

Evaluation Methods for Hydrogen Pick-up in Irradiated High Burnup Fuel Rod Claddings

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Abstract

The hydrogen content of zirconium alloy cladding of irradiated fuel rods affects in several ways their in-reactor performance. For this reason, not only the total amount of hydrogen in the cladding has to be determined but also the topology of the delta-hydride precipitates has to be determined. Two techniques and the experience gained during their application to the determination of the hydrogen content of highly irradiated PWR and BWR-claddings are described and their quantitative results compared. The two techniques are:

- ◆ Hot extraction to determine the total hydrogen amount in the material;
- ◆ and Scanning Electron Microscopy (SEM) to measure the area fraction of the hydride platelets.

Furthermore, a procedure to quantify the amount of hydrogen in the oxide layer is discussed. The experimental results revealed a hydrogen concentration in the oxide of about 750 ppm.

Keywords: Spent fuel; cladding; high burnup, zirconium hydrides

1. Introduction

The concentration of hydrogen in zirconium alloy cladding and the structural components of light water reactor (LWR) fuel assemblies is an important parameter during and after irradiation [1-3].

The presence of hydrogen in zirconium alloys results mainly from its oxidation in the hot primary coolant during irradiation. The chemical reaction can be written as



Only a part of the hydrogen formed diffuses into the cladding. This so-called pick-up fraction depends on the alloying components in the zirconium and may vary between 5 and 25 wt %. In zirconium alloys a certain amount of hydrogen can be in solid solution depending on temperature. For example, at an operating temperature of 350 °C about 150 ppm of hydrogen is dissolved.

In the case of high corrosion, i.e., high hydrogen production, and/or low temperatures, the hydrogen precipitates as delta-hydride platelets ($\text{ZrH}_{1.9}$). Length and orientation of the hydride platelets may determine the mechanical properties of the zirconium alloy. High hydrogen concentrations in zirconium alloys can also affect the corrosion rate. Steep temperature gradients in the rod cladding can support the formation of highly concentrated, dense hydride rims at the cladding outer surface. As a result of the formation of these dense hydride rims, corrosion can be accelerated.

For industry and technology it is therefore obvious that all technical developments that increase corrosion due to a change of materials or geometries have to be evaluated with regard to the resulting content and distribution of hydrogen. In the following, the main impacts of hydrogen and the corresponding measuring techniques to quantify the hydrogen concentration are described.

2. Impact of hydrogen on the material behaviour

Hydrogen affects the material behaviour on two main areas:

- ◆ Mechanical response (ductility, delayed hydrogen cracking (DHC), creep, defect behaviour, and
- ◆ Corrosion behaviour as a result of the different corrosion rates of the different zirconium alloys and $\text{ZrH}_{1.9}$

From the viewpoint of measurement it is important to choose an appropriate technique for characterisation and quantification of the hydrogen in the alloy. For phenomena with homogeneous hydrogen distribution an integral technique is well suited. Figure 1 shows the ductility behaviour of cladding and structural components at operational and room temperature as a function of the integral hydrogen content.

For a local phenomenon, such as accelerated corrosion due to increased local hydrogen content in the vicinity of the metal-oxide interface, a local characterisation of the hydride distribution is needed. Figure 2 shows different hydride precipitate densities at the metal-oxide interface and the acceleration of the corrosion rate in the case of higher hydride concentration.

Total elongation [%]

