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A novel technique to remove deuterium from CANDU pressure tubes

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Abstract

Deuterium ingress into the pressure tubes of a Canada deuterium uranium (CANDU) nuclear reactor can cause the pressure tubes to crack prematurely. A novel technique, based on the rapid diffusion of deuterium in zirconium alloys, and subsequent preferential segregation of deuterium at the surface, has been developed to remove dissolved deuterium. This technique involves a simple continuous plasma treatment of the surface of a pressure tube, and can remove as much as 70% of the dissolved deuterium from the entire wall thickness of a pressure tube in realistic time scales. The proposed technique has considerable economic incentive: it may extend the life of pressure tubes without channel replacement. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Canada deuterium uranium (CANDU) nuclear reactors are fuelled by natural uranium and moderated by heavy water (D_2O). Pressure tubes in a CANDU reactor contain fuel bundles as well as the D_2O coolant, working at about 300 °C and 9.6 MPa. The pressure tubes are made of Zr–2.5% Nb alloy due to the low neutron absorption cross-section and the high corrosion resistance at elevated temperatures of zirconium alloys [1]. During reactor service, D_2O may dissociate, resulting in deuterium (D) ingress into the pressure tubes. If D-ingress exceeds the terminal solid solubility (TSS), hydrides (deuterides) can precipitate which are brittle and which can lead to delayed hydride cracking (DHC) under stress. This D-ingress problem can thus result in failures, and it has become a major contributor to limiting the in-service life of operating pressure tubes.

Before operation, the pressure tube is generally filmed by a passive oxide layer which serves as a barrier to deuterium uptake. However, despite these protective barrier films, deuterium still permeates into, and accumulates in, the underlying alloy. The concentration of deuterium is, in fact, reaching the point at which pressure tubes in a number of CANDU reactors need replacing, a very costly process.

It is therefore desirable to develop new techniques which can rehabilitate pressure tubes in situ by removal of the dissolved deuterium from the material. It is estimated that removal of 20% deuterium from a pressure tube with deuterium content close to the TSS value could extend the lifetime by several years [2]. This deuterium removal technique should be able to remove a sufficient amount of deuterium from a local region or from the entire tube in reasonable times; it must preserve the microstructures of pressure tube material, and not introduce any chemicals that might lead to enhanced corrosion in the heat transport system. In addition it should utilise simple techniques and be based upon a solid scientific understanding of the processes involved, so it can be reliably modelled.

In the following, we describe a novel technique which can remove as much as 70% of the dissolved deuterium from a pressure tube in a day. This technique is based on our previous studies and the understanding of the segregation and diffusion of deuterium in zirconium alloys, and it involves a plasma treatment of the surface of a

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pressure tube at temperatures at which no deleterious microstructural changes occur.

1.1. Basis of removal method

Once deuterium has entered a pressure tube, it is difficult to remove. One obvious way is to heat the pressure tube under a vacuum and pump the deuterium away. Unfortunately, it turns out that this method works best only at pressures and temperatures which are not feasible for an in situ removal process in a CANDU reactor. The partial pressure P (Pa) of deuterium in equilibrium with a Zr alloy containing C_D (atomic fraction) of deuterium at the temperature T (K) is given by [3] [1]

$$P = 2.1 \times 10^{10} C_D^2 \exp(-12962/T). \tag{1}$$

UHV conditions ($<2.7 \times 10^{-6}$ Pa) are required, if the targeted concentration of deuterium is 20 ppmw at 300 °C. Raising the temperature (>600 °C) would help, but microstructural changes will occur and thus this is not an acceptable process that could be used in-reactor.

There are, however, two properties of Zr and its alloys that provide a route for removal at 300 °C. First, diffusion of deuterium in zirconium alloys is a fast process. The diffusion coefficient D_D (cm^2/s) is given by [4,5],

$$D_D = 1.55 \times 10^{-3} \exp(-4217/T). \tag{2}$$

At 300 °C for instance, deuterium atoms would move on average 1.2 mm in an hour (given approximately by $2(D_D t)^{1/2}$).

