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Hydrogen uptake and corrosion behavior of Zr–2.5Nb pressure tubes in Wolsong Unit 1

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Abstract

The hydrogen uptake behavior of Zr–2.5Nb pressure tubes in Wolsong Unit 1 was analyzed in terms of reactor operating factors including the longitudinal location, coolant temperature and time, and compared with those obtained from other CANDU reactors. The amount of deuterium uptake was higher at the outlet of the pressure tubes which were subjected to a higher coolant temperature and became enhanced with increasing reactor operation time. The Zr–2.5Nb pressure tubes in Wolsong Unit 1 showed stable hydrogen uptake behavior up to 13 effective full power years (EFPY). However, scattering of the deuterium uptake tends to increase with increasing operation time. Furthermore, the hydrogen charged Zr–2.5Nb specimens were subjected to corrosion at 400°C under 10 MPa H_2O with an aim of evaluating the effect of absorbed hydrogen on the corrosion of pressure tubes in the later stage of life. The absorbed hydrogen seems to have a negligible effect on the corrosion behavior of Zr–2.5Nb pressure tubes. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Zr–2.5wt% Nb (hereafter referred to Zr–2.5Nb) alloy has been used [1] as pressure tube material for Wolsong Unit 1 reactor for 17 years. All of the Zr–2.5Nb CANDU pressure tubes are manufactured by extrusion at a temperature of about 815°C, in the $(\alpha+\beta)$-phase field. They are then cold-drawn about 27% and finally stress relieved for 24 h at 400°C. The tubes have a dual phase α-Zr and β-Zr structure. Even though the Zr–2.5Nb pressure tubes were designed to operate for 30 years, they have often been replaced due to several life-limiting problems. Three pressure tubes in Wolsong Unit 1 were retubed in 1994 after 10 effective full power years (EFPY) of operation according to an inspection program [2].

The hydrogen and deuterium uptakes and the concomitant delayed hydride cracking are the most important factors in the lifetime of a pressure tube. The hydrogen and deuterium contents in the pressure tube increase significantly as the service life increases in the reactor. Therefore, periodic measurement of the hydrogen and deuterium concentrations is required to ensure that the hydrogen equivalent concentration (H_{eq}) will not exceed the terminal solid solubility (TSS) in the CANDU Zr–2.5Nb pressure tube at operation temperature.

Originally, the only opportunity to determine the hydrogen and deuterium concentrations of in-service pressure tubes occurred when the occasional tube was removed from service. One alternative is the scrape sampling method retrieving a sample from the inner surface of in-service pressure tube for chemical analysis [3]. The obtained scrape geometry yields approximately 45 mm long, 9 mm wide and 0.08 mm thick. Over the past several years, this technique has been developed to a very effective method in obtaining the rate of hydrogen and deuterium uptakes in pressure tubes [3].

All the hydrogen and deuterium analyses of the pressure tube off-cuts which were obtained from the

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both sides of pressure tubes at the initial installation stage in 1990, 10 pressure tubes by scrape sampling in 1992, three removed pressure tubes in 1994, and four pressure tubes by scrape sampling in 1998 were carried out for Wolsong Unit 1 as an inspection program [2,4,5].

In this study, the deuterium uptake behavior of Zr–2.5Nb pressure tubes in Wolsong Unit 1 reactor was analyzed in terms of operating factors including the longitudinal location, coolant temperature and time, and was also compared with those of Canadian reactors. Furthermore, the hydrogen uptake behavior of the Zr–2.5Nb alloy in a gas environment and the effect of hydrogen uptake on its oxidation behavior were investigated in terms of the effects of microstructure and the corrosion rate to understand the hydrogen uptake behavior of Zr–2.5Nb pressure tubes.

2. Deuterium uptake of Wolsong-1 pressure tubes

Fig. 1 shows the deuterium pick-up measured in Wolsong Unit 1, compared with those obtained in Canadian CANDU pressure tubes [3,6]. The deuterium uptake in the pressure tubes is plotted as a function of EFPY. The deuterium uptake is greatly dependent on the material of the pressure tube. Zr–2.5Nb pressure tubes exhibit much lower rates of deuterium ingress compared with Zircaloy-2 pressure tubes used in the earlier CANDU reactors. In contrast to the catastrophic increase in the 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 2 ppm D/yr (1 ppm H_{eq}/yr) 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 scrape samples are consistent with those from pellets taken from the full wall thickness of removed pressure tubes. Therefore, the results from scrape sampling can be used in the analyses of pressure tube integrity.