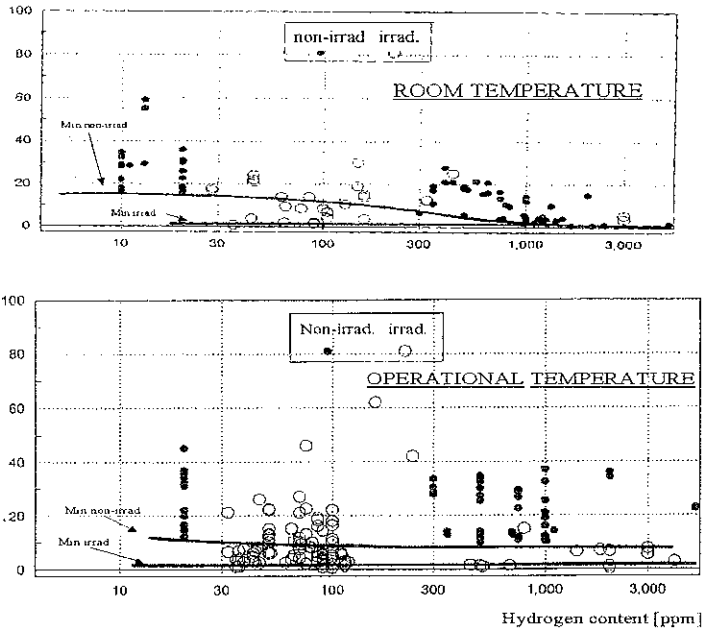


Figure 1. Hydrogen has a temperature dependent impact on ductility /4/.

Oxide layer thickness

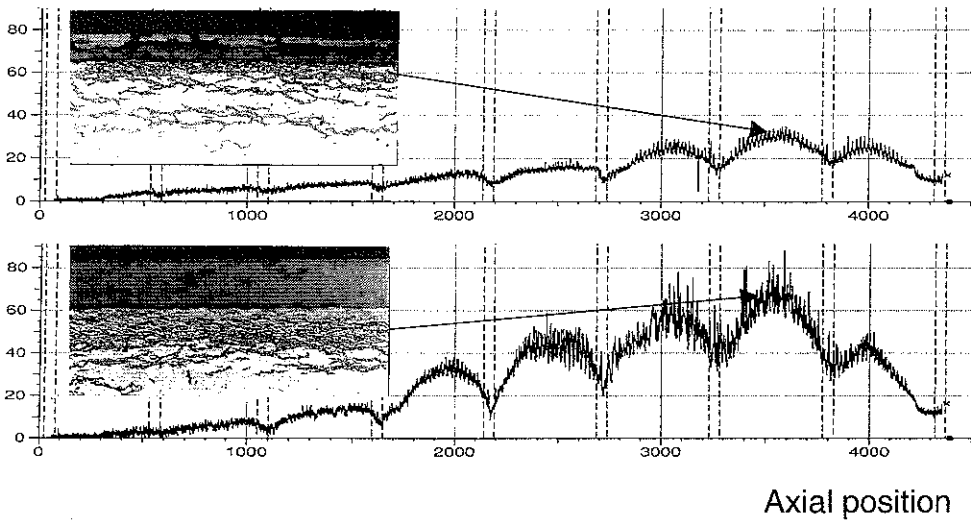


Figure 2. Dense hydride rims: higher corrosion caused by the thicker hydride rim. /5/.

3. Measurement techniques

3.1. Integral determination

3.1.1. Hot extraction

The integral method used at the Institute for Transuranium Elements is hot vacuum extraction (HVE) under a carrier gas where the mean hydrogen concentration in the sample is determined without distinguishing between dissolved hydrogen and hydride.

3.1.1.1. Methodology

The weighed sample is heated to melting in order to release hydrogen from dissolved hydrogen and decomposed hydrides. The hydrogen released is carried under inert gas flow to a thermal conductivity cell where the total amount of hydrogen in the sample is determined by integration. The result divided by the sample weight yields the concentration.

The apparatus, an adapted DINIMAT 401 from Ströhlein, Germany, was used after minor modifications for remote control working conditions. Only the furnace is mounted in a hot cell. The gas and supply unit with the thermal conductivity cell are installed outside the hot cell.

3.1.1.2. Calibration and Standards

The machine is calibrated by injecting a known volume of hydrogen into the gas line (either N₂ or Ar gas flow) leading to the oven. In addition, at the beginning and end of each series of measurements on zirconium alloys, a certified Ti sample (of known hydrogen content) is measured to verify the calibration and the consistency of the measurements during each series. As a supplementary check a number of certified Zr and externally supplied Zry-hydrogen reference samples are available.

