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Effect of β-Zr decomposition on the solubility limits for H in Zr–2.5Nb

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Abstract

The zirconium alloy Zr–2.5Nb (Zr–2.5 wt.% Nb) is used to fabricate pressure tubes for CANDU®[1] nuclear reactors. The microstructure of the as-extruded tubes consists of elongated h.c.p. α-Zr grains surrounded by a network of b.c.c. β-Zr containing at least 20 wt.% Nb. The β-Zr phase is *meta*-stable at temperatures below 900 K and gradually dissociates into its constituent elements α-Zr and β-Nb. The aim of this study was to determine the effect of β-Zr decomposition on the terminal solid solubility for dissolution (TSSD) for H in Zr–2.5Nb. Specimens of Zr–2.5Nb were charged to different hydrogen concentrations and aged at temperatures ranging from 673 to 773 K for 30 to 6000 min, to decompose their β-Zr component by different amounts. Hydride dissolution temperature and hydrogen concentration were determined using differential scanning calorimetry and hot vacuum extraction mass spectrometry, respectively. The results show that the as-extruded pressure tube structure, with the β-Zr almost intact, has the highest TSSD and that the TSSD for structures with fully decomposed β-phase is the lowest and approaches that of unalloyed Zr.

Keywords: Hydrogen; Solubility; Zr–Nb alloys; TSS; CANDU®

1. Introduction

Due to low neutron absorption cross section of Zr, Zr-based alloys such as the Zircaloy-2, Zircaloy-4 and Zr–Nb alloys are used for reactor core components. However, the terminal solid solubility (TSS) for H in Zr [1–4] is very low and the components may become susceptible to delayed hydride cracking, blister formation and reduction in fracture toughness if H concentration exceeds the TSS [5,6]. In Zr–2.5Nb (Zr–2.5 wt.% Nb), a two phase alloy used for pressure tubes in CANDU® power reactors, the TSS is less than 0.7 at.% H (about 70 wt. ppm) at 573 K [7]. The pressure tubes pickup hydrogen in a slow but continuous process during operation (e.g. due to high temperature corrosion). Therefore, higher TSS contributes to longer lifetime for the pressure tubes and great savings for the industry.

The microstructure of the as-extruded pressure tubes consists of elongated grains of hexagonal close-packed α-Zr (90% of volume) which contains about 0.6 wt.% Nb surrounded by a network of body-centred cubic β-Zr (10%) which contains at least 20 wt.% niobium [8]. The β-Zr phase is *meta*-stable at temperatures below 900 K and gradually transforms to the constituent elements α-Zr and β-Nb [9,10]. Earlier studies have shown that the TSS for hydrogen in the β-Zr (Zr–20 wt.% Nb) phase is higher than in α-Zr [11,12] and that the relative solubility of hydrogen in Zr–20Nb to that in zirconium is greater than unity [11–13]. (Note that the term ‘solubility’ should not be confused with the term ‘solubility limit’ or TSS. Solubility is related to the Sievert’s constant and is a measure of affinity of a solid for hydrogen). A number of these studies [11,13] have also shown that the TSS for hydrogen in the β-Zr and the relative solubility decreases with the decomposition of the β-phase. Since knowledge of the variation of the TSS due to changes in the microstructure of the alloy is essential in assessing the operating and end-of-life behavior of the pressure tubes, a systematic study was conducted of the TSS for hydrogen in Zr–2.5Nb pressure tube alloy as a function of β-Zr decomposition. Results of this study are discussed here.

2. Experimental

Specimens of Zr–2.5Nb (60×4×2 mm) were machined

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from an as-extruded pressure tube. This pressure tube was fabricated from a β-quenched ingot and was, in the final stage of fabrication, 27% cold worked (it was not stress relieved following cold working). Chemical analysis of the ingot identified the major impurities as: O, Fe, C, Si, Al and N at 1100, 800, 190, 65, 55 and 35 wt. ppm, respectively. The specimens were charged to different hydrogen concentrations from the gas phase. The charging was carried out at moderate temperatures (about 523 K), using an Ni plating technique [14], to remove the possibility of microstructural transformation during charging. They were subsequently aged at temperatures ranging from 673 to 773 K for 1 to 100 h, to decompose their β-Zr component by different amounts. After aging, coupons of about 2×4×4 mm were cut and analyzed for TSS dissolution (TSSD) temperature using differential scanning calorimetry (DSC).

