

## Hydrogen Trapping in