3.1.1.3. Analysis principles

After the calibration has been performed and a Ti standard tested, the samples are analysed. The samples, rings of cladding about 2 mm thick, are cut into up to eight pieces (see Fig. 3) and analysed one or two pieces at a time. The results are averaged to give a mean value for the ring.

The sample is weighed in a metallic container and the weight recorded. It is then dropped through a funnel into the preheated crucible in the furnace and the empty container re-weighed. This is recorded and the sample weight calculated.

The hydrogen release is detected as an increase in thermal conductivity of the gas flow by the cell and registered on a pen recorder. The resulting peak height is noted and read-off from the calibration curve as ppm H₂ at NTP. At least three analyses are made on samples from the same cladding ring in order to determine a mean hydrogen concentration.

3.1.1.4. Influence of sample features

Since corrosion is the main source of hydrogen in the metal, a corrosion layer is typically associated with most of the samples to be analysed. Its presence influences the measurement, because the concentration of hydrogen in ZrO₂ is generally different from that found in the metal [6,7]. Knowing the oxide layer thickness and its hydrogen content, the effect of the oxide layer on the measurement can be easily corrected.

Small amounts of UO₂ fuel attached to the cladding add to the total weight, but since the fuel contains little or no hydrogen it will yield an overall estimated hydrogen concentration in the sample slightly below that of the real value. This effect is considered to be negligible.

3.1.1.5. Hydrogen in oxide layers

Since it is the mechanical properties and hydrogen pick-up of the metallic wall that is of interest, it is

desirable to eliminate the hydrogen contained in the oxide layer. This can be done mechanically by removing the oxide layer or thermally by evaporation of the physically absorbed water.

At a first glance, the mechanical method appears to be the most straightforward one, but under hot cell conditions it is difficult to mechanically remove the oxide layer on a tube with an accuracy of a micron without taking away part of the dense hydride rims. Such a stringent demand can be principally eliminated by thermal homogenisation of the hydride rim. However, the dissolution of dense hydride rims may need very high temperatures and the result of this procedure has to be monitored. Therefore, instead of mechanically removing the oxide layer, a thermal method, that evaporates the adsorbed water from the oxide and which also allows the existing HVE technique to be employed, has been tested:

The measurements were performed with irradiated and non-irradiated samples. The non-irradiated samples were hydrogen charged samples with known hydrogen contents of 200 and 800 ppm. These

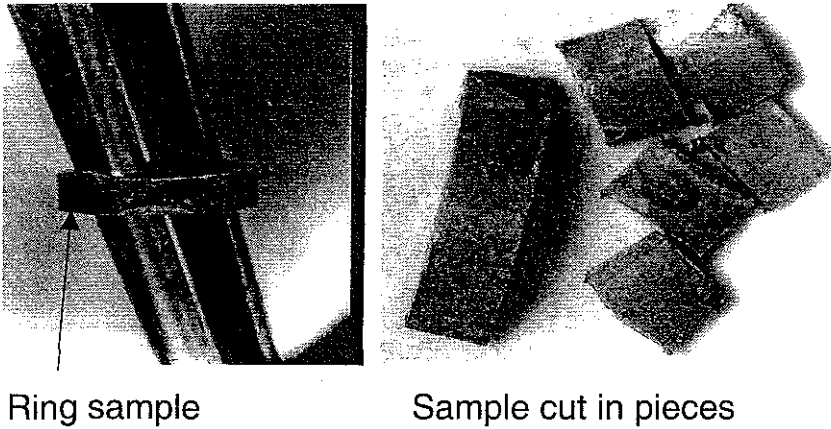


Figure 3. A ring sample (left) is cut in pieces (right) for hot extraction measurements.

