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Diffusion of deuterium in Zr–2.5Nb alloy under neutron irradiation

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ABSTRACT

Pressure tubes of cold-worked Zr–2.5Nb (Zr–2.5 wt% Nb) material are used in the core of CANDU®[1] reactors to contain the fuel bundles and the heavy water (D_2O) heat transport fluid. Deuterium diffusion in unirradiated Zr–2.5Nb pressure tube material has been measured both in and out of neutron flux to determine the magnitude of any irradiation effects. The measurements were carried out at about 530 and 580 K using the U-2 Loop of NRU reactor at the Chalk River Laboratories. The results show that deuterium diffusion in Zr–2.5Nb pressure tube material during irradiation at a fast neutron flux of $\sim 5 \times 10^{17}$ nm^{-2} s^{-1} is not significantly different from that measured in the absence of neutron flux. This supports the use of deuterium diffusivities determined from out-reactor tests for modeling deuterium mobility in unirradiated pressure tubes and other reactor core components made from zirconium alloys.

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1. Introduction

Pressure tubes of cold-worked Zr–2.5Nb (Zr–2.5 wt% Nb) material are used in the core of CANDU®[1] reactors to contain the fuel bundles and the heavy water (D_2O) heat transport fluid. The pressure tubes operate at temperatures ranging from about 520 K at the inlet to about 580 K at the outlet [1]. Over time they absorb deuterium released by the corrosion reaction between the D_2O and the Zr. Predicting deuterium concentrations in a pressure tube over its lifetime requires models that describe both deuterium pickup from corrosion process and its distribution in the tube. To model its distribution correctly, the effects of fast neutron irradiation on the diffusivity of deuterium must be measured and accounted for.

Early studies in Zircaloy-4 [2] and austenitic steel [3] had shown that neutron irradiation can cause a substantial increase in the diffusivity of hydrogen. However, a subsequent study had reported no influence of irradiation on the mobility of tritium in Zircaloy-2 [4]. Due to these conflicting results, the present experiments were designed to measure simultaneously the diffusion coefficient of deuterium in Zr–2.5Nb pressure tube material both in and out of neutron flux to determine the magnitude of any irradiation effects. The measurements were carried out at about 530 and 580 K using the U-2 Loop of NRU reactor at the Chalk River Laboratories. Preliminary results obtained at about 570 K were reported earlier [5]. This paper summarizes all the results.

2. Experimental

Samples, 3 mm wide × 3 mm thick and with lengths of 60, 102 and 124 mm, were machined from the longitudinal direction of a piece of unirradiated Zr–2.5Nb pressure tube. The tube was manufactured from a quadruple-melted ingot, cold-worked 28% and stress relieved at 673 K for 24 h. According to the chemical analysis the hydrogen and oxygen concentration in the tube were 2 and 1100 mg/kg alloy, respectively. The specimens were coated with palladium, using an electroless process [6], at one end and charged with deuterium at 523 K for about 1 week. (Since U-2 is a light water loop, deuterium was chosen instead of hydrogen to avoid any complications arising from possible absorption of hydrogen through the side walls of the specimens during the experiment as a result of exposure to high temperatures.) The palladium layer acted as a window to allow the deuterium to penetrate the sample only through the coated surface. Metallography showed a deuteride layer 200–400 μm thick at the end of these samples with a diffusion layer of about 1 mm. (Calculations show that when the specimens are held for 60 days at 573 K, an initial deuteride layer of 100 μm at one end of them is sufficient to produce a diffusion profile with some remaining deuteride layer at the end of the exposure period.) After the diffusion anneal in the U-2 Loop, metallographic examination showed a remaining deuteride layer of 150–300 μm. This observation confirmed that there was an ample source of deuterium to continuously feed the rest of the specimen during the experiment.

Initially, two specimens (one 124 mm long and one 60 mm long), were placed in-flux and two similar ones out-of-flux in the U-2 Loop (Fig. 1). In the in-flux position the fast neutron flux ($E > 1$ MeV) and the temperature were estimated to be $\sim 5 \times 10^{17}$ nm^{-2} s^{-1} and 573 ± 2 K, respectively. The temperature in the out-of-flux region was estimated to be 579 ± 2 K. In a later exposure, two specimens of 102 mm length (Fig. 2) were placed in an in-flux position with the neutron flux and the temperature estimated at $\sim 4.5 \times 10^{17}$ nm^{-2} s^{-1} and 536 ± 2 K, respectively. In both occasions the exposure period was ~50 days and the integrated dose received by the in-flux specimens was $\sim 2 \times 10^{24}$ nm^{-2}. After the exposure the specimens were sectioned to ~3 mm long segments and analyzed for deuterium distribution by hot vacuum extraction mass spectrometry (HVEMS) [7].

