated TSS value for the same bulk concentration [H+D]. These results indicate that only a fraction of the [H] in excess to $c_{\alpha:\delta}$ at T_{op} precipitate at room temperature as zirconium hydrides in the irradiated material. Both, the low TSSd values and its tendency to reach the TSS unirradiated value has been interpreted assuming that a hydrogen trapping mechanism operates in the two phase field of the Zr–H equilibrium diagram [1–5]. The mechanism considers that a fraction of the hydrogen isotope concentration remains trapped in crystalline defects induced by fast neutron fluxes [6]. That fraction is gradually annihilated by the post-irradiation thermal treatments, leaving these atoms free for precipitate as zirconium hydrides during the cooling down step of the thermal treatment.

P. Vizcaíno · A. D. Banchik · J. P. Abriata
Comisión Nacional de Energía Atómica, Av. Del Libertador
8250, C.P.:1429 Buenos Aires, Argentina

P. Vizcaíno (✉)
LMFAE, UACN, Centro Atómico Ezeiza, Presbítero Juan
González y Aragón No. 15, B1802 AYA Ezeiza, Buenos Aires,
Argentina
e-mail: vizcaino@cae.cnea.gov.ar

Within this context, the aim of the present work was to confirm the behavior observed by the DSC experiments following the evolution of the hydride crystalline structure with the annealings and attempt to quantify the amount of hydrogen *effectively precipitated* at room temperature as hydrides in the irradiated material. The approach was first intended using conventional X-ray diffraction techniques, but, owing to the limitations of the diffractometer[1] to detect small hydride contents (hydrogen concentrations lower to 2 at. hydrogen %), the experiments were carried out using the high intensity beam of the LNLS. The following paragraphs summarize the results of this experience.

Experimental

Materials

Four unirradiated Zircaloy-4 pieces of 10 × 10 × 1.7 mm were cut from a fully recrystallized Zircaloy-4 sheet with a grain size of (20 ± 5) µm. The alloying elements of the Zircaloy-4 are: 1.50 wt.% of Sn, 0.31 wt.% of Fe + Cr and the rest is zirconium, the base metal of the alloy.

The samples were hydrided with the cathodic technique using a H_2SO_4 diluted aqueous solution at 82 °C. Subsequent to the growth of a zirconium hydride layer at the two surfaces the samples were annealed 3 h at 550 °C to homogenize the bulk hydride distribution. After removing with SiC abrasive papers a possible residual hydride layer, the hydrogen contents of the samples were measured by a gas chromatograph LECO RH-404 (±4 wppm).

The irradiated Zircaloy-4 samples were taken from the Zircaloy-4 thermal column of a cooling channel that was removed from the CNA-1 reactor core after 10,3 fepy [2]. The thermal column of the cooling channels act (a) as a fuel channel keeping the fuel elements in the right position and (b) as an isolating cylindrical wall between the coolant at 250–300 °C and the moderator at 180–230 °C. The Zircaloy-4 microstructure is fully recrystallized and has an equiaxial grain size of 20 µm.

Due to the oxidation reaction of the Zircaloy-4 tubes with the D_2O coolant, a layer of ZrO_2 and deuterium gas (D) are produced by the corrosion reaction, a fraction of which is incorporated into the Zr matrix. Thus, the irradiated samples have about (20 ± 5) wppm of hydrogen, which was incorporated into the Zr matrix during the tubing fabrication and deuterium incorporated during reactor operation. The amount of D depends on the fast neutron fluency and the operating temperature. Owing to this, as the neutron flux varies on the radial and vertical directions of the reactor core and the temperature only on the vertical position, the [D] in each cooling channels varies along the vertical direction. Then, the total hydrogen isotope concentration, [H] in so far, is calculated adding the hydrogen and the deuterium concentration according [H] = 20 wppm + 0.5 [D]. The [D] was measured with a gas chromatograph for hydrogen (LECO RH-01; ±4 wppm) calibrated with D_2 instead of H_2 gas, the global error of [H] is estimated in 10 wppm. Details of the calibration process are given elsewhere, [2]. Before making the gas content analysis the samples were mechanically polished with SiC abrasive paper to remove the ZrO_2 layers.

