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Cold neutron prompt gamma activation analysis, a non-destructive technique for hydrogen level assessment in zirconium alloys

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ABSTRACT

We propose a novel use of a non-destructive technique to quantitatively assess hydrogen concentration in zirconium alloys. The technique, called Cold Neutron Prompt Gamma Activation Analysis (CNPGAA), is based on measuring prompt gamma rays following the absorption of cold neutrons, and comparing the rate of detection of characteristic hydrogen gamma rays to that of gamma rays from matrix atoms. Because the emission is prompt, this method has to be performed in close proximity to a neutron source such as the one at the National Institute of Technology (NIST) Center for Neutron Research. Determination shown here to be simple and accurate, matching the results given by usual destructive techniques such as Vacuum Hot Extraction (VHE), with a precision of ±2 $\mathrm{mg\,kg^{-1}}$ (or wt ppm). Very low levels of hydrogen (as low as 5 $\mathrm{mg\,kg^{-1}}$ (wt ppm)) can be detected. Also, it is demonstrated that CNPGAA can be applied sequentially on an individual corrosion coupon during autoclave testing, to measure a gradually increasing hydrogen concentration. Thus, this technique can replace destructive techniques performed on "sister" samples thereby reducing experimental uncertainties.

1. Introduction

With increased burnups and longer life times in nuclear reactors, uniform corrosion of zirconium alloy nuclear fuel cladding and the associated hydrogen pick-up can become a life-limiting degradation mechanism in existing and advanced light water reactors, since the ingress of hydrogen and precipitation of hydrides can cause cladding embrittlement [1,2]. Thus, it is of great interest to limit cladding embrittlement by decreasing overall corrosion and/or by decreasing the amount of hydrogen ingress for a given corrosion rate. The corrosion reaction is given by:

$$\mathrm{Zr} + 2\mathrm{H_2O} \rightarrow \mathrm{ZrO_2} + 2\mathrm{H_2} \tag{1}$$

Some of the hydrogen generated during corrosion can enter the metal. The hydrogen picked up by the metal during reactor or autoclave exposure is normalized to the hydrogen generated in the corrosion reaction. We define the hydrogen pick-up fraction f_H as the ratio of the hydrogen absorbed by the metal over the total generated hydrogen:

$$f_H = \frac{H_{absorbed}}{H_{generated}} \tag{2}$$

Despite extensive research, the mechanisms of hydrogen pick-up and especially the influence of the alloy composition and microstructure on f_H are not at all well understood [3–6]. In addition, there is evidence that f_H may vary during the corrosion process, such that different values occur at different stages of oxide film growth [7]. Part of the difficulty in developing mechanistic understanding of hydrogen pick-up is that accurate and precise measurements of hydrogen pick-up during corrosion are difficult to obtain. The purpose of this study is to demonstrate the use of Cold Neutron Prompt Gamma Activation Analysis (CNPGAA) to investigate the variations of f_H with alloy composition, corrosion time and alloy microstructure. In order to achieve this goal, differences as low as 5 $\mathrm{mg\,kg^{-1}}$ need to be accurately measured in zirconium alloys. Note that because the hydrogen masses, alloying element content and weight gain due to corrosion are very low, mass fraction in units of $\mathrm{mg\,kg^{-1}}$ (the SI unit) is for all practical purposes equal to wt ppm which is the common unit of hydrogen in zirconium. Both units will be displayed for the reader's convenience.

Many techniques have been traditionally used to measure hydrogen content in zirconium. Destructive techniques such as Vacuum Hot Extraction (VHE) or Inert Gas Fusion (IGF) have been widely used in past research [3–5,8]. These techniques are well developed, fast and inexpensive. In these experiments, zirconium samples are heated either to 1200 °C in the case of VHE (causing significant alloy microstructure changes, since the zirconium transition from α to β phase occurs at 865 °C) or to a temperature above the melting point in the case of IGF. Thus, both VHE and IGF are

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destructive techniques, which preclude further analyses on the sample. Hence, sister samples (identical samples coming from the same batch of material) must be used to evaluate the hydrogen pick-up variation as a function of corrosion time, which inherently spreads the results and makes the induced error difficult to evaluate. Also, the sample size analyzed in VHE and IGF (a piece of approximately 4 mm × 8 mm) is much smaller than a standard corrosion coupon (25 mm × 20 mm). Thus, spot-to-spot hydrogen concentration variations within the coupon may falsify the results. Finally the precision of these destructive techniques at these low hydrogen concentration levels is not well established.

Various non-destructive techniques have been used for evaluating hydrogen content in zirconium alloys. The EMAR method (electromagnetic acoustic resonance) [9] is ideal for in situ measurement but is not very precise. Also ultrasonic measurement coupled with eddy current testing [10], or neutron transmission technique [11] have been applied to this problem. However none of these techniques have the level of reliability and precision required to detect low hydrogen mass fractions in zirconium alloys.

