



Regular article

The association of hydrogen with nanometre bubbles of helium implanted into zirconium



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ABSTRACT

Electron energy-loss spectroscopy (EELS) is used to investigate the association of hydrogen with helium bubbles in zirconium. Conventional EELS data yield a signal at 13.5 eV (similar to the hydrogen K-edge, 13 eV), which is spatially distributed around the peripheries of bubbles and may correlate with the concentration of hydrogen/deuterium in the material. Ultra-high energy resolution EELS yields a signal at 148.6 meV (comparable to a range of Zr–H bonds, 130–156 meV) from a region containing bubbles and no visible hydrides. These signals are interpreted in the context of either bubble surface chemisorption or bubble stress field trapping mechanisms.

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As an impurity, hydrogen can play a significant role in the degradation and embrittlement of structural metals [1], including steels [2], aluminium [3], titanium [4] and zirconium [5]. Understanding the location and nature of hydrogen in zirconium alloys is important because hydrogen absorbed during aqueous corrosion can lead to property degradation [6] and delayed hydride cracking [7]. Techniques like hot vacuum extraction [8] provide bulk hydrogen measurements, whilst Raman [9], secondary ion-mass [10,11], laser induced plasma spectroscopies [12] and X-ray diffraction [13–15] have sub-micron to millimetre resolutions and can detect hydrogen (or hydrides). However, the majority of potential traps for hydrogen in zirconium are smaller than the resolutions afforded by these techniques and detecting hydrogen on nanometre scales is immensely challenging.

This study addresses this issue by examining the association of hydrogen with nanometre-scale helium bubbles in a zirconium alloy matrix. Literature on iron/steel, aluminium, iron, nickel, copper, molybdenum, palladium and tantalum systems [16–20] suggests that hydrogen can be bound at, or close to, helium bubble surfaces. In those

cases, this trapping is thought to occur either through chemisorption [18] or as a product of the stress fields surrounding bubbles [16,21], but no equivalent studies have been performed on zirconium alloys. Aside from bubbles, there are many other potential microstructural traps for hydrogen including vacancies [22], dislocations [23], substitutional species [24] and irradiation-induced matrix defects [25,26], but these are not considered in this paper.

In this work, the association of hydrogen with helium bubbles is explored using Electron Energy-Loss Spectroscopy (EELS). This technique has been successfully used to identify ~50–100 nm diameter hydrogen bubbles formed in biological samples under electron irradiation [27]. Their hydrogen content was confirmed from spectral evidence of the hydrogen K-shell ionisation edge. In inorganic matter, similar evidence for the K-edge has been reported for nano-bubbles both of hydrogen in focused ion beam treated diamond [28] and bubbles in silicon carbide irradiated with H_2^+ and He^+ ions [29]. In both cases, the K-edge signal was taken to indicate the presence of molecular hydrogen.

Recent advances in ultra-high resolution EELS in a new generation of monochromated scanning transmission electron microscopes have enabled vibrational spectroscopy to be performed with nanometre spatial resolutions [30]. As the lightest element, hydrogen yields vibrational peaks of the highest energy, theoretically making it the element most

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easily detectable using vibrational spectroscopy [31]. However, the spatial resolution of the technique is limited by the delocalised nature of the vibrational features, in that the signal contains a component that is apparent nanometres away from the source [31]. Nonetheless, this technique has been used to detect signals arising from the binding of hydrogen in both titanium hydride and epoxy resin [32].

Zircaloy-4 was studied in 'as-received' and 'deuterium charged' states (charging conditions: 0.1 M KOH and D_2O , 0.1 A·cm⁻², 24 h, 20–40 °C). These contained ~10 wt.ppm(H) or ~10 wt.ppm(H) plus ~120 wt.ppm(D), respectively. Approximately 10 wt.ppm(H) is intrinsic to manufacturing of Zircaloy-4 and was measured using Hot Vacuum Extraction (HVE). ~120 wt.ppm(D) was calculated from weight gain measurements after cathodic charging. Discs with electron transparent regions were prepared by mechanical punching, grinding and electropolishing (5% perchloric acid in methanol, -40 to -60 °C). Electropolishing introduces a small further quantity of hydrogen, which cannot be quantified using HVE because of the low material volume. Henceforth, the two sample conditions are termed 'Low H/D' and 'High H/D', as production of a hydrogen-free sample was unrealistic.

The discs were implanted with 10 keV He⁺ ions using the Microscope and Ion Accelerator for Materials Investigations (MIAMI) facility [33]. A beam current of 0.06–0.10 nA (flux of $\sim 2.75 \times 10^{14}$ to 5×10^{14} ions·cm⁻²·s⁻¹) achieved 300 nC (fluence of 1.5×10^{18} ions·cm⁻²). Bubbles were typically \varnothing 1–7 nm, although some bubbles approaching \varnothing 10 nm were observed. SRIM [34] calculations indicated helium implantation throughout the thickness of the regions considered suitable for EELS data acquisition. Sample temperatures were maintained at 300 °C during implantations, dissolving ~56 wt.ppm of H/D [35] and providing sufficient diffusion mobility for interaction with the forming bubbles.

Samples studied using conventional EELS were first oxygen plasma cleaned. A JEOL ARM-200CF TEM with a Gatan Quantum 965ER electron energy-loss spectrometer was utilised at The University of Glasgow. The instrument was operated at 200 kV and had a Zero-Loss Peak (ZLP) Full-Width at Half-Maximum (FWHM) of ~0.5 eV. The convergence and collection semi-angles were 29 and 36 mrad, respectively.

