

Role of hydrides on the oxidation and deuterium pickup of Zr–2.5Nb in D₂O at 573 K

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Abstract

This study was initiated to determine the role of hydrides on the oxidation and D-pickup rates of Zr–2.5Nb pressure tubes used in CANDU[®] reactors. Coupons of Zr–2.5Nb pressure tube material were charged to H concentrations ranging from 5 to 800 mg H/kg metal. A continuous layer of hydride was also introduced on the surface of some coupons. Tests were conducted in lithiated D₂O at 573 K for about 4 years. The coupons were removed at certain intervals for oxide thickness, D-pickup and various other evaluations such as metallography. All the coupons, except those with a surface hydride layer, showed comparable oxidation and D-pickup rates. The coupons with a surface hydride layer showed oxidation and D-pickup rates of about a factor of two higher than the other coupons. These findings, as well as results from the other examinations are reported in this paper.

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1. Introduction

The oxidation rate of Zircaloy-4 fuel cladding material has shown acceleration after long-term corrosion tests in 633 K water [1–3]. A substantial increase in the corrosion rate is also observed for long-term exposure of fuel claddings in the pressurized water reactors (PWRs) [4]. This increase in the oxidation rate of Zircaloy-4 fuel cladding is thought to be partially related to the onset of hydride precipitation at the metal-oxide interface [2]. The possibility that the presence of hydrides in the metal-oxide interface could increase the corrosion rate of zirconium alloys was suggested about 50 years ago [5], but tests performed soon after showed inconsistent results [6–8]. While one test had shown an increase in the oxidation rate of Zircaloy-2 with increase in hydrogen concentration of the metal [6], other tests, using Zircaloy-2 samples with up to 3000 ppm hydrogen, had not indicated

any significant change in the corrosion rate of the alloy [7,8]. Recently more attention has been paid to this problem as the nuclear fuel is left in the PWRs for progressively longer periods to achieve higher burn-up levels [9]. Consequently, new tests have been carried out, and they show that an increase in the oxidation rate of Zircaloy-2 and -4 occurs only if a massive surface hydride layer is present [10–12].

The Zirconium alloy Zr–2.5Nb (Zr–2.5 (wt.%) Nb) is used to fabricate pressure tubes for CANDU[®] nuclear reactors. The pressure tubes are located in the core of the reactor and contain the fuel bundles and the heavy water (D₂O) heat transport fluid [13]. The pressure tubes operate at temperatures ranging from 520 K at the inlet to 580 K at the outlet. Under such conditions the pressure tubes oxidize and in the process deuterium is released from the water molecule. A fraction of the deuterium is absorbed by the metal and when the deuterium plus initial hydrogen concentration in the metal exceeds the solubility limit hydrides/deuterides precipitate. This study was initiated to determine if dispersed hydrides or a layer of hydride over the surface of Zr–2.5Nb CANDU[®] pressure tube material have any effect on its oxidation and deuterium pickup behaviour.

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¹ CANDU[®]—CANada Deuterium Uranium is a registered trademark of Atomic Energy of Canada Ltd.

Table 1
Preparation history, nominal bulk hydrogen concentration and surface hydride layer thickness of the coupons prior to corrosion tests

Coupon type	Preparation history	Nominal bulk [H] (mg H/kg metal)	Nominal thickness of surface hydride layer (μm)
A	As received and chemically polished	7	None
B	Chemically polished, charged from gas phase and chemically polished again	130	None
C	Chemically polished, charged from gas phase and chemically polished again	200	None
D	Chemically polished, charged from gas phase and chemically polished again	700	None
E	Chemically polished and cathodically charged	7	30
F	Chemically polished, cathodically charged and annealed at 553 K for 24 h	57	20
G	Chemically polished, cathodically charged, annealed at 553 K for 24 h and chemically polished to remove the hydride layer	57	None

