

Hydrogen Absorption Behavior of Zr-2.5Nb Pressure Tubes in Wolsong Unit 1

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Abstract

The deuterium uptake behavior of Zr-2.5Nb pressure tubes in Wolsong Unit 1 was analyzed in terms of longitudinal location, operation time, and coolant temperature. The results were compared with those obtained from Canadian CANDU reactors. The amount of deuterium uptake was higher at the outlet part than at the inlet part and was also higher when subjected to a longer operation time and a higher coolant temperature. The hydrogen uptake of Zr-2.5Nb in a hydrogen gas atmosphere was dependent on the microstructure of the alloy. The aged Zr-2.5Nb consisting of α -Zr and β -Nb phases showed higher hydrogen uptake than that consisting of α -Zr and β -Zr phases. The hydrogen in the alloy decreased the rate of oxidation. This could be explained in terms of the cathodic controlled reaction of Zr-2.5Nb oxidation.

1. Introduction

The Zr-2.5wt%Nb (hereafter referred to Zr-2.5Nb) alloy has been used [1] as pressure tube material for the CANDU reactors, including the Wolsong Units 1 and 2, and for the RBMK reactors of the USSR. Even though the Zr-2.5Nb pressure tube was designed to operate for 30 years, they have been often replaced due to several life-limiting problems. Three pressure tubes in Wolsong Unit 1 had been retubed in 1994 after 10 effective full power years (EFPY) of operation according to a inspection program [2].

The hydrogen and deuterium uptakes and the concomitant hydride formation are most crucial in controlling the mechanical properties and failure behavior of Zr-2.5Nb pressure tubes. The average

hydrogen and deuterium contents in the pressure tube increases significantly above the as-fabricated level as the service life increases in the reactor. Therefore, periodic measurement of the hydrogen and deuterium concentration is required to ensure that the maximum safe value is not exceeded in the CANDU Zr-2.5Nb pressure tube. The equivalent concentrations of hydrogen and deuterium (H_{eq}) have been determined as a significant measure of the CANDU pressure tube fitness for service [3]. However, although the RBMK Zr-2.5Nb pressure tubes have been used at higher coolant temperatures than the CANDU Zr-2.5Nb pressure tubes, there is no clear evidence for any degradation from the hydrogen uptake [4]. Thus, it is important to understand the deuterium uptake behavior of the pressure tubes on the basis

of the operation conditions and the microstructure of the tubes.

In the present work, firstly, the deuterium uptake data of Wolsong Unit 1 pressure tubes obtained from periodic inspections have been analyzed in terms of operation factors and also were compared with those of Canadian reactors. Secondly, the hydrogen uptake behavior of the Zr-2.5Nb alloy in a gas environment and the effect of hydrogen uptake on its oxidation behavior have been investigated. It is the purpose of this paper to analyze the deuterium uptake data obtained from Wolsong Unit 1 and to discuss the data with respect to the current understanding for Zr-2.5Nb corrosion and hydrogen uptake behavior.

2. Deuterium Uptake Behavior of Wolsong Unit 1 Pressure Tubes

The hydrogen and deuterium contents of the Zr-2.5Nb pressure tubes in Wolsong Unit 1 increased continuously during reactor operation of about 14 EFPY for several reasons [2,5]. During operation times, the concentration of H_{eq} has been checked to see whether it exceeds the solubility limit of pressure tubes to prevent tube failure due to DHC (Delayed Hydride Cracking). Thus, all CANDU reactors, including Wolsong Unit 1, were recommended to evaluate the deuterium concentration in their pressure tubes periodically. If there is any possibility of contact between the pressure tube and calandria tube, the operation of the reactor will be permitted after proving that a hydride blister will not form until the next evaluation [6]. Analyses of the hydrogen concentration of the pressure tube off-cuts in 1990, the hydrogen and deuterium analyses of pressure tubes by scrape sampling and integrity analysis of pressure tubes in 1992, and the hydrogen and deuterium analyses of removed pressure tubes in 1994 were carried out for

