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Journal of Alloys and Compounds 293–295 (1999) 324–328

Journal of
ALLOYS
AND COMPOUNDS

Influence of neutron irradiation on H diffusion in Zr–2.5Nb alloy

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Abstract

Deuterium diffusion in Zr–2.5Nb pressure tube material was measured in- and out-of-flux in the U-2 Loop of the NRU reactor at Chalk River Laboratories. The results show that deuterium diffusivity at a neutron flux of about $5 \cdot 10^{17} \text{ n.m}^{-2} \text{ s}^{-1}$ is similar to that measured out-of-flux. This result suggests that deuterium diffusivities determined from out-reactor tests are sufficient for modeling deuterium ingress and its redistribution in pressure tubes and other reactor components made from zirconium alloys. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Zirconium; Deuterium; Diffusion; Irradiation; CANDU

1. Introduction

In CANDU^{®1} nuclear power reactors, pressure tubes of cold-worked Zr–2.5Nb (Zr–2.5 wt% Nb) material are used in the reactor core to contain the fuel bundles and the heavy water (D₂O) coolant. 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 D₂O and the Zr. If the total hydrogen isotope concentration in the tubes exceeds the terminal solid solubility the tubes can become susceptible to a crack initiation and propagation process called delayed hydride cracking. Predicting deuterium concentrations in pressure tubes over their lifetimes requires models that describe both deuterium ingress and its distribution in the tube. To model its distribution correctly, the effect of fast neutron flux on the diffusivity of deuterium must be accounted for.

Diffusion coefficients are normally obtained by annealing specimens made of two zones with different hydrogen concentrations and subsequently measuring the hydrogen concentration along its length. Such measurements have been carried out in α -Zr, the Zircalloys and Zr–2.5Nb in a number of out of reactor experiments (i.e. in the absence of any irradiation) [2–6]. There have been limited measurements carried out in Zircaloy-4 [7], austenitic steel [8] and Zircaloy-2 [9] under neutron irradiation. In two of

these references, a substantial enhancement in the diffusivity of hydrogen in Zircaloy-4 and austenitic stainless steel due to neutron irradiation was reported [7,8]. However, in the third reference, no influence of irradiation on the mobility of tritium in Zircaloy-2 was reported. Based on these results, it was thought that neutron irradiation may have some effects on the diffusion of hydrogen in Zr–2.5Nb material. Therefore, the present experiments were designed to measure simultaneously the diffusion coefficient of deuterium in Zr–2.5Nb alloy both with and without neutron irradiation to determine the magnitude of any irradiation effects.

2. Experimental

Samples, 3×3×124 and 3×3×60 mm, were machined from the longitudinal direction of a piece of Zr–2.5Nb pressure tube # RX095. 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⁻¹ respectively.

The specimens were coated with palladium at one end and charged with deuterium at 523 K for about one week. (Deuterium was chosen instead of hydrogen to avoid any problem arising from possible absorption of hydrogen during the experiment.) 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 to 400 μm thick at the end of these

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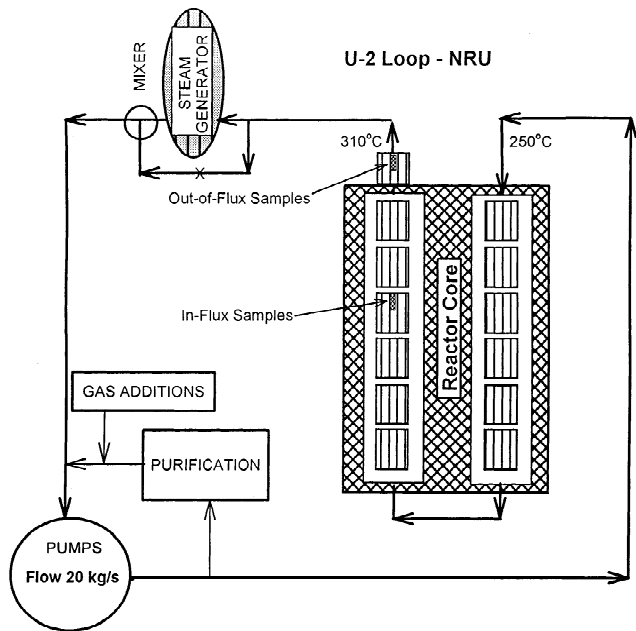


Fig. 1. Schematic diagram of U-2 Loop (NRU reactor) at the Chalk River Laboratories showing the in-flux and out-of-flux specimen positions.

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 metallographic examination showed a remaining deuteride layer of 150 to 300 μm . This observation confirmed that there was an ample source of deuterium to continuously feed the rest of the specimen during the experiment.