2. Experimental

Coupons of Zr–2.5Nb (10 mm \times 25 mm \times 1.8 mm) were machined from an extruded and 28% cold worked pressure tube (No. 1980). The tube was fabricated from a non- β -quenched ingot. In the final stages of fabrication, the tube was stress relieved at 673 K in \sim 1 MPa steam for 24 h. Based on chemical analysis of the ingot, the major impurities were O, Fe, C, Si, Al and N at 1130, 636, 150, 96, 73 and 50 wt. ppm, respectively. To have the same surface finish, the coupons were chemically polished by immersing them in a solution of 45 parts lactic acid ($\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$), 45 parts nitric acid (HNO_3) and 2 parts hydrofluoric acid (HF) for 1 min at room temperature. Some of the coupons were charged to nominal hydrogen concentrations of 130, 200 and 700 mg/kg (mg H/kg metal) using hydrogen gas. To avoid the possibility of any microstructural transformation during hydrogen charging, the coupons were charged at about 523 K using a Ni plating technique [14]. Other coupons were charged by electrolytic techniques (cathodic charging) to introduce a continuous hydride layer on the coupon surface. These coupons were charged for 24 h in a 0.2 M H_2SO_4 acid bath at 333 K with a current density of 200 mA/cm². The resultant hydride layer was about 30 μm thick. Some of these coupons were sealed under \sim 10^{−6} Torr vacuum in a glass tube and annealed at 553 K for 24 h to allow some of the hydrogen from the surface hydride layer to diffuse into the bulk of the coupons. Finally, the surface hydride layer of a number of the annealed coupons was removed by chemically polishing prior to corrosion tests. As a result, a total of seven types of coupons were prepared for testing, which were designated as A, B, C, D, E, F and G type (Table 1). Cross-section specimens were prepared from each coupon type and examined using optical metallography. Prior to the examination, the surface of the cross-sectioned specimens was chemically polished using a solution of 50 parts nitric acid, 45 parts lactic acid and 5 parts hydrofluoric acid to reveal the hydride morphology. Optical

micrographs from four different types of coupons are shown in Fig. 1.

Corrosion tests were conducted in lithiated D₂O ($\text{pH}_a = 10.4^2$, $[\text{Li}^+] = 0.6$ ppm) at 573 K for a period of about 4 years. Note that since the coupons were already charged with hydrogen, performing the corrosion tests in D₂O allows for the determination of the amount of deuterium pickup by the coupons during corrosion with much higher accuracy than if the corrosion tests were carried out in H₂O. The coupons were removed from test at certain intervals for oxide thickness measurements. The thickness of oxide films was calculated from the weight gain of the coupons and occasionally verified using the Fourier Transform Infrared Reflection Spectroscopy technique [15]. The whole coupon surface area was used in calculating the oxide thickness from the coupon weight gain. A sample of \sim 100 mg was cut from each coupon at certain intervals for hydrogen and deuterium concentration measurements using the hot vacuum extraction mass spectrometry (HVEMS) technique [16]. The samples were analyzed for hydrogen and deuterium concentrations without removing their oxide or hydride layer. Occasionally, a suitable sample was also cut for metallography.

3. Results and discussion

3.1. Oxidation results

The oxidation results of coupons of different types are plotted in Fig. 2. Each data point in the figure is the average of 5 coupons for up to 77 d, 4 coupons for up to 175 d and 3 coupons for the remaining corrosion periods. After 77 d and 175 d exposures one coupon of each type was removed from the test to be archived for [H] and [D] measurements and metallography. The standard deviations, shown as error

² pH_a stands for apparent pH. It is the pH of a heavy water (D₂O) solution measured with a standard pH meter calibrated in a light water (H₂O) buffer.