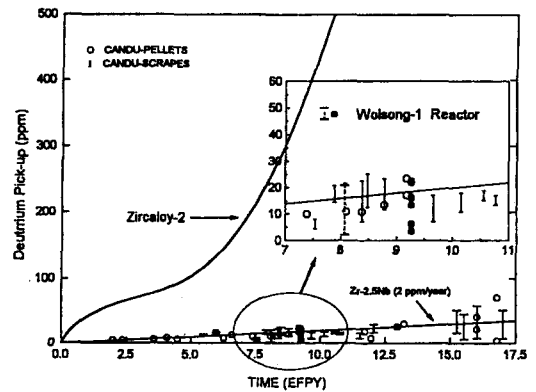


Fig. 1. Deuterium Concentration in Zircaloy-2 and Zr-2.5Nb Pressure Tubes

Wolsong Unit 1 as an inspection program [2,5].

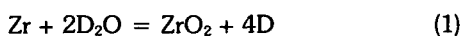
In this work, the deuterium uptake data obtained from Wolsong Unit 1 were analyzed with respect to the distance from the pressure tube inlet, coolant temperature, and operation time. The data were also compared with that of Canadian CANDU reactors.

Fig. 1 shows the deuterium pick-up measured in Wolsong Unit 1, compared to those obtained in Canadian CANDU pressure tubes [3,7]. The deuterium uptake in the pressure tubes is plotted as a function of operation time. Zr-2.5Nb pressure tubes exhibit much lower rates of deuterium ingress compared to Zircaloy-2 pressure tubes operating under similar conditions in the earlier CANDU reactors. In contrast to the catastrophic increase of deuterium uptake rate of Zircaloy-2 pressure tubes, the Zr-2.5Nb pressure tubes show much lower rates of deuterium uptake up to 17 EFPY operation time. Based on the database, the deuterium uptake model of 2ppm D/year was introduced to analyze the deuterium uptake amount of pressure tubes during reactor operations [3]. The figure also shows that the results from deuterium analyses of scrap samples are consistent with those from pellets taken from the full wall thickness of removed pressure tubes.

Therefore, the results from scrap sampling can be used in the analyses of pressure tube integrity.

The results obtained from Wolsong Unit 1 show good agreement with the proposed deuterium uptake model for Zr-2.5Nb pressure tubes. Even though the deuterium uptake behavior of Zr-2.5Nb pressure tubes seems to be within the general deuterium uptake model, there is a slight scattering phenomenon of deuterium uptake that increases as the reactor operation time increases. The scattering was relatively small in the initial operation time of less than 12.5 EFPY, but increased gradually as the operation time increased. The most severe scattering was reported in Pickering Unit 3, resulting in the retubing of that tube [7].

Zirconium alloys are normally protected against hydrogen (including deuterium) ingress by the surface oxide film, which presents a good barrier both to ingress, and to the egress of hydrogen already in the metal. However, this oxide film offers little protection under straining conditions at a notch, and zirconium alloys are susceptible to rapid cracking in hydrogen [8]. There are three different processes by which hydrogen isotopes can enter a Zr-2.5Nb pressure tube. The first is by diffusion in the zirconium alloy via a direct metallurgical contact with another metal. The other two ingress routes operate through the surface of oxide film; the absorption of environmental hydrogen gas and hydrogen uptake during corrosion. Among the three processes, the hydrogen uptake that occurs as part of the normal oxidation process in the high temperature coolant is usually regarded as the main cause of the hydrogen ingress into the tubes. The zirconium alloys are susceptible to significant corrosion during high temperature reactor service :



The deuterium produced by reaction (1) may be either released as deuterium gas molecules or absorbed in the oxide and metal matrix. The feature that the oxidation rate of the Zr-2.5Nb pressure tubes was close to be linear with no acceleration in the rate and the feature that the Zircaloy-2 pressure tubes showed clear evidence for an acceleration in the oxidation rate [7] are very similar to the deuterium uptake behavior, as shown in Fig. 1, indicating that the deuterium uptake into the pressure tube is mainly attributed to corrosion of the pressure tube in the coolant.