For details of the DSC analysis see Ref. [11]. Each specimen was analyzed for the TSSD temperature in at least three consecutive thermal cycle runs. The runs consisted of a heatup from a temperature of ~300 K to a maximum temperature (T_{max}) not exceeding 600 K, a hold-time of 5 min at T_{max} followed by a cooldown to ~300 K. In all runs, the heatup/cooldown rate was 30 K/min. T_{max} was chosen to be <600 K to minimize the potential transformation of *meta*-stable β-Zr structure during measurements and it was chosen to be at least 30 K higher than the estimated hydride dissolution temperature so that the DSC heatflow signal would include the completion of the hydride dissolution process. The first run served

Table 1
[Nb] (the niobium concentration in the β-phase), T_{TSSD} (the TSSD temperature) and [H] (the hydrogen concentration) for 10 sets of Zr–2.5Nb pressure tube samples with different heat treatments

Sample condition	[Nb] (wt.%)	T_{TSSD} (K)	[H] (mg/kg)	Sample condition	[Nb] (wt.%)	T_{TSSD} (K)	[H] (mg/kg)	Sample condition	[Nb] (wt.%)	T_{TSSD} (K)	[H] (mg/kg)
As-received	27	491.8	27	Aged at 673 K for 24 h	57	492.3	24	Aged at 673 K for 400 h	76	521.0	32
	27	509.0	38		57	547.4	52		76	551.6	50
	27	521.6	44		57	502.4	26		76	513.8	24
	27	471.5	28		57	477.2	17		76	506.9	25
	27	464.1	26		57	479.3	18		76	545.6	48
	27	487.4	24		57	506.3	27		76	535.6	42
	27	509.8	36		57	508.2	29		76	513.7	28
	27	469.3	19		57	477.8	18		76	506.5	27
	27	554.6	67		57	566.2	69		76	538.6	41
	27	514.9	37		57	527.8	39		76	522.8	31
Aged at 673 K for 1 h	32	491.6	26	Aged at 673 K for 48 h	65	509.9	28	Aged at 723 K for 70 h	80	526.6	34
	32	510.9	36		65	540.4	44		80	546.2	47
	32	486.2	23		65	529.8	38		80	513.4	27
	32	475.5	19		65	510.1	29		80	495.1	20
	32	475.0	20		65	548.5	53		80	550.7	49
	32	484.4	23		65	497.3	23		80	505.6	24
	32	501.0	30		65	521.0	34		80	516.5	29
	32	475.0	19		65	500.9	25		80	512.3	27
	32	553.6	64		65	553.7	56		80	520.1	31
	32	535.6	51		65	503.2	26		80	514.5	27
Aged at 673 K for 2 h	34	491.4	26	Aged at 673 K for 96 h	71	516.3	30	Aged at 773 K for 100 h	94	526.4	33
	34	525.0	43		71	548.7	50		94	540.0	42
	34	509.3	33		71	516.5	31		94	529.3	34
	34	472.8	19		71	494.1	21		94	522.6	31
	34	479.3	21		71	540.4	46		94	527.9	33
	34	487.5	23		71	509.6	27		94	531.5	36
	34	504.2	31		71	520.1	32		94	528.4	34
	34	484.4	22		71	522.4	33		94	522.2	30
	34	561.5	70		71	523.2	33		94	526.8	33
					71	560.1	61		94	538.0	39
Aged at 673 K for 8 h	41	487.6	23								
	41	541.4	51								
	41	488.7	22								
	41	474.3	18								
	41	470.3	16								
	41	493.6	24								
	41	509.8	31								
	41	482.9	21								
	41	562.6	68								

to condition the specimens (i.e. to anneal out any stressed regions due to cutting and also produce fine homogeneously distributed hydrides) to a similar state prior to any subsequent runs, since prior thermal history can affect the results. If the responses of the last two of three runs were similar and the hydride dissolution temperatures were within 1 K, the results were considered acceptable. The instrument was calibrated prior to measurements using melting points of indium (429.76 K), tin (505.04 K) and lead (600.65 K).

