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Exploiting Adsorption Dynamics in Atom Probe Tomography for accurate Measurements of Hydrogen Concentrations

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Understanding the behaviour of hydrogen within a material microstructure is key to many branches of research, such as the hydrogen embrittlement of metals and hydrogen storage. However, undertaking effective microanalysis on this element is challenging, due to its volatility and weak interaction which electron beams. Therefore, the development of alternative microscopy methods to characterise hydrogen within an increasingly wide range of materials is vital to advance an array of research topics.

Atom Probe Tomography (APT) detects all elements with the same sensitivity and is therefore in principle well suited for imaging of hydrogen. However, hydrogen is also a common contaminant in virtually every APT experiment, obscuring hydrogen that is actually contained in the sample. In previous studies, this problem could be mitigated through use of deuterium for sample preparation and the application of pulsed voltage evaporation [1, 2]. Unfortunately, this restricts the method to the analysis of materials where such an evaporation mode is feasible, and, in particular, where sample preparation with deuterium as proxy for naturally abundant hydrogen is possible.

Previous research has shown that the contaminant hydrogen in APT is dependent on the evaporation rate and the pulse frequency: More evaporated ions per time ("ion flux") are correlated with less contaminant hydrogen [3, 4]. In this study, we conduct experiments where we repeatedly change evaporation rate or pulse frequency during APT experiments, and monitor the change in the contaminant hydrogen, which we find to be highly linear. This indicates that, extrapolating to the case of a theoretical experiment with infinitely high evaporation rate, no contaminant hydrogen is expected [5]. Whilst APT experiments with infinitely high rate are not possible, it is possible to estimate hydrogen contents under such theoretical conditions.

Figure 1 shows the total (ionic) detected hydrogen in two tungsten APT specimens, respectively, whilst cycling the amount of time between evaporation events. One of the specimens is free from any hydrogen other than that introduced as a contaminant, the other specimen has been implanted with deuterium. It is seen that the fractions of all contaminant hydrogen ions decrease with the time between evaporation events, meanwhile the amount of sample hydrogen (deuterium) in the deuterated sample is stable. This allows for an estimate for the amount of deuterium in the deuterated sample.

The method is not limited only to measurements of the global amount of hydrogen within a sample, extensions to a layer-by-layer based extrapolation (i.e. depth profiles) or voxelization (3D distribution) are both possible. Figure 2 shows a nominally hydrogen-free steel sample where extrapolation was applied to H+ voxel-wise to obtain an accurate measure of the hydrogen content. As seen, the extrapolated amounts are not uniformly distributed throughout the sample, but enriched at the tip, due to a hydrogen-rich oxide cap on the sample.

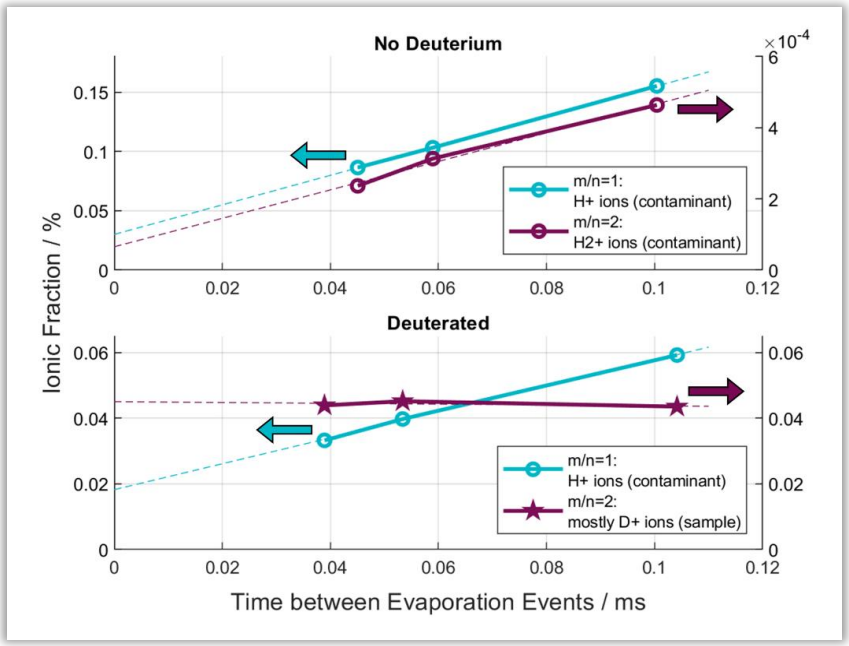

Figure 1: Extrapolation of hydrogen in a nominally hydrogen free (top figure) and deuterated tungsten sample (bottom figure). It is seen that contaminant hydrogen ions decrease with time between evaporation events and extrapolate to near 0 in a theoretical, infinitely fast experiment. Sample hydrogen (bottom diagram, m/n=2 events) is unaffected.

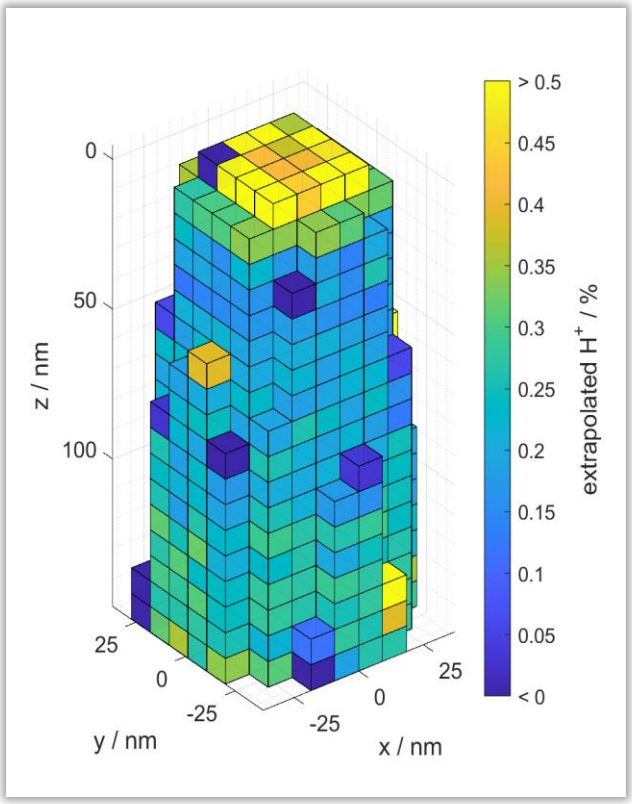

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Figure 2: Extrapolation of H+ ions in a nominally hydrogen-free steel sample. It is seen that the extrapolated amounts of H+ are not uniformly distributed, but enriched at the tip of the sample, presumably due to a hydrogen-rich oxide cap.

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