However, the data obtained from Wolsong Unit 1 indicate the ingress of hydrogen, as well as deuterium. The source of hydrogen is still unclear. Generally, deuterium uptake has been much less than 20% of theoretical values for Zr-2.5Nb pressure tubes [7]. But a much higher deuterium uptake up to 70% of theoretical value in Pickering Unit 3 and up to 100% in the Zircaloy-2 tubes from Pickering Units 1 and 2 was reported. The theoretical value is the amount of hydrogen produced due to zirconium oxidation stoichiometrically calculated by reaction (1). The deuterium uptake behavior during the corrosion has also been reported to be dependent on the microstructure of the alloy [9]. Thus, it is suspected that some other sources of deuterium could exist. More systematic researches are required to quantify the contributions from each source.

Figs. 2 and 3 show the deuterium concentration versus the distance from the pressure tube inlet for Zr-2.5Nb pressure tubes removed from Pickering Units 3 and 4, Bruce Units 1 and 2, and Wolsong Unit 1, respectively. The range of deuterium concentrations for Zircaloy-2 pressure tubes removed from the high flux channels of Pickering Units 1 and 2 is also shown in Fig. 2. All Zr-2.5Nb tubes showed an increase in deuterium concentration from the inlet end to the outlet end.

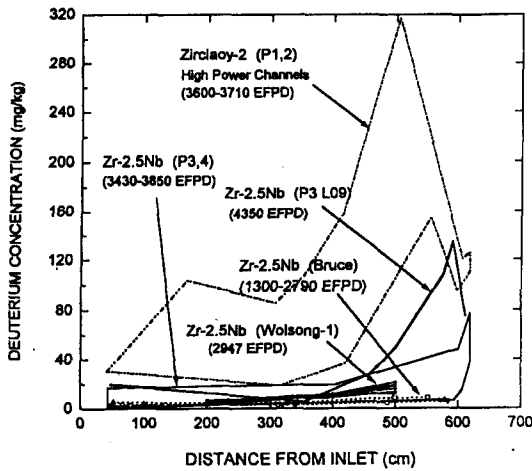


Fig. 2. Deuterium Concentration in Zircaloy-2 and Zr-2.5Nb Pressure Tubes from Pickering, Bruce and Wolsong-1 NGSs

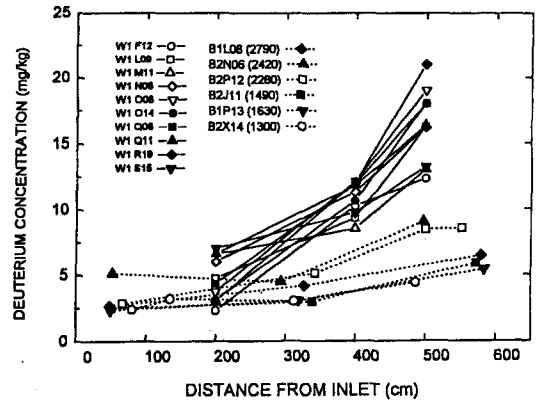


Fig. 3. Deuterium Concentration Along Zr-2.5Nb Pressure Tubes from Bruce(1300-2790 EFPD) and Wolsong-1 (2947EFPD) NGSs

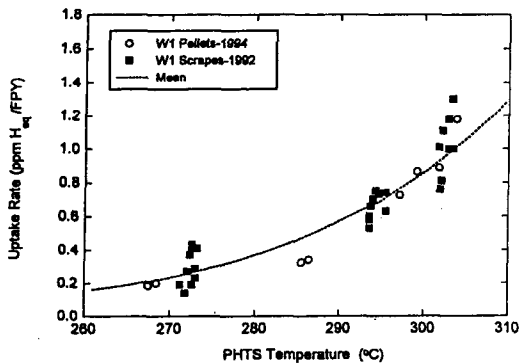


Fig. 4. Equivalent Hydrogen Uptake Rate Related to Temperature of Zr-2.5Nb Pressure Tubes from Wolsong-1

Only one removed Zr-2.5Nb pressure tube (P3L09) shows a deuterium concentration profile with a peak near the outlet end. The trend becomes more clear as the operation time increased, as shown in Fig. 3. The pressure tubes in Wolsong Unit 1 showed a steeper increase of deuterium concentration from the inlet to the outlet end than Bruce Units 1 and 2 having lower operation time. Therefore, it is concluded that the deuterium uptake of a pressure tube increases from the outlet end to the inlet end and the effect

becomes more clear as operation time increases.

