Quantification Challenges for Atom Probe Tomography of Hydrogen and Deuterium in Zircaloy-4

Isabelle Mouton1, Andrew J. Breen1, Siyang Wang2, Yanhong Chang1, Agnieszka Szczepaniak1, Paraskevas Kontis1, Leigh T. Stephenson1, Dierk Raabe1, M. Herbig1, T. Ben Britton2 and Baptiste Gault1*

1Max-Planck-Institut für Eisenforschung, Max-Planck-Straße 1, 40237 Düsseldorf, Germany and 2Department of Materials, Royal School of Mines, Imperial College London, London, SW7 2AZ, UK

Abstract
Analysis and understanding of the role of hydrogen in metals is a significant challenge for the future of materials science, and this is a clear objective of recent work in the atom probe tomography (APT) community. Isotopic marking by deuteration has often been proposed as the preferred route to enable quantification of hydrogen by APT. Zircaloy-4 was charged electrochemically with hydrogen and deuterium under the same conditions to form large hydrides and deuterides. Our results from a Zr hydride and a Zr deuteride highlight the challenges associated with accurate quantification of hydrogen and deuterium, in particular associated with the overlap of peaks at a low mass-to-charge ratio and of hydrogen/deuterium containing molecular ions. We discuss possible ways to ensure that appropriate information is extracted from APT analysis of hydrogen in zirconium alloy systems that are important for nuclear power applications.

Key words: atom probe tomography, deuterium, hydrogen, nuclear materials, quantification, zirconium alloy

(Received 9 July 2018; revised 5 November 2018; accepted 5 December 2018)

Introduction
Atom probe tomography (APT) combines a time-of-flight mass spectrometer with a projection microscope (Müller et al., 1968). The technique provides atomic scale chemical information with nanometer spatial resolution has a high sensitivity and equal efficiency across a wide range of mass-to-charge-state ratios. The main strength of APT lies in its capacity to provide a precise account of where atoms of a specific species were located within a 3D volume of probed material and provide quantitative microstructural data at the atomic scale (Kelly & Miller, 2007; Devaraj et al., 2018).

As a mass spectroscopy technique, APT has the inherent capacity to detect light elements, including hydrogen. Yet its application to measuring hydrogen composition within metals has been hampered by the presence of hydrogen in the residual gas in the ultrahigh vacuum chamber of the APT microscope. This hydrogen generates noise in the data, as the hydrogen may be adsorbed onto the tip, subsequently migrating toward the specimen apex and gets finally field desorbed and ionized (Sundell et al., 2013). This produces characteristic peaks at 1, 2, and 3 Da, corresponding respectively to H+, H2, and H3+, as well as some events uncorrelated to a pulse contributing to the general background. This “background” signal provides significant uncertainty when tracking the presence of hydrogen within the original material.

In principle the “background” hydrogen challenge can be overcome with isotopic marking, using deuterium, as the natural abundance of deuterium is very low (only 0.015%). Isotopic marking, through the use of deuterium or heavy water during microstructural formation, has been used to distinguish between residual hydrogen from the chamber and solute hydrogen, the deuterium, originating from the specimen itself (Gemma et al., 2007, 2011; Takahashi et al., 2010, 2018; Chen et al., 2017; Li et al., 2018).

An added complexity is that the relative amounts of the H+, H2, and H3+ peaks are highly dependent on the amplitude of the electrostatic field and on the nature of the surface (Tsong et al., 1983), making it difficult to ensure that no H gets identified as D. This problem is made more prominent as the community increasingly uses laser-pulsing, which results in operating the instrument under lower electrostatic fields [as evaporation occurs at higher temperatures (Kellogg, 1981; Marquis & Gault, 2008; Vurpillot et al., 2009)] where the relative amount of H2 is expected to be higher (Tsong et al., 1983).

Therefore instead of looking for a small concentration of trapped H solute, we used APT to investigate stable bulk hydrides and deuterides in Zircaloy-4, and compare this with the hydrogen-free alloy. From a technological point of view, Zr-based alloys are among the materials most affected by hydrogen embrittlement when they are employed as nuclear fuel cladding in water-based nuclear reactors. Zr alloys are used in these applications as they have a low neutron absorption cross section, good corrosion resistance, and appropriate mechanical strength. However, during service they corrode and pick up hydrogen and risk being affected by delayed hydride cracking (Bair et al., 2015; Suman et al., 2015). The solubility of hydrogen in α-Zr is less than 10 wt. ppm.
at room temperature (McMinn et al., 2000), and the driving force for segregation to interfaces and to form secondary phases is high. The phase diagram for the Zr–H system indicates at least four ZrH_x phases at temperatures below 550°C a hexagonal close packed ζ with x = 0.25–0.5, a face-centered tetragonal (FCT) γ with x = 1, a face-centered cubic δ with x ≈ 1.5–1.65 and another FCT phase ε with x ≈ 1.75–2 (Grosse et al., 2008; Li et al., 2017).

Little is known so far of the field evaporation behavior of bulk hydrides, with only few reports on systematic studies (Takahashi et al., 2009; Chang et al., 2018). Yet, the compositional accuracy of APT is known to be strongly dependent on an appropriate set of experimental parameters, as extensively discussed for carbides, nitrides, oxides (Sha et al., 1992; Kitaguchi et al., 2014; Mancini et al., 2014; Gault et al., 2016), but also for metallic alloys (Miller, 1981; Yao et al., 2011). Voltage pulsing has typically been used for analyzing solute H, in order to maximize the electrostatic field, reduce the proportion of H_2, and possibly mitigate surface diffusion. Here, this pulsing mode led to a premature fracture of atom probe specimens and did not entirely prevent the detection of H-containing molecular ions. We performed an investigation of the results obtained from laser-pulsed APT. Following precise decomposition of the peaks in the mass-to-charge spectrum, we discuss the parameters influencing the quality of the measurement. Our results point to the need to better understand the reasons for the variations in the amount of detected residual H in comparison with solute H or D, so as to enable direct analysis with no need for isotopic marking.

Experimental

Experiments were conducted on a rolled and recrystallized plate of a commercial Zircaloy-4 with a composition of Zr–1.5Sn–0.2Fe–0.1Cr wt.%. The alloy was heat treated at 800°C for 2 weeks to form large “blocky-alpha” grains with a typical grain size larger than 200 μm, as described in Tong & Britton (2017). Samples were electrochemically charged with hydrogen or deuterium using galvanostatic charging at a current density of 2 kA/m², using a solution of 20 wt.% HClO_4:methanol = 1:9 (vol.) with 30 V applied voltage at room temperature (McMinn et al., 2000), and the driving force for segregation to interfaces and to form secondary phases is high. An inverse pole figure (IPF) map rendered with respect to the surface normal is shown for a typical intergranular hydride formed at a twin boundary in Figure 1b. The misorientation angle is approximately 85° between the parent and twin α-Zr grains, which indicates that they are [1012]<1011> extension twins, for which the theoretical misorientation angle about the c-axis is ~85.22°. An orientation gradient can be easily identified within the pink hydride packet in the IPF implying misfit strain between the matrix and the δ hydrides.

The preparation protocol is summarized in Figures 1c–1e, with the hydride clearly visible both in the secondary electron micrograph of the lifted out bar sliced onto a flat specimen support (Si post) in Figure 1d and of the final specimen in Figure 1e. The ruggedness of the interface is evident from the side views. APT results were obtained on a local electrode atom probe (LEAP) 5000 XR from Cameca Madison, WI, USA. UV laser pulsing was thus used, which drastically improved yield compared to voltage mode where the specimen fractured prematurely. A base temperature of 60 K, laser pulse energy of 60 pJ, pulse repetition rate of 250 kHz, and a detection rate of 1–2 ions per 100 pulses were used during the experiments.

Methods

Based on the natural abundances of the different elements it is possible to perform a decomposition of the mass peaks. This alleviates quantification issues associated with the overlap of peaks corresponding to different isotopic species that have the same mass-to-charge ratio (Miller, 2000). We implemented an automated peak decomposition procedure, akin to maximum likelihood method proposed in London et al. (2017). Peak decomposition is performed on the total number of counts for each mass peak (defined by a specific range of values). The signal used for deconvolution is thus in the form of a histogram, represented in gray in Figure 2, with coarser bins than typically used to represent mass spectra obtained from APT analysis. Peaks are then fitted with the combination of the total ion count obtained for each overlapping species groups, taking into account all isotopes with their respective isotopic abundance. The background level due to ions evaporating between pulses and detector noise is subtracted prior to performing this procedure. This procedure was either applied to the entire reconstruction or to individual bins of a composition profile. Typical results are displayed in the form of a histogram, as shown in Figure 2, where the number of ions ^{10}N in the peak with mass/charge of mDa is determinate (^{10}N in the peak at 45 Da). Each peak is a combination of the natural abundance of the Zr (^{96}Zr) and the proportion of Zr^{2+}, ZrH^{+}, and ZrH_2^{+} which can be written as:

\[
\begin{bmatrix}
45N & 45.5N & 46N & 46.5N & 47N & 47.5N & 48N & 48.5N & 49N
\end{bmatrix} = \begin{bmatrix}
A^{+}_{96Zr} & 0 & 0 \\
A^{+}_{95Zr} & A^{+}_{95Zr} & 0 \\
A^{+}_{94Zr} & A^{+}_{94Zr} & A^{+}_{94Zr} \\
A^{+}_{93Zr} & A^{+}_{93Zr} & A^{+}_{93Zr} \\
A^{+}_{92Zr} & A^{+}_{92Zr} & A^{+}_{92Zr} \\
A^{+}_{91Zr} & A^{+}_{91Zr} & A^{+}_{91Zr} \\
A^{+}_{90Zr} & A^{+}_{90Zr} & A^{+}_{90Zr} \\
A^{+}_{89Zr} & A^{+}_{89Zr} & A^{+}_{89Zr} \\
0 & A^{+}_{88Zr} & A^{+}_{88Zr} \\
0 & 0 & A^{+}_{87Zr}
\end{bmatrix} = \begin{bmatrix}
N^{+}_{96Zr} \\
N^{+}_{95Zr} \\
N^{+}_{94Zr} \\
N^{+}_{93Zr} \\
N^{+}_{92Zr} \\
N^{+}_{91Zr} \\
N^{+}_{90Zr} \\
N^{+}_{89Zr} \\
N^{+}_{88Zr} \\
N^{+}_{87Zr}
\end{bmatrix}.
\]
As this is an overdetermined system of linear equations, a least squares solution was numerically found. Explicitly, we minimized by trial the sum of squared residuals between the number of ions in each peak [left term in equation. (1)] and the combination of the number of ions $Z_{r2}^{2+}$, $Z_{rH2}^{2+}$ and their abundancy [right term in equation. (1)].

The precision of the decomposition depends on the residual number of ions after decomposition. The resulting decomposition is presented as colored bars which represent the relative amplitude of each of the identified species. The histogram in Figure 2 was obtained from an uncharged sample, and yet some $Z_{rH2}^{2+}$ can be seen, whereas no peak of $Z_{rH2}^{2+}$ or $Z_{rD}^{2+}$ can be measured.

**Results and Discussion**

**Species Distribution**

Thin slices (10 nm) through the tomographic reconstructions from representative APT datasets for the metal–hydride and metal–deuteride interfaces are shown in Figures 3a and 3b. This allows for direct comparison of the detection of H and D within a stable phase and as solute in the metallic matrix. Similar features can be observed in both, with a segregation of Sn at a very rough interface, as reported in a separate article (Breen et al., 2018). This segregation at the growth front of the hydride into the metal has been recently reported. Sections of the mass spectrum obtained for these two datasets are displayed in Figures 3c and 3d. For the hydride (in black), peaks appear at 1 and 2 Da, corresponding to $H^+$ and $H_2^+$ as expected. For the deuteride (in red), the amplitude of the peak at 2 Da corresponding most likely to $D^+$ is higher relative to the $H^+$ peak. This peak likely also contains a certain amount of $H_2^+$ which is undetermined. Additional peaks at 3 and 4 Da corresponding to $HD^+$ and $D_2^+$ are also apparent.

As evidenced by the mass spectrum of the H-charged sample, the presence of triple ions ($H_3^+$ and so $DH_2^+$) is negligible. The possible combinations of molecular ions in this range of mass-to-charge ratios are listed in Table 1.

Peaks corresponding to H- and D-containing molecular ions, e.g. $Z_{rH2}^{2+}/Z_{rD}^{2+}$ are also present in both datasets, as seen in Figure 3d. The $Z_{rH2}^{2+}/Z_{rD}^{2+}$ are present in the region of the dataset corresponding to the H/D-rich phase but surprisingly also within the $\alpha$-Zr phase. This is seen in Figure 4, which shows the results from the peak decomposition procedure described above applied to regions of interest extracted from the $\alpha$-Zr and the H/D-rich phase in datasets of both the hydrogenated and deuterated samples. In the H-charged specimen ($\alpha$ matrix phase in Fig. 4a and H-rich phase in Fig. 4c), peaks associated with Zr and ZrH are measured, but none for ZrH$_2$. Whereas in the D-charged specimen ($\alpha$ matrix phase in Fig. 4b and D-rich phase in Fig. 4d), the same peaks appear but high peaks labeled as ZrH$_2$, likely corresponding mostly to ZrD, are also present. The difference in the relative amplitude of the peaks from the different species is evident between the two samples. Interestingly, the $\alpha$-Zr matrix consistently contains a relative high level of H or D.

---

**Fig. 1.** a: Polarized light optical micrograph of the hydride microstructure showing both intragranular and intergranular hydrides. b: IPF map of the selected twin boundary hydride, rendered with respect to the surface normal. Secondary electron micrographs (c) of the marked hydride to ensure that this specific hydride was analyzed; (d) of a slice of the “Toblerone-shaped” bar containing the hydride lifted-out from the material and mounted on the support Si post; (e) final specimen. The dark contrast reveals the presence of the hydride in the final specimen.

**Fig. 2.** Typical histogram resulting from the decomposition of the mass peaks based on the elements’ natural abundances.
In the accurate measurement of the composition of H/D in the different phases there are two major challenges. First, the amount of H originating from residual gases and/or the specimen needs to be established and, second, the possible overlap between H$_2$ and D needs to be disentangled.

The presence of a significant amount of hydrogen in the analysis of both the uncharged and D-charged sample may first be related to:

- Residual H from within the APT chamber that can be field ionized or field desorbed from the specimen in the form of atomic, homomolecular, or heteromolecular ions (Sundell et al., 2013).
- Partial hydration during deuteration or the subsequent exchange of D by H as the specimen was kept in air for several weeks after preparation.
- The preparation of the specimens themselves. Samples have been mechanically polished using water-based solution which is known to cause hydride formation (Kestel, 1986). This is also known to occur via FIB-based specimen preparation of Zr and Ti (Shen et al., 2016; Chang et al., 2018).

A combination of these effects likely explains the ZrH$_{2+}$ peaks, as well as the H peaks (not shown here), observed for data obtained respectively from an uncharged sample (Fig. 2) and from a D-charged sample (Figs. 4b and 4d).

H quantification in the $\alpha$ and H/D-Zr phase can be obtained from composition profiles along rectangular regions-of-interest positioned perpendicularly to the interface. Because of the roughness of the interface, readily visible in Figure 3, only thin slices with long sections parallel to the interface were considered, the precise size is $15 \times 25 \times 75$ nm$^3$ and $15 \times 60 \times 100$ nm$^3$ for H- and D-charged samples respectively. Figures 5a and 5b represent the composition profiles across the hydride/$\alpha$-Zr and deuteride/$\alpha$-Zr interface for respectively Zr and H after application of the complete peak decomposition protocol. As the mass spectrum obtained for the H- or D-charged sample is different, two separate peak decompositions are performed to quantify H or D as indexed in Table 1 (two last columns). For the H-charged sample (Fig. 5a), the H peak was quantified as coming all from the sample, ignoring the residual H from the ultra-high vacuum chamber. Therefore, the H composition in both $\alpha$ matrix and hydride phases will be slightly overestimated. For the D-charged sample (Fig. 5b), there is significant uncertainty regarding the possible overlap between H$_2$ and D, and its amplitude. In this case, the peak at 2 Da was considered as being exclusively D. The absolute composition of D reported here is hence likely overestimated.

### Compositional Analysis

In the accurate measurement of the composition of H/D in the different phases there are two major challenges. First, the amount of H originating from residual gases and/or the specimen needs to be established and, second, the possible overlap between H$_2$ and D needs to be disentangled.

The presence of a significant amount of hydrogen in the analysis of both the uncharged and D-charged sample may first be related to:

- Residual H from within the APT chamber that can be field ionized or field desorbed from the specimen in the form of atomic, homomolecular, or heteromolecular ions (Sundell et al., 2013).
- Partial hydration during deuteration or the subsequent exchange of D by H as the specimen was kept in air for several weeks after preparation.
- The preparation of the specimens themselves. Samples have been mechanically polished using water-based solution which is known to cause hydride formation (Kestel, 1986). This is also known to occur via FIB-based specimen preparation of Zr and Ti (Shen et al., 2016; Chang et al., 2018).

A combination of these effects likely explains the ZrH$_{2+}$ peaks, as well as the H peaks (not shown here), observed for data obtained respectively from an uncharged sample (Fig. 2) and from a D-charged sample (Figs. 4b and 4d).

H quantification in the $\alpha$ and H/D-Zr phase can be obtained from composition profiles along rectangular regions-of-interest positioned perpendicularly to the interface. Because of the roughness of the interface, readily visible in Figure 3, only thin slices with long sections parallel to the interface were considered, the precise size is $15 \times 25 \times 75$ nm$^3$ and $15 \times 60 \times 100$ nm$^3$ for H- and D-charged samples respectively. Figures 5a and 5b represent the composition profiles across the hydride/$\alpha$-Zr and deuteride/$\alpha$-Zr interface for respectively Zr and H after application of the complete peak decomposition protocol. As the mass spectrum obtained for the H- or D-charged sample is different, two separate peak decompositions are performed to quantify H or D as indexed in Table 1 (two last columns). For the H-charged sample (Fig. 5a), the H peak was quantified as coming all from the sample, ignoring the residual H from the ultra-high vacuum chamber. Therefore, the H composition in both $\alpha$ matrix and hydride phases will be slightly overestimated. For the D-charged sample (Fig. 5b), there is significant uncertainty regarding the possible overlap between H$_2$ and D, and its amplitude. In this case, the peak at 2 Da was considered as being exclusively D. The absolute composition of D reported here is hence likely overestimated.

### Table 1. Likely Combinations of Possible Species Detected in the Range of 1–4 Da for the Hydrided and Deuterated Samples.

| Mass-to-Charge (Da) | Combinations of Possible Species | Uncharged or H-Charged | D-Charged |
|---------------------|---------------------------------|------------------------|-----------|
| 1                   | H$^+$                           | 1H                     | 1H        |
| 2                   | H$_2$ + D$^+$                    | 2H                     | 1D        |
| 3                   | H$_3$ + DH$^+$                   | 3H                     | 1D + 1H   |
| 4                   | H$_4$ + DH$_2$ + D$_2$           | 2D                     |           |

**Fig. 3.** Distribution of species for Zr, Sn, $^3$H, and $^2$H at the (a) hydride/$\alpha$-Zr interface and (b) deuteride/$\alpha$-Zr interface. Sections of the mass spectrum in the range of (c) 1–6 Da and (d) 44–50.5 Da obtained for the hydride (black) and the deuteride (red).

**Table 1.** Likely Combinations of Possible Species Detected in the Range of 1–4 Da for the Hydrided and Deuterated Samples.

| Mass-to-Charge (Da) | Combinations of Possible Species | Uncharged or H-Charged | D-Charged |
|---------------------|---------------------------------|------------------------|-----------|
| 1                   | H$^+$                           | 1H                     | 1H        |
| 2                   | H$_2$ + D$^+$                    | 2H                     | 1D        |
| 3                   | H$_3$ + DH$^+$                   | 3H                     | 1D + 1H   |
| 4                   | H$_4$ + DH$_2$ + D$_2$           | 2D                     |           |
the stable hydride or deuteride phases is in the range of 60–65 at%.

The level of H or D in the α-Zr matrix is surprisingly high, in the range of approximately 18–22 at%, which is well above the expected maximum solubility of approximately 2 at% (Giroldi et al., 2009). Contrary to the uncharged Zr sample (Fig. 2), the high content of H/D in the α-Zr for the H/D charged sample mainly arises from the decomposition of ZrH and ZrD, shown in Figures 5b and 5d respectively. Therefore, H/D atoms are likely introduced during the charging process, but the presence of H/D may also be related to a different maximal solubility under electrochemical-charging conditions. The chemical potential of the H/D in the solution is rather different to that in the gaseous environment that is usually employed to perform charging and solubility measurements (Yamanaka et al., 1995). The presence of defects near the polished surface or strain caused by the growth of the hydride in the matrix near the precipitate can also influence the solubility of H (Christensen et al., 2015).

**Electrostatic Field Dependence**

The evolution of the relative charge-states of a single element can be used as a tracer to investigate the local variations of the electrostatic field within a single dataset (Kingham, 1982; Shariq et al., 2009; Müller et al., 2011). Here, the relative amplitude of Zr$^{3+}$ to Zr$^{2+}$ across the interface was measured. In Figure 6, the composition of H- or D-containing species is plotted against this ratio. A higher electrostatic field is observed within the hydride and deuteride, as compared to the matrix. In the composition profile obtained from the H-charged sample, shown in Figure 6a, the progressive drop in amplitude of ZrH as the electrostatic field increases likely indicates a field-assisted dissociation of this molecular ion (Tsong et al., 1983; Gault et al., 2016). A similar behavior is observed in the D-charged sample composition profile for the peak labeled ZrH$_2$, likely to be almost exclusively ZrD, in Figure 6b.

Interestingly, the behavior of H (at 1 Da) in the H (or D) rich phase is different for samples charged with either hydrogen or deuterium. For the hydrided sample, the composition of both H and H$_2$ is increasing with the electrostatic field, whereas for the deuterated sample, the composition of D (at 2 Da) increases and H (at 1 Da) progressively drops as the field increases. This observation proves that a major portion of the H$_2$/D signal (at 2 Da) is coming from the deuterium ions introduced during charging. The evolution of the H signal (at 1 Da) in the deuteride phase is likely due to residual H, presumably generated from within the APT chamber, as it decreases with increasing local electrostatic field. The amount of H under high electrostatic field conditions appears to be above 10 at%, which is far from negligible and cannot originate from the residual H content within the APT chamber. Thus, we assume that the deuterated sample contains both D and H after charging. Charging was performed under D rich conditions, and so it is unlikely that H is introduced here. It is more likely that H is introduced during metallographic sample polishing or APT specimen preparation. This extra H signal significantly complicates quantification of hydrogen and its isotopes within materials.

**General Considerations**

The analyses presented showcase the difficulties inherent to quantifying hydrogen within the microstructure of a metallic alloys, even when there is a stable hydride-rich phase present.

First, separation of the overlap of H$_2$ and D, and, to a lesser extent, separation of the overlap of H$_3$ and DH is not straightforward.
The strong dependence on the electrostatic field of the atomic and the molecular nature of the ions detected makes it difficult (if not impossible) to distinguish residual H from solute H. Earlier work, particularly by Tsong and co-workers, highlighted the diversity of parameters that contribute to fluctuations in the relative composition of H\(^+\), H\(_2\)\(^+\), and H\(_3\)\(^+\), including the nature of the surface that is likely to have a catalytic effect on the formation of H\(_3\) or the splitting of H\(_2\) for example (Ai & Tsong, 1984; Chi-fong Ai & Tsong, 1984). The relative amounts of H\(_2\) and H\(_3\) are highly dependent on the local magnitude of the electrostatic field that can fluctuate significantly across the field-of-view and over time during an experiment. This is clearly demonstrated in Figure 6. These problems can be made more prominent by the use of laser pulsing that often results in more pronounced variations of the electrostatic field across the field of view (Gault et al., 2010) and field evaporation at higher temperature.

Performing a local analysis is possible, but reducing the sample size reinforces the relative importance of statistical fluctuations, making the measurement potentially significantly less precise. Using D-charging as a replacement for H is good solution to locate the H ions in the microstructure (provided that physical differences between H and D during microstructure formation can be assumed to be negligible). Nevertheless, dependent on the material and the experimental conditions (cryo preparation, analysis with laser pulse), D charging can increase the complexity of quantification. Thus, although isotopic marking by deuteration is elegant and attractive, it is not a miraculous solution. This supports previous work Sundell et al. (2013). Indeed, a significant fraction of the H/D is detected as part of molecular ions, and their respective proportions are highly dependent on the amplitude of the electrostatic field.

A preferred route would be to gain a better understanding of how residual and solute hydrogen behave during the course of the analysis, thereby potentially allowing us to distinguish between the two with no need for deuteration. The supply of the residual gas to the ionization or field desorption zone is mostly related to the diffusion of adsorbed hydrogen on the surface of the specimen (Sundell et al., 2013). However, the detailed mechanisms are still poorly understood in the case of very low partial pressures of gas and when multiple phases intersect the surface (Orloff, 2008). Overall, our results agree with reports on other materials which find that a maximized electrostatic field will tend to reduce the influence of the residual hydrogen both in the form of molecular hydrogen and H-containing molecular ions. There might also be a possibility to find appropriate descriptors and track their evolution locally during the experiment. The electrostatic field is clearly one such descriptor, which was discussed at length herein, but others may exist. The deployment
of machine learning techniques can provide a data reduction strategy where data are combined and simplified, and in practice can build upon solution to the overdetermined system of equations presented within equation (1), but may provide a faster methodology for less constrained analysis of complex material systems. However, these new algorithms should be trained and evaluated within simple systems first, to demonstrate efficacy, and furthermore deployment of these new analysis methods could later lead to interesting findings in this area.

Conclusions

In summary, we have characterized stable Zr-hydrides and deuterides by APT, and their interface with the α-Zr matrix, in electrochemically charged Zircaloy-4. We highlighted the dependence of the detected atomic or molecular ionic species on the local strength of the electrostatic field at the specimen’s surface. The influence of the residual H from the ultra-high vacuum chamber was shown to become less pronounced as the electrostatic field increases, which indicates that the field condition should be maximized for H quantification. Finally, we discussed isotopic marking which helps with assessing the locations of high concentrations of hydrogen within the microstructure, but adds to the complexity associated with quantifying H by APT.

Author ORCIDs. Isabelle Mouton, 0000-0002-2202-4033; Baptiste Gault, 0000-0002-4934-0458

Acknowledgments. Uwe Tezins and Andreas Sturm are thanked for their support in the FIB and APT facilities at MPIE. IM, LTS, DR, and BG designed the study. IM, AS, and YC prepared the specimens. IM, AS, YC, and AJB conducted the APT experiments. SW and TBB performed the hydridation and the study. IM, AS, YC, and AJB acknowledge the Deutsche Forschungsgemeinschaft (DFG) for partially funding this research through SFB 761 “Stahl ab-initio”. AB also acknowledges the Alexander von Humboldt Foundation (AvH) for partially funding this research. The authors are grateful for the Max-Planck Society and the BMBF for the funding of the Laplace and the UGSLiT projects respectively. TBB thanks the Royal Academy of Engineering for support of his Research Fellowship. TBB and SW acknowledge support from the HexMat programme grant (EP/K034332/1). The raw APT data are available upon request to the corresponding authors.

References

Ai CF & Tsong TT (1984). A study of the temperature dependence of a surface catalyzed and field enhanced formation of H3 and NH3 on metal surfaces. J Chem Phys 81, 2845–2854.

Bair J, Asle Zaeem M & Tonks M (2015). A review on hydride precipitation in zirconium alloys. J Nucl Mater 466, 12–20.

Birch R, Wang S, Tong V & Britton TB (2018). The effect of cooling rate and grain size on hydride formation in Zircaloy-4. arXiv:1807.11927 [cond-mat]. Available at http://arxiv.org/abs/1807.11927 (retrieved October 10, 2018).

Brein AJ, Mouton I, Lu W, Wang S, Szczepaniak A, Kontis P, Stephenson LT, Chang Y, da Silva AK, Liebscher CH, Raabe D, Britton TB, Herbig M & Gault B (2018). Atomic scale analysis of grain boundary deuteride growth front in Zircaloy-4. Scr Mater 156, 42–46.

Chang Y, Brein AJ, Tarzimoghaddam Z, Künsterne P, Gardner H, Ackerman A, Radecka A, Bagot PAJ, Lu W, Li T, Jägle EA, Herbig M, Stephenson LT, Moody MP, Rugg D, Dye D, Ponge D, Raabe D & Gault B (2018). Characterizing solute hydrogen and hydrides in pure and alloyed tantalum at the atomic scale. Acta Mater 150, 273–280.

Chen Y-S, Haley D, Gerstl SSA, London AJ, Sweeney F, Wepf RA, Rainforth WM, Bagot PAJ & Moody MP (2017). Direct observation of individual hydrogen atoms at trapping sites in a ferritic steel. Science 355, 1196–1199.

Chi-fong A & Tsong TT (1984). Field promoted and surface catalyzed formation of H3 and NH3 on transition metal surfaces: A pulsed-laser imaging atom-probe study. Surf Sci 138, 339–360.

Christensen M, Wolf W, Freeman C, Wimmer E, Adamson RB, Hallstadius L, Cantonwine PE & Mader EV (2015). H in α-Zr and in zirconium hydrides: Solubility, effect on dimensional changes, and the role of defects. J Phys: Condens Matter 27, 025402.

Devaraj A, Perea DE, Liu J, Gordon LM, Prosa TJ, Parikh P, Diercks DR, Meher S, Kolli RP, Meng YS & Thevuthasan S (2018). Three-dimensional nanoscale characterisation of materials by atom probe tomography. Int Mater Rev 63, 68–101.

Gault B, La Fontaine A, Moody MPMP, Ringer SPSP & Marquis EEAA (2010). Impact of laser pulsing on the reconstruction in an atom probe tomography. Ultramicroscopy 110, 1215–1222.

Gault B, Saxey DW, Ashton MW, Sinnott SB, Chiaramonti AN, Moody MP & Schreiber DK (2016). Behavior of molecules and molecular ions near a field emitter. This work is a partial contribution of the US Government and therefore is not subject to copyright in the United States. New J Phys 18, 33011.

Gemma R, Al-Kassab T, Kirchheim R & Pundt A (2007). Studies on hydrogen loaded V–Fe8 4% films on AlOx substrate. J Alloys Compd 446–447, 534–538.

Gemma R, Al-Kassab T, Kirchheim R & Pundt A (2011). Analysis of deuterium in V–Fe5 at.% film by atom probe tomography (APT). J Alloys Compd 509, 5872–5876.

Giroldi JP, Vizzaino P, Flores AV & Banchik AD (2009). Hydrogen terminal solid solubility determinations in Zr–2.5Nb pressure tube microstructure in an extended concentration range. J Alloys Compd 474, 140–146.

Grosse M, Steinbrueck M, Lehnemann E & Vontobel P (2008). Kinetics of hydrogen absorption and release in zirconium alloys during steam oxidation. Oxid Met 70, 149–162.

Kellogg GL (1981). Determining the field emitter temperature during laser irradiation in the pulsed laser atom probe. J Appl Phys 52, 5320.

Kelly TF & Miller MK (2007). Invited review article: Atom probe tomography. Rev Sci Instrum 78, 031101.

Kestel BJ (1986). Non-acid electrolyte thins many materials for TEM without causing hydride formation. Ultramicroscopy 19, 205–211.

Kingham DR (1982). The post-ionization of field evaporated ions: A theoretical explanation of multiple charge states. Surf Sci 116, 273–301.

Kitaguchi HS, Lozano-Perez S & Moody MP (2014). Quantitative analysis of carbon in cementite using pulsed laser atom probe. Ultramicroscopy 147, 51–60.

Li S, Wang Y, Che Z, Liu G, Ren Y & Wang Y (2017). Investigations of deformation-induced ζ-γ phase transformation in zirconium hydride by in situ high-energy X-ray diffraction. Acta Mater 140, 168–175.

Li T, Kiasian O, Cherevko S, Zhang S, Geiger S, Scheu C, Feller P, Raabe D, Gault B & Mayrhofer KJ (2018). Atomic-scale insights into surface species of electrolytacasts in three dimensions. Nat Catal 1, 300–305.

London AJ, Haley D & Moody MP (2017). Single-ion deconvolution of mass peak overlaps for atom probe microscopy. Microsc Microanal 23, 300–306.

Mancini I, Amiri²far N, Shinde D, Blum I, Gilbert M, Vella A, Vurpillot F, Lefebvre W, Lardé R, Talbot E, Pareige P, Portier X, Ziani A, Daunesne C, Durand C, Eymery J, Butte R, Carlin J-F, Grandjean N & Riguitti L (2014). Composition of wide bandgap semiconductor materials and nanostructures measured by atom probe tomography and its dependence on the surface electric field. J Phys Chem C 118, 24136–24151.

Marquis EEAA & Gault B (2008). Determination of the tip temperature in laser assisted atom-probe tomography using charge state distributions. J Appl Phys 104, 084914.

McMinn A, Darby EC & Schofield JS (2000). Terminal solid solubility of hydrogen in zirconium alloys. In Proc 12th Int Symp on Zirconium in the Nuclear Industry ASTM STP 1354, Sabol GB & Moan GD (Eds.), West Conshohocken, USA: ASTM, 173–194.

Miller MK (1981). An atom probe study of the anomalous field evaporation of alloys containing silicon. J Vac Sci Technol 19, 57.
Miller MK (2000). Atom Probe Tomography: Analysis at the New, Atomic Level. York: Kluwer Academic/Plenum Publishers.

Müller EW, Panitz JA, McLane SB & Müller EW (1968). Atom-probe field ion microscope. Rev Sci Instrum 39, 83–86.

Müller M, Saxey DWW, Smith GDWDW & Gault B (2011). Some aspects of the field evaporation behaviour of GaSb. Ultramicroscopy 111, 487–492.

Orloff J (2008). Handbook of Charged Particle Optics, 2nd ed. Boca Raton, USA: CRC Press.

Sha W, Chang I, Smith GDWDW, Mittemeijer EJJ, Liu C & Mittemeijer EJJ (1992). Some aspects of atom-probe analysis of Fe-c and Fe-n systems. Surf Sci 266, 416–423.

Shariq A, Mutas S, Wedderhoff K, Klein C, Hortenbach H, Teichert S, Kücher P & Gault B (2009). Investigations of field-evaporated end forms in voltage- and laser-pulsed atom probe tomography. Ultramicroscopy 109, 472–479.

Shen HH, Zu XT, Chen B, Huang CQ & Sun K (2016). Direct observation of hydrogenation and dehydrogenation of a zirconium alloy. J Alloys Compd 659, 23–30.

Suman S, Khan MK, Pathak M, Singh RN & Chakravartty JK (2015). Hydrogen in Zircaloy: Mechanism and its impacts. Int J Hydrogen Energy 40, 5976–5994.

Sundell G, Thuvander M & Andrén H-O (2013). Hydrogen analysis in APT: Methods to control adsorption and dissociation of H₂. Ultramicroscopy 132, 285–289.

Takahashi J, Kawakami K & Kobayashi Y (2018). Origin of hydrogen trapping site in vanadium carbide precipitation strengthening steel. Acta Mater 153, 193–204.

Takahashi J, Kawakami K, Kobayashi Y & Tarui T (2010). The first direct observation of hydrogen trapping sites in TiC precipitation-hardening steel through atom probe tomography. Scr Mater 63, 261–264.

Takahashi J, Kawakami K, Otsuka H & Fujii H (2009). Atom probe analysis of titanium hydride precipitates. Ultramicroscopy 109, 568–573.

Thompson K, Lawrence D, Larson DJ, Olson JD, Kelly TF & Gorman B (2007). In situ site-specific specimen preparation for atom probe tomography. Ultramicroscopy 107, 131–139.

Tong VS & Britton TB (2017). Formation of very large 'blocky alpha' grains in Zircaloy-4. Acta Mater 129, 510–520.

Tseng TT, Kinkus TJ & Ai CF (1983). Field induced and surface catalyzed formation of novel ions: A pulsed-laser time-of-flight atom-probe study. J Chem Phys 78, 4763–4775.

Vurpillot F, Houard J, Vella A & Deconihout B (2009). Thermal response of a field emitter subjected to ultra-fast laser illumination. J Phys D: Appl Phys 42, 125502.

Yamanaka S, Higuchi K & Miyake M (1995). Hydrogen solubility in zirconium alloys. J Alloys Compd 231, 503–507.

Yao L, Cairney JM, Zhu C & Ringer SP (2011). Optimisation of specimen temperature and pulse fraction in atom probe microscopy experiments on a microalloyed steel. Ultramicroscopy 111, 648–651.