3. Results

Details of data analysis and results of the initial exposure (in-flux at 573 K and out-of flux at 579 K) have been reported earlier [5].

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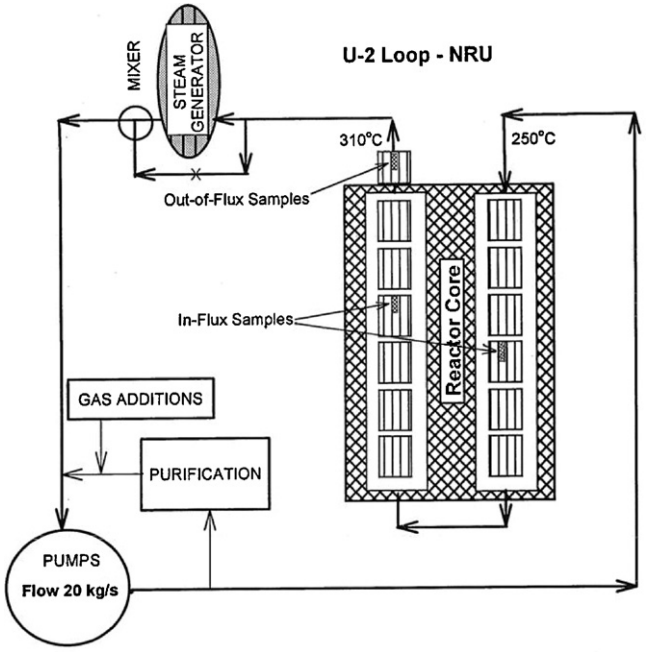

Fig. 1. Schematic diagram of U-2 loop, located at the NRU reactor of the Chalk River Laboratories, showing the in-flux and out-of-flux specimen positions.

The deuterium distribution profile along the length of a 102 mm long specimen exposed in-flux at 536 ± 2 K for 50 days is shown in Fig. 3. The figure shows that these specimens were sufficiently long to be considered as semi-infinite. Therefore the data were analyzed using the following diffusion equation derived for a semi-infinite medium [8].

$$C(x,t) = (C_1 - C_0)erfc\left(\frac{x}{2\sqrt{Dt}}\right) + C_0 \quad (1)$$

In this equation $C(x,t)$ is the concentration at distance x from hydride layer at time t, C_1 is the concentration of dissolved hydrogen in equilibrium with the hydride layer at the anneal temperature and D is the diffusion coefficient. Results of the analyses for the two 102 mm samples annealed at an in-flux position at 536 ± 2 K are given in Table 1.

Based on the average diffusion coefficients obtained at 536 K (Table 1) and at 573 K [5] the following diffusion equation for deuterium in Zr–2.5Nb pressure tube material in fast neutron flux is derived:

$$D_D = 9.65 \times 10^{-9} \exp\left(\frac{-2.27 \times 10^4}{RT}\right) \quad (2)$$

where D_D is in $m^2\,s^{-1}$, T is in K and R is 8.314 J mol^{-1} K^{-1}. This equation may be used to derive diffusion coefficients within the temperature range of 520–580 K. To extrapolate beyond this temperature range may result in erroneous diffusion coefficients.

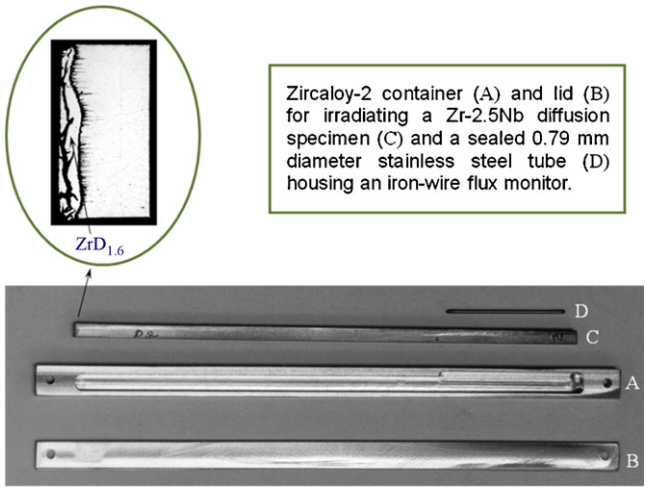

Fig. 2. A photograph showing the specimen housing (A and B), specimen (C) and a neutron flux monitor (D). The inset shows the deuteride ($ZrD_{1.6}$) layer at the end of the specimen.