Fig. 4 shows the equivalent hydrogen (H_{eq}) uptake rate versus the temperature of pressure tubes for pressure tubes removed from Wolsong Unit 1. The hydrogen uptake rate increased with the temperature of the pressure tubes. This explains that the higher hydrogen uptake at the outlet end of a pressure tube, shown in Figs. 2 and 3, is due to the higher temperature of the outlet region. It is conceivable that the higher temperature caused the higher corrosion rate of the pressure tube with coolant and thereby resulting in the higher amount of hydrogen uptake. It is also substantiated by the fact that the oxide thickness of the outlet end is thicker than that of the inlet end [7]. The higher deuterium concentration of pressure tubes in Wolsong Unit 1 compared to that of Bruce reactors at a similar operation time can also be explained by this temperature effect. The maximum coolant temperature of Bruce Unit 1 is 308°C, which is lower than the 312°C temperature of Wolsong Unit 1. According to the mean curve in Fig. 4, the hydrogen uptake rate at 308°C is 1.20 H_{eq} /FPY, whereas the hydrogen uptake rate at

Table 1. Design Data of CANDU Nuclear Reactors.

	NPD	Douglas Point		Pickering 1 and 2		Kanupp	Pickering 3 and 4		Bruce 1-4		Pickering 5-8		Bruce 5-8		600(1) MW		Darlington		Cernavoda		
		25	200	540	540		125	540	750	750	540	540	540	750	750	600	600	850	850	1-4	1-5
Power Output, MW	25	200	540	540	125	540	750	750	540	540	540	750	750	600	600	850	850	600	600		
Number of Channels	132	306	390	390	208	390	480	480	390	390	390	480	480	390	390	480	480	380	380		
Annulus Gas	Air	Air	N ₂	N ₂	CO ₂	N ₂	CO ₂	CO ₂	N ₂	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂
Annulus Spacer Material	Ix750	ZrNbCu	ZrNbCu	ZrNbCu	Ix750	ZrNbCu	ZrNbCu	ZrNbCu	ZrNbCu	ZrNbCu	ZrNbCu	ZrNbCu	ZrNbCu	ZrNbCu	ZrNbCu	Ix750	Ix750	Ix750	Ix750	Ix750	Ix750
Number of Spacers	1	2	2	2	2	2	2 (1,2) 4 (3,4)	2	2	2	2	4	4	4	4	4	4	4	4	4	4
Coolant Pressure MPa	7.6	9.65	9.65	9.6	10.9	9.6	10.2	10.2	9.6	9.6	9.6	10.3	10.3	11.1	11.1	11.1	11.1	11.1	11.1	11.1	11.1
Coolant Temperature K (maximum)	548	572	570	570	572	570	581	581	570	570	570	581	581	585	585	586	586	585	585	585	585
Pressure Tube Material (2)	A	A	A	C	B	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Wall Thickness mm	4.2	3.9	5.0	4.1	4.0	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2
Internal Diameter mm	82.5	82.5	103	103	82.5	103	103	103	103	103	103	103	103	103	103	103	103	103	103	103	103
First Power from Reactor	1962	1967	1971	1971	1971	1971	1977/79	1977/79	1982/85	1982/85	1982/85	1984/87	1984/87	1982	1982	1989/92	1989/92	1992	1992	1992	1992

(1) Gentilly-II, Point Lepreau, Embalse, Wolsong.

(2) A is Zircaloy-2, B is heat treated Zr-2.5 wt% Nb, C is cold worked Zr-2.5 wt% Nb.