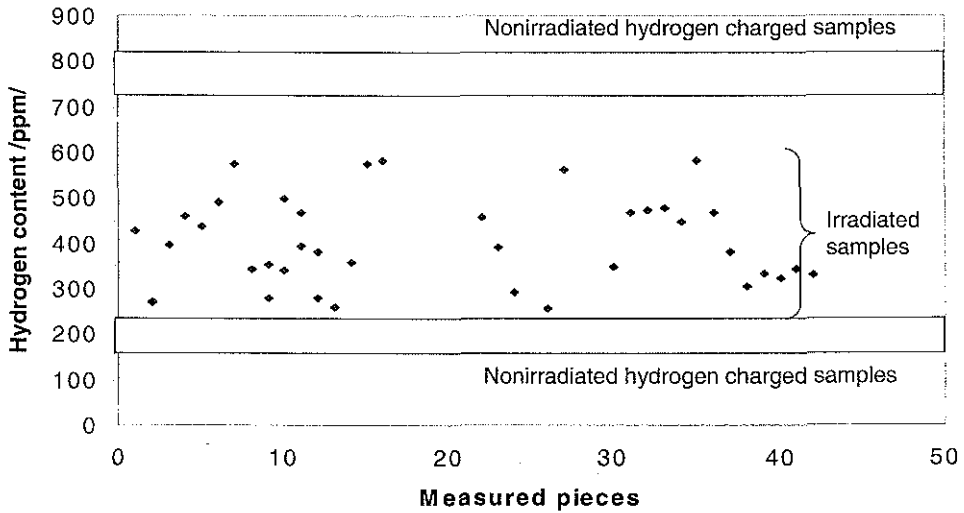


Figure 4. Hydrogen measurements on irradiated and hydrogen charged non-irradiated sample pieces after annealing above 500 °C.

samples were intended to benchmark the hydrogen determination technique and to assure that annealing did not influence the hydrogen content in the metallic phase. The irradiated ring samples were cut from a fuel rod with locally about 40 μm oxide layer thickness.

Figure 4 summarises the result of all HVE measurements on sample pieces that were heat-treated for 6 to 24 h at 510 - 550 $^{\circ}\text{C}$. The results on the non-irradiated pieces reflect the high homogeneity of the original specimen, a good reproducibility of the hydrogen content obtained in the cold laboratory and no indications for an influence of the heat-treatment. The irradiated ring samples (a total of three samples at the same axial location) were cut at the most into eight pieces, but measured in 4-5 batches of 3 or 4 pieces each. The scattering of the hydrogen content is remarkably high and can be attributed to a slightly inhomogeneous temperature distribution around the cladding in combination with the high diffusivity of hydrogen in zirconium alloys. The average value obtained for the three samples was 380 ± 9 ppm.

Three irradiated samples which were cut nearby but not heat-treated were used as reference samples with an average hydrogen content of 416 ± 14 ppm. By comparison of the heated and non-heated samples, the hydrogen content in the oxide was determined to be 36 ± 17 ppm. On the basis of an oxide layer of 40 μm and a metallic wall thickness of 690 μm the hydrogen concentration in the oxide was determined to be about 750 ± 360 ppm. This value lies between the results obtained by /6,7/. However, the statistical error of such small samples is very high due to the inhomogeneity of the hydrogen in the cladding.

3.2. Local determination

3.2.1. Metallography

Metallography is an ideal tool to reveal the distribution of zirconium hydrides in the component. Figure 5 shows typical distributions seen in the cladding of highly irradiated PWR and BWR claddings.

However, the quantitative determination of local hydride content is of limited accuracy, because the chemical etching introduces variations in the thickness of the hydrides. The extent of hydride formation at the cladding rim can be assessed from a measurement of the thickness of the zone exhibiting dense