In this study we use CNPGAA to analyze low levels of hydrogen in zirconium. CNPGAA has not been routinely used to detect hydrogen in zirconium alloys, as it is time consuming and can only be performed in a specialized facility. As will be shown, this technique is non-destructive, precise, measures the average hydrogen concentration in the whole sample and can detect very low levels of hydrogen (as low as 5 mg kg^{-1} (or wt ppm) [12]).

The initial results from CNPGAA are presented in this paper.

2. Experimental procedures

2.1. VHE and IGF apparatus

Vacuum Hot Extraction and Inert Gas Fusion have been performed by LUVAK, Inc. at Boylston, MA. An NRC Model 917[1] apparatus [13] has been used for VHE. A weighed sample is introduced through a vacuum lock into a molybdenum crucible in a vacuum line system. Prior to analysis, the sample is cleaned with ether and allowed to dry to remove any surface contamination. Heat is then applied to the crucible through an induction coil, to heat the sample and crucible to just below the melting point of the sample and with the aid of high-speed diffusion pumps, the hydrogen released is extracted from the sample and collected within the system. The amount of hydrogen present is then measured using a McLeod gauge and results are reported in units of mass fraction (mg kg^{-1}).

A Leco RH-404 Hydrogen Analyzer[1] apparatus [14] has been used for IGF. A weighed sample is melted in a graphite crucible in a stream of high-purity argon. Molecular hydrogen is released from the sample and is separated from any carbon monoxide and nitrogen liberated from the sample. A thermal conductivity cell determines the hydrogen content from which the mass fraction of hydrogen in the sample is calculated. The calibration of the VHE and IGF hydrogen determinations is verified with a NIST standard reference material of hydrogen into titanium [15].

2.2. CNPGAA apparatus

CNPGAA was performed at National Institute of Standards and Technology (NIST), Gaithersburg, in one of the cold neutron beam lines. A scheme of the instrument is presented in Fig. 1 and precise details on the apparatus are described elsewhere [16–18]. A brief description of the technique is presented here. The CNPGAA detection technique is based on the emission of characteristic prompt gamma rays emitted by a given nucleus when it absorbs a neutron. Thermal neutrons exit the reactor ($\bar{E}_{neutrons} \cong 0.025$ eV) and enter a liquid hydrogen cold moderator ($T_{moderator} \approx 25$ K), which shifts the neutron spectrum to lower energy ($\bar{E}_{neutrons} \cong 5$ meV). In a slightly curved neutron guide over a distance of 41 m, gamma rays and fast neutrons travel straight out the guide while cold neutrons are efficiently reflected and guided to the sample, thus providing a nearly pure beam of cold neutrons on the sample. These neutrons pass a collimator and are incident on the sample on a circular area of approximately 3.14 cm^2. The neutrons go through the sample, so the hydrogen content is averaged through the sample thickness. Some neutrons are absorbed by the sample, some by the chamber, and some pass through the chamber without being absorbed (the probability of absorption depends on the cross sections). Better sensitivity is obtained with cold neutrons since the absorption rate increases significantly when the neutron velocity decreases. Indeed, the hydrogen capture cross section is inversely proportional to the velocity at thermal neutron energies, such that neutrons from a moderator at 30 K yield an approximately threefold higher hydrogen reaction rate than those from a 300 K source. Absorption of cold neutrons by hydrogen results in the emission of one characteristic gamma ray at the energy of 2223 keV, due to the single hydrogen nucleus de-excitation ($^1\mathrm{H}(n,\gamma)\ ^2\mathrm{H}$) with a half-life of 10^{-9} seconds. This gamma ray is then detected and the signal can be converted to the hydrogen concentration of the sample. The neutron flux at the CNPGGA target position is approximately $8 \times 10^8\ \mathrm{cm}^{-2}\ \mathrm{s}^{-1}$.

The inner chamber (24.1 cm × 17.1 cm × 24.8 cm) is made of aluminum and magnesium alloys which have small neutron absorption cross section. This minimizes the gamma ray background from neutron capture by the walls of the sample box. The chamber is evacuated to minimize the gamma ray background due to neutron capture by nitrogen and hydrogen in atmospheric water vapor. Samples irradiated inside the chamber are suspended by Teflon strings between the prongs of an aluminum fork (again to minimize the instrumental background). The samples are thin enough to avoid gamma ray attenuation and self-shielding inside the sample.

Gamma rays emitted by the sample are measured using a high-purity germanium detector mounted vertically into a bismuth germanate (BGO) Compton suppressor (which improves the signal-to-noise ratio by decreasing the baseline background coming from Compton gamma rays).

Accounting for all of these features, the maximum background noise at the hydrogen gamma-ray energy is 5 mg kg^{-1} (or wt ppm), such that very low concentrations of hydrogen in the samples are detectable. This background is principally coming from other gamma-rays produced by neutron capture in hydrogenous materials present in the germanium and BGO detectors.