312°C is 1.41 H_{eq}/FPY. Thus, the hydrogen uptake value of 0.44~1.13 H_{eq} (ppm)/yr that was used in the integrity analysis for Wolsong Unit 1 pressure tubes in 1992 seems not to be conservative. The higher hydrogen uptake rate in the higher coolant temperature shows the limit of present Zr-2.5Nb pressure tubes. The increased outlet temperature is one of modern trends in nuclear power development, as shown in Table 1. The higher coolant temperature causes a higher hydrogen uptake, resulting in the increase of susceptibility to DHC.

Up to now, the pressure tubes in Wolsong Unit 1 have shown stable behavior. However, considering their 30 year design life and the fact that Wolsong Unit 1 was one of the CANDU reactors to operate at the high coolant temperature of 312°C, the hydrogen uptake behavior with operation time should be strictly checked and analyzed.

3. Hydrogen Uptake and Oxidation Behavior of Zr-2.5Nb Alloy

The hydrogen uptake and the concomitant hydride formation are most crucial in controlling the failure behavior of the Zr-2.5Nb pressure tubes. The hydrogen content in the pressure tubes increases significantly as the service life increases in the reactor. Therefore, it is recommended to check the hydrogen content periodically [10]. Among the proposed hydrogen uptake processes, the hydrogen uptake that occurs as part of the normal oxidation process in the high temperature coolant is usually regarded as the main cause of the hydrogen ingress into the tubes. Thus, it is important to understand the correlation between the corrosion and hydrogen uptake of the Zr-2.5Nb alloy. Generally, the deuterium uptake of the Zr-2.5Nb pressure tubes during the corrosion has been much less than 20% of

theoretical ones, with the exception of one pressure tube in the Pickering Unit 3 reactor (P3L09) that showed a deuterium uptake of 70% theoretical value [7]. These results are confined to the commercial Zr-2.5Nb pressure tube, and are therefore not enough to permit an understanding of the microstructure effects on hydrogen uptake behavior of the Zr-2.5Nb alloy. Although the close dependence of corrosion behavior on the microstructure of the Zr-2.5Nb alloys has been reported [9,11], there have only been a few studies made on the effect of microstructure on hydrogen uptake [9].

The hydrogen absorbed above the solubility limit of the matrix is known to precipitate as hydride and the hydride was reported to be susceptible to coolant corrosion, resulting in an acceleration of the corrosion rate [12]. Whereas, hydrogen within the solubility limit will exist as a solid solution state. Considering the major role of hydrogen on the corrosion mechanism of zirconium alloys and the increase of hydrogen amount in the pressure tube with operation time, the role of matrix hydrogen on the corrosion processes has to be elucidated to understand the hydrogen uptake processes of the Zr-2.5Nb pressure tubes.

In the present work, the Zr-2.5Nb alloy was heat treated to have various phases of the Zr-Nb binary system and was hydrogen-charged in the H₂ gas atmosphere. The weight gain of hydrogen-charged specimens in 400°C steam has been investigated and analyzed in terms of the hydrogen effect on the corrosion rate of the alloy. The present work has been done to contribute to the understanding of the role of the microstructure on the hydrogen uptake behavior of the Zr-2.5Nb pressure tube. The different hydrogen uptake behaviors of the CANDU and RBMK pressure tubes were also discussed in terms of the current understanding of hydrogen uptake processes.

Table 2. Summary of Heat Treatments Given to Zr-Nb Alloys.

Heat	Treatment	Microstructure
Annealed	850°C for 1 hour, followed by air cooling	α -Zr, β -Zr
Aged	1000°C for 15 min, followed by water quenching, followed by heating at 550°C for 10 days	α -Zr, β -Nb

3.1. Experimental Procedures

The Zr-2.5Nb alloy sheets were ordered from CEZUS Co (France). The sheet specimens (15 x 30 x 2 mm) were sealed in quartz capsules and given heat treatments, as shown in Table 2. Metallographic and X-ray examinations of the heat-treated specimens were performed and the results are summarized in Table 2. More detailed information on these examinations can be referenced from our previous work [13]. The heat-treated specimens were mechanically polished to a 1200 grit finish with SiC paper, and then hydrogen-charged up to an average of 100 ppm hydrogen in a H₂ Gas atmosphere at 400°C. Hydrogen analyses were performed after hydrogen-charging. Oxidation tests at 400°C under 10MPa H₂O steam atmosphere were performed in order to determine whether or not the hydrogen uptake affects the oxidation reaction.

