

## The Effect of Heating Zirconium Hydrides Studied by Electron Energy Loss Spectroscopy

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Zirconium alloys are used as nuclear materials, especially as fuel cladding, for most Light water reactors as well as CANDU's. One of the "in-service" degradation phenomena for these materials is oxidation and hydrogen ingress into the base metal. The latter will cause hydride precipitation and thus embrittlement of fuel cladding. Because of this an interest in the properties and characteristics of Zirconium hydride exists in the research community. The interest in the role of temperature and its variations on the cladding and the hydrides within has been driven by the need to better understand the long term behaviour of the cladding in service, as well as the impact of hydrides, during the Loss of Coolant Accidents. Furthermore, the fuel rod transport, intermediate storage and long term storage are of importance.

In this study, in order to examine the behaviour of a reference hydride, as a function of temperature, in situ heating has been carried out in a JEOL2200 FEG-TEM, using a heating stage from "DENSsolution" the so called "Wildfire". EELS spectra are obtained in the low loss region, using the plasmon peaks of the material as a fingerprint. In previous studies, Woo and Carpenter (1992) [1] have used the low loss region of EELS spectra to identify and characterise Zirconium hydrides. Three hydride phases were identified (as listed in Table 1). Zhao et al. (2008) [2] identified a new fourth hydride structure ( $\zeta$ -hydride) (Table 1). These data are used for comparison to evaluate the type of hydride present at different temperatures.

Two samples have been studied; one sample was heated, only for one cycle and the other for two cycles. First sample ramped up from room temperature to 1000°C in 30 minutes, and EELS spectrum acquired at that temperature. Another sample has been heated once to 1100°C, then once more to 700°C, and then held for approximately 45 minutes before being allowed to cool back to room temperature. EELS low loss spectra were acquired in the second cycle throughout the heating and also once the sample had returned to room temperature. Knowing the characteristic peaks, the aim of this study was to determine the shifts brought to the peaks' positions by heating the sample. The spectra will also be compared with other zirconium hydrides from standards and post reactor irradiated cladding.

Figure 1(a,b) shows four of the spectra mentioned above. Whilst the form of the spectra is very similar for all, before and after each heating ramp a definite shift is observed. The analysis of the peak positions shows a gradual shift towards lower energies (Table 1). This work gives suggestions of the reasons for observed peak shifts. Studies performed on partially and/or fully oxidised Zirconium found values between 13.5 eV and 14.4 eV [3] and most attribute it to the bulk plasmon loss peak. Similar experiments which involve heating zirconium hydrides in a vacuum [4], [5] have seen hydrogen beginning to desorb between 425°C and 500°C depending on experimental conditions but have not witnessed any oxidation. In this study, as the temperature has been higher than the above mentioned studies, and seemingly longer dwell times have been applied, a possible oxidation in the case of the second cycling can be assumed. Work is in progress, to further explore this aspect of the results. Results till present indicate a first hydrogen desorption followed by a subsequent oxidation.

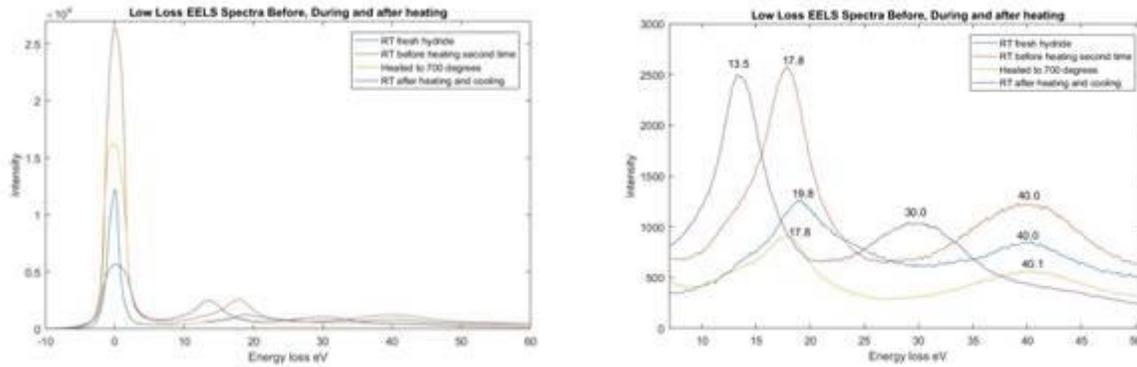


Figure 1a. Low loss EELS spectra showing the fresh hydride, after heating the first time, held at 700 degrees during the second ramp and after heating and cooling. Figure 1b. Plasmon peaks from Low loss EELS spectra showing the fresh hydride, after heating the first time, held at 700 degrees during the second ramp and after heating and cooling. Peak positions are noted on figure.

State of sample	1 <sup>st</sup> peak	2 <sup>nd</sup> peak	3 <sup>rd</sup> peak
Fresh hydride	19.8	-	40.0
Heated once to 1000°C	19.7	-	39.8
RT after first cycle	17.8	-	40.0
Heated 2 <sup>nd</sup> time to 700°C	17.8	-	40.1
RT after 2 <sup>nd</sup> cycle	13.5	30.0	-
Epsilon $\epsilon - ZrH_{1.7-2}$ [1]	19.6 ( $\pm 0.2$ eV)	-	$\approx 40^*$
Delta $\delta - ZrH_{1.5-1.66}$ [1]	19.2 ( $\pm 0.2$ eV)	-	$\approx 40^*$
Gamma $\gamma - ZrH$ [1]	18.3 ( $\pm 0.2$ eV)	-	$\approx 40^*$
Zeta $\zeta - ZrH_{0.25-0.5}$ [2]	17.4 ( $\pm 0.2$ eV)	-	$\approx 40^*$
ZrO2 mono [3]	14.4	25.8	41.2
ZrO2 tetra [3]	14.4	25.4	42.3
Zirconium matrix $\alpha - Zr$ [1]	16.8 ( $\pm 0.2$ eV)	-	$\approx 40^*$

Table 1: Summary of the peak positions for the different heated samples and the different hydrides and oxides as reference. \*Although the exact value peak position is not stated spectra shown indicate presence of such peak.

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