2.3. Fitting programs

During the experiment a gamma-ray spectrum is acquired in which each peak is originated from a given gamma ray of a given nucleus de-excitation. Although the hydrogen nucleus undergoes only one characteristic nuclear de-excitation (at 2223 keV), zirconium undergoes multiple de-excitations which generate numerous peaks in the gamma-ray spectrum. A typical example of the full gamma ray spectrum of a hydrided zirconium alloy is shown in Fig. 2, with a zoom on the hydrogen peak energy region given in Fig. 3. The zirconium 934 keV peak has been chosen as the reference zirconium peak. Different types of fitting programs have been used to analyze the results. Indeed, since the detected hydrogen concentrations can be very low, the choice of the fitting programs could affect the results. To verify this, three different fitting programs were used:

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[1] The identification of certain commercial equipment, instruments, or materials does not imply recommendation or endorsement by the National Institute of Standards and Technology. These identifications are made only in order to specify the experimental procedures in adequate detail.

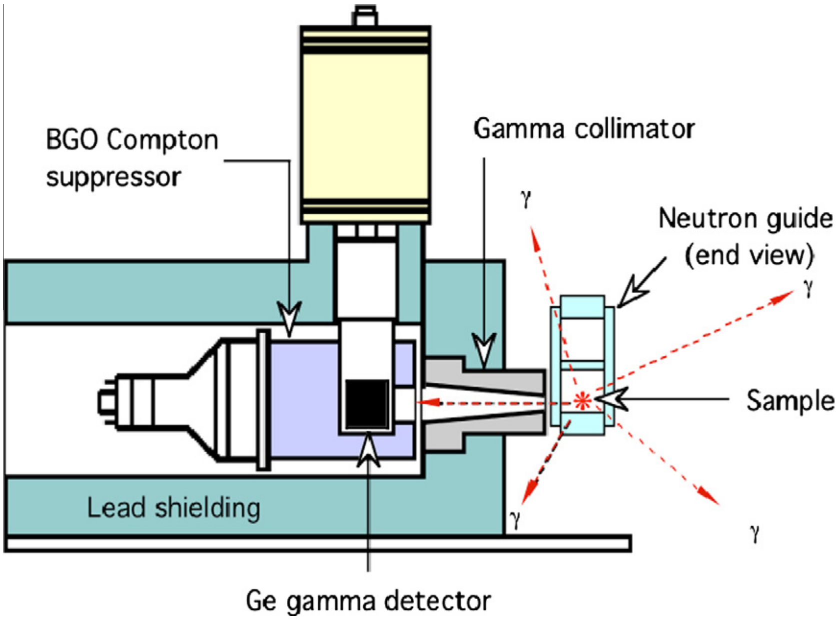

Fig. 1. Schematic of the cold neutron PGAA instrument located at the NIST Center for Neutron Research.

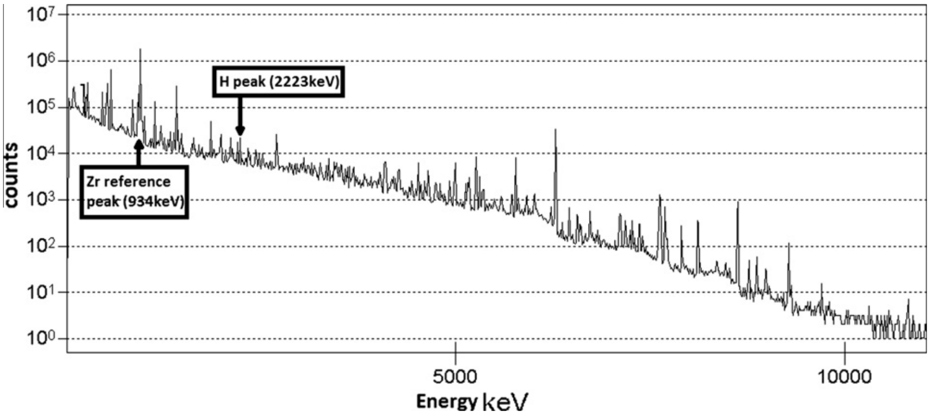

Fig. 2. Gamma ray counts versus gamma ray energy obtained during measurement of a Zr–1Nb–1Sn–0.1Fe sample after 105 days of corrosion in pure water at 360 °C and plotted using a commercial peak search program. In gray and indicated by arrows, are the zirconium reference peak (934 keV) and the hydrogen peak (2223 keV).

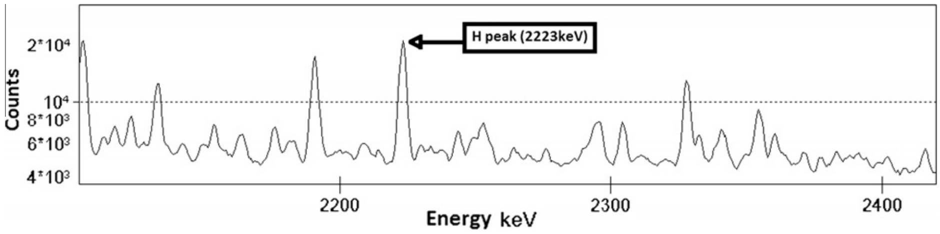

Fig. 3. Zoom of the gamma ray spectrum (number of counts in function of gamma ray energy) on the hydrogen energy peak region of Zr–1Nb–1Sn–0.1Fe after 105 days of corrosion in pure water at 360 °C, plotted using a commercial peak search program. The hydrogen peak is indicated by an arrow. The calculated hydrogen concentration of this alloy after 105 days of corrosion is 49 mg kg^{-1} (or wt ppm).