3.2. Hydrogen-Charging Effect on Oxidation

The hydrogen contents of the heat treated Zr-2.5Nb sheet specimen and tube specimen after hydrogen-charging are summarized in Table 3. The aged alloy consisting of α -Zr and β -Nb phases showed higher amount of hydrogen-charging than the annealed alloy and the pressure tube material, both of them are consisting of α -Zr and β -Zr

Table 3. Hydrogen Contents of Zr-2.5Nb Alloys After Hydrogen-Charging.

Specimen	Microstructure	H Content (ppm)
Annealed Zr-2.5Nb Plate	α -Zr, β -Zr	43 (17) ¹
Aged Zr-2.5Nb Plate	α -Zr, β -Nb	132 (15)
Pressure Tube (Zr-2.5Nb)	α -Zr, β -Zr	62 (6)

1) Hydrogen Content Before Hydrogen-charging

phases. The hydrogen atoms exist in a solid solution state within the solubility limit, but the amount of hydrogen above the limit will precipitate as a hydride form. The terminal solid solubility (TSS) of hydrogen in a zirconium alloy has been investigated by many researchers and the Kearns' heat-up line [14] that is obtained from the database is now used in the integrity analysis of the CANDU pressure tubes. As the hydrogen TSS of the Zr matrix at 400°C is 196 ppm according to the Kearns' line, all hydrogen in these specimens will exist in a solid solution state.

It was reported [15,16] that the amount of hydrogen uptake into the β -Zr phase with a BCC structure in a H₂ gas atmosphere is higher than that of α -Zr having a HCP structure, and that the diffusion coefficient of hydrogen in the β -Zr phase is much faster than in the α -Zr phase. Considering the similar BCC structure of the β -Nb phase, the higher hydrogen uptake of the aged specimen is mainly attributed to the β -Nb phase. However, this does not explain the higher hydrogen uptake of the aged specimen than the annealed specimen. The higher amount of the hydrogen uptake by a pressure tube than an annealed specimen having the same phases can be ascribed to the continuous β -Zr phase that appears to make an easy path for the hydrogen uptake (the β -Zr phase in an annealed specimen exists as a discrete form).

Fig. 5 shows the changes in weight gain with oxidation time obtained from the isothermal oxidation tests at 400°C under 10MPa H₂O steam on the aged and annealed Zr-2.5Nb alloys. The

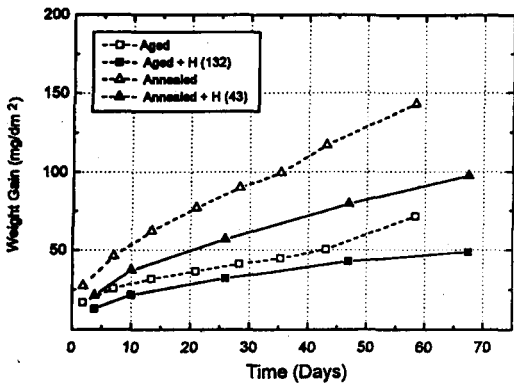


Fig. 5. Effect of Hydrogen-Charging on the Oxidation of the Heat-treated Zr-2.5Nb Alloy in H₂O Steam of 10MPa at 400 °C

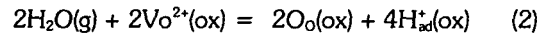
oxidation behaviors of hydrogen-charged alloys are compared. The weight gain of the aged alloy consisting of α -Zr and β -Nb phases was lower than the annealed alloy consisting of α -Zr and β -Zr phases, irrespective of hydrogen content. It is also noted that the weight gains of hydrogen-charged specimens were lower than those of the specimens that weren't hydrogen-charged.