Second, deuterium is known to have a very strong tendency to segregate at the surfaces of zirconium and relevant alloys [6,7]. For example, the equilibrium concentration of deuterium on the surface θ_s can be four orders of magnitude higher than the bulk concentration θ_b, at 300 °C. This arises from the approximate equation

$$\theta_s = \theta_b \exp(\Delta E_s/RT), \tag{3}$$

where ΔE_s, the heat of segregation is defined as the enthalpy difference (negative) between the segregated D-atoms and those in the bulk; it is estimated to be 43.5 kJ/mol [7].

Our method is then based upon these two important properties of Zr and its alloys: fast diffusion and strong segregation of D. First the deuterium has to diffuse to the surface where it will segregate, thus greatly enhancing its local concentration. The segregated D must then be efficiently removed at a rate at least equal to the segregation rate, which is limited by bulk diffusion. This is achieved by sputtering. The requirement for a simple process indicates that a plasma is suitable. A second requirement is that the sputtering conditions do not erode the Zr–alloy to any great extent. The maximum energy (1000 V) chosen took this into account; the sputter coefficient for Zr is small compared to that for D using Ar as the plasma gas. As the segregated D atoms are sputtered away by the plasma, more deuterium atoms migrate from the bulk and refill the now-vacant surface traps. Continuation of this process will eventually deplete the entire sample of deuterium.

2. Experimental

2.1. Methods for measuring D

High vacuum extraction mass spectroscopy (HVEMS) is a qualified method for determination of the bulk deuterium concentrations in alloys [8]. The sample is degassed in a calibrated volume at an elevated temperature. Under ultrahigh vacuum (UHV) conditions, the entire pressure increase can be attributed to the release of dissolved gases which are analysed by a mass spectroscopy. However, since HVEMS is inherently a destructive technique, it is unsuitable for monitoring the changes of deuterium concentration during a process designed to remove deuterium nondestructively.

Nuclear reaction analysis (NRA) is generally a nondestructive ion beam technique used to determine the elemental composition, and in some cases the depth profiles, of light elements in bulk materials from the first few hundred Angstroms up to a few micrometres depth in the sample [9]. A conventional NRA experiment using low energy, e.g., 0.63 MeV incident ^{3}He$^+$ beams and a detector with a thin depletion depth (~0.1 mm) measures only the total proton yield within <1 μm of the sample surface. Since deuterium is known to concentrate at free surfaces and defects that may occur near surfaces because of sample preparation such as cutting and polishing [10], the conventional method may yield deuterium concentration values unrepresentatively higher than the true bulk value.

In order to determine the bulk deuterium concentration quantitatively by NRA, the 'energy spectrum' method (NRA-ESM) was introduced. Details of the method were described in [10]. Briefly, 2 MeV ^{3}He$^+$ ions bombard the sample under analysis, and the energy spectrum of the emitted protons from the reaction D(^{3}He, p)^{4}He is measured by a silicon charged particle detector with a depletion depth of 2 mm which is larger than the projected range of the energetic protons in silicon (~1.3 mm). The spectrum is further compared with a simulated spectrum which assumes a uniform deute-

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[1] These values have been obtained for hydrogen, but the isotopic differences are not large [4].

rium distribution. The simulation takes into account the kinematic broadening arising from the finite detector size, as well as the energy loss and energy loss straggling, and requires a knowledge of the stopping power and the cross-section of the reaction. This analysis provides not only the averaged deuterium composition but also the depth profile up to a few micrometres depth in the sample.

2.2. Plasma etching

A plasma is a partially (of the order of 10^{-5}) ionized gas containing ions, electrons, radicals, excited molecules, and neutral molecular species [11]. Plasmas occurs in nature. In practical applications, such as dry etching, surface modification, and deposition of thin films, the plasma is typically produced by application of an electric field to a gas maintained at low pressures (0.1–133 Pa) in a chamber. The plasma etching proceeds by two mechanisms: physical bombardment of a sample surface by energetic positive ions, and chemical reaction by the radicals in the plasma with the atoms at or near the sample surface. If an inert gas is used, removal of the surface material is primarily by physical sputtering.

