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Site specific dependencies of hydrogen concentrations in zirconium hydrides

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ABSTRACT

Zircaloy-4 specimens were H-charged up to 1230 wppmH. Intra-, inter- and trans-granular zirconium hydride precipitates (or ZrH_{2-x} where 1/(2 - x) is the Zr/H molar ratio) were observed throughout the α -Zr matrix. Transmission Electron Microscopy and electron diffraction confirmed that the ZrH_{2-x} precipitates were face-centred cubic structures consistent with the δ - ZrH_{2-x} phase. Electron Energy Loss Spectroscopy analysis of the δ - ZrH_{2-x} precipitates at three different nucleation spots displayed shifts in the plasmon energy loss peaks that can be attributed to local variations of the H content of the δ - ZrH_{2-x} precipitates rather than the presence of different ZrH_{2-x} phases as has previously been assumed.

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Zirconium alloys can be described as the principal nuclear fuel cladding materials for Light-Water Reactors (LWRs) because of their low thermal neutron absorption cross-section, acceptable mechanical and thermal properties with good corrosion resistance under the normal operational conditions of LWRs [1-3]. During LWR operation, Zr has a high susceptibility to incorporate H due to oxidation reactions with the primary coolant [4]. When the H concentration exceeds the solubility limit for the hexagonal close-packed phase (α -Zr), radial and circumferential hydrides (ZrH_{2-x}) are prone to form in the microstructure [5,6].

The nucleation and growth of ZrH_{2-x} phases impact the fuel cladding performance by means of two interconnected effects [7,8]: (i) the deterioration of mechanical properties (embrittlement), and (ii) crack growth via Delayed Hydride Cracking (DHC) which occurs preferentially at high stress regions such as a grain boundary or crack tip. Both mechanisms have been responsible for several observed failures of nuclear reactor components throughout the history of nuclear engineering. Major implications also lie in the logistics of Spent Nuclear Fuel (SNF) transportation, where high mechanical stresses posed by moving and transporting the embrittled Zr cladding may initiate cracks resulting in fractures and subsequent release of fission gases and radioactive material to the environment.

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https://doi.org/10.1016/j.scriptamat.2018.08.044 1359-6462/© 2018 Elsevier Ltd. All rights reserved. Understanding the physicochemical nature of ZrH_{2-x} is of paramount importance for nuclear engineering [9-12].

The relationships between ZrH_{2-x} and the α -Zr matrix are of high interest, but owing to the high systematic complexity that arises from the H association with Zr, many areas are still not completely understood [4,13]. The face-centred cubic (FCC) hydride (δ -ZrH_{2-x}) is considered to be stable at room temperature and is often reported in literature to be the most commonly observed phase [13]. δ -ZrH_{2-x} forms under slow cooling, with H equilibrium concentrations around $1.5 < H_{\gamma} \le 1.9$ and temperatures in the range of 273 to 1173 K. Within the alloy microstructure, ZrH_{2-x} are generally found to be attached to α -Zr grain boundaries in the form of needle- or plateletlike precipitates [14]. Additional phases were also reported for the Zr-H binary system. A face-centred tetragonal (FCT) phase, γ -ZrH_{2-x} with c/a > 1, is metastable under thermal cycling and nucleates under faster cooling rates and via shearing of the hexagonal parent phase at lower H concentration levels than the δ -ZrH_{2-x} phase [19]. For higher concentration levels $(1.71 < H_y \le 2)$, there is another FCT phase, ϵ -ZrH_{2-x} with c/a <1. To date, for all reported ZrH_{2-x} phases, the physical and thermodynamic conditions behind their formation as well as their characterisation are still subject to further investigation, despite considerable research effort [11,15-19].

Conventional and Synchrotron X-ray diffraction (XRD) have been used to characterise ZrH_{2-x} precipitates, their crystal structure, and to identify the various phases present [20-22]. XRD studies in combination with Electron BackScatter Diffraction (EBSD) have been used to investigate the orientation relationship of ZrH_{2-x} and the matrix,







the influence of the α -Zr matrix on the nucleation and growth, fracture mechanisms, and to extract information on mechanical behaviour [21]. Electron Energy Loss Spectroscopy (EELS) is a well-established technique for the use in fingerprinting of materials, e.g. [23], and efforts have been made to probe the crystal structures of ZrH_{2-x} by means of analysing the low-loss energy regime of the EELS spectrum; in particular, the shifts in the plasmon frequency that occur due to the H association with Zr [15,24]. However, no definitive study which validates EELS measurements with a detailed microstructural investigation using conventional transmission electron microscopy (TEM) exists.