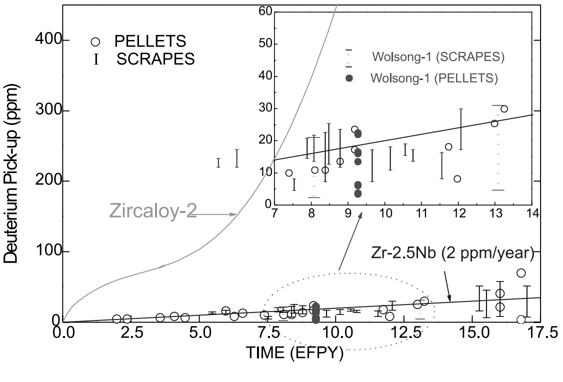

Fig. 1. Deuterium concentration in Zircaloy-2 and Zr–2.5Nb pressure tubes including Wolsong-1 reactor.

The results obtained from Wolsong Unit 1 show good agreement with the proposed deuterium uptake model for Zr–2.5Nb pressure tubes up to 13 EFPY. 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 in deuterium uptake, including Wolsong Unit 1, 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. Therefore, the deuterium uptake behavior of Zr–2.5Nb pressure tubes in Wolsong Unit 1 reactor should be monitored and analyzed for the remaining operation time, especially in terms of scattering behavior.

The features that the oxidation rate of the Zr–2.5Nb pressure tubes was close to being linear with no acceleration and that the Zircaloy-2 pressure tubes showed clear evidence for an acceleration in the oxidation rate [6] are very similar to the deuterium uptake behavior, as shown in Fig. 1. From the facts, it has been insisted that the deuterium uptake into the pressure tube is mainly attributed to the corrosion of the pressure tube in the coolant [6,7].

Table 1 shows the hydrogen and deuterium concentrations of Q06 and S15 channels that were scrape-sampled both in 1992 and 1998. Although the deuterium concentration increases as the reactor operation time increases, the hydrogen concentration remains nearly constant. This fact also substantiates that the deuterium uptake into the pressure tube is mainly attributed to the corrosion of the pressure tube. However, the source of hydrogen in Wolsong Unit 1 is still unclear. Generally, deuterium uptake has been much less than 20% of the theoretical values that are stoichiometrically calculated by the corrosion reaction of Zr–2.5Nb pressure tube. But a much higher deuterium uptake, up to 70% of the theoretical value in Pickering Unit 3 and up to 100% in the Zircaloy-2 tubes from Pickering Units 1 and 2, was reported [6]. The deuterium uptake behavior during the corrosion has also been reported to be dependent on the microstructure of the alloy [8]. Thus, it is suspected that some other sources of deuterium could exist. More systematic researches are required to quantify the contributions from each source.

Fig. 2 shows the deuterium concentration versus the distance from the pressure tube inlet for Zr–2.5Nb pressure tubes in Wolsong Unit 1 compared with those obtained in Bruce Units 1 and 2. Generally, the deuterium uptake of a pressure tube increases from the inlet end to the outlet end and the effect becomes more clear as operation time increases. Fig. 3 shows the temperature dependence curve of hydrogen uptake rate of the Zr–2.5Nb pressure tubes in Wolsong Unit 1. The

Table 1
Hydrogen and deuterium concentrations in scrape samples of Q06 and S15 channels in Wolsong-1 [4]

Channel ID	Axial Location (m)[a]	[D] (mg/kg)		[H] (mg/kg)		$[H]_{initial}$ (mg/kg)
		1992	1998	1992	1998	
Q06	2.0	4.3	4.6	17	9.8	9.0
	4.0	11.9	19	14	13.2	
	5.0	18	31	12.9	12.3	
	5.6	–	25	–	9.9	
S15	2.0	7	5.9	10.1	10.1	6.8
	4.0	9.7	18	11.5	11.5	
	5.0	13.2	23	13.3	12.3	
	5.6	–	23	–	12.4	

[a] The axial location was measured from the inlet end of pressure tube.