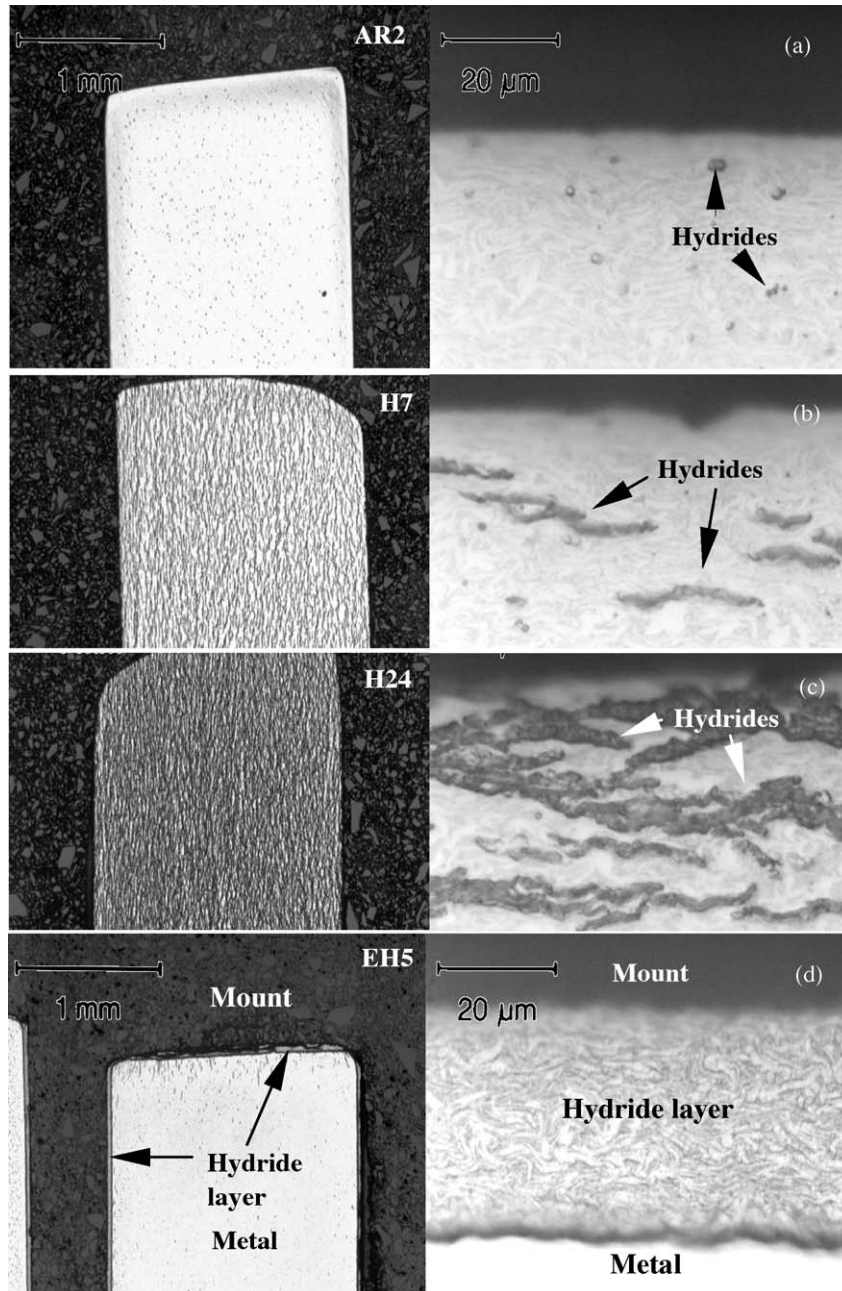


Fig. 1. Optical micrographs showing the initial microstructure of the Zr–2.5Nb coupons. (a) Coupon AR2, type A with [H] of 7 mg/kg. (b) Coupon H7, type C with [H] of 230 mg/kg. (c) Coupon H24, type D with [H] of 590 mg/kg. (d) Coupon EH5, type E with a surface hydride layer of $\sim 30 \mu\text{m}$. Note that the microstructure of each coupon is shown both in low (left) and high (right) magnifications.

bars in Fig. 2, indicate that (except in the case of type A coupons) coupon-to-coupon variation of oxide film thickness is relatively small.

Fig. 2 indicates that all the coupons, except the ones with a continuous hydride layer on their surface (E and F types), have comparable oxidation rates ($\sim 6.4 \times 10^{-3} \mu\text{m/d}$). It is surprising to observe that coupons with such a large range of hydrogen concentrations (5 to over 800 mg/kg) have similar corrosion rates. This indicates that a large number of hydrides distributed homogeneously in the bulk of a Zr–2.5Nb

pressure tube will not have a major effect on its corrosion rate. The coupons with a continuous surface hydride layer with (type F) and without (type E) initial annealing at 553 K show comparable oxidation rates ($\sim 1.2 \times 10^{-2} \mu\text{m/d}$). This result is expected, because, even though E and F type coupons had different preparation histories, after one day at the test temperature (573 K) both types would have comparable hydride morphologies with a bulk [H] of 74 mg/kg and a remaining surface hydride layer. Fig. 2 also shows that the oxidation rate of the coupons with a