an algorithm for hand fitting of peaks (SUM) written at NIST [19], a standard commercial peak search program which locates peaks and integrates peaks automatically, and the program PEAKFIT 4.0*, a manual program in which the fitting is made peak by peak and is used to double check the automatic fitting processes used in the other programs. One significant difference between the SUM algorithm and the standard peak search is that using SUM, the background and peak regions are chosen by hand, while the peak search program chooses a few channels on either side of the peak for background calculation. This different way to consider the background affects the results of the standard peak search, which are always a few mg kg^{-1} lower than the results obtained by SUM.

2.4. Materials examined

2.4.1. Standards

The first major challenge to performing quantitative hydrogen analysis is to calibrate the results with standards so they can be quantified. The peaks have different sensitivities to the neutron absorption. Sensitivities (the number of counts per seconds per milligrams of the considered element exposed to the beam) are directly related to the neutron absorption cross sections and to the probability of a given de-excitation path compared to another one (for instance going from energy level 1 to 3 directly, by passing energy level 2). The hydrogen mass fraction in mg kg^{-1} in a zirconium sample is given by the following equation:

$$C_{\mathrm{H}}^{sample} = \left(\frac{\frac{A_{2223}}{t} - \mathrm{H}_{bkgd}}{S_{2223}^{\mathrm{H}}}\right) \times \left(\frac{S_{934}^{\mathrm{Zr}}}{\frac{A_{934}}{t}}\right) \times \frac{10^{-6}}{\omega_{\mathrm{Zr}}}\ \mathrm{mg\ kg}^{-1} \qquad (3)$$

where C_{H}^{sample} is the hydrogen concentration in the sample in mg kg^{-1}(or wt ppm), A_{2223} is the area of the 2223 keV peak in counts, H_{bkgd} is the hydrogen background in counts per second, S_{2223}^{H} is the hydrogen sensitivity in cps mg^{-1}, t is the acquisition time in seconds, S_{934}^{Zr} is the 934 keV reference zirconium peak sensitivity, A_{934} is the area of the 934 keV reference peak and ω_{Zr} is the mass fraction of zirconium. Considering the extremely low of alloying elements in a sample, and the small fraction that oxide mass represents of total mass of the sample, we will consider that $\omega_{\mathrm{Zr}} \cong 1$ for all alloys during the corrosion process (and thus mg kg^{-1} is approximately equal to wt ppm).

The determination of the sensitivities is of primary importance to the determination of hydrogen concentration. These sensitivities are determined using standards.

Because NIST certified standards of hydrogen into zirconium do not exist (only reference values exist), a combination of different standards was used: a pure zirconium foil ($m_{\mathrm{Zr}} = 218$ mg), a titanium foil ($m_{\mathrm{Ti}} = 14$ mg) and a graphite/urea/titanium powder sample (%Ti = 12.55% and %H = 3.171% mass fractions). Using this combination of standards, the sensitivities have been calculated using Eqs. (4)–(8):

$$S_{1381}^{\mathrm{Ti}} = \frac{A_{1381}}{(m_{\mathrm{Ti}} \times t)} \qquad (4)$$

where S_{1381}^{Ti} is the sensitivity of the 1381 keV titanium peak, A_{1381} is the area of the 1381 keV peak and t the acquisition time.

$$S_{934}^{\mathrm{Zr}} = \frac{A_{934}}{(m_{\mathrm{Zr}} \times t)} \qquad (5)$$

where S_{934}^{Zr} is the sensitivity of the 934 keV zirconium peak.

The hydrogen background H_{bkgd} is determined before running the samples by acquiring a 48 h spectrum with no sample inserted in the evacuated chamber:

$$\mathrm{H}_{bkgd} = \frac{A_{2223}^{bkgd}}{t} \qquad (6)$$

where A_{2223}^{bkgd} is the area of the 2223 keV peak during this experiment.

The ratio of Ti and H sensitivities is determined using the graphite/urea/titanium powder according to:

$$\frac{S_{2223}^{\mathrm{H}\,powder}}{S_{1381}^{\mathrm{Ti}\,powder}} = \left(\frac{\left(\frac{A_{2223}}{t} - \mathrm{H}_{bkgd}\right)}{\%\mathrm{H}}\right) \times \left(\frac{\%\mathrm{Ti}}{(A_{1381} \times t)}\right) \qquad (7)$$

Finally:

$$S_{2223}^{\mathrm{H}} = \frac{S_{2223}^{\mathrm{H}\,powder}}{S_{1381}^{\mathrm{Ti}\,powder}} \times S_{1381}^{\mathrm{Ti}} \qquad (8)$$

The results obtained using the various fitting programs for the analysis and calculation of area are in good agreement with each other. The peak search program gives us the smallest error range and consequently the best confidence. Thus, we will only display the results given by this peak search program. The sensitivities are given in Table 1.