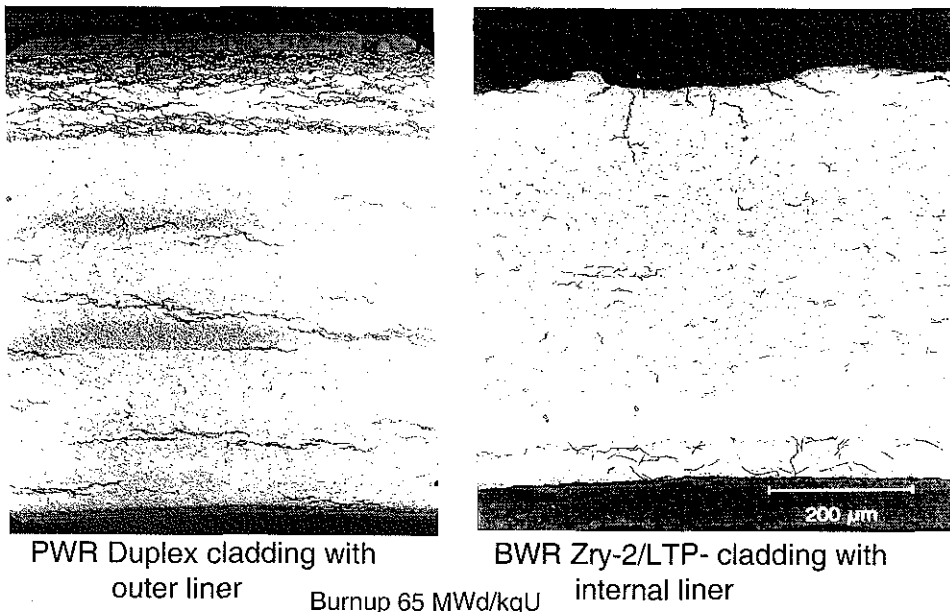


Figure 5. Radial hydride distributions in the cladding of high burnup PWR and BWR fuels.

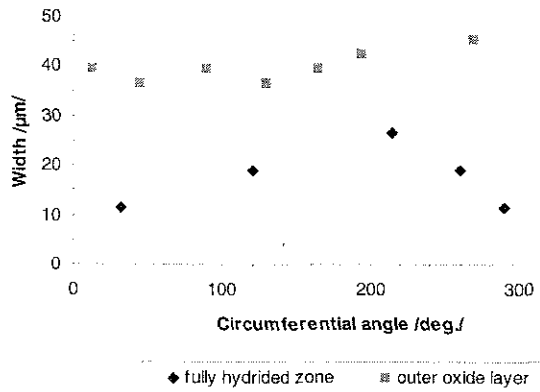


Figure 6. Comparison of oxide layer and hydride dense zone thickness on the cladding periphery.

hydride formation, Fig. 6, but is also sensitive to the etching procedure and therefore difficult for general comparison.

3.2.2. Scanning Electron Microscopy

Scanning electron microscopy (SEM) with backscattered electron imaging (BSEI) allows a microstructural investigation of the amount, location and morphology of the Zr-hydrides to be performed. Because of a density difference there is a visible contrast difference between the hydrides and the matrix, and the platelets are clearly distinguished by BSEI in the cladding cross-section. With image analysis software with feature sizing, the area fraction of hydrides in the area under investigation can be estimated using grey level segmentation. Pores and image artifacts can be excluded from the calculation by their size and shape. The average of a number of area fraction values represents the volume fraction with sufficient accuracy, and knowing the chemical composition of the hydrides the overall hydrogen content of the sample can be calculated and compared with the value determined by HVE.

The procedure for estimating by SEM the area fraction of Zr-hydride platelets in zirconium alloy cladding is as follows:

- 1) Obtain BSE images of the polished cladding cross-section at an appropriate magnification and covering an appropriate surface area.
- 2) Using image analysis software, obtain a grey level histogram on each image. When the BSEI brightness and contrast settings are correctly adjusted, there will be two distinct maxima in the histogram, one for the hydrides and the other for the zirconium alloy matrix.
- 3) Perform grey level segmentation to determine the area fraction of the hydride platelets.

The resulting hydride area fraction values are used to obtain the distribution along the radius or, if sampled along the periphery, to obtain the peripheral distribution.

Averaging several radial distributions per cladding sample should give a satisfactory estimate of the total area fraction. This value can be converted into the integral hydrogen content by the formula (2), proposed by Schrire and Pearce /8/:

$$Wt_H = Wt_\delta \cdot F \left[\frac{\rho_\delta}{\rho_{Zr}(1-F) + \rho_\delta \cdot F} \right] \quad (2)$$

where Wt_H = wt ppm hydrogen, Wt_δ = wt ppm hydrogen in δ -phase hydride (from chemistry), F = measured hydride area fraction, ρ_δ = density of δ -phase hydride (5.65 g/cm³, RT) and ρ_{Zr} = density of α -phase metal (6.54 g/cm³, RT). It is assumed that all the hydrides are present as δ -phase hydrides. Hydrogen in solid

solution can be neglected because at room temperature the solubility is very low (<1 ppm) and the slow in-reactor cooling facilitates hydride precipitation.