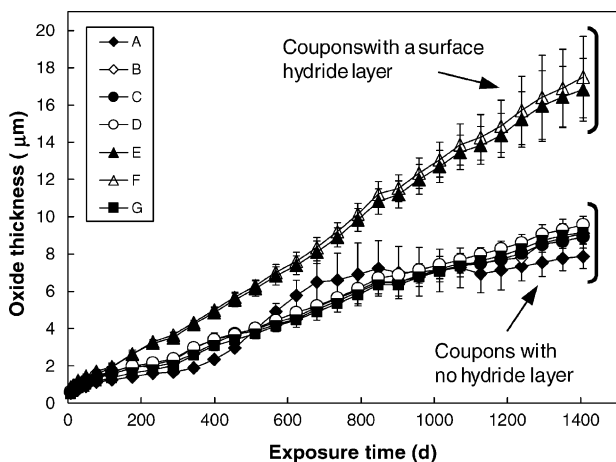


Fig. 2. Comparison of oxidation of Zr–2.5Nb coupons with different initial hydrogen concentrations and hydride morphologies (see Table 1 for hydrogen concentration and preparation history of the coupon types A–G) oxidized in lithiated D₂O (pH_a = 10.4, [Li⁺] = 0.6 ppm) at 573 K. Coupon types E and F (showing higher oxidation) are the only ones with a continuous surface hydride layer. The oxide thickness was obtained by measuring the weight gain of the coupons resulting from corrosion. Error bars represent the standard deviation for coupons.

continuous surface hydride layer is about twice the oxidation rate of those without such hydride layer. These results are in agreement with the results of recent corrosion tests conducted using Zircaloy-2 and -4 coupons, which also showed that an increase in the oxidation rate occurs only if a surface hydride layer is present [10–12].

At 573 K (the test temperature) the solubility limit for hydrogen in Zr–2.5Nb pressure tube material, stress relieved at 673 K for 24 h, is 74 mg/kg [17]. Therefore, except for the A and G type coupons, which initially had < 74 mg/kg, all the coupons would have hydrides present at the test temperature. The number of hydrides present depends on the [H] of the coupons and, as Fig. 1 shows, it is the greatest in the case of the D type coupons. In some cases the [H] of the D type coupons was in excess of 800 mg/kg. It is worth noting that charging the bulk of the coupons homogeneously to such high concentrations of hydrogen at moderate temperatures (523 K) is only possible with the nickel-plating technique mentioned in Section 2. The earlier work cited above used only coupons charged at elevated temperatures (743 K) up to [H] less than 400 mg/kg. The present tests have extended the investigations to coupons with much higher hydrogen concentrations than previously available.