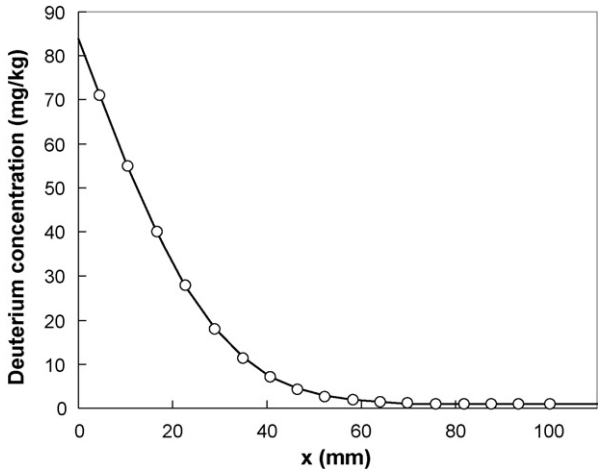

Fig. 3. Deuterium concentration profile along the length of a 102 mm long specimen after 1212 h at 536 K and under a fast neutron flux of ~4.5×10^{17} nm^{-2} s^{-1}. The open circles represent the data points and the solid curve is obtained as a result of a least squares fit to Eq. (1).

Table 1
Diffusion coefficient (D_D) for deuterium in unirradiated Zr–2.5Nb pressure tube material measured at 536 ± 2 K under a neutron flux of ~4.5×10^{17} nm^{-2} s^{-1}.

Sample	No. 1	No. 2	Average
D_D ($m^2\,s^{-1}$)	6.04×10^{-11}	5.80×10^{-11}	5.92×10^{-11}

4. Discussion

The diffusion coefficients measured in- and out-of-flux at 579 K are entered in Table 2 along with the values calculated from data of Léger [9], Sawatzky et al. [10] and Skinner and Dutton [11] obtained in the absence of irradiation. Note that, for ease of comparison, all the diffusion coefficients in the table are given for hydrogen (converted from the present measurements for deuterium and the measurements of Skinner and Dutton for tritium)

Table 2
Comparison of in-flux and out-of-flux diffusion coefficients for deuterium in Zr–2.5Nb CANDU® pressure tube material obtained at 579 K.

	Diffusion coefficient D_D ($m^2\,s^{-1}$)	Source
Out-of-flux	1.09×10^{-10}	Sawatzky et al. [10]
	1.41×10^{-10}	Léger [9]
	7.69×10^{-11} to 5.96×10^{-10} [a]	Skinner and Dutton [11]
	1.25×10^{-10} [b]	Khatamian et al. [5]
In-flux	1.30×10^{-10} [b]	Eq. (2)

[a] Note that, Zr–2.5Nb is an alloy with two phases, α and β. The β-phase is metastable and the diffusion rate of hydrogen in this alloy depends on the level of the β-phase decomposition [10,11]. Skinner and Dutton measured the diffusion rate in pressure tube specimens with a range of β-phase decomposition by a tritium tracer technique and then obtained the diffusion rate for hydrogen by multiplying the measured value by the square root of 3 (the tritium to hydrogen mass ratio).

[b] This value is obtained by multiplying the measured D_D value by the square root of 2 (the deuterium to hydrogen mass ratio).

in Zr–2.5Nb pressure tube material. The table shows that the previously measured values, in the absence of any irradiation, at 579 K range from 7.69×10^{-11} to 5.96×10^{-10} and that the present values, whether measured in-flux or out-of-flux, are within these ranges. The results of the present work in Table 2 also show that at 579 K the difference between the diffusion coefficients measured in- and out-of-flux is less than 4%. This indicates that a fast neutron flux of $\sim 5 \times 10^{17}$ nm^{-2} s^{-1}, up to an accumulated fluence of $\sim 2 \times 10^{24}$ nm^{-2}, does not have any significant effect on the diffusivity of deuterium in Zr–2.5Nb pressure tube material.

As stated in the introduction, Frisius et al. [2] have examined the influence of fast neutron irradiation on the diffusion of hydrogen in Zircaloy-4. They used diffusion couples made of two square sheets (about 2 mm thick) welded together, one sheet being pre-charged with hydrogen. The specimens were then diffusion annealed under a fast neutron flux of $\sim 1.2 \times 10^{17}$ nm^{-2} s^{-1}. Before and after the diffusion anneal, the hydrogen concentration profile along the length of the specimens were determined using neutron scattering. The data were analyzed using a one-dimensional diffusion model. (Note that the diffusion couples were made of two square sheets and far from being one-dimensional.) The results obtained from two similar specimens showed about 25% difference and they attributed this difference to a possible variation in the crystallographic texture of the two specimens. They compared these results with those of Kearns [12] and their own [13] earlier measurements of the diffusion coefficients for Zircaloy-4 without irradiation. This comparison showed an enhancement of about a factor of two, which they attributed to the fast neutron irradiation.