Based on the obtained results, the difference of the hydrogen uptake behavior between the CANDU and RBMK pressure tubes can be partially explained. The RBMK pressure tube consists of α -Zr and β -Nb. Therefore, its corrosion rate is lower than the CANDU pressure tube, which consists of α -Zr and β -Zr, resulting in lower hydrogen uptake on the basis that the hydrogen uptake into the pressure tube is mainly attributed to the corrosion of the pressure tube in the coolant as discussed in Fig. 1. Moreover, the higher coolant temperature of the RBMK pressure tubes (outlet temp. 335-340°C) and the retarding effect of the hydrogen in the matrix on the oxidation rate will afford the higher hydrogen uptake limit.

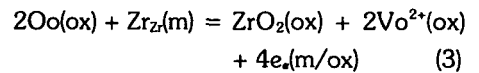
The oxidation of Zr-based alloys at elevated temperatures in H₂O can be divided into 3 partial

reactions, the proton production, anodic and cathodic reactions, as follows :

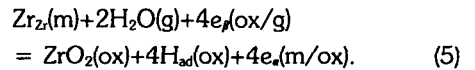
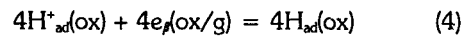
Proton Production/Oxygen Vacancy Annihilation



Anodic Reaction



Cathodic Reaction



Hydrogen adsorbed on the oxide, H_{ad}(ox), may be either released as hydrogen gas molecules,



or absorbed in the oxide phase,



- where, Vo²⁺(ox) ; Oxygen vacancy
 O_o(ox) ; Oxygen ion in matrix oxide
 H_{ad}⁺(ox) ; Hydrogen ion adsorbed on matrix oxide surface
 H_{ab}(ox) ; Hydrogen atom absorbed in matrix oxide
 Zr_{Zr}(m) ; Zirconium atom at a regular metal site

Except the initial stage of oxidation, the oxidation rate of the Zr-2.5Nb binary alloys has been

suggested to be controlled by a cathodic reaction [9]. Therefore, hydrogen existing in the matrix will retard the reaction (6b), resulting in a decrease in the total cathodic reaction rate. In this respect, hydrogen in the Zr matrix within the TSS is suggested to retard the oxidation rate of the Zr alloy at elevated temperatures in H₂O. It also means that the hydrogen uptake rate into the CANDU pressure tube during the operation can be decreased as operation time increases. The increase of hydrogen content in the matrix with operation time will retard the hydrogen uptake rate.

However, considering the fact that the hydrogen content in the β -Zr phase was higher than that in the α -Zr phase and the fact that hydride is preferentially corroded [12], the increase in the hydrogen content of the CANDU pressure tubes might cause great increases in the corrosion rate, resulting in a catastrophic increase of hydrogen content, as shown in the P3L09 pressure tube. To confirm this possibility, more sophisticated research should be performed.

4. Conclusions

The deuterium uptake behavior of the Zr-2.5Nb pressure tubes in Wolsong Unit 1 shows good agreement with the proposed deuterium uptake model derived from the obtained results of Canadian CANDU reactors. There is some scattering in deuterium uptake behavior, and the width of this scattering seems to widen as operation time increases. To ensure the integrity of Wolsong Unit 1 for a design life of 30 years, the hydrogen and deuterium content should be checked periodically and more systematic research should be performed.

The deuterium uptake in the pressure tubes is sensitive to operation factors such as location from the inlet end, coolant temperature, and operation

time. The amount of deuterium uptake in a pressure tube increases as the location goes to the outlet end, as the operation time increases, and as the coolant temperature increases.

The amount of hydrogen uptake in an aged alloy consisting of α -Zr and β -Nb phases is higher than that consisting of α -Zr and β -Zr. The increase of the hydrogen content in the Zr-2.5Nb alloy within the TSS decreases the oxidation rate at 400°C H₂O steam and especially in an annealed alloy consisting of α -Zr and β -Zr phases. It can be well accounted for in terms of the cathodic controlled oxidation reaction of Zr-2.5Nb alloy.

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