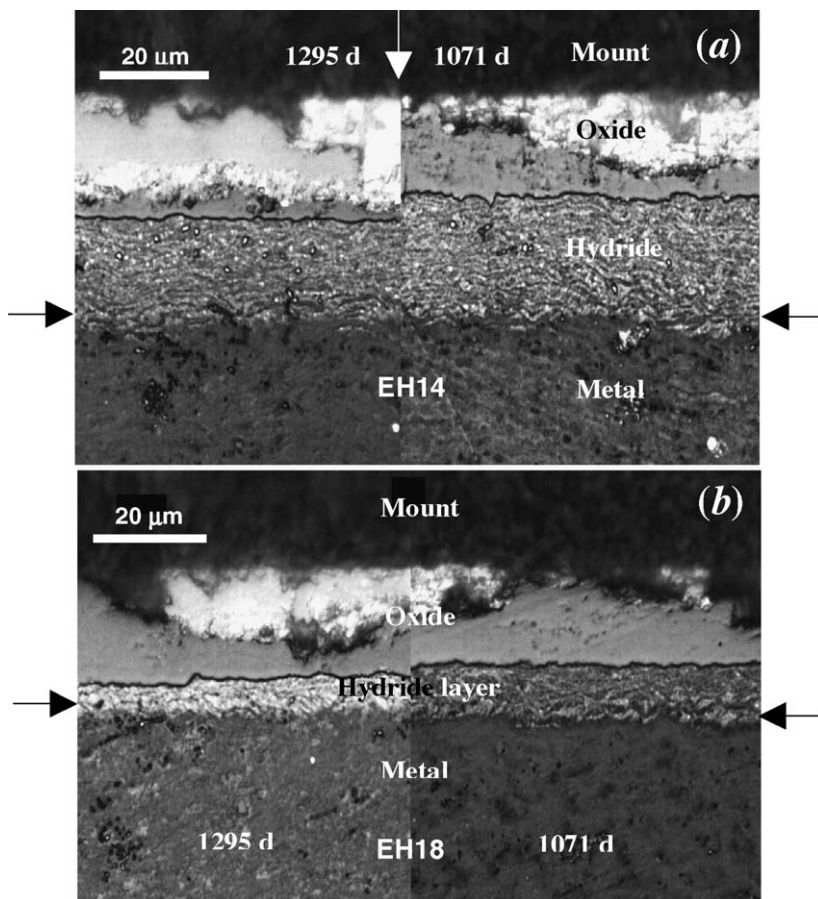


Fig. 3. Optical micrographs showing cross section of: (a) EH14, a type E coupon and (b) EH18, a type F coupon taken after 1071 d (right) and 1295 d (left) corrosion periods. The metallographic samples were cut with care so that the cross sections to be examined after the two corrosion periods would be close to each other. Note that in both cases the metal-hydride interfaces (shown by arrows) have intentionally been lined up by adjusting the micrographs. This alignment of the micrographs makes it easier to illustrate that as the oxide grows thicker the hydride layer gets thinner.

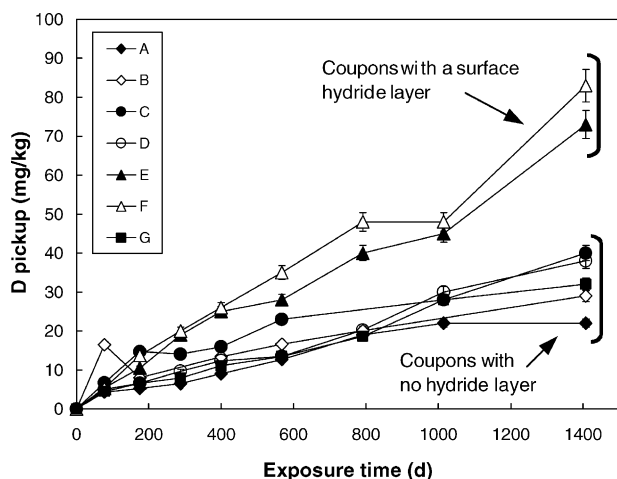


Fig. 4. Deuterium concentration of Zr–2.5Nb coupons with different initial hydrogen concentrations and hydride morphologies (see Table 1 for hydrogen concentration and preparation history of the coupon types A–G) oxidized in lithiated D₂O (pH_a = 10.4, [Li⁺] = 0.6 ppm) at 573 K. Coupon types E and F are the only ones with an initial continuous surface hydride layer. The error bars ($\pm 5\%$) are the uncertainties in measured values.

Fig. 3 shows optical micrographs in cross section of a type E and a F coupon taken after 1071 d and 1295 d corrosion periods. The figure shows that in both cases the oxide grows on top of the hydride layer and at the expense of the hydride layer (i.e. as the oxide grows thicker the hydride layer gets thinner). At some point in time the hydride layer will disappear and the oxidation rate is expected to decrease to the level of the oxidation rate of coupons with no surface hydride layer. The tests are continuing to ascertain this possibility.

3.2. Deuterium pickup

Results of hydrogen and deuterium concentration measurements from different coupon types are given in Table 2. Each entry in the table is obtained from only one sample except in the case of six entries marked with an (a), which

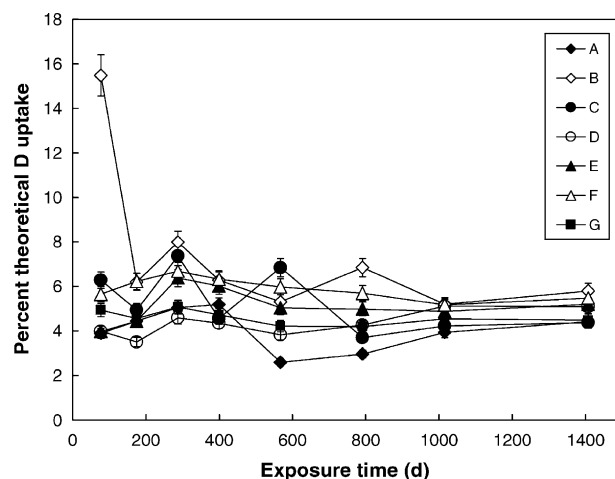


Fig. 5. Percent theoretical deuterium pickup for Zr–2.5Nb coupons with different initial hydrogen concentrations and hydride morphologies oxidized in lithiated D₂O (pH_a = 10.4, [Li⁺] = 0.6 ppm) at 573 K. The percent theoretical deuterium pickup values are calculated using the data given in Figs. 2 and 4. It should be noted that the first point for type B is high because of an unexpectedly high measured value of D (Fig. 4).