Dobrozemsky et al. [3] have measured permeation of hydrogen through a 500 mm long stainless steel tube (25 mm O.D. and 1 mm wall thickness) imbedded in a reactor core to investigate the irradiation effects on the diffusivity of hydrogen in stainless steel. The measurements were done under different irradiation fluxes achieved by varying the reactor power from 0 to 7.5 MW. A monotonous increase in the permeation of hydrogen with increase in the irradiation dose rate was observed. The maximum enhancement in the permeation was a factor of three at the fast neutron flux of 1.0×10^{17} nm^{-2} s^{-1} achieved at 7.5 MW. Even though no diffusion coefficients are reported in the paper, both permeation and diffusion coefficients were suggested to be enhanced. In view of the fact that permeation is the product of the diffusivity and the hydrogen solubility, it is not clear how the diffusion coefficients were calculated without the knowledge of the irradiation effects on the solubility of hydrogen in austenitic steel. It is also possible that the terms "permeation" and "diffusion" are used interchangeably in their paper. They estimate the variation in the specimen temperature during the permeation experiment to be <10 K, while they indicate that an error in the temperature of about 100 K is needed to cause a three-fold increase in the permeation. It is possible that the temperature variation along such a long specimen was more than the estimated value of 10 K and, partly, the reason for the large variation in permeation.

In contrast, Kunz et al. [4] have shown that, within their experimental errors, the irradiation damage induced by a neutron fluence of $\sim 10^{18}$ nm^{-2} does not affect the diffusion rate of tritium in Zircaloy-2. They implanted a 5-mm wide region of the specimens (50 mm × 10 mm × 0.25 mm size) with tritium generated by irradiating a copper disk with 100 MeV α-particles. The α-beam was focused in such a way that one half of the specimen was irradiated by the neutrons produced during the tritium generation process. The diffusion rates in two halves of the specimen were compared after diffusion anneals at a given temperature. They also examined the effects of irradiation hardening on the diffusivity of tritium in Zircaloy-2 by irradiating the specimens with 1–5 MeV protons to a total dose of 1.3×10^{20} pm^{-2}. Again, the tritium diffusion coefficients obtained for these specimens with an increased level of irradiation dose were similar to the ones obtained for unirradiated material. One should note that the specimens used by Kunz et al. [4] were annealed after being irradiated, whereas the specimens mentioned in the above works [2,3] and the ones in the present tests were diffusion annealed during the exposure to irradiation.

The results of the present measurements are in accord with the findings of Kunz et al. [4], but do not agree with irradiation enhancement of hydrogen diffusion in Zircaloy-4 and in austenitic steel reported by Frisius et al. [2] and Dobrozemsky et al. [3], respectively. The data presented here are for Zr–2.5Nb, a two-phase alloy. One may reason that the different effects observed are due to the type of materials used in the test. However, Kunz et al. [4] have used Zircaloy-2, a single-phase alloy similar to Zircaloy-4. Then again, as stated above, the measurements carried out by Kunz et al. only show the effect of integrated flux (fluence) after the irradiation, whereas the other studies include the flux effects. Further measurements with pre-irradiated specimens are needed to investigate this point.

Almost all of the work reported on the effects of irradiation on diffusion [14] deal with the self-diffusion or tracer-diffusion of heavier atoms than hydrogen. The understanding is that the enhancement in diffusion results from irradiation-induced increase in vacancies and unoccupied interstitials and not by collisions. As it has also been discussed previously [5], this idea may only apply for the cases where majority of the lattice sites (metals and alloys) or the interstitial sites (oxides and hydrides) are occupied and a small increase in the number of vacant sites would increase the diffusion rate. In the case of Zr–2.5Nb pressure tubes the diffusion of hydrogen mainly takes place via the interstitial sites in the alloy. At low hydrogen concentration limits, applicable to the alloy conditions in the nuclear industry ([H] ≤ 1 at.%) and the samples used in the present and above mentioned tests, more than 99% of the interstitial sites are vacant and are readily available for hydrogen to use in the diffusion process. As a result, irradiation could not increase the available interstitial sites by more than 1%, and therefore, it is reasonable that in the present study the effects of irradiation on the enhancement of diffusivity of hydrogen in Zr–2.5Nb were not discernible.

5. Summary

Effects of fast neutron irradiation on the diffusivity of deuterium in unirradiated Zr–2.5Nb pressure tube material was examined by simultaneously exposing specimens at 573 and 579 K at in- and out-of-flux locations in the U-2 Loop of the NRU reactor at the Chalk River Laboratories. In a separate test a second set of specimens were exposed at 533 K at an in-flux location of the loop. The duration of each test was ~50 days. The results show that a fast neutron flux of about 5×10^{17} nm^{-2} s^{-1}, up to an accumulated fluence of $\sim 2 \times 10^{24}$ nm^{-2}, does not have any significant effect on the diffusivity of deuterium in unirradiated Zr–2.5Nb pressure tube material.

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