The samples for the XRD experiments were carefully conditioned. The pieces of tube were mechanical polished with SiC abrasive paper until the wall thickness was reduced to about ~0.3 mm. Then, the flatten pieces were chemically pickled in a solution of distilled water (50%), nitric acid (45%) and hydrofluoric acid (5%) to improve the final surface smoothness of the X-ray samples.

Eight irradiated pieces of 7 × 7 × 0.3 mm were chosen for the experiments. They were taken from three regions of a Zircaloy-4 thermal column having the following neutron fluences[2]:

(a) 0.05×10^{22} n/cm^2 (LF group)
(b) 0.7×10^{22} n/cm^2 (MF) and
(c) 0.9×10^{22} n/cm^2 (HF)

Post-irradiation thermal treatments, made in a vacuum chamber (10^{-5} torr) to avoid oxidation, were applied to some of the samples. One sample of the LF and one of the MF groups were annealed at 400 °C for 1/2 h and other three, one per group; were annealed at 600 °C for 4 h. The rest of the samples were keep in the same condition they were received from the reactor plant, or ''as received'' condition.

X-ray diffraction experiments

The diagrams were obtained at the D12A-XRD1 line of the LNLS, with the diffractometer in the θ–2θ layout and a photon beam energy of 8.08 keV corresponding to a wavelength $\lambda = 1.542484$ Å ($\Delta\lambda = 0.000001$ Å), similar to the CuK_α line. The scans were made in 0.05° steps along the interval $20° \leq 2\theta \leq 130°$. The X-ray flat samples were polycrystalline sheets having the typical crystalline texture of cold rolled and fully recrystallized Zircaloy-4. The *c* axis of the α-Zr hcp cell was quasi-perpendicular to the sample surface and the pole figure have symmetry under 180° rotations. Therefore, two diffraction diagrams were made for each sample in order to discriminate the texture effects between positions rotated at 90°.

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[1] Diffractometer Philips PW 3710.

[2] The calculus only consider the fast neutron flux, that is En > 1 Mev, which produces the radiation damage in the zirconium matrix.

Results and discussion

The X-ray diffraction diagrams of four unirradiated samples containing 560, 450, 290 and 20 wppm of hydrogen were taken and several intense peaks of the δ-hydride phase (δ-$ZrH_{1.5}$, 1995 JCPDS 08-0218) were observed. The most intense are: $(111)_\delta$ (100%) at $2\theta = 32.4°$, $(220)_\delta$ (70%) at $2\theta = 54.4°$, $(200)_\delta$ (60%) at $2\theta = 37.6°$, $(311)_\delta$ (60%) at $2\theta = 64.8°$ and others of lower intensity. All of them are indexed in the Fig. 1.

Owing to the excellent resolution of the X-ray diagrams it was possible to measure in all the samples the area under the most intense peaks, the $(111)_\delta$ and $(220)_\delta$ of the hydride phase. Nevertheless, the closeness between the $(111)_\delta$ and the $(110)_\alpha$ (α-Zr, 1995 JCPDS 05-0665) and its overlapping in the ''as received'' condition of the irradiated samples restricts the number of peaks to only one, the $(220)_\delta$. A linear regression curve between [H] and the area under the $(220)_\delta$ was made with the three samples having the higher [H]. That line is good enough to extrapolate the results to the low [H] region. The value of the area of the sample with the lowest [H] value was not included in the regression line calculation because of its high area dispersion. These area values were normalized by that of the 560 wppm sample. The results are shown in Fig. 2.

On the other hand Fig. 3 shows the peak $(111)_\delta$ for the irradiated samples of the MF group in the three metallurgical conditions: as received, annealed at 400 °C and annealed at 600 °C. Qualitatively, the area under the peak of the as received sample and the one annealed at 400 °C are quite similar, being both smaller than the area of the sample annealed at 600 °C. The peak $(220)_\delta$ shows a similar trend in Fig. 4. The same behavior was observed for the samples of the lowest (LF) and highest (HF) fluence regions.