SEM parameters that greatly influence the area fraction values are beam energy, beam current and working distance, all these affect directly the brightness and contrast of the image. These parameters have to be optimised for each particular working environment and then kept as constant as possible to obtain comparable results between individual samples. Some of the very small round features in the BSE images, which are excluded from the calculation, may be small hydride precipitates. However, their contribution to the total hydride area appears to be insignificant. One problem not considered so far is the so-called "edge effect", where details with sharp edges in the images, e.g., edges of pore cross-sections, become very bright compared with the surrounding material. The grey level increases from black in the pores to high brightness at the pore edges. In between there is an area where the grey level unavoidably is the same as that of the hydrides. If the hydride density is low and the pore density high, this effect can cause a notable error.

As an example, one SEM image analysis result for the total area fraction of hydrides for a cladding sample is given in Table 1 along with the bulk hydrogen content determined by HVE. Automatic grey level segmentation, a facility provided by the proprietary software of the instrument, was used, and reasonable results were obtained only if there was an area of total blackness in the image, i.e., the oxide layer.

Table 1 Comparison of total hydrogen content as determined by SEM and HVE.

Method	SEM	HVE
Total [H] wt ppm	744	681

Consequently, the SEM method was applied only to the outermost one-third of the cladding cross-section, with eight areas each of about 220 μm square along the rim averaged, giving an area fraction examined of 0.115. For the rest two-thirds of the cladding cross-section, where there were only very few hydrides, light optical microscopy was used with four areas each of about 300 μm square averaged. Assuming that etching quadruples the hydride platelet cross-section, an area fraction 0.01 was obtained for this part. The values given by the two independent methods are in satisfactory agreement.

Figure 7 shows the distribution of the hydrogen content based on the measured area fraction values along the periphery in the sample mentioned above. The area examined covers the outermost third

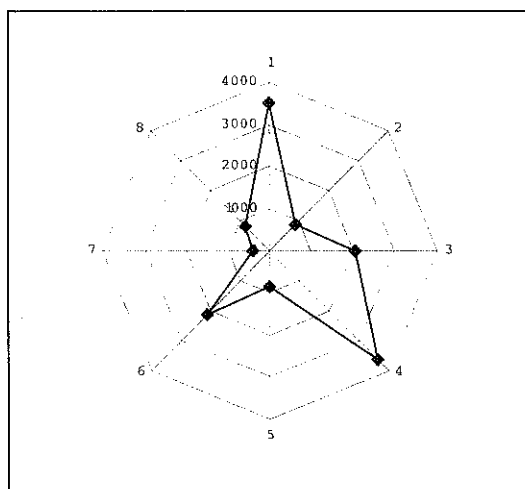


Figure 7. Hydrogen content in wt ppm at eight evenly spaced positions along the rim calculated from the area fraction of hydrides in the outermost third of the cross-section measured by SEM.

of the cross-section and the sampling was done at eight evenly spaced positions along the rim. It is evident that there are very significant variations in the amount of hydrides along the cladding periphery.

Our results show that by applying image analysis methods to SEM backscattered electron micrographs of zirconium alloy cladding cross-sections a satisfactory estimate of the total hydrogen content can be obtained. By sampling along the radius or periphery the corresponding hydride distribution or hydrogen content can be evaluated. Work is in progress to improve the reproducibility and accuracy of the method.

4. Conclusion

Hot vacuum extraction in combination with metallographic examination is a reliable standard tool for a general assessment of the influence of hydrogen on the mechanical and corrosion behaviour of zirconium alloy claddings. Techniques to evaluate the local hydrogen concentration in the oxide and metal are available to further improve this knowledge. One such technique that may be used to determine the radial and circumferential distribution of hydrogen from the local hydride content of the cladding is phase analysis of backscattered electron images obtained in the scanning electron microscope.

5. References

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