Experimental report

10/04/2024

Proposal:	**DIR-271**		**Council:**	10/2022
Title:	Hydrogen diffusion measurement on biphasic Zr alloy			
Research area:	Materials			

This proposal is a new proposal

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Samples: Zr-2.5Nb

Instrument	Requested days	Allocated days	From	To
NEXT	1	1	18/05/2023	19/05/2023

Abstract:

Hydrogen diffusion in Zr alloys is a fundamental process involved in many deleterious phenomena during the service of nuclear components, such as delayed hydride cracking and blistering.

As neutron imaging has proven to be a very suitable technique to quantify hydrogen diffusion in Zr alloys with high spatial resolution, the aim of this proposal is to determine the hydrogen diffusion coefficient in a Zr-2.5Nb alloy with two very different microstructural conditions of ß phase (continuous and discontinuous), in order to elucidate the effect of ß phase continuity on the DHC mechanism. Experiments on off situ heat treated samples and in situ diffusion experiments are proposed to account for detailed temporal variations

Experimental Report DIR 271 - Hydrogen diffusion measurement on biphasic Zr alloy

Introduction:

Delayed Hydride Cracking (DHC) is a degradation mechanism that affects the structural integrity of zirconium-alloy components used in fission nuclear power reactors, particularly in Zr-2.5Nb pressure tubes (PT) of CANDU reactors. DHC is a thermally activated process promoted by hydrogen diffusion under a stress gradient originated by stress-concentrating effect on a crack-tip. Under certain conditions of temperature and hydrogen concentration, a hydride particle can precipitate and grow in front of the crack tip. Then, the hydride fracture occurs when critical conditions are achieved (critical values of stress concentration and hydride dimensions), and the repetition of this process generates the crack propagation. Phenomenological models have been developed to predict the behavior of different alloys in service operation. These models depend of several parameters, being the hydrogen diffusion coefficient the most important and the hardest to determinate by standard techniques.

The microstructure of the as–extruded and cold drawn Zr–2.5Nb PT is biphasic, consisting of elongated deformed α-Zr (hcp) grains with a continuous network of metastable β-Zr (bcc, approximately 20wt%Nb) surrounding the α-Zr grains. Annealing heat treatments produce a decomposition of the metastable β-Zr phase into α-Zr and β-Nb (over 95wt% Nb), and the continuous β-Zr network becomes discontinuous. It is well known that hydrogen terminal solid solubility (TSS) and hydrogen diffusivity differ remarkably between alpha and beta phases, but there is no agreement as regards the effect of the continuity of beta phase on hydrogen diffusion. Then, the development of new and precise measurements is needed to clarify the effect of β-Zr continuity on hydrogen diffusion coefficient in biphasic Zr alloys, parameter that rules the DHC mechanism.

Due to the differences in the neutron attenuation coefficient between Zr and hydrogen, the neutron imaging technique offers a direct method to determine the hydrogen diffusion in Zr alloys components.

Previous results:

Hydrogen diffusion coefficient in Zr alloys was determined in different microstructural conditions by several techniques. Specifically, regarding the effect of β phase continuity on hydrogen diffusion coefficient, some publications showed opposite results [1, 2]. Moreover, there is previous experience at ANTARES Neutron Imaging facility in the determination of in-situ hydrogen diffusion in Zr alloys at high temperatures [3], and also in the capability of measuring very low H contents in Zr alloys with a precision of ~5 wt ppm H and a spatial resolution around 30 μm [4]. Regarding the effect of the hydrogen diffusion coefficient on DHC, we have experimental evidences and some studies with theoretical models that support the hypothesis that the continuity of beta phase plays a key role in hydrogen diffusion [5].

Objective:

Based on the previous work [4], the measurements of H diffusion by neutron imaging are expected to have a high accuracy. The aim of this proposal is to determine the hydrogen diffusion coefficient in a Zr-2.5Nb alloy with two very different microstructural conditions of β phase (continuous and discontinuous), in order to elucidate the effect of β phase continuity on the DHC mechanism. Experiments on off situ heat treated samples and in situ diffusion experiments are proposed to account for detailed temporal variations.

Performed experiment:

Both experiments consist in taking neutron images of Zr-2.5Nb samples (4x6x22)mm^3 having each a hydride layer on one face. The schematic of the experimental setup and dimensions of a typical sample is shown in Fig. 1. For ambient temperature measurements, 7 samples from as-received material (continuous β phase) and 7 of annealed material (discontinuous β phase) were prepared by varying the diffusion temperature of each sample in the typical temperature range of CANDU reactor operation. In addition, for the in situ experiments, two samples were prepared, one from each metallurgical condition. Furthermore, 13 calibration samples with homogeneous hydrogen content were produced.

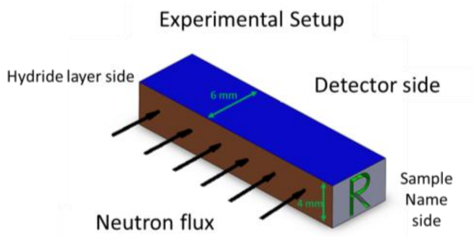

Figure 1. Scheme of experimental setup.

Preliminary results:

Calibration

Of the 13 samples intended for calibration, only 11 were measured. Preliminary results show that the calibration line of attenuation vs hydrogen concentration can be represented with a single fit line for the material in the two metallurgical states. Figure 2 shows the least squares fit to the experimental data. The values obtained from the fitting equation are in accordance with similar calibrations by other authors [4].