Following the DSC measurements, the degree of decomposition of the β-phase of the specimens was established by determining the Nb concentration of the β-phase using X-ray diffraction [15]. The specimens were then analyzed for hydrogen using the hot vacuum extraction mass spectrometry (HVEMS) technique [16].

3. Results and discussion

Three temperatures are identified on a typical DSC heatflow curve involving hydride dissolution in Zr–Nb alloys [11]; namely the peak temperature (PT), the maximum slope temperature (MST) and the completion temperature (CT). It has been shown [11] that the PT represents the hydride dissolution temperature, T_{TSSD}, more closely than the MST or the CT. Therefore, all the TSSD temperatures reported in this work are based on the PT.

The hydrogen solubility limits in 10 sets of coupons with different amounts of β-phase decomposition were examined in the temperature range 460 to 570 K. The results for each sample condition (heat treatment) and the corresponding [Nb] (Nb concentration in the β-Zr phase) for each set are given in Table 1. Initially the best fit to each set of data was determined by a linear regression of log C_H (hydrogen concentration) versus $1/T$ (inverse temperature in K), using the following equation:

$$C_H = C_0 \exp(-Q/RT) \tag{1}$$

where C_H is in mg of H/kg of alloy, T is in K and R is 8.314 J K^{-1} mol^{-1} and where C_0 and Q are the fit parameters. The approximate functional forms of the dependence of C_0 and Q on [Nb] were then determined. The results showed that the functional forms of C_0 and Q are exponential and linear, respectively. Subsequently, all the data were fitted to a surface function with two independent variables T and [Nb]. The best fit resulted in:

$$C_0 = 45\,072 \exp(0.0173 \cdot [\mathrm{Nb}]) \tag{2}$$

and:

$$Q = 29\,653 + 98.01 \cdot [\mathrm{Nb}] \tag{3}$$

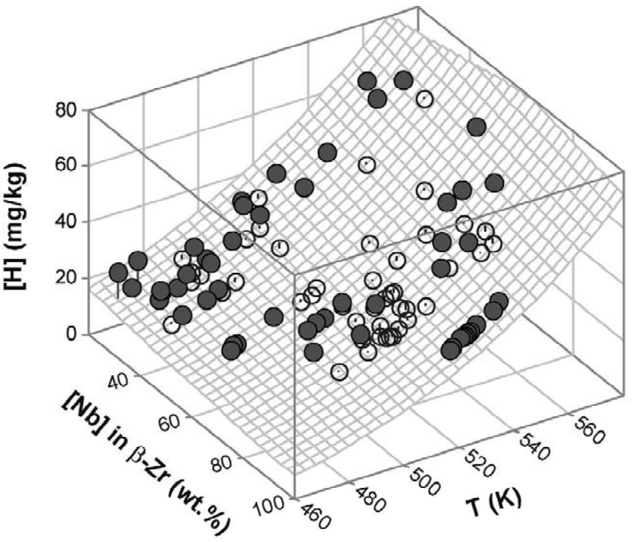

Fig. 1. TSSD for hydrogen in Zr–2.5Nb pressure tube material as a function of T and [Nb] in the β-Zr phase. The mesh surface is the best fit to the data (see Eqs. (1)–(3)). The open and filled circles represent data points below and above the mesh surface, respectively.

where [Nb] is in wt.%. The results of the fit are shown in Fig. 1 (mesh surface). In the figure, the open and filled circles represent data points below and above the mesh, respectively. The figure shows that the fit is very good and, except for two filled circles at the low [Nb] and low [H] corner, all the data points lie in close proximity to the fit surface.

