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Letter to the Editors

Thermal behaviour of hydrogen in Zircaloy corrosion layers

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Abstract

The behaviour of hydrogen present in the oxide scale on corroded Zircaloy was investigated at different temperatures by gravimetry and FTIR spectroscopy. Hydrogen is leaving the oxide beginning slowly at 300 °C. At about 500 °C hydrogen is quickly removed from the oxide scale by cracking OH bonds. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Corrosion and accumulation of hydrides in fuel claddings are the limiting factors in reaching higher burnups and longer irradiation periods in nuclear power plants. The current method to measure the hydrogen concentration in cladding samples is by hot gas extraction of cladding parts including the oxide scale. This method overestimates hydrogen in fuel claddings because part of it is located in the zirconia corrosion layer [1]. Using the temperature–time behaviour of hydrogen evolution from corroded claddings samples a method has been developed which allows (within one fusion step) one to differentiate between the hydrogen fraction in the corrosion layer vs. the amount dissolved or precipitated in the base metal [2]. As a prerequisite the thermal behaviour of hydrogen in zirconium corrosion layers was investigated.

2. Experiment

Stress-relieved Zircaloy-4 tubing samples were autoclave corroded at 340 °C/160 bar in 0.5 M lithiated water to an oxide thickness of 100 μm. One sample was divided into five consecutive ring specimens of 2.5 mm width. By investigating oxide thickness and hydrogen distribution of another sample of the same batch a uniform oxidation was confirmed. Thus, the five ring samples are comparable between each other. After a general treatment of the five samples at 80 °C/1 h to remove moisture each of the ring samples was heated separately in air at different temperatures during different time intervals (Table 1).

3. Results

From the data listed in Table 1 follows, that the hydrogen remaining in the oxide scale after drying is stable with further heating at 80 or 158 °C (samples 1 and 2). At 300 °C (sample 3) a slight weight loss was measured after 2 h heating indicating that hydrogen slowly moves out of the oxide. Sample 4 showed a weight loss of 2 mg/g after 2 h heating at 500 °C and no change with further heating. Obviously after removing the greater part of hydrogen within the first 2 h heating, further hydrogen loss and air oxidation are compensating. At 675 °C air oxidation overcompensates hydrogen loss (sample 5). By extrapolating air oxidation (assuming constant rate) to the start of heating a weight loss of 2.36 mg/g was calculated related to hydrogen (value in parentheses).

Fig. 1 shows the FTIR spectra after heating of samples 2 (the spectra of samples 1 and 2 were completely identical!), 3, 4 and 5. Looking at the FTIR spectra of Fig. 1 the results of Table 1 can be interpreted in more detail. After heating at 80 or 158 °C the inverse peak at 3600 cm^{-1} can be related to the OH stretching

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Table 1
Weight loss of corroded Zircaloy-4 cladding with temperature

Sample	Weight (mg)	Temperature (°C)	Time on temperature (h)	Weight loss (mg/g)
1	1444.6	80	1	–
2	1435.7	158	4	–
			7	–
3	1442.3	300	2	0.97
			3.75	0.90
			6	0.83
4	1355.8	500	2	2.0
			3	2.0
			5.5	2.0
5	1409.3	675	1.5	1.21 (2.36)
			12	−9.22[a]

[a] Negative weight loss means weight gain!

mode [3]. Obviously OH bonds are mainly responsible for the presence of hydrogen in the zirconia scale on Zircaloy [3]. After 6 h heating at 300 °C (sample 3) the peak is still present with some diminished depth according to the measured small weight loss (Table 1). In the spectrum of sample 4 heated 5.5 h at 500 °C only a small inverse peak indication is left at 3600 cm^{-1} in accordance with the greater weight loss. Finally, the OH indication at 3600 cm^{-1} is completely absent in the FTIR spectrum of sample 5 heated at 675 °C. This finding is in agreement with the fractionated hydrogen determination in corroded fuel cladding samples where hydrogen in the oxide evolved out of the sample at about 500 °C and was detected as single peak besides the main hydrogen peak originated from the base metal [2,4]. The additional inverse peak appearing at about 1600 cm^{-1} after heating at 300 °C and higher temperatures cannot be explained with certainty at this time, but it is known that a peak at that wave number appears in zirconium alloy samples corroded in lithiated water [5]. It is explained by absorption of CO_2 from the air and related to the C–O bond and, apparently, this reaction is stronger at higher temperatures.

It is assumed that the OH bonds are cracked to H_2O and pure oxide and that hydrogen leaves the oxide scale as H_2O. Hydrogen determinations on samples 1, 3 and 4 by the current method (see above) revealed a loss of hydrogen of (118 ± 36) wt ppm (sample 3) and (137 ± 42) wt ppm (sample 4), respectively. These values correspond to a weight loss of about 1.06 mg/g and 1.23 mg/g (as H_2O, calculated based on the above outlined interpretation) and have to be compared to 0.97 and 2.0 mg/g, respectively, found by gravimetry (see Table 1). It should be noted that the presented data do not exclude a second hydrogen species present within the oxide [6].

From the outlined results we can conclude, that hydrogen is leaving the water corrosion oxide scale on Zircaloy beginning slowly at 300 °C. At a temperature of

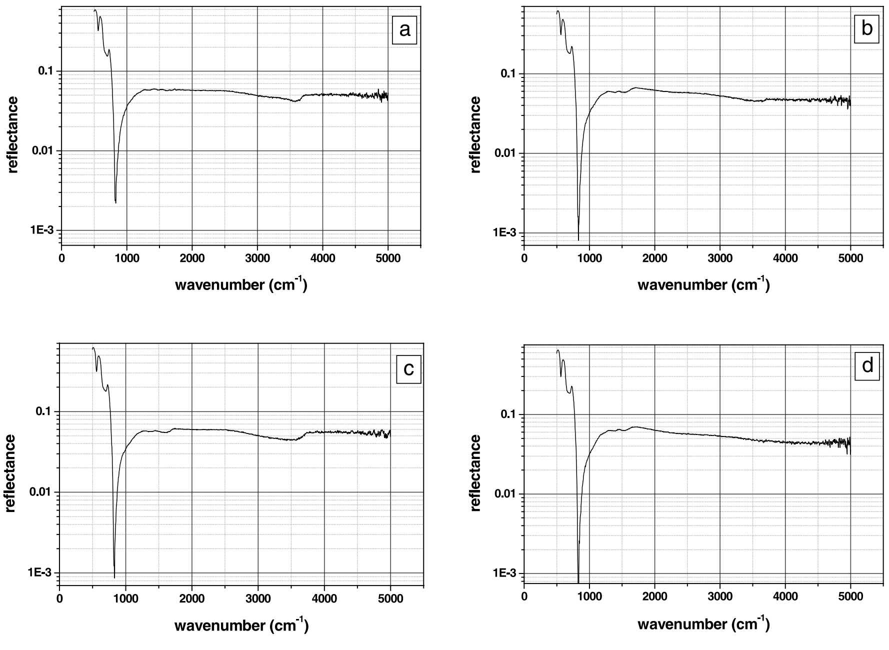

Fig. 1. Infrared reflection spectra after heating of samples 2 (a), 3 (b), 4 (c) and 5 (d).

about 500 °C and higher hydrogen is quickly removed from the oxide scale by cracking OH bonds.

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