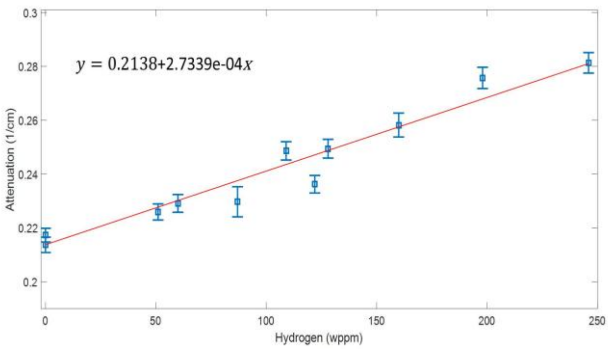

Figure 2. Hydrogen content calibration line.

Diffusion Profiles

A total of 10 samples were measured with previous diffusion thermal treatments at different temperatures and times. In the aged material 4 were measured and in the as received material the remaining 6 were measured. From each diffusion profile obtained from the attenuation as a function of distance, the value of the hydrogen diffusion coefficient for each temperature was calculated. With this information, as shown in Figure 3, in Arrhenius type graphs, the hydrogen diffusion coefficient was calculated for each metallurgical state. It is observed that there is a clear separation between the two states but the values of the material as received are lower than those reported by other authors previously. From the preliminary analysis of the data it is clear that the decomposition of the metastable beta zirconium phase would have an effect on the decrease in the value of the hydrogen diffusion coefficient. It remains to be clarified whether the effect is due only to a morphological change or whether there is also a component of the chemical composition.

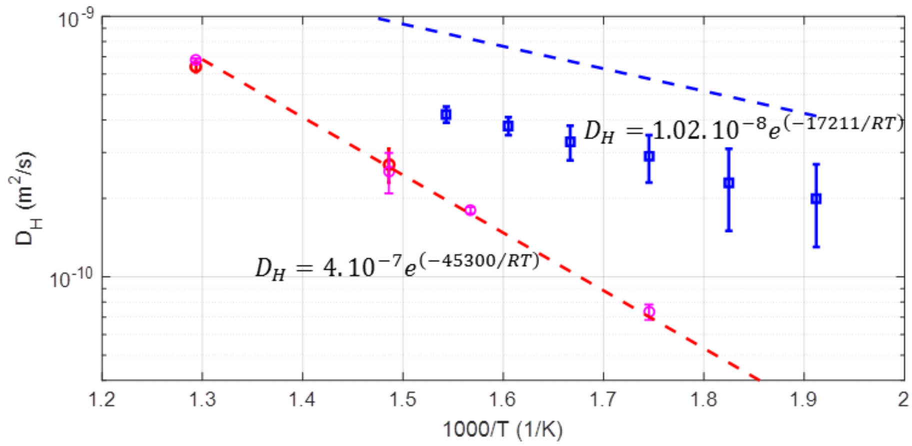

Figure 3. Experimental measurement of the hydrogen diffusion coefficient in a Zr-2.5Nb pressure tube at two different metallurgical conditions. In red is the as-received material and in blue is the aged material. The dotted lines represent previous measurements by other authors for similar metallurgical conditions.

The other part of the experiment consisted of measuring in-situ the hydrogen diffusion coefficient in two samples, one aged and the other as received, inside an oven at a constant temperature of 400ºC for 7 hours. Three images were taken per minute and averaged, giving a total of 450 images throughout the experiment.

After correcting the background of the images by eliminating the attenuation due to surface oxide growth, the profiles shown in Figure 4 are observed for one of the metallurgical states, the other is equivalent. It is observed that the beginning of all the profiles is unique, and this is consistent with the terminal solid solubility of hydrogen must be the same since the temperature does not vary. Finally, the observation of the profiles fits with very good agreement to the theoretical solution of the Fick equation for an infinite layer at all observed times, clearing up the doubts that existed about whether the diffusion mechanism could involve some fast path kinetics.

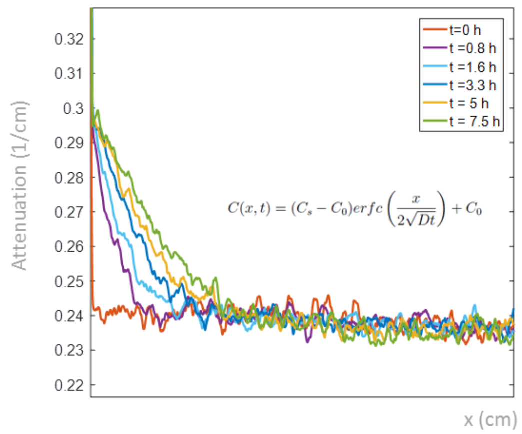

Figure 4. Diffusion profiles measured in-situ at different times.

[1] B.C. Skinner, R. Dutton, "Hydrogen Diffusivity in α-β Zirconium alloys and its role in Delayed Hydride Cracking", Hydrogen Effects on Material Behavior (1990) 73-83.

[2] G.A.Mc Rae,et al., J. Nuclear Materials510 (2018) 337-347.

[3] M. Grosse, et al, Nucl. Instr. Meth A 651 (2011) 253–257.

[4] N. L Buitrago,J. Nuclear Materials 503 (2018) 98-109.