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Atomic scale analysis of grain boundary deuteride growth front in Zircaloy-4

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ABSTRACT

Zircaloy-4 (Zr-1.5%Sn-0.2%Fe-0.1%Cr wt%) was electrochemically charged with deuterium to create deuterides and subsequently analysed with atom probe tomography and scanning transmission electron microscopy to understand zirconium hydride formation and embrittlement. At the interface between the hexagonal close packed (HCP) α-Zr matrix and a face centred cubic (FCC) δ deuteride ($ZrD_{1.5–1.65}$), a HCP ζ phase deuteride ($ZrD_{0.25–0.5}$) has been observed. Furthermore, Sn is rejected from the deuterides and segregates to the deuteride/α-Zr reaction front.

Zircaloy-4 is primarily used as a fuel cladding material in water based nuclear reactors due to its low neutron absorption cross section, good mechanical properties and corrosion resistance. However, the alloy is susceptible to hydrogen embrittlement (HE) through a mechanism known as delayed hydride cracking (DHC) or hydrogen-induced delayed cracking (HIDC) [1, 2]. Hydrogen ingress occurs during service due to exposure with the water coolant. Zirconium has a relatively high oxidation potential and will readily form a ZrO_2 layer when in contact with water – through this process, hydrogen is released, some of which is absorbed into the underlying alloy [3]. The terminal solid solubility (TSS) of hydrogen in α-Zr is low, <10 wt ppm at room temperature and ambient pressure [4], and so there is a high driving force for excess hydrogen to precipitate as a brittle solid zirconium hydride. The severity of the embrittlement is dependent on several factors, for instance, an increase in the volume fraction and size of the hydrides and a decrease in the strain rate are known to be more deleterious [2, 5, 6]. The orientation of hydride platelets also has a significant influence on toughness, with those perpendicular to the tensile-axis being more deleterious [7]. The atomic structure and interfacial chemistry are also expected to play a critical role. In particular it is interesting to note that Northwood and Gilbert [8] report that during DHC, crack initiation occurs within the hydride itself and not at the hydride/α-Zr interface. It therefore follows that knowledge of the internal structure and chemistry is of utmost importance to elucidating the mechanisms of DHC.

However, despite many decades of research on hydrogen interaction in zirconium alloys, including Zircaloy-4, there is still a lack of atomic-scale structural and compositional characterisation of the hydrides including the growth front, which is a focus in this letter. Significant uncertainty also exists in the thermodynamics of the Zr-H system and variation in the proposed phase diagrams is evident, particularly below the eutectic temperature of 550 °C [3, 9, 10]. Currently, four different zirconium hydride phases have been reported. In terms of crystal structure and approximate stoichiometry ZrH_x, these are referred to as hexagonal close packed (HCP) ζ ($x = 0.25–0.5$), face-centred tetragonal (FCT) γ ($x = 1$), face-centred cubic (FCC) δ ($x \approx 1.5–1.65$) and FCT ε ($x \approx 1.75–2$) [11–13]. ζ is fully coherent with the α-Zr matrix with a c-axis twice as long, and may play a critical role as the intermediate phase in the dissolution and precipitation processes of the more stable δ-hydride [14, 15]. The ambiguity in identifying the various hydride phases, particularly ζ, has been brought about, in part, by the much lower diffraction intensities of the hydride relative to the α-Zr matrix [14]. However, with the advent of aberration corrected transmission electron microscopy (TEM), greater clarity of atomic structure is now possible [16].

Atom probe tomography (APT) is another powerful microanalytical technique that offers a unique opportunity to reconstruct the three-dimensional position and elemental identity of atoms from a material specimen with sub-nm spatial resolution [17]. The technique has already been used to observe solute segregation, including H, at grain boundaries and the metal/oxide interface in zirconium alloys [18–22] but has had limited application to the study of zirconium hydrides

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directly. This is likely partially due to the technical challenges involved in identifying and quantifying hydrogen using APT. Background H from the analysis chamber, typically in the range of 0.5–5 at.% [23], is routinely observed in the mass spectra. Ambiguity arises in determining which hydrogen atoms are from the chamber or the sample being analysed. Yet, recently, Chang et al. [24], reported on successfully using APT to characterise hydrides in the thermodynamically similar system of Ti-H – here we demonstrate that it can also be used to gain insights into the Zr-H system as well. A way to mitigate the challenges associated to H-quantification, as employed in this study, is to charge the material with the isotope deuterium (D or ^{2}H), to minimise overlap with the background hydrogen peaks [23, 25–27]. As a consequence, H analysis in atom probe is starting to emerge as a promising means of directly observing hydrogen in metals. Coupled with aberration corrected TEM as well as electron channelling contrast imaging (ECCI) [28] and electron back-scattered diffraction (EBSD) in the scanning electron microscope (SEM) – a multiscale approach to zirconium hydride analysis is presented herein.

Commercial Zircaloy-4 (Zr-1.5%Sn-0.2%Fe-0.1%Cr wt%) was received as a rolled and recrystallized plate with a typical split basal texture and average grain size of ~11 μm. The sample was then heat treated at 800 °C for two weeks to form large 'blocky-alpha' grains >200 μm similar to that recently reported by Tong and Britton [29]. The sample was then electrochemically charged with deuterium (galvanostatic charging, current density = 2 kA/m^2) using a solution of 1.5 wt% D_2SO_4 in D_2O at 65 °C for 24 h. After this process, a hydride layer of approximately 20 μm thickness formed at the surface. Annealing at 400 °C for 5 h followed by furnace cooling of 0.5 °C/min was then used to redistribute the D from the surface into the bulk of the sample. The microstructure was then inspected using polarised light microscopy and a Zeiss Merlin scanning electron microscope (SEM).

Fig. 1 provides an overview of the microstructure after D charging and annealing. Fig. 1 a is a polarised light-optical micrograph showing the different types of deuterides that have evolved. The grain boundary deuterides are the most common and the focus of further characterisation. Fig. 1 b is an ECCI image of a deuteride at higher magnification. Here, contrast changes are observed within the hydride and suggest a high dislocation density and internal strain as well as possible phase separation. The complex nature of the contrast in ECCI does not allow for directly assessing the size and nature of the various phases, but what seems like a single deuteride appears to be complex in nature and will be hereafter referred to as a deuteride packet. Fig. 1 c is an EBSD IPF map of the same region, the deuteride is indexed as δ and follows the $\{0001\}_\alpha \parallel \{111\}_\delta$, $\langle 11{-}20\rangle_\alpha \parallel \langle 110\rangle_\delta$ orientation relationship with the bottom matrix grain. This is in agreement with previous reports [14, 30]. Fig. 1 d is a misorientation to grain average orientation map which suggests an orientation gradient within the deuteride packet that is associated with a high dislocation density and internal strain. This deuteride packet also likely contains other hydrides, e.g. ζ, as well as metallic inclusions, but with respective volume fractions that do not allow for direct imaging at this scale, hence TEM was pursued.

An overview of the TEM results is shown in Fig. 2. A TEM specimen was hence prepared from within the same grain boundary deuteride packet using a FEI Helios 600i dual-beam scanning electron microscope/focused-ion beam (SEM/FIB). The FIB was used to lift out a section of the grain boundary deuteride, as indicated in Fig. 2 a, and was subsequently thinned until it was electron transparent. Scanning transmission electron microscopy (STEM) imaging was conducted in an aberration-corrected STEM/TEM (FEI Titan Themis) at 300 kV. For high-resolution high-angle annular dark field image (HAADF) imaging, a probe semi-convergence angle of 17 mrad and inner and outer semi-collection angles ranging from 73 to 200 mrad were chosen. Fig. 2 b is a high-angle annular dark field image (HAADF) of the grain boundary deuteride growth front from this sample. Within the α-Zr grain, 100–200 nm ahead of the growth front, variations in contrast suggest

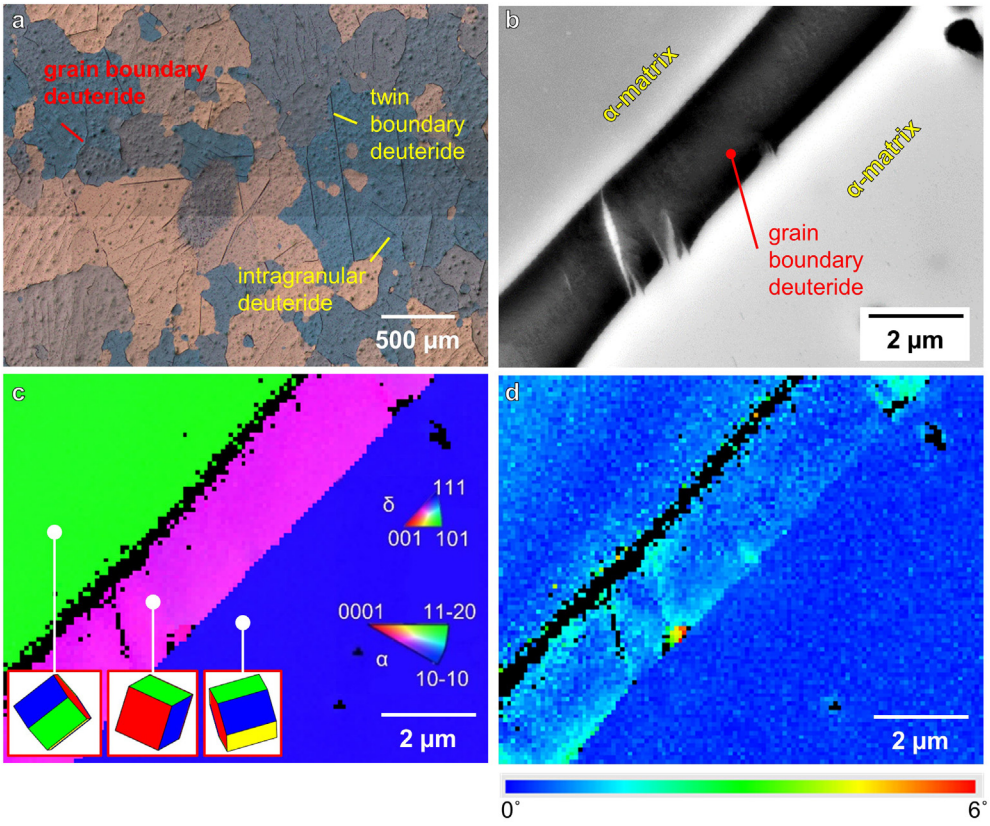

Fig. 1. (a) Polarised light micrograph of Zircaloy-4 after deuterium charging showing evidence of deuteride formation. (b) SEM-ECCI image of the same grain boundary deuteride indicated in (a). (c) Relative crystal orientation EBSD map and unit cell orientations of the detected δ and α phases. (d) Misorientation to grain average orientation map. IPF: Inverse pole figure.