Two of the specimens (one 124 mm long and one 60 mm long), were placed in-flux and two similar ones were placed out-of-flux in the U-2 Loop (Fig. 1) of the NRU reactor at the Chalk River Laboratories. During the exposure the average fast neutron flux at the in-flux region was about $5 \cdot 10^{17} \text{ n.m}^{-2} \text{ s}^{-1}$ ($E > 1 \text{ MeV}$). The exposure period was 1146 h (48.8 days) during which the in-flux and the out-of-flux regions were at 573 ± 2 and 579 ± 2 K respectively. The integrated dose received by the in-flux specimens was $2 \cdot 10^{24} \text{ n.m}^{-2}$. After the exposure the specimens were sectioned to about 3 mm long segments and analyzed for deuterium distribution by hot vacuum extraction mass spectrometry [10].

3. Analysis of results

A long specimen with a thin hydride layer at one end, acting as a source of hydrogen during the diffusional anneal, can be modeled as a one dimensional semi-infinite medium which initially is at a uniform concentration C_0 and its surface is constantly maintained at a concentration

C_1 . Solving the diffusion equation with these boundary conditions results in the following simple solution [11]:

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

where $C(x,t)$ is the concentration at distance x from hydride layer at time t and D is the diffusion coefficient. Note that C_1 is the concentration of dissolved hydrogen in equilibrium with the hydride layer at the anneal temperature.

For a short specimen, where the assumption of a semi-infinite medium is not valid, the following equation, which is the solution of the diffusion equation for a finite medium [11], must be used:

$$C(x,t) = C_1 - \frac{4(C_1 - C_0)}{\pi} \sum \frac{(-1)^n}{2n+1} \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{4l^2}\right) \cos\left(\frac{(2n+1)\pi(l-x)}{2l}\right) \quad (2)$$

where l is the length of the specimen.

4. Results

The deuterium distribution profile along the length of a 124 mm long specimen is shown in Fig. 2. The figure shows that these specimens were sufficiently long to be considered as semi-infinite and, therefore, the data were analyzed using Eq. (1).

Fig. 3 shows the deuterium distribution profile from a 60 mm long specimen. The figure shows that in this case the anneal period is more than sufficient for the deuterium to

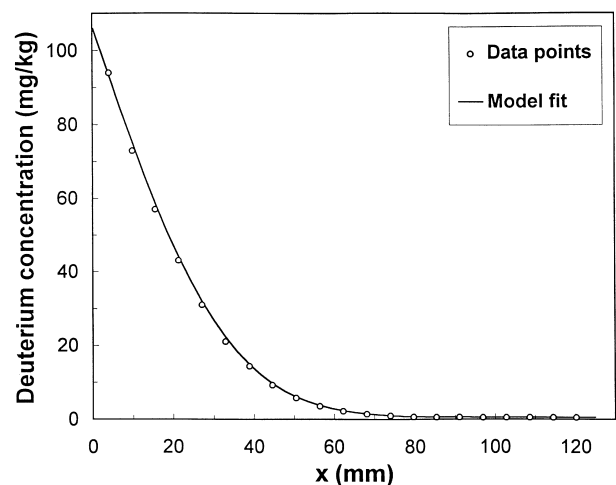


Fig. 2. Deuterium concentration profile along the length of a 124 mm long specimen (semi-infinite) after 1146 h at 573 K and under a fast neutron flux of about $5 \cdot 10^{17} \text{ n.m}^{-2} \text{ s}^{-1}$. The open circles represent the data points and the solid curve is obtained as a result of a least squares fit to Eq. (1).

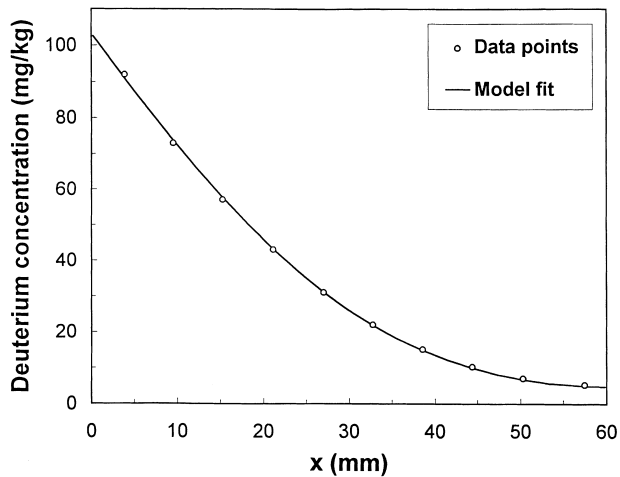


Fig. 3. Deuterium concentration profile along the length of a 60 mm long specimen (finite) after 1146 h at 573 K and under a fast neutron flux of about $5 \cdot 10^{17} \text{ n.m}^{-2} \text{ s}^{-1}$. The open circles represent the data points and the solid curve is obtained as a result of a least squares fit to Eq. (2).