are the average of two samples with similar hydrogen concentrations. In the following discussion, it is assumed that the hydrogen concentration values are the initial hydrogen content of the coupons and that only deuterium was picked up during the corrosion tests. This assumption is confirmed by the fact that the hydrogen concentration of the type A coupons (containing very little hydrogen) did not change during the corrosion tests (Table 2). The [D] values are plotted in Fig. 4. The figure shows that the deuterium pickup data, as in the case of the oxidation data (Fig. 2), clusters in two groups. The first group constitutes the data from the A, B, C, D and G type coupons. These coupons do not have a continuous surface hydride layer (Table 1) and clearly have picked up much less (generally < 1/2) deuterium than the ones with a continuous surface hydride layer (the E and F types). The coupons of the first group also show some variation in deuterium pickup. However, due to inadequate statistics and the lack of a clear

Table 2

Hydrogen and deuterium concentrations of Zr–2.5Nb coupons with different initial hydrogen concentrations oxidized in lithiated D₂O (pH_a = 10.4, [Li⁺] = 0.6 ppm) at 573 K

Corrosion period (day)	Coupon type													
	A		B		C		D		E		F		G	
	H	D	H	D	H	D	H	D	H	D	H	D	H	D
77	5.0	4.3	135	16.5	190	6.7	720	5.0	530	5.4	700	5.3	54	4.5
175	7.0	5.2	142	8.0	230	14.7	590	6.6	560	10.5	870	13.7	51	6.6
287	5	6.5	—	—	174 ^a	14.1 ^a	610	9.5	750	19	860	20	52	7.9
399	7	9	127	13.4	148	15.9	620	12.4	740	25	830	26	53	11.1
567	6	12.7	104	16.6	159	23.0	470	13.5	590	28	740	35	57	13.5
791	6	19	99 ^a	20.1 ^a	—	—	540	20.2	620	40	730	48	58	18.6
1015	6.6	22	—	—	220 ^a	28.0 ^a	810	30	440	45	360	48	53	28
1407	6.6	22	82	29.0	149	40.0	640	38	630	73	720	83	63	32

Each entry is obtained from one sample except in the case of the entries with an (a), which are the average of two samples with similar hydrogen concentrations. The uncertainty in H and D values is $\pm 5\%$. H and D represents hydrogen and deuterium concentrations (mg/kg), respectively.

^a Average of two specimens with similar hydrogen concentrations.

trend, further data are required to clearly establish the extent of this variation.

The “percent theoretical deuterium pickup³” is calculated for each coupon using its measured [D] and oxygen pickup via oxidation. This parameter is plotted in Fig. 5. While the deuterium pickup rates for the two groups of coupons (with and without surface hydride layer) are quite different, Fig. 5 shows that the percent theoretical deuterium pickup is fairly similar for all the coupons with different hydrogen concentrations and/or hydride morphologies. After a long corrosion period the percent theoretical deuterium pickup data seem to cluster about 5%, which is within the range of values observed for Zr–2.5Nb pressure tube material [18].

4. Conclusions

Coupons of Zr–2.5Nb, machined from a non-irradiated CANDU[®] reactor pressure tube, were charged to different hydrogen concentration from a gas phase. Some coupons were also charged by electrolytic techniques to form a continuous hydride layer on their surface. Corrosion tests were conducted in lithiated D₂O (pH_a = 10.4, [Li⁺] = 0.6 ppm) at 573 K for a period of about 4 years. Results indicate that all the coupons, except the ones with a continuous surface hydride layer, have comparable oxidation rates. They also show that the oxidation rate of the coupons with a continuous surface hydride layer is about twice the oxidation rate of those without such a hydride layer. Optical micrographs of the coupons with a continuous surface hydride layer taken after different corrosion periods show that the oxide grows on top of the hydride layer. They also show that as the oxide grows thicker the thickness of the hydride layer decreases.

The deuterium concentrations of a number of coupons measured periodically show that the deuterium-pickup rate of the coupons with a continuous surface hydride layer is more than twice the pickup rate of the other coupons. However, the percent theoretical deuterium pickup, calculated for each coupon using its measured [D] and oxygen pickup via oxidation, is about 5% for all the coupons with different hydrogen concentrations and/or hydride morphologies.

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³ Amount of D-picked up as a percent of the total amount of D released in the corrosion process $Zr + 2D_2O \rightarrow ZrO_2 + 4D$.