Table 1
Hydrogen and zirconium sensitivities and hydrogen background determined for CNPGAA measurements.

Parameter	Peak centroid (keV)	Peak search program
Zirconium sensitivity (counts s^{-1} mg^{-1})	934	$9.91 \times 10^{-2} \pm 7.8 \times 10^{-4}$
Hydrogen sensitivity (counts s^{-1} mg^{-1})	2223	$13.12 \pm 2.9 \times 10^{-1}$
Hydrogen background (counts s^{-1})	2223	$6.3 \times 10^{-2} \pm 1.1 \times 10^{-3}$

Table 2
Hydrogen concentration in (mg kg^{-1} or wt ppm) obtained with VHE and CNPGAA on 10 Zr alloys (25 mm × 20 mm × 0.8 mm) uncertainties are 1 s, based on counting statistics, sensitivity measurement, and peak fitting, as discussed in the text.

Alloys	Exposure time (days)	Hydrogen concentration (mg kg^{-1} or wt ppm) by VHE	Hydrogen concentration (mg kg^{-1} or wt ppm) by CNPGAA
Zr–0.2Fe–0.1Cr	0	11 ± 1	39.8 ± 0.6
	7	24 ± 1	52.9 ± 1.0
	173	64 ± 3	92.0 ± 1.3
Zr–0.4Fe–0.2Cr	493	129 ± 6	160.0 ± 2.1
Zircaloy-4: Zr–0.2Fe–0.1Cr–1.3Sn	0	9 ± 1	37.3 ± 0.6
	28	23 ± 1	50.0 ± 0.8
	55	25 ± 2	55.4 ± 0.9
	240	75 ± 4	108.0 ± 1.7
Zr–0.2Nb	326	69 ± 3	96.9 ± 1.6
Zr–2.5Nb	326	134 ± 6	165.0 ± 2.2

2.4.2. Zirconium alloys samples

Corrosion tests were performed at Westinghouse Laboratory in Monroeville, PA. The zirconium alloys samples studied are in the form of corrosion coupons (25 mm × 20 mm × 0.8 mm) and their composition is listed in Table 2 (where the alloying content is indicated in percent mass fraction). The processing of these alloys is described elsewhere [20]. The coupons of various zirconium alloys (including ZrFeCr model alloys, ZrNb and Zircaloy4) were corroded in 360 °C pure water in a single static 4 l autoclave in saturated pressure condition at 18.7 MPa (2708.6 psi) according to ASTM G2-88 [21]. The alloys underwent different corrosion exposure times and thus exhibit various oxide thicknesses and hydrogen concentrations.

3. Results

3.1. Comparison with destructive techniques

One of the advantages of the CNPGAA technique is that it does not require any information such as precise thickness of the sample or sample mass since the ratios are measured. Using the element ratio method also largely negates the effect of uncertainties concerning neutron interactions (absorption, scattering, etc.) on the results. Indeed, sources of uncertainties associated with the neutron flux such as beam attenuation, temporal differences in the neutron flux, variation in sample area coverage by the beam or attenuation of the beam into the sample due to neutron absorption will vary from experiment to experiment. However, for a single experiment, these uncertainties are canceled by the element ratio method since they affect equally the hydrogen and the zirconium peaks [22]. If we recall Eq. (1) the variations described above associated with one particular experiment are denoted by the factor I:

$$C_{\mathrm{H}}^{Sample}(I)=\left(\frac{\frac{I\times A_{2223}}{t}-\frac{I}{t}\times \mathrm{H}_{bkgd}}{S_{2223}^{\mathrm{H}}}\right)\times\left(\frac{S_{934}^{\mathrm{Zr}}}{\frac{I\times A_{934}}{t}}\right)=C_{\mathrm{H}}^{Sample} \tag{9}$$

For benchmarking, ten uncut corrosion coupons were examined using first Cold Neutron Prompt Gamma Activation Analysis and then Vacuum Hot Extraction. The results of this comparison between the two techniques are shown in Table 2. The uncertainty in VHE shown in Table 2 is the total experimental uncertainty taking into account the error coming from the VHE technique and other uncertainties such as the area-to-area variation of hydrogen concentrations in a coupon. This error is difficult to evaluate, but using the error given by the company [23] and VHE measurements on various spots of the same coupon, the overall error has been estimated to be 5% of the hydrogen content. The error in CNPGAA comes from the error in A_x given by the different fitting programs and the composition errors of the standards. Using propagation error formulas the final error is given by:

$$\Delta C_{\mathrm{H}}^{sample}=C_{\mathrm{H}}^{sample}\times\left(\left(\left(\frac{\sqrt{\left(\left(\frac{\Delta A_{2223}}{t}\right)^{2}+\left(\Delta \mathrm{H}_{bkgd}\right)^{2}\right)}}{\frac{A_{2223}}{t}-\mathrm{H}_{bkgd}}\right)^{2}+\left(\frac{\Delta S_{2223}^{\mathrm{H}}}{S_{2223}^{\mathrm{H}}}\right)^{2}\right)^{2}+\left(\left(\frac{\Delta S_{934}^{Zr}}{S_{934}^{Zr}}\right)^{2}+\left(\frac{\Delta A_{934}}{A_{934}}\right)^{2}\right)^{2}\right)^{\frac{1}{2}} \tag{10}$$

where Δx denotes the error associated with x.