Table 1
Results of the least squares fit to the diffusion data

Specimen	Diffusion coefficient D in $\text{m}^2 \text{ s}^{-1}$		
	Out-of-flux at $579 \pm 2 \text{ K}$	Out-of-flux at $573 \pm 2 \text{ K}^a$	In-flux at $573 \pm 2 \text{ K}$
124 mm long	$9.16 \cdot 10^{-11}$	$8.38 \cdot 10^{-11}$	$8.19 \cdot 10^{-11}$
60 mm long	$8.57 \cdot 10^{-11}$	$7.84 \cdot 10^{-11}$	$8.16 \cdot 10^{-11}$
Average	$8.86 \cdot 10^{-11}$	$8.11 \cdot 10^{-11}$	$8.17 \cdot 10^{-11}$

^a Normalized to 573 K using the activation energy given in Ref. [3].

diffuse through the entire length of the specimen. These specimens were treated as finite-length and Eq. (2) was used in analyzing the data. Depending on the specimen type the data were fit by least squares to either Eq. (1) or Eq. (2) with varying D , C_1 and C_0 . The resulting diffusion coefficients for both specimen types are given in Table 1.

The diffusion coefficients obtained from the 124 mm (semi-infinite) and the 60 mm (finite-length) specimens agree very well and show that both models are consistent. Since the temperatures of the in-flux and the out-of-flux regions are different, the out-of-flux diffusion coefficients are normalized to 573 K, using the activation energy given in Ref. [3], and presented in the table for comparison.

Table 2
Diffusion coefficient (D_{H}) for H in unirradiated Zr–2.5Nb pressure tube material measured at 573 K

Reference	This work ^a	Léger [3]	Sawatzky et al. [4]	Skinner and Dutton [5] ^b
D_{H} ($\text{m}^2 \text{ s}^{-1}$)	$1.15 \cdot 10^{-10}$	$1.29 \cdot 10^{-10}$	$1.01 \cdot 10^{-10}$	$8.1 \cdot 10^{-11}$ to $1.6 \cdot 10^{-10}$

^a This value is obtained by multiplying the value in Table 1 by the square root of 2 (the deuterium to hydrogen mass ratio).

^b Skinner and Dutton measured the diffusion rate of tritium by a 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).

5. Discussion

The diffusion coefficient measured in the out-of-flux region is compared in Table 2 with the values reported in the literature for Zr–2.5Nb pressure tube material. The table shows that the previously measured values range from $8.1 \cdot 10^{-11}$ to $1.6 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and that the present value is within this range. Skinner and Dutton [5] have shown that this observed range is due to the varied state of the β -Zr phase in the material. They demonstrated that the presence of the β -Zr phase in Zr–2.5Nb enhances hydrogen mobility in this material compared with α -Zr phase (pure Zr) and that the level of enhancement decreases as the β -Zr phase decomposes due to prolonged heat-treatment at moderate temperatures. Our specimens were stress relieved at 673 K for 24 h prior to diffusion measurements. Such a heat-treatment is common in the final stage of the CANDU pressure tube fabrication process and is possible that the specimens used by Sawatzky et al. [4] and Léger [3] were subjected to a similar heat-treatment (no heat-treatment information is provided in these two papers).

The last row in Table 1 shows that at 573 K the difference between the deuterium diffusion coefficients measured in in- and out-of-flux positions is less than 2%. This indicates that a fast neutron flux of about $5 \cdot 10^{17} \text{ n.m}^{-2} \text{ s}^{-1}$, up to an accumulated fluence of about $2 \cdot 10^{24} \text{ n.m}^{-2}$, does not have any observable effect on the diffusivity of deuterium in Zr–2.5Nb pressure tube material. In the following paragraphs, these results are compared with three other measurements reported in the literature.