The plasma apparatus is shown schematically in Fig. 1. It consists of a counter electrode positioned about 50 mm from the sample (which itself forms the other electrode), a stainless steel sample holder which is surrounded by a heater made of Nichrome wires, and pumping and gas inlet systems. Argon was chosen as the etchant gas. The pressure of the system was maintained at 13.3 Pa with the Ar flow rate at 40 sccm (cc per minute at standard conditions). The plasma can be sustained by either dc or ac supplies. We used 1000 V dc to maintain the plasma discharge as well as to provide a negative bias voltage on the sample. However, RF and microwave sources can also be used. Only the front surface of the sample was exposed to the plasma, the other sides being protected by a close fitting holder. The sample temperature was measured by a K-type thermocouple spot directly welded to the reverse side of the sample. The sample heating power was effectively provided by both the actual heater and the power absorbed from the plasma.

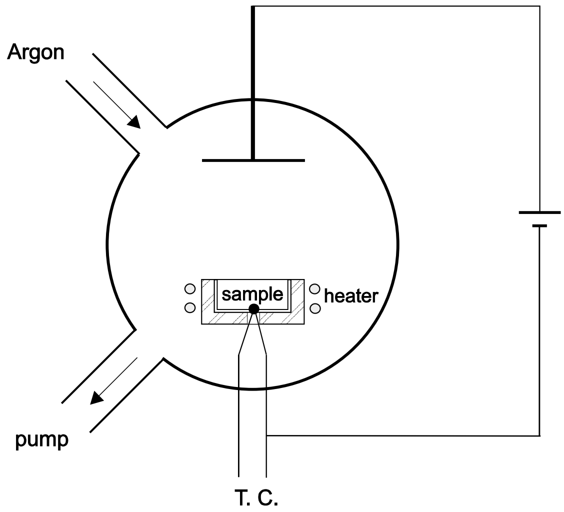

Fig. 1. Schematic of plasma treatment unit.

2.3. Sample treatment and analysis

Samples were off-cuts of CANDU pressure tubes (Zr–2.5% Nb alloy). These samples were subjected to a flow of 1% D_2O in ultrahigh purity (UHP) Ar at a flow rate of 10 sccm for 4 d, followed by thermal annealing in UHP Ar for 16 d, all at 300 °C. The average concentration of deuterium is ~100 ppmw (parts per million by weight) in the loaded material. The samples were then cut into pieces each of the size $4.6 \times 4.2 \times 9.8$ mm^3 by a low speed diamond saw using water as a coolant.

An as-received sample was first analysed by NRA-ESM, and the result was used as the starting reference. The deuterium content of each sample was measured again after each plasma treatment to determine the fraction of deuterium removed. During plasma treatments, five out of the six surfaces of the sample were protected by the walls of the sample holder, leaving only one surface (the front) to be exposed to the plasma. The NRA-ESM analyses were only carried out on the surfaces of two sides of the sample which were never exposed to the plasma. Two spots were measured on each side, each of 1.5×1.5 mm^2. In order to obtain the concentration value characteristic of the bulk, all calculations were averaged (integrated) over a 1.4–3.9 μm depth from the surface, which was known to be deeper than the region of surface-enhanced D concentration. The final results of NRA-ESM were further confirmed by HVEMS analyses on specified samples.

3. Results and discussion

The deuterium depth distribution obtained by NRA-ESM for a typical Zr–2.5% Nb alloy loaded with ~100 ppmw D, is shown in Fig. 2. The error bar includes the statistical error in the yield together with estimates arising from uncertainties in the cross-section, detector angle, etc., as well as the contribution that comes from the heterogeneity of deuterium in the sample as represented by the standard deviation of the spots analysed. It is apparent that a strong near-surface enhancement of deuterium exists up to a depth of ~1.3 μm. Beyond the

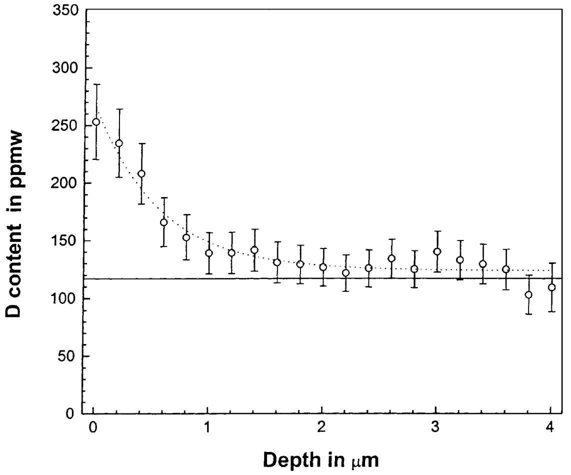

Fig. 2. Depth profile of deuterium ((○) extracted from NRA-ESM, (———) analysed by HVEMS).

surface-enhanced region, the distribution becomes constant and is in good absolute agreement with the average bulk D concentration obtained by HVEMS (117 ppmw, shown as the horizontal solid line).