In Figs. 2 and 3 the present results are compared with data obtained earlier [7] using Zr–2.5Nb samples with similar β-Zr phase composition to the present ones, but with different grain morphologies. The earlier samples were annealed at 1123 K for 1 h to regenerate the β-Zr phase prior to aging at 673 or 773 K. Such a heat treatment transforms the microstructure of the sample from one in

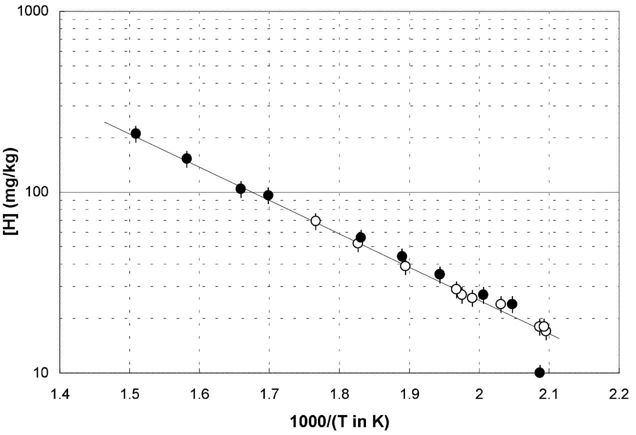

Fig. 2. TSSD for hydrogen in Zr–2.5Nb as-extruded pressure tube material aged at 673 K for 24 h (open circles). The line is obtained using Eqs. (1)–(3) and [Nb] = 57 wt.%. The results are compared with the data obtained by Khatamian [7] (filled circles), using Zr–2.5Nb pressure tube material annealed at 1123 K for 1 h and aged at 673 K for 24 h.

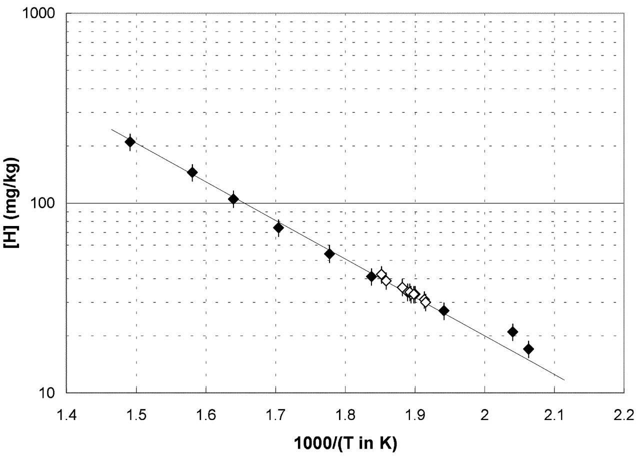

Fig. 3. TSSD for hydrogen in Zr–2.5Nb as-extruded pressure tube material aged at 773 K for 100 h (open diamonds). The line is obtained using Eqs. (1)–(3) and [Nb] = 94 wt.%. The results are compared with the data obtained by Khatamian [7] (filled diamonds), using Zr–2.5Nb pressure tube material annealed at 1123 K for 1 h and aged at 773 K for 1000 h.

which the elongated α-Zr grains are surrounded by a network of β-Zr grains (as a result of extrusion) to an equiaxed structure where β-Zr is recrystallized in isolated zones at triple-points of the α-Zr grains [17]. In the figures the straight lines are drawn using the global fit (Eqs. (1)–(3)) and [Nb] values given in Table 1. Both figures show that the present results are in good agreement with the previous ones. This agreement also indicates that the grain morphology of the alloy has very little effect on TSSD.

