

Direct observations of stable hydrides to solute hydrogen in metals using atom probe tomography

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Understanding the interaction of hydrogen in metals has been a topic of particular interest in materials science for many decades. This is due, in part, to hydrogen embrittlement (HE) phenomena, which is problematic to many engineering alloys. The ingress of hydrogen, either during fabrication or service, can cause a sudden drop in ductility and premature fracture in a variety of applications. Zircaloy-4 (Zr-1.5%Sn-0.2%Fe-0.1%Cr wt. %), which finds application as a cladding material for water based nuclear fuel rods, is an example of a non-ferrous alloy that is susceptible to the formation of stable hydrides in aqueous environments and failure through a delayed hydride cracking mechanism (DHC). Until now, the understanding of HE has been predominantly based on theoretical modelling and indirect experimental observations. Directly observing the position of atomic hydrogen in a metal has been a formidable challenge, owing to it being the smallest, most ubiquitous element found in nature, usually with very high diffusion rates so that it may egress from a sample before it can even be analysed. However, such information is of vital importance for elucidating the fundamental interactions of hydrogen in metals and understanding HE mechanisms.

Atom probe tomography (APT) is one experimental technique that holds much promise in alleviating this roadblock in understanding. The technique enables the position and chemical identity (including H) of millions of atoms from a material specimen to be reconstructed in 3D. However, there have been significant technical challenges that have prevented widespread adaptation for H analysis. Residual H within the analysis chamber complicates H quantification, sample preparation techniques may also have an influence on hydride formation and H in solution. In an attempt to mitigate these challenges, samples can be charged with deuterium which can act as a tracer for information on segregation and partitioning behaviour. However, the diffusion rate is often so fast that cryogenic transfer directly after charging must be used in order to observe any D still trapped within the material.

In this presentation, recent developments in H/D analysis using APT and other complementary techniques including transmission electron microscopy (TEM) will be presented. In particular, successful observations of stable hydrides and deuterides in Zircaloy-4 will be shown. Several hydride phases are observed, including δ (ZrH_{1.66}) and ξ (Zr₂H), with the latter found within a broad and diffuse interfacial region between δ and the Φ #177;-matrix. Detailed information on the structure and segregation behaviour at matrix-hydride interfaces as well as hydride-hydride interfaces will be given and this will be directly combined with crystallographic information to inform phase and crystallographic character of interfaces. Preliminary observations on solute D, utilising recently acquired state-of-the-art cryogenic transfer capabilities at the Max Planck Institute for Iron Research (MPIE), will also be presented. The challenges and implications for using APT to study H interaction in metals, and in particular, elucidate the controlling mechanisms of HE will be discussed.

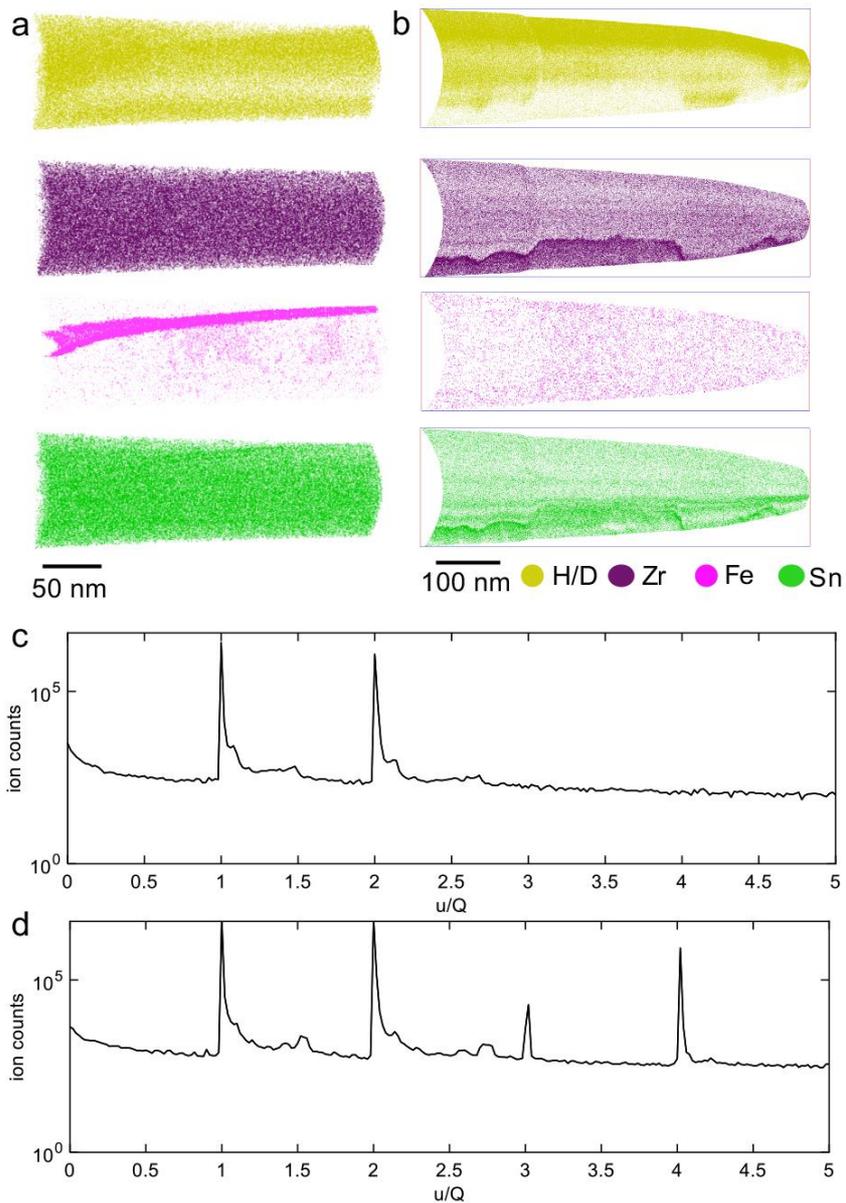


Figure 1 (a) APT reconstruction of Zircaloy-4 hydride interface. (b) APT reconstruction of Zircaloy-4 Deuteride interface (c) and (d) mass spectra of (a) and (b) respectively - note the peaks at $u/Q = 3$ and 4 in (d) signifying successful D detection.