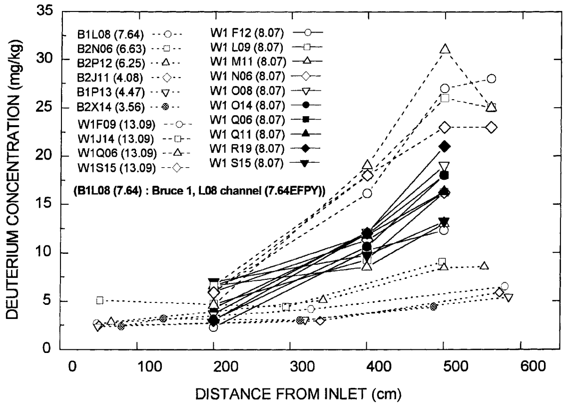

Fig. 2. Deuterium concentration along Zr–2.5Nb pressure tubes from Bruce (3.56–7.64 EFPY) and Wolsong-1 (8.07/13.09 EFPY) NGSs.

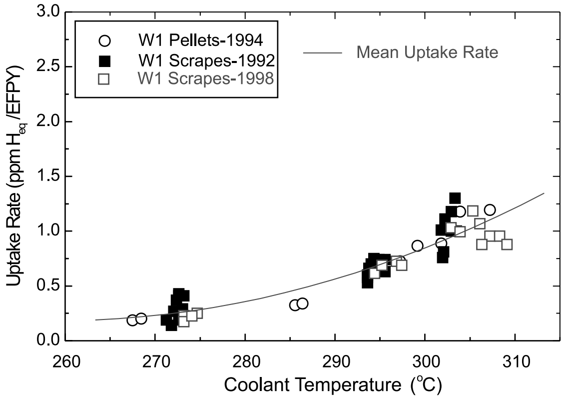

Fig. 3. Temperature dependence of hydrogen uptake rate of the Zr–2.5Nb pressure tubes in Wolsong-1 reactor.

deuterium uptake rate was increased with the operation temperature of the pressure tube. This figure explains that the higher deuterium uptake at the outlet end of a pressure tube, shown in Fig. 2, 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, thereby resulting in a higher amount of deuterium uptake. It is also substantiated by the fact that the oxide thickness of the outlet end is thicker than that of the inlet end [6]. 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 [7]. According to the temperature dependence curve of hydrogen uptake as shown in Fig. 3, the hydrogen uptake rate at 308°C is 1.20 H_{eq}/EFPY, whereas the hydrogen uptake rate at 312°C is 1.41 H_{eq}/EFPY. Thus, the hydrogen uptake value of 0.615 H_{eq}ppm/yr that was used in the integrity analysis for Wolsong Unit 1 pressure tubes in 1992 [4] and 1.0 H_{eq}/yr introduced in Fig. 1 do not seem to be conservative.

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

3. Effect of hydrogen uptake on oxidation of Zr–2.5Nb

The hydrogen content in the pressure tubes increases significantly as the service life increases in the reactor. 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 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. Although the close dependence of corrosion behavior on the microstructure of the Zr–2.5Nb alloy has been reported [8–11], there have only been a few studies made on the effect of matrix phase on the hydrogen uptake of the alloy [8,12].

Considering the major role of hydrogen on the corrosion mechanism of zirconium alloys [8,13] 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.

3.1. Experimental procedures

The Zr–2.5Nb alloy sheets were ordered from CEZUS Co (France). The sheet specimens ($15 \times 30 \times 2\ \mathrm{mm}^3$) 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 [11]. The heat-treated specimens were mechanically polished and then hydrogen-charged up to 30, 100, 250 ppm hydrogen in a H_2 gas atmosphere at 400°C. Hydrogen analyses were performed after hydrogen gas charging. Oxidation tests at 400°C under 10 MPa H_2O steam atmosphere were performed in order to determine whether or not the hydrogen uptake affects the oxidation reaction. X-ray examinations of the oxide formed on the specimens were performed after 1-, 4-, 10-, and 71-day oxidation.

3.2. Hydrogen charging effect on oxidation

The hydrogen contents of the heat-treated Zr–2.5Nb sheet specimens after hydrogen charging are summarized in Table 2. The aged alloy consisting of α-Zr and β-Nb phases showed higher amount of hydrogen-charging than the annealed alloy consisting of α-Zr and β-Zr 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. As the TSS of hydrogen in a Zr matrix at 400°C is 196 ppm according to the Kearns' line [14], the hydrogen exceeding the TSS in the highly hydrogen-charged specimens will exist as hydrides during corrosion tests.

It was reported [15] that the amount of hydrogen uptake into the β-Zr phase with a BCC structure in a H_2 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.