Fig. 3 shows the fraction of deuterium remaining after 24 h etching by the plasma at various temperatures. Up to the highest temperature investigated (i.e., 350 °C), the higher the temperature, the faster the rate of removal of dissolved D. At 350 °C, the highest temperature at which the pressure tube can be maintained without deleterious microstructural changes, the treatment removed about 70% of deuterium from the sample in a day. We estimate that the maximum erosion depth of the alloy itself during this period, to be on the order of a micrometre.

3.1. Simple model of D removal

As described above, the removal of deuterium from pressure tubes by plasma treatment depends on the bulk diffusion of deuterium in the material, segregation of the deuterium to the surface, plasma sputtering of the segregated D, and thermal desorption of deuterium from the surface (although this is very small at all of our reported temperatures). The following simple model considers bulk diffusion only, and would therefore provide an *upper bound* to the removal rate of the technique, because the removal must be eventually limited by long range diffusion. We assume that the rate is not limited by sputtering.

The plasma etching experiment was performed under conditions which guaranteed that only one face of the sample could be sputtered by the plasma. Since loss of D from the surfaces of the sample which are protected by the walls of the sample holder is negligible, we consider a planar sample, one end of which is isolated and the other is kept at zero concentration for all times by the plasma treatment. By solving the diffusion equations, the removal rate $r(t)$, defined as the fraction of deuterium removed after time t, is obtained as (Appendix A)

$$r(t) = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-\frac{(2n+1)^2\pi^2 D_{\mathrm{D}} t}{4l^2}\right], \tag{4}$$

where l is the thickness of the sample ($l = 4.2$ mm in our example).

Fig. 4 shows both the experimental removal rates and the calculations at various temperatures as a func-

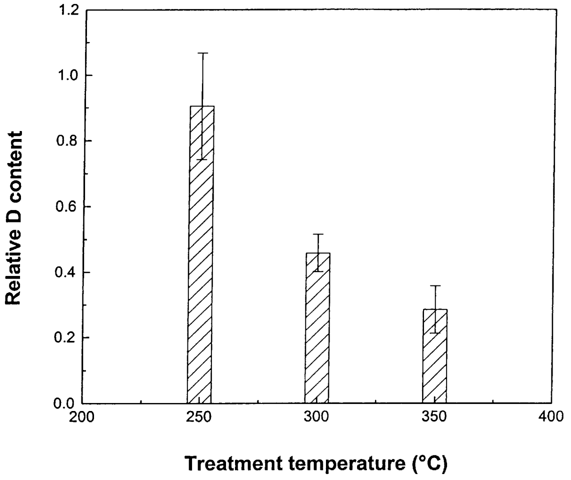

Fig. 3. Relative D content after 24 h treatment at various temperatures.

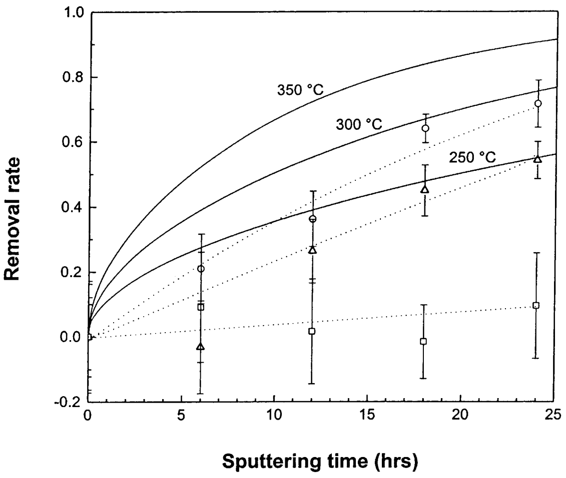

Fig. 4. D-removal rate at various temperatures (theoretical: (———) Eq. (4); experimental: (□) 250 °C, (△) 300 °C, (○) 350 °C, the dotted lines are for guiding the eye only).