The behavior observed in Figs. 3 and 4 is compatible with the results obtained in recent works, where a strong effect of the neutron radiation was observed on the hydrogen solubility in irradiated Zircaloy-4. The temperatures of terminal solid solubility in dissolution measured by a DSC were much smaller than the unirradiated values for samples of similar hydrogen contents [1, 2]. These values seem to be metastable and the solubility of the unirradiated Zircaloy-4 was gradually recovered performing annealings

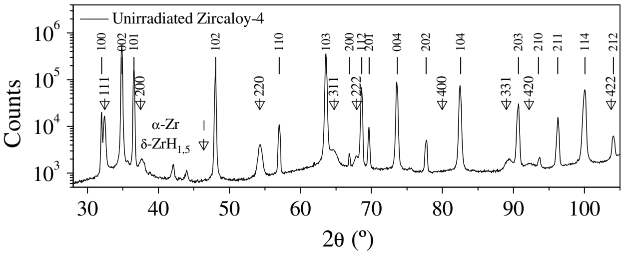

Fig. 1 XRD diagram of an unirradiated Zircaloy-4 sample (450 wppm). Many peaks of the δ phase (inverted triangles) and α-Zr phase (bars) are observed. The two small peaks placed at 42° and 43.9° corresponds to the $Zr(Fe,Cr)_2$ precipitates

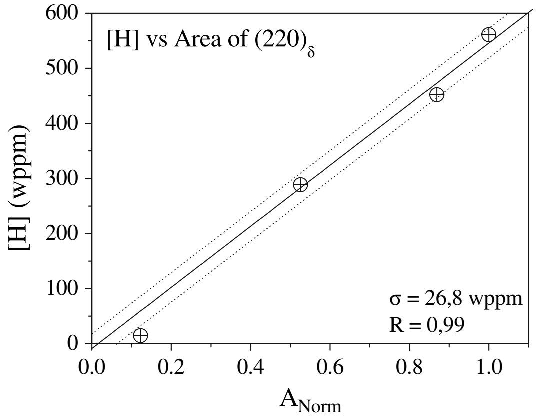

Fig. 2 Linear relation between the area of the peak $(220)_\delta$ and [H] for the unirradiated samples

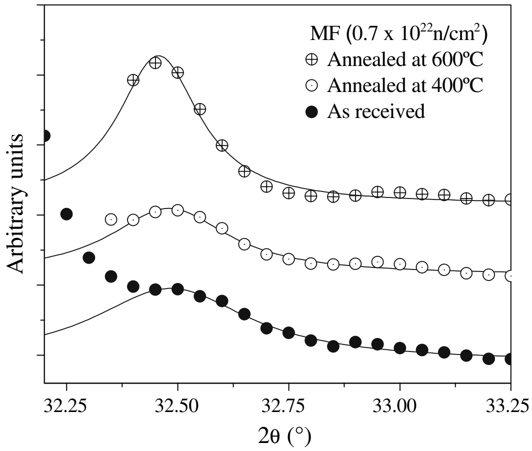

Fig. 3 Peaks $(111)_\delta$ of the three samples of the MF group (0.7×10^{22} n/cm^2)

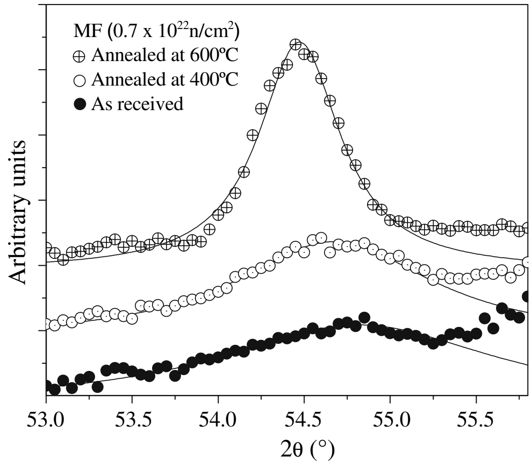

Fig. 4 Peaks $(220)_\delta$ of the three samples of the MF group (0.7×10^{22} n/cm^2)

of many hours (up to 80 h) at 600 °C [1, 2]. The overall behavior was explained by posing a hydrogen atom-defect interaction assuming that a fraction of the hydrogen atoms remained trapped at the crystalline defects created by irradiation which are gradually released due to the irradiation defect annihilation by the annealings [6].

McMinn et al. has suggested that <a> component dislocation loops play a significant role in hydrogen trapping [3]. Calorimetric results obtained studying hydride dissolution shown that the terminal solid solubility temperature increases with runs up to relatively low temperatures (380 °C), recovering the hydrogen solubility partially [1, 2]. The solubility of LF samples reaches the unirradiated values by short annealing at 400 °C, while longer annealing at 600 °C were needed to be applied to the HF samples to reach the unirradiated solubility [2]. Then, based on the trapping mechanism, the results observed in the LF samples can be explained assuming that the annihilation of the <a> loops during the runs up to T_{max} = 400 °C releases practically all the trapped H atoms.