Eqs. (1)–(3) are used to create 10 lines in Fig. 4 representing the 10 sets of samples with different amounts of β-Zr decomposition. (In essence, this figure is obtained by intersection of the fit surface with fixed [Nb] planes). In Fig. 4 the results for unalloyed Zr (α-Zr) obtained by Khatamian and Ling [11] and Kearns [2] and for Zr–2.5Nb pressure tube material obtained by Slattery [3] are also presented for comparison. The figure shows that TSSD for hydrogen in the as-extruded pressure tube material (set No. 1) is the highest and that, as the β-Zr phase of the alloy decomposes, TSSD decreases and approaches a limit representing the material with fully decomposed β-Zr (set No. 10). The reason for this variation in the TSSD is that β-Zr has a higher affinity (solubility) for hydrogen than α-Zr [6,7] and traps some of the hydrogen. The dashed line in Fig. 4 is the TSSD line obtained by Slattery [3] for Zr–2.5Nb alloy. This line is closer to the present results for the aged specimens than for the annealed ones, but it has a slightly lower activation energy (lower slope) than the present results. Generally, the agreement is good due to the fact that the specimens used by Slattery were also aged during preparation. Since Slattery's specimens with higher H concentrations were prepared at higher temperatures the level of the β-phase decomposition increased with the hydrogen concentration of the specimens resulting in the lower activation energy for his TSSD line. The TSSD line for the fully aged Zr–2.5Nb, due to complete decomposi-

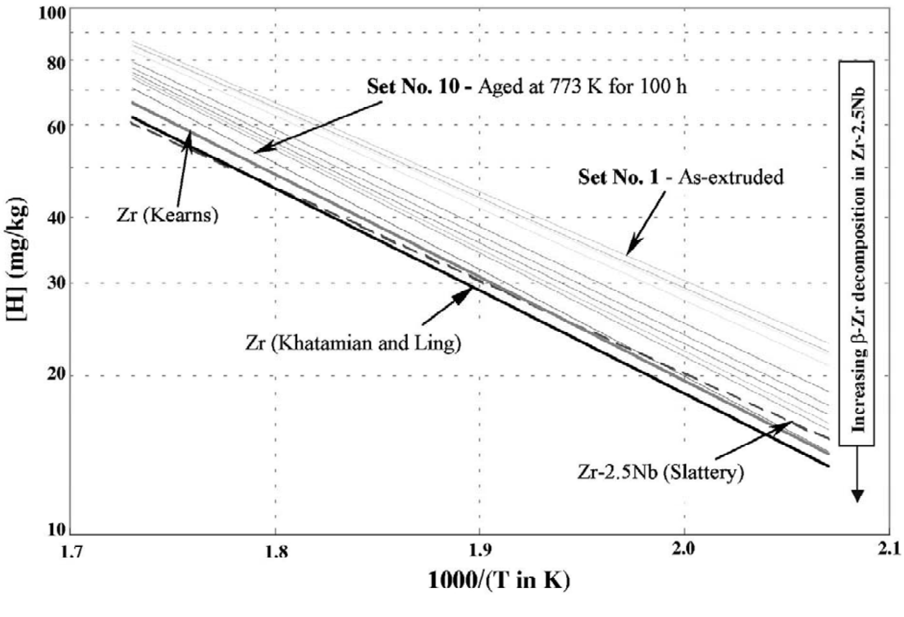

Fig. 4. TSSD lines for hydrogen in Zr–2.5Nb pressure tube material with different amounts of aging. The 10 lines for the 10 sets of samples are obtained using Eqs. (1)–(3) and [Nb] given in Table 1. The lines for unalloyed Zr (α-Zr) obtained by Kearns [2] and Khatamian and Ling [11] and for Zr–2.5Nb obtained by Slattery [3] are shown for comparison.

tion of the β-Zr phase, is very close to the lines for pure Zr (α-Zr) obtained by Khatamian and Ling [11] and Kearns [2] (Fig. 4).

4. Conclusions

The effect of the decomposition of the *meta*-stable β-Zr (Zr–20Nb) on the solubility limit of hydrogen in Zr–2.5Nb pressure tube material has been measured using differential scanning calorimetry, X-ray diffraction and hot vacuum extraction mass spectrometry. It was found that:

1. The solubility limit for hydrogen in the as-extruded pressure tube, with β-Zr phase only very slightly decomposed, is the highest and decreases as the β-Zr phase gradually decomposes as a result of exposure to elevated temperatures.
2. The hydrogen solubility limit in the fully-aged pressure tube material, with fully-decomposed β-Zr phase, is the lowest and is slightly above the values for unalloyed Zr (α-Zr).

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