The High H/D material was studied using Ultra-High-Resolution (UHR) EELS and vibrational spectroscopy, using the Nion UltraSTEM 100 MC 'Hermes' at the SuperSTEM Laboratory [36]. The microscope was operated at 60 kV and had a ZLP FWHM of 0.3 eV, which was improved to 0.02 eV, following monochromation. The convergence and collection semi-angles were 31 and 44 mrad, respectively. Some data were collected using an aloof beam, where delocalised vibrational modes were detected using a beam passing through the vacuum in close proximity to a sample. This effectively removes the spectral background associated with the beam passing through material, thus improving the signal-to-noise ratio.

Analyses were performed using Gatan Digital Micrograph (with additional functionality provided by the EELSTools plugin [37]) and MathWorks Matlab. Zero-loss peak misalignment was calibrated in all data and pixel-to-pixel energy drift (arising from instability in the beam) was corrected for, where necessary. The Principal Component Analysis feature of the Multivariate Statistical Analysis tool [38] was used to remove random noise from conventional EELS data; this tool could not be successfully applied to the UHR EELS data.

Spectral deconvolution analyses were performed using the spectral difference method [39]. This involved subtracting a matrix spectrum from a bubbles spectrum (after scaling to account for thickness differences), yielding the spectral difference. A scaling window of ~45–50 eV was used, encompassing the high energy shoulder of the Zr N_{2,3} edge. Components were identified from the difference spectra, which could be mapped by applying energy-selected windows to the spectrum images. Vibrational modes were extracted from UHR EELS data by subtracting a background function (the sum of two power laws) from the zero-loss peak, yielding difference spectra.

Implanted bubbles are visible as approximately circular regions of darker contrast in Fig. 1a, indicating a reduced material density. Sparse hydrides were also observed at room temperature in the implanted regions (Fig. 1), indicating that for both hydrogen concentrations the bubbles did not suppress hydride formation. The presence of hydrides does not preclude the association of hydrogen with bubbles, as the region of implantation in each electropolished disc is very small, so it would not be sufficient in size to influence the hydrogen concentration in the non-implanted bulk significantly. Consequently, were the bubbles to 'trap' hydrogen at the 300 °C implantation temperature, Fickian diffusion from the non-implanted bulk would ensure the equilibrium solute hydrogen concentration was maintained in the matrix interstices in the implanted region. Upon post-implantation cooling, the non-trapped interstitial hydrogen would then form hydrides in the implanted region as the solubility limit decreased with temperature.

EELS data characteristic of the matrix and bubbles are presented in Fig. 2. The two most prominent signals are the zirconium bulk plasmon oscillation (maximum at 16.6 eV) and the zirconium N_{2,3} shell ionisation edge (reported onset of 29 eV [40], with a delayed maximum observed at 41 eV in the present data). Subtraction of the matrix spectrum from corresponding bubble spectrum yields spectral differences that clearly include the helium K-shell ionisation edge. This feature has a sharp onset reported at 22 eV [41], with an experimentally observed maximum at 23.4 eV, followed by a gradually diminishing tail.

Another signal is apparent to the left of the zirconium bulk plasmon in the spectral difference. This feature is broad, of comparable magnitude to the helium K-edge, has an apparent maximum at 13.5 eV, but appears to be a delayed edge that has an onset around 6 eV. The position of this signal is close to that reported for the hydrogen K-shell ionisation edge (13 eV [42]), but the morphology of this feature differs from that reported elsewhere [28,42]. This may indicate that it arises from, or is superposed upon, signals from another source.

With observed energy ranges for the known helium and possible hydrogen K-shell ionisation edge signals, it becomes possible to map spatially the intensity of these signatures by applying energy-selected windows to the spectrum images. The maps for these energy ranges are given in Fig. 3 for the High H/D and Low H/D samples.

As seen clearly for the High H/D sample (upper in Fig. 3), the feature at 13.5 eV is spatially distributed as rings of intensity around the peripheries of bubbles and will henceforth be referred to as 'halos'. Interestingly, those bubbles mapped from the High H/D sample (upper in Fig. 3) generally appear to possess a stronger halo than those of comparable sizes in the Low H/D sample (lower Fig. 3). This is unlikely to be an artefact of mapping or imaging parameters (such as magnification and resolution), since the pixel sizes are comparable between the maps (0.36 × 0.36 nm for High H/D versus 0.40 × 0.40 nm for Low H/D), as are the foil thicknesses (inelastic mean free path range of 0.36–0.66 for High H/D versus 0.42–0.59 for Low H/D). This observation holds true for other datasets not presented here, suggesting that there may be a correlation between hydrogen concentration and halo intensity. However, the present collection of datasets is not sufficiently large to state a robust correlation between hydrogen/deuterium concentration and halo intensity.

If not originating from hydrogen, the observed halos could be cavity (if gaseous bubbles) or interface (if solid bubbles) plasmon oscillations arising from matrix-bubble interfaces [43,44]. David et al. attributed the observation of 12.3–13.3 eV halos around helium nano-bubbles in silicon to originating from cavity plasmon oscillations [45]. However, it is difficult to produce silicon specimens devoid of hydrogen, so those halos observed by David et al. may actually be characteristic of hydrogen associated with the bubbles. Indeed, a later publication by those authors [46] shows a "burst" bubble (containing no helium) that does not have an associated halo. As a burst bubble would still be expected to yield a surface plasmon, its absence suggests that it originates from hydrogen. Although the work of Heyward et al. [20]

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