Fig. 4 shows the changes in weight gain with oxidation time obtained from the isothermal oxidation tests at 400°C under 10 MPa H_2O steam on the differently heat-treated Zr–2.5Nb alloys. The oxidation behavior of Zr–2.5Nb alloy was mainly sensitive to the microstructure which in turn is influenced by heat treatment as discussed in our previous results [8,11]. The weight gain of the quenched alloy increased almost linearly with time. In contrast, it increased linearly with logarithmic time for the aged and annealed alloys. 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 increase of the hydrogen content in the Zr–2.5Nb alloy has a negligible effect on the oxidation rate. Fig. 5 shows the X-ray examinations of the oxide formed on the annealed Zr–2.5Nb having 204 ppm hydrogen

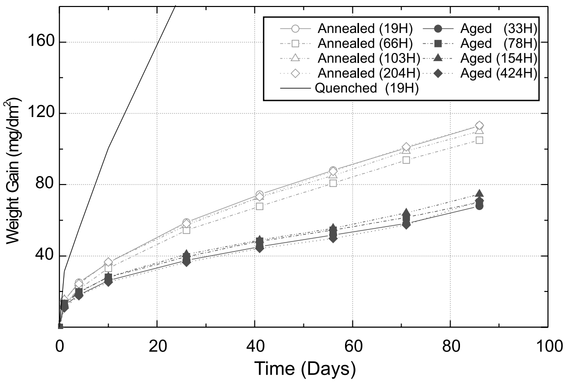

Fig. 4. Change in weight gain with oxidation time obtained from the Zr–2.5Nb alloys in H_2O steam of 10 MPa at 400°C.

Table 2
Heat treatments and hydrogen content of Zr–Nb alloys

Heat treatment		Microstructure	H Content (wt. ppm)
Quenching	1000°C, 15 min → water quenching	α′-Zr[a]	19
Ageing	Quenching → 550°C, 10 days	α-Zr, β-Nb	33/78/154/424[b]
Annealing	850°C, 1 h → air cooling	α-Zr, β-Zr	19/66/103/204[b]

[a] α′-Zr: α-Zr martensite.

[b] Hydrogen charging targets are 0, 30, 100, 250 ppm, respectively.

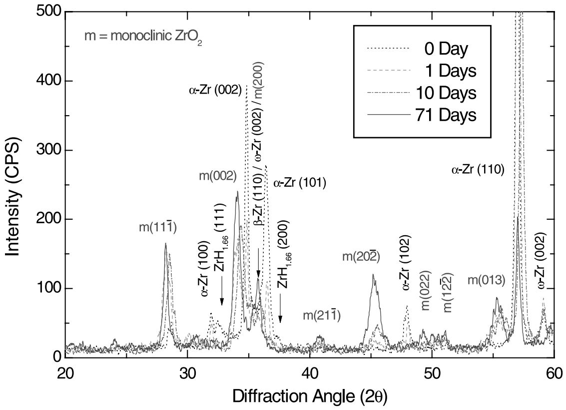

Fig. 5. X-ray diffraction patterns of oxide grown on annealed Zr–2.5Nb (204 ppm H) in H_2O steam at 400°C for 0, 1, 10, 71 days.

after 1-, 4-, 10-, and 71-day oxidation tests. The hydride of the specimen disappeared after 1 day's oxidation, and the monoclinic ZrO_2 was growing on the matrix phases as oxidation time increased. There was no apparent change in the X-ray examinations of the Zr–2.5Nb specimens by hydrogen charging up to 424 ppm. These results suggest that the deuterium buildup in the Zr–2.5Nb pressure tubes during reactor operation seems to have a negligible effect on the current stable deuterium uptake behavior of the tubes.

However, considering the fact that the hydrogen content in the β-Zr phase was higher than that in the α-Zr phase and the report that hydride is preferentially corroded [16], more sophisticated research should be performed.

4. Conclusions

1. The deuterium uptake behavior of the Zr–2.5Nb pressure tubes in Wolsong Unit 1 up to 13 EFPY 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.
2. 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.
3. The amount of hydrogen uptake in the aged Zr–2.5Nb alloy consisting of α-Zr and β-Nb phases is higher than that in the annealed alloy consisting of α-Zr and β-Zr in a H_2 atmosphere at 400°C.
4. The oxidation behavior of Zr–2.5Nb alloy is mainly sensitive to the microstructure, irrespective of hydrogen content. The increase of the hydrogen content in the Zr–2.5Nb alloy seems to have a negligible effect on the oxidation rate at 400°C H_2O steam.

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