We notice a consistent difference of 29.4 mg kg^{-1} (or wt ppm) with a standard deviation of 1.1 mg kg^{-1} (or wt ppm) between the VHE and CNPGAA results. This difference is rationalized and explained below.

3.2. Hypothetical underlying peak of zirconium

A consistent discrepancy is observed between CNPGAA results and those given by VHE which is necessary to rationalize. The first hypothesis considered was that not all the hydrogen was extracted during VHE so that some hydrogen remained in the sample, leading to a lower value in VHE measurement. To test this hypothesis, we used IGF on the same samples, which should release all the hydrogen. We obtained the same results as in VHE, which confirmed that no hydrogen remained in the samples after VHE.

The second hypothesis considered is that there is an underlying peak at the hydrogen gamma-ray energy (since the discrepancy is constant among the different zirconium alloys investigated, it should be a zirconium peak). However no zirconium peak is referenced at this energy [24] and no effects such as a double-escape peak, pair-production or Bremsstrahlung escape peaks could explain it. It is likely that this particular peak of zirconium has never been previously reported because all zirconium samples contain a small amount of hydrogen and researchers may have ascribed that peak to the hydrogen [25]. Indeed, hydrogen is very stable in zirconium and is normally present in zirconium after the processing of the material [26]. According to VHE results on bare alloys in Table 2, the initial hydrogen concentration after processing is usually on the order of 10 mg kg^{-1} (or wt ppm). The previous studies using CNPGAA on zirconium alloys to detect other elements than hydrogen would not have examined this particular peak which was supposed to be only due to hydrogen. To check if there was an unknown underlying peak of zirconium we first performed VHE on four different zirconium alloys to obtain hydrogen-free zirconium samples, which were then examined using CNPGAA. The hydrogen-free zirconium samples also showed a constant peak at the hydrogen energy, which supports the hypothesis of the unknown underlying zirconium peak. Note that to perform VHE on the samples, it has been necessary to cut them using a low speed diamond saw to a size of 4 mm × 8 mm × 0.8 mm. Likely because of this or because of some remaining traces of hydrogen in the degassed samples, the value of the observed peak in free hydrogen samples was slightly higher than that in the full-sized hydrided samples used in Table 2.

To conclude, for samples in which the neutron beam area is entirely covered by the sample or larger, the offset between the CNPGAA and VHE techniques due to the hypothetical underlying zirconium peak is equal to 29.4 ± 1.1 mg kg^{-1} (or wt ppm) of hydrogen. Taking into account this potential peak of zirconium and as long as the sample area fully covers the neutron beam,

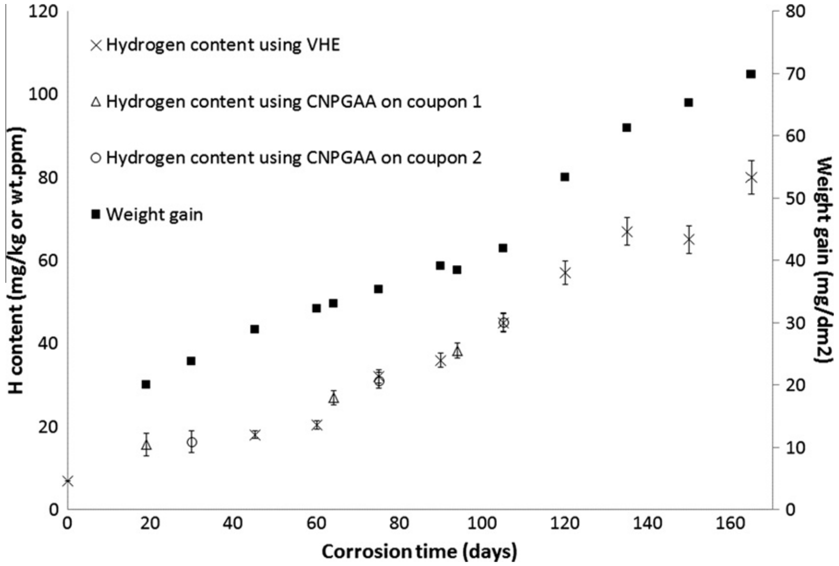

Fig. 4. Hydrogen concentration (mg kg^{-1} or wt ppm) in ZIRLO coupons as function of corrosion time using VHE on sister samples and successive CNPGAA measurements on two different individual coupons, plotted along with the weight gain of the corresponding sample. Error bars represent uncertainties based on equation 10 for CNPGAA measurements and equal to 5% of the hydrogen content for VHE measurements as discussed in the text.

CNPGAA technique accurately matches the results given by conventional destructive techniques such as VHE.