However, a second trapping mechanism seems to be necessary to explain the evolution for the HF samples.

A recent work of Chung et al. by TEM in irradiated Zircaloy fuel cladding material with fluence levels similar to those of the HF samples give a hint about this traps [7]. The authors observed 'microscopic' hydrides precipitated in association with the <c> type dislocations. The density of these microscopic hydrides is a few orders of magnitude higher than the macroscopic hydrides density. They observed that these hydrides were stable at least up to 333 °C. The association between microscopic hydrides and <c> loops observed by Chung, under the light of Yang's [8] and Krueger's [9] analysis on the high temperature stability of <c> loops, which showed that no changes take place in the <c> loops density after 1 h at 560 °C or 575 °C and only a reduction of 50% is observed after 1 h at 675 °C, allow to assume that during reactor operations irreversible hydrogen traps related with the <c> loops are created in the Zircaloy-4 structural component for fluences higher than 10^{20} n/cm^2, which can only be completely reverted at temperatures as high as 600 °C.

With the aim to achieve a quantitative comparison, the areas under the peaks $(220)_\delta$ were measured for the samples of the three groups. They are shown in Table 1.

The values A_{Norm} of Table 1 were calculated making the ratio between the peak area of irradiated material and the area of an unirradiated sample having 560 wppm. With that normalization it is possible to calculate the [H] *effectively precipitated* as hydrides using the regression line shown in Fig. 2. As an example, the area of the sample 3, belonging to the HF group and annealed at 600 °C have a normalized area A_{Norm} = 0.29 (ΔA_{Norm} less than 5%). Then, according to Fig. 2 that A_{Norm} value corresponds to a [H] = 152 wppm, while the sample 1, belonging to the same group but being in the ''as received'' condition, has a normalized peak area of A_{Norm} = 0.17, which corresponds to a [H] = 85 wppm. Thus, about 65 wppm of hydrogen have not precipitated as hydrides when the irradiated material was cooled down from the operating temperature at T_{op} = 250–300 °C. This means that as the material during irradiation is at the two-phase field of the Zr–H equilibrium diagram, that amount of H atoms should be at T_{op} at same kind of traps that prevent the H atoms to precipitate as hydrides at room temperature. Certainly, as in the case of the previous example, the [H] estimated for the samples annealed at 600 °C for 4 h are still lower than the bulk values measured by the gas chromatograph, Table 1 but, as it has been shown, the hydrogen solubility of unirradiated Zircaloy-4 is recovered at 600 °C after much more longer annealing time than 4 h [2].

Table 1 A_{Norm} values obtained normalizing the area of the peak $(220)_\delta$ for the irradiated samples by the area of the same peak of the unirradiated sample of 560 wppm

Group	Sample	[H] (wppm)	$(220)_\delta$ A_{Norm}
LF	1		0.20
	2	185 ± 15	0.19
	3		0.29
MF	1		0.26
	2	178 ± 15	0.24
	3		0.31
HF	1	166 ± 15	0.17
	2		0.29

In summary, the results obtained by the synchrotron X-ray diffraction experiments have shown in a direct way the effects of the neutron irradiation on the hydride formation. In addition, they quantify the estimations made by DSC in previous works.

Conclusion

The LNLS X-ray diffraction capability successfully detects the δ-phase zirconium hydrides in unirradiated samples containing [H] as low as 0.2 at.% H.

The zirconium hydride phase that develops in the irradiated material has been identified as the cubic δ-phase of the equilibrium diagram of the Zr–H system.

The evolution of the $(111)_\delta$ and $(220)_\delta$ peaks with the post irradiation thermal treatments have shown that the fast neutron fluence affects that amount of zirconium hydrides that could precipitate in the irradiated Zr matrix.

The peak area increment with the post irradiation annealing at 600 °C observed in Zircaloy-4 samples with a

[H] higher than the $c_{\alpha:\delta}$ (T_{op}) implies that an amount of H atoms between 35 and 65 wppm does not precipitate as zirconium hydrides in the irradiated samples. Then, that amount should be at the operating temperature of the reactor in same kind of traps that prevent the precipitation of the δ-hydrides.

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