tion of the sputtering time. The solid lines represent calculations from Eq. (4). All experimental curves lie below the limit of the theory. A much slower rate was observed for the lowest temperature (250 °C) than the theoretical prediction. This is probably due to the low solubility of deuterium at 250 °C (∼35 ppmw, [12]). At that temperature, most of the deuterium in the sample exists in the form of deuterides which must dissolve before the deuterium atoms can diffuse. This will slow down the whole process of the removal, resulting in much slower removal rate than the prediction of the diffusion model which assumes that all deuterium is in solution.

3.2. Hydrogen ingress

Our early results showed removal of deuterium from the sample by plasma treatment, but indicated that hydrogen (H, protium) ingress into the sample occurred at the same time. Such H-pickup during plasma treatment comes from the hydrogen content in the plasma, which arises from dissociation of H_2O. Water vapour exists because of the poor vacuum conditions of our original setup which was pumped by a mechanical pump (base pressure ∼ 13.3 Pa).

H-pickup can be controlled by more effective pumping using a molecular drag pump. A molecular drag pump can operate at pumping speed of 10–20 L/s at a gas pressure of 13.3 Pa; i.e., at about 100 times higher pressure than other clean pumps such as a conventional turbo molecular pump. This reduces the impurities in the plasma, and as a result, H-ingress during treatment is also much reduced. Table 1 shows the concentrations of hydrogen before and after plasma treatment in the apparatus which was pumped either by a mechanical or a molecular drag pump.

It is clear that the molecular drag pump effectively reduces the H-pickup, as expected. We emphasize that it is not necessary to have excellent vacuum in any practical implementation of this process. All that is necessary is to establish a flow of Ar free from components that might release hydrogen into the plasma. Water is the most important contaminant. In-reactor one can envisage a recirculating system with stages to dry the Ar and remove molecular D_2 and H_2, before reinjecting the Ar into the plasma.

Table 1
H content analysed by HVEMS

H content (ppmw)	Mechanical pump	Molecular drag pump
Before treatment	3.6	5.3
After treatment	118.0	12.7

4. Conclusions

The present D-removal technique, which is feasible for implementation in a reactor, has a considerable economic incentive: it may extend the life of pressure tubes without channel replacement. Based on the rapid diffusion and preferential segregation of deuterium in zirconium alloys, this technique involves a plasma treatment of the surfaces of the pressure tubes at temperatures which preserve their microstructure. It can remove deuterium from the entire wall thickness of pressure tubes at realistic rates: as much as 70% deuterium was removed in a day. The H-pickup during plasma treatments comes from the hydrogen content in the plasma, and can be controlled by improvement of the purity of the Ar in the plasma, for example by more rapid pumping using a molecular drag pump. A recirculating Ar pumping system with continual drying and H_2 and D_2 removal could be used for practical engineering developments.

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Appendix A

We consider a planar sample of which one end is isolated and the other keeps at zero concentration for all times. The diffusion equation and initial and boundary conditions are written as

$$\begin{aligned}
&\frac{\partial}{\partial t}C(x,t) = D\frac{\partial^2}{\partial x^2}C(x,t),\\
&C = C_0, \quad (0 < x < l, t = 0),\\
&\frac{\partial C}{\partial x} = 0, \quad (x = 0, t \geqslant 0),\\
&C = 0, \quad (x = l, t \geqslant 0),
\end{aligned} \tag{A.1}$$

where C_0 is the initial concentration, l is the thickness of the sample, and D is the diffusion coefficient. The solution of the Eq. (A.1) has the form of

$$C(x,t) = \frac{4C_0}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}\exp\left[-\frac{(2n+1)^2\pi^2 Dt}{4l^2}\right]\cos\frac{(2n+1)\pi x}{2l}. \tag{A.2}$$

The removal rate $r(t)$, defined as the fraction of deuterium removed after time t, then is obtained by integrating Eq. (A.2),

$$r(t) = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{(2n+1)^2 \pi^2 D t}{4 l^2} \right]. \tag{A.3}$$

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