Frisius et al. [7] have examined the influence of fast neutron irradiation on the diffusion of hydrogen in Zircaloy-4. They used diffusion couples made of two sheets ($30 \times 30 \times 2 \text{ mm}$) welded together, one sheet being precharged with hydrogen. The specimens were then annealed at 673 K for 336 h under a fast neutron flux of $\sim 1.2 \cdot 10^{17} \text{ n.m}^{-2} \text{ s}^{-1}$ (fluence of $1.5 \cdot 10^{23} \text{ n.m}^{-2}$). Before and after the diffusion anneal, the hydrogen concentration profiles 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 far from being one-dimensional specimens.) There was about 25% difference between the diffusion constants obtained for the two similar specimens they examined 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

[2] and their own [5] earlier measurements of the diffusion coefficients for Zircaloy without irradiation. This comparison showed a factor of about two enhancement due to the fast neutron irradiation.

Dobrozemsky et al. [8] have used permeation of hydrogen through a 500 mm long tube (25 mm O.D. and 1 mm wall thickness) imbedded in a reactor core to study the effects of irradiation on the diffusivity of hydrogen in stainless steel 4301. The measurements were carried out at 840 K and under different irradiation fluxes achieved by varying the reactor power from 0 to 7.5 MW. At all reactor powers other than 7.5 MW, the temperature of the long specimen was maintained by additional ohmic heating. The fast neutron flux at 7.5 MW was $1.0 \cdot 10^{17} \text{ n.m}^{-2} \text{ s}^{-1}$. 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. Although no diffusion coefficients are reported in the paper, the permeation- as well as the diffusion-coefficients were suggested to be enhanced. Since 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. There is also the possibility that they use the terms “permeation” and “diffusion” interchangeably. By varying the temperature, under no irradiation, they show that an error in the temperature of about 100 K is needed to cause such an increase in the permeation. The variation in the specimen temperature during the permeation experiment was estimated to be less than 10 K. However, the temperature variation along the specimen may have been more than the estimated value of 10 K.

Unlike the measurements by Frisius et al. [7] and Dobrozemsky et al. [8], Kunz et al. [9] have shown that, within their experimental errors, the irradiation damage induced by a neutron fluence of about $\sim 10^{18} \text{ n.m}^{-2}$ does not affect the diffusion rate of tritium in Zircaloy-2. Their specimens ($50 \times 10 \times 0.25 \text{ mm}$ size) were prepared by implanting a well defined region of the specimen (about 5 mm wide) with tritium generated by irradiating a copper disk with 100 MeV α -particles. In some of their experiments, 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 both 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 by irradiating the specimens with 1–5 MeV protons to a total dose of $1.3 \cdot 10^{20} \text{ p.m}^{-2}$. 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 in Refs. [7,8] were diffusion annealed during the exposure to irradiation whereas in Ref. [9] they were annealed after being irradiated.

The present measurements disagree with irradiation

enhancement of hydrogen diffusion observed in Zircaloy-4 by Frisius et al. [7] and in austenitic steel by Dobrozemsky et al. [8]. Since the present work used Zr–2.5Nb, a two phase alloy, one may argue that the different effects observed are due to the type of materials used in the test. On the other hand, Kunz et al. [9] have used Zircaloy-2, an alloy similar to Zircaloy-4, and in agreement with the present results have seen no effects of irradiation in hydrogen diffusion. However, as stated above, the measurements carried out by Kunz et al. only show the effect of fluence whereas the other studies include the flux effects. Further measurements with preirradiated specimens are underway to investigate this point. More tests are being performed at other temperatures to improve confidence and the applicability of the results.

A great deal of work has been reported on the effects of irradiation on diffusion [12–14], however, almost all of them 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 interstitial and vacancies and not by collisions. 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, however, the diffusion of hydrogen mainly takes place via the interstitial sites in the α -Zr phase. In this phase the maximum hydrogen concentration at 573 K is about 0.7 at.% (the hydrogen solubility limit). This low number of atoms in solution means that more than 99% of the interstitial sites are normally vacant and are readily available for hydrogen to jump to and that irradiation may enhance the process by not more than 1%. Therefore, it is understandable that in the present study no irradiation enhancement of diffusion was observed.

6. Conclusions

Deuterium diffusion in Zr–2.5Nb pressure tube material was examined at about 573 K by simultaneously exposing specimens at in- and out-of-flux locations in the U-2 Loop of the NRU reactor at the Chalk River Laboratories. During the 48 days exposure the average fast neutron flux was about $5 \cdot 10^{17} \text{ n.m}^{-2} \text{ s}^{-1}$. The results show that deuterium diffusivity under fast neutron irradiation is similar to that measured in the absence of irradiation.

Acknowledgements

The authors would like to thank V.C. Ling, G.A. Ledoux, R.C. Stothers, T.G. Lamarche and A.D. Lepage for technical assistance, B.C. Skinner for helpful discussions and C.E. Coleman for many useful comments on the

paper. This work was funded by AECL CANDU R and D Program 5.

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