Here, H-charged Zircaloy-4 samples have been characterized using conventional TEM methods, combined with EELS. In particular, focus was made to the electron energy loss energy range from 10-50 eV – the plasmon peak range – to investigate local valence electron density variations of ZrH_{2-x} precipitates located at different precipitate nucleation regions within the α -Zr microstructure.

Tensile specimens of Zircalov-4 (initial bulk composition given in Table 1) were H-charged using a gas-solid reaction. Titanium hydride (TiH₂, Alfa-Aesar 99.9% pure) was heated to 773 K and the evolved H₂ reacted with the Zr specimens. The specimens were cooled to 700 K at a rate of 20 K/h and were held at this temperature for 30 min to avoid H desorption. Samples were then furnace-cooled to room temperature. LECO combustion analysis indicated that the bulk hydrogen concentration was approximately 1230 wppmH and recent XRD measurements with Reitveld refinement revealed the presence of δ -ZrH_{2-x} precipitates in an α -Zr matrix [25]. TEM samples were produced using the conventional focused ion beam (FIB) lift-out technique [26]. Thin foils were analysed using a JEOL 2100F transmission electron microscope (with Schottky Field Emission Gun) operating at 200 keV. The TEM is equipped with a 11 MPx Orius CCD for imaging, and a Gatan 963 GIF Quantum Electron Energy Loss Spectrometer. At 200 keV, the EELS resolution - measured at the full width at half maximum (FWHM) of the zero-loss peak (ZLP) - was in the range of 1.1 to 1.3 eV using a 5 mm aperture. Crystallographic indexing of the selected area electron diffraction (SAED) patterns was performed by matching calculated diffraction patterns using the CrystalMaker software and crystal structure data available in the scientific literature [27,28] to the experimentally obtained SAED patterns.

Bright-Field TEM (BFTEM) micrographs revealed elongated ZrH_{2-x} precipitates – consistent with needle- and platelet-like shaped precipitates - distributed throughout the matrix, yet associated with different microstructural features throughout the α -Zr matrix. Examples of trans-, inter-, and intra-granular hydrides are shown in Fig. 1. Associated SAED patterns for both the α -Zr and ZrH_{2-x} precipitates are shown inset of the individual micrographs shown in Fig. 1. The circles indicate the approximate locations from where the SAED patterns and EELS spectra were recorded. The experimental diffraction patterns for all precipitates analysed were indexed to be face-centred cubic consistent with the δ -ZrH_{2-x} phase, in agreement with the previous XRD analysis of the same material [25] and also consistent with the fact that δ -ZrH_{2-x} phase is favoured to form in Zr alloys (and similarly in Ti alloys) when both H and O (>1000 ppm) concentrations are high [19]. Due to the precipitates all having the same crystal structure and direction, and the surrounding matrix being equivalent, the orientation between relationship precipitate and matrix are approximately the same in each case, allowing for direct comparisons to be made. For each δ -ZrH_{2-x}

(a) 242. 220 0 0110 0 022 1111/2rH 100 132. 100 232 200 nm 242. 220 110 0 232 101/2rH 120 111 0 022 1111/2rH 120 111 0 022 1111/2rH 120 011 0 022 1111/2rH 110 022 1111/2rH 110 022 1111/2rH 110 022 1111/2rH 110 022 1111/2rH

Fig. 1. BFTEM micrographs of the δ -ZrH_(2-x) observed in the α -Zr matrix at (a) trans-, (b) inter- and (c) intra-granular positions. Inset of each micrograph are SAED patterns recorded from the precipitate (ZrH) and the matrix (HCP).

analysed, three sets of ten spectra were acquired from different points along the length of the precipitate. Additionally, matrix spectra were taken from locations close to the hydride precipitate for reference.

The results of the average low-loss EELS spectra obtained from the matrix and the three different δ -ZrH_{2-x} at the locations shown in the micrographs shown in Fig. 1 are presented in Fig. 2. A Fourierlog deconvolution was applied to all spectra to remove the multiple inelastic scattering [29]. All the δ -ZrH_{2-x} EELS spectra were recorded at the [111] FCC zone axis. The plasmon peaks have clearly shifted towards higher energy losses when the δ -ZrH_{2-x} were analysed at the different nucleation spots within the α -Zr matrix.

Plasmon resonances can be used to interpret the plasmon energy shifts observed in the EELS measurements of the δ -ZrH_{2-x}. Electrons of a material can be excited by the incident electron beam through momentum transfer which induced collective electronic oscillations that, at the quantum level, can be described as quasi-particles known

Zircaloy-4 elemental composition as-received (weight percent, wt.%).

Table 1

Zr	Sn	Fe	Cr	FeCr	0	Н	Major impurities
Balance	1.55	0.22	0.12	0.34	0.14	4 wppm	Ta, C and Si ($\approx 100wppm)$

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