3.3. Hydrogen concentration as function of corrosion time using CNPGAA

Since the above measurements show that CNPGAA technique and VHE techniques agree once the offset due to the hypothetical underlying peak of zirconium is taken into account, we used CNPGAA to measure hydrogen content on two individual ZIRLO coupons (2.5 mm × 3.0 mm × 0.8 mm) at different times during the corrosion process. The ZIRLO coupons were corroded under the same conditions as the alloys shown in Table 2: 360 °C pure water in a single static autoclave of 4 l in saturated pressure condition at 18.7 MPa (2708.6 psi). Several ZIRLO sister samples were inserted in the autoclave to study the evolution of hydrogen uptake using VHE. The results are presented in Fig. 4 which plots the weight gain (mg dm^{-2}, on the right scale) caused by the uptake of oxygen during the corrosion reaction for every samples analyzed by VHE or CNPGAA at that particular corrosion time. The hydrogen contents (on the left vertical axis) were measured using both CNPGAA and VHE. The results shown in Fig. 4 indicate that taking out one ZIRLO coupon, performing CNPGAA on it and then inserting it back to the autoclave does not appear to alter the corrosion process. For instance, after 75 days of corrosion, one of the sister samples used in VHE (cross) and coupon two (circle) contain, at that particular corrosion time, the same amount of hydrogen, even though coupon two underwent two CNPGAA measurements (one at 35 days and on at 75 days). The examination of the evolution of hydrogen content among the different samples allow us to conclude that CNPGAA coupons behave similarly to sister samples, and thus the CNPGAA measurement does not alter the corrosion process and hydriding of ZIRLO samples. One should note that the uncertainty in CNPGAA measurements decreases with hydrogen content whereas that of VHE increases, which indicates that CNPGAA is more precise than VHE for levels of hydrogen higher than 40 mg kg^{-1} (or wt ppm). The hydrogen concentrations and mass gains measured can be used to calculate the hydrogen pick-up fraction as a function of corrosion time. This has been done using the values from Fig. 4 and hydrogen pick-up fraction is plotted in Fig. 5. This means that the technique can be used for measuring hydrogen uptake during corrosion of zirconium alloys, which will be the subject of upcoming publications.

At the beginning of the corrosion process, corrosion rate is high and the pick-up fraction increases rapidly to reach a value of approximately 5%. The hydrogen pick-up fraction remains approximately 5% in this pre-transition regime following a decrease in the corrosion rate (see weight gain curve in the right scale). Then, after approximately 70 days of corrosion, it starts to increase again up to approximately 12%. This increase occurs before the corrosion weight gain transition, which occurs around 95 days of corrosion. The overall hydrogen pick-up fraction in the post transition regime (approximately 12% after 100 days of corrosion) is consistent with former published data of ZIRLO corrosion in water autoclave [27]. The hydrogen pick-up fraction increases before the sudden loss of protectiveness occurring at the weight gain transition, which indicates that, even if the corrosion rate is still low, a greater fraction of the hydrogen is picked-up by the sample. After the weight gain transition, the hydrogen pick-up fraction remains constant but at a higher value compared to that before the transition. This general behavior has already been reported by Harada and Wakamatsu [7]. However, no satisfactory mechanism has been found to explain it. Additional experiments are being done to understand the mechanism leading to this hydrogen pick-up fraction behavior.

4. Conclusion

The Cold Neutron Prompt Gamma Activation Analysis method was applied to non-destructive hydrogen level assessment in Zr alloys. CNPGAA has been shown to be a reliable, accurate and precise method to measure hydrogen pickup in zirconium alloys. The method measures hydrogen concentrations comparable to VHE if one is careful to take into account the offset between the techniques, potentially due to a non-referenced underlying peak of zirconium at the hydrogen gamma-ray energy of 2223 keV, in calculating the hydrogen concentration and ensuring that the sample completely covers the beam. The CNPGAA technique is nondestructive, and measures the hydrogen concentration of the whole coupon, thus avoiding any spot-to-spot variation of hydrogen concentration (which can become significant close to the oxide transition). Experimental evidence shows that the measurement does not affect the corrosion process. Also, CNPGAA can precisely

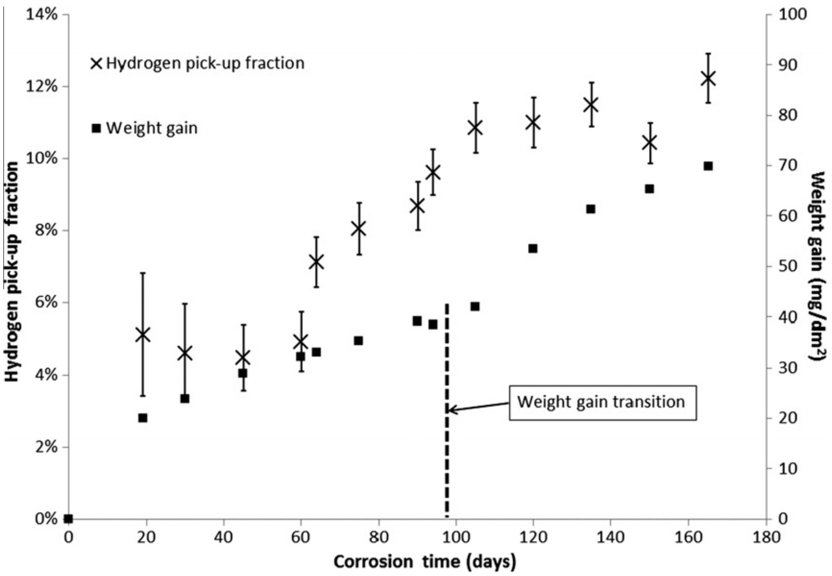

Fig. 5. Hydrogen pick-up fraction in ZIRLO coupons as function of corrosion time, plotted along with the weight gain of the corresponding coupon. Error bars represent uncertainties based on equation 10 for CNPGAA measurements and equal to 5% of the hydrogen content for VHE measurements as discussed in the text.

detect low levels of hydrogen (as low as 5 mg kg^{-1} (or wt ppm)) and can be used to measure the variations of hydrogen concentration in a single sample which makes it more attractive than other non-destructive techniques developed. The hydrogen pick-up fraction of ZIRLO samples has been investigated using CNPGAA and VHE. It is shown that the hydrogen pick-up fraction undergoes marked evolutions, both at the beginning of the corrosion process and slightly before the weight gain transition. The increase in hydrogen pick-up fraction before the weight gain transition is not well understood and is currently under investigation.

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References

[1] Corrosion of Zirconium Alloys in Nuclear Power Plants, IAEA-TECDOC-684, Vienna, 1993.
[2] Waterside Corrosion of Zirconium Alloys in Nuclear Power Plants, IAEA-TECDOC-996, Vienna, 1998.
[3] S. Kass, J. Electrochem. Soc. 107 (1960) 594–597.
[4] H.H. Klepfer, Corrosion 19 (1963) 285.
[5] W.E. Berry, D.A. Vaughan, E.L. White, Corrosion 17 (1961) 109.
[6] B. Cox, J. Nucl. Mater. 264 (1999) 283–294.
[7] M. Harada, R. Wakamatsu, in: Zirconium in the Nuclear Industry: 15th International Symposium, ASTM STP 1505, 2008, pp. 384.
[8] E.A. Gulbransen, K.F. Andrew, J. Electrochem. Soc. 116 (1969) 659–664.
[9] M. Nakatsuka, S. Ishimoto, Y. Ishii, A. Miyazaki, J. Nucl. Sci. Technol. 43 (2006) 1142–1148.
[10] M.P. Gómez, G. Domizzi, M.I.L. Pumarega, J.E. Ruzzante, J. Nucl. Mater. 353 (2006) 167–176.
[11] L. Bennun, J. Santisteban, J. Díaz-Valdés, J.R. Granada, R.E. Mayer, Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 263 (2007) 468–472.
[12] R. Lindstrom, R. Paul, D. Vincent, R. Greenberg, J. Radioanal. Nucl. Chem. 180 (1994) 271–275.
[13] Methods of Chemical Analysis of Zirconium and Zirconium Alloys (Silicon, Hydrogen, and Copper), ASTM E146-83.
[14] Standard Test Method for Determination of Hydrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Thermal Conductivity/Infrared Detection Method, ASTM E1447-09.
[15] W.P. Reed, Certificate of Analysis Standard Reference Material 352c, National Institute of Standards and Technology, 1990.
[16] R. Paul, Analyst 122 (1997) 35R–41R.
[17] R. Paul, R. Lindstrom, A. Heald, J. Radioanal. Nucl. Chem. 215 (1997) 63–68.
[18] R. Paul, R. Lindstrom, C. Brocker, E. Mackey, J. Radioanal. Nucl. Chem. 278 (2008) 697–701.
[19] R. Lindstrom, Biol. Trace Elem. Res. 43–45 (1994) 597–603.
[20] A.T. Motta, M.J. Gomes Da Silva, A. Yilmazbayhan, R.J. Comstock, Z. Cai, B. Lai, in: Zirconium in the Nuclear Industry: 15th International Symposium, ASTM STP 1505, 2009, pp. 486.
[21] Standard Test Method for Corrosion Testing of Products of Zirconium, Hafnium, and Their Alloys in Water at 680 F or in Steam at 750 F, ASTM G2-88, 2002.
[22] E.A. Mackey, R.L. Paul, R.M. Lindstrom, D.L. Anderson, J. Radioanal. Nucl. Chem. 265 (2005) 273–281.
[23] D. Gaskill, Vice President General Manager LUVAK. Inc., Personal Communication, 2010.
[24] Database of Prompt Gamma Rays from Slow Neutron Capture for Elemental Analysis, IAEA STI/PUB/1263, 2007.
[25] S. Nakamura, H. Harada, S. Raman, P.E. Koehler, J. Nucl. Sci. Technol. 44 (2007) 21–28.
[26] E.A. Gulbransen, K.F. Andrew, J. Electrochem. Soc. 101 (1954) 474–480.
[27] G.P. Sabol, G.R. Kilp, M.G. Balfour, R. Elwyn, in: Zirconium in the Nuclear Industry: Eighth International Symposium, ASTM STP 1023, Philadelphia, 1989, pp. 227–244.