doi:10.1017/S1431927622006432
Microsc. Microanal. 28 (Suppl 1), 2022

Hydrogen Localisation in Metallurgical Samples With High Resolution Secondary Ion Mass Spectrometry (NanoSIMS)

Katie Moore[1*], Yasser Aboura[1], Chris Jones[1], David Martelo[1], Roberto Morana[2], Robert Akid[1] and Michael Preuss[1,3]

[1.] Department of Materials, University of Manchester, Manchester, UK.
[2.] BP Exploration Operating Company Limited, Sunbury on Thames, UK.
[3.] Monash University, Clayton, Victoria, Australia.
* Corresponding author: katie.moore@manchester.ac.uk

Hydrogen embrittlement of high strength alloys can cause catastrophic or premature failure in highly demanding environments such as the oil and gas, nuclear and aerospace industries and many different mechanisms of hydrogen embrittlement have been proposed [1]. To better understand the mechanisms responsible and mitigate for the detrimental effects of hydrogen it is essential to be able to localize hydrogen at the scale of the microstructure. However, hydrogen mapping is challenging due to its small mass, high diffusivity and significant embrittlement effect at low concentrations.

High-resolution secondary ion mass spectrometry (NanoSIMS) is emerging as a powerful tool to study not only complex problems in materials science but is one of only a few techniques that is able to localise hydrogen and deuterium at microstructurally relevant length scales [2]. The NanoSIMS is capable of chemical mapping at <100 nm spatial resolution with detection limits in the ppm range and can detect almost all elements in the periodic table including isotopes. It uses a 16 kV Cs^+ ion probe to generate secondary ions from the sample surface which are collected and analysed in a magnetic mass spectrometer. The NanoSIMS has seven detectors allowing simultaneous detection of different elements and isotopes along with an ion-induced secondary electron image giving topographical information [2].

One of the major problems with detecting and localising hydrogen is that it can be difficult to determine the origin of the hydrogen, especially in high vacuum instrumentation, for example did the hydrogen come from residual hydrogen in the vacuum system, sample preparation or storage? To reduce uncertainty in the detection of hydrogen, the metal samples were exposed to deuterated water as the natural abundance of deuterium is very low (0.0115%) [3].

Hydrogen/deuterium localisation in three different metallurgical systems was investigated, a 625+ nickel alloy, a 303 stainless steel and two zirconium alloys. The steel and nickel alloys were electrochemically charged and the zirconium alloys were oxidised in an autoclave to simulate nuclear reactor conditions. Sample preparation was relatively straightforward and just required a very good metallurgical polish. Correlative NanoSIMS and SEM was used to help identify microstructural features (Figure 1).

In the nickel alloy, 625+, deuterium was localised at dislocation slip bands, σ continuous grain boundary precipitates and twin boundaries (Figure 1). Hydrogen transport by dislocation movement was revealed by performing NanoSIMS on an in-situ deuterium charged single edge notched tension sample. Without dislocation movement or the presence of pre-strained regions, no localised deuterium was observed [4].

In zirconium, deuterium was found to be localised around second phase particles (SPPs) in Zircaloy-2 and Zircaloy-4 (Figure 2), this had not previously been seen but this observation is important for understanding the degradation of these alloys due to hydrogen ingress during service [5].

The complexities associated with hydrogen/deuterium detection in the NanoSIMS and how they have been overcome, such as outgassing of the samples, due to a lack of a cryo stage on the NanoSIMS, ion beam damage and amorphization of the sample, will be discussed [3,6].

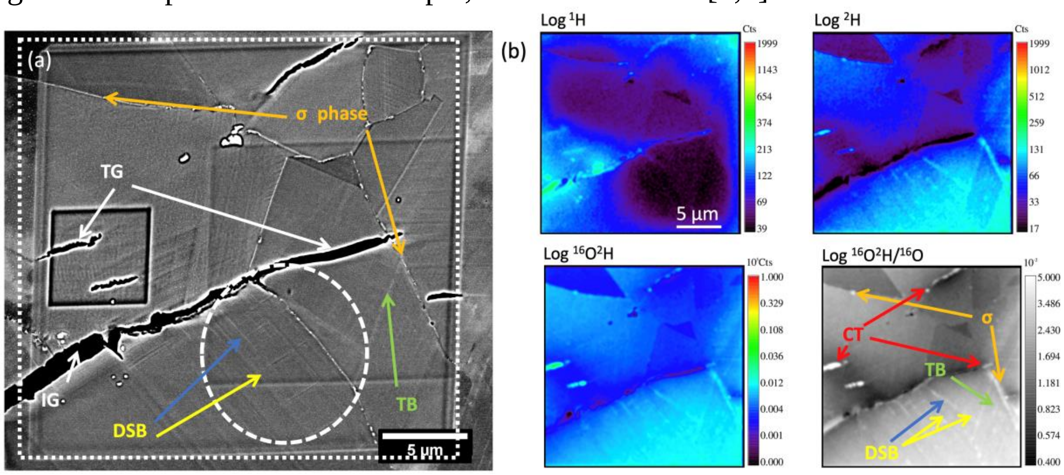

Figure 1. SEM of the cracked Nickel 625+ sample after NanoSIMS analysis. b) NanoSIMS Log ^{1}H, Log ^{2}H, Log ^{16}O^{2}H and ^{16}O^{2}H /^{16}O ion and ratio maps of the selected region. TB: Twin bands, DSB: Dislocation slip bands, CT: Crack tip TG: Transgranular and IG: intergranular [4].

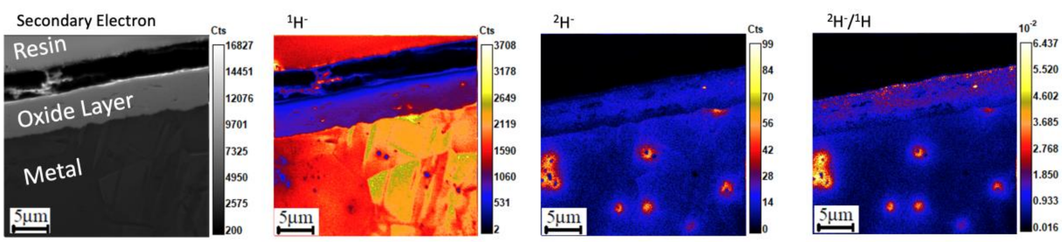

Figure 2. NanoSIMS secondary electron, ^{1}H, ^{2}H and ^{2}H/^{1}H ion and ratio maps from a Zircaloy-4 sample showing deuterium localised around secondary phase particles in the metal [5].

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[6] The authors acknowledge funding from BP through the BP International Centre for Advanced Materials (BP-ICAM) and the Engineering and Physical Sciences Research Council (EPSRC) (EP/L01680X) through the Materials for Demanding Environments Centre for Doctoral Training. This work was also supported by the Henry Royce Institute for Advanced Materials (EP/R00661X/1, EP/S019367/1, EP/P025021/1 and EP/P025498/1) and the MIDAS Zr grant EP/S01702X/1. We would like to thank Jacobs for supplying the autoclave facilities and financial support.