The Observation of H Isotope in Fe-Cr-Ni Model Stainless Steels at the Nano Scale using Atom Probe Tomography

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Stainless Steels (SS) are ubiquitous in consumer, industrial, and laboratory applications due to the combination of relatively high toughness, low cost, and especially corrosion resistance in many common aqueous environments. SS's, however, when subjected to hydrogen embrittlement (HE), can suffer a reduction of ductility that can be detrimental. Under sufficient embrittlement through hydrogen-electrochemical reactions, ductility in SS decreases by over 50% [1]. Understanding the fundamental mechanisms of HE in SS can help potentially mitigate the damaging circumstance.

Measuring the spatial concentration of H in metals may not be done using standardized techniques. Thermal desorption analysis may provide bulk measurements of H but cannot measure H spatially. X-ray energy dispersion spectroscopy cannot be used to measure low-Z elements. Mass spectrum techniques are best qualified to measure H. Secondary ion mass spectroscopy has shown that H segregates to cracks in SS during yielding [2]. Improving the resolution of H concentration measurement towards nano-scale features including dislocations, grain boundaries, or other defects will improve our understanding of hydrogen embrittlement. H at this resolution can be measured using atom probe tomography (APT).

Hydrogen may be measured in APT; however artificial hydrogen not present in the original material is routinely detected and cannot be delineated from hydrogen originally existing in the material. This is in part due to hydrogen desorbing from the vacuum chamber and adsorbing onto the sample [3]. The most common method to avoid the hydrogen artifact is by charging with deuterium. Deuterium's electronic structure allows it to operate similarly to hydrogen in metal while the ^{2}H isotope can be more easily delineated from the ^{1}H peak in the mass-to-charge spectra in APT. Hydrogen via deuteration has been successfully measured using APT in several alloys including ferritic and pearlitic steel [4-6] as well as Al [7]. Any hydrogen or deuterium measurements in austenitic SS using APT have not been previously reported.

We report a study of background H measurement by sweeping measurement parameters of model SS alloys in APT using Pure Fe, Fe-18Cr-10Ni (wt. %), and Fe-18Cr-14Ni (wt. %). An increase of both pulse rate and detection rate (events/pulse) decreases the measured H concentration in materials (Figure 1). We also report the measurement of deuterium in electrochemically charged SS followed by plunge quenching and transferring the sample into the APT analysis chamber via a cryo transfer system in PNNL (Figure 2). This capability to study the distribution of deuterium in model steels, if correlated with nanomechanical testing, transmission electron microscopy, and in situ synchrotron deformation experiments can provide unprecedented understanding of hydrogen embrittlement mechanisms [8].
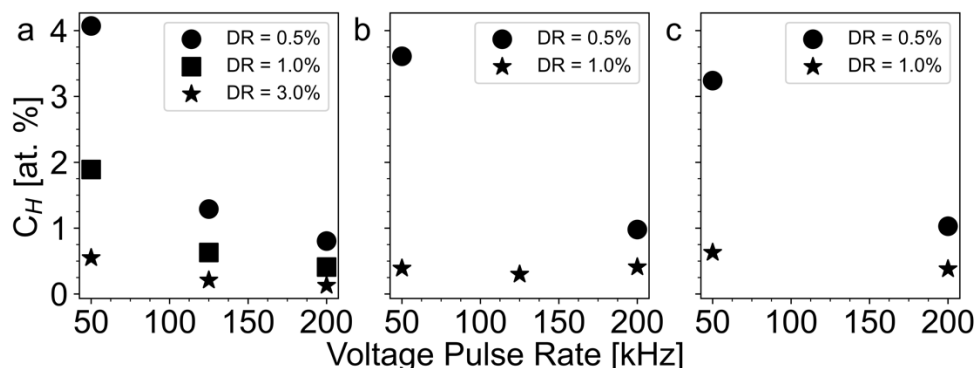
Figure 1. Concentration of hydrogen (at. %) measured with APT using using voltage mode with a pulse fraction of 20% of different alloys: **a.)** Pure Fe **b.)** Fe-18Cr-10Ni, and **c.)** Fe-18Cr-14Ni.
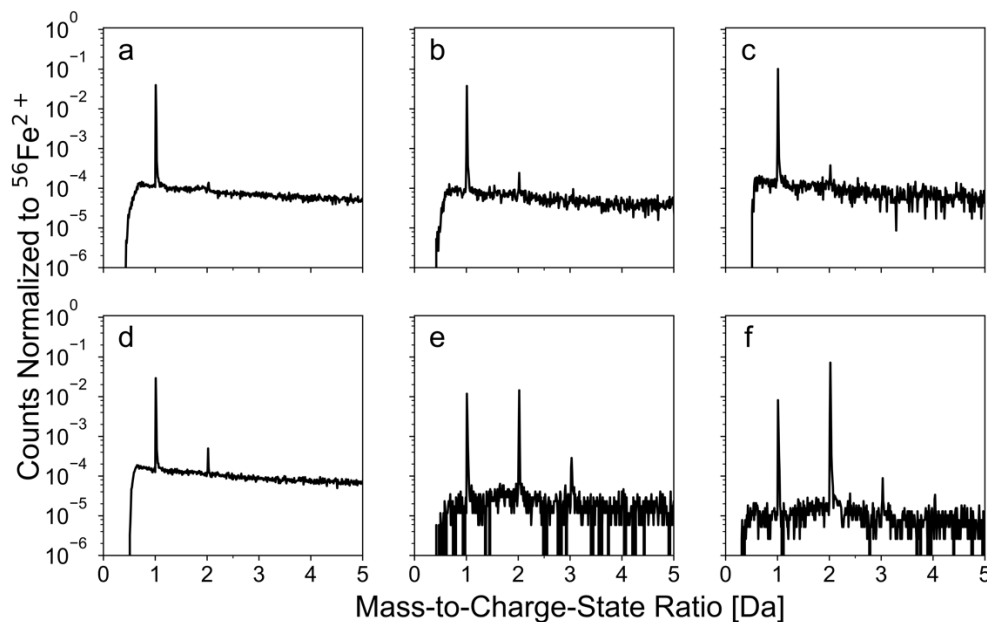
Figure 2. Mass-to-charge spectra of samples that have been electrochemically charged with deuterium. **a)**, **b)**, and **c)** are without charging including: **a)** Pure Fe, **b)** Fe-18Cr-10Ni, and **c)** Fe-18Cr-14Ni. **d.) e.)**, and **f.)** are with deuterium charging including: **d.)** Pure Fe, **e.)** Fe-18Cr-10Ni, and **f.)** Fe-18Cr-14Ni. Counts are normalized to $^{56}Fe^{2+}$.

References:

[1] S Sugiyama et al., Journal of Nuclear Materials **283-287** (2000), p. 863.
[2] O. Sobol et al., Materials Science and Engineering: A **676** (2016), p. 271.
[3] S-H Yoo et al., New Journal of Physics (2021).

[4] Y-S Chen et al., International Journal of Hydrogen Energy **44**(60) (2019), p. 32280.

[5] J Takahashi, K Kawakami and Y. Kobayashi, Acta Materialia **153** (2018), p. 193-204.

[6] A.J. Breen et al., Acta Materialia **188** (2020), p. 108.

[7] H. Zhao et al., Nature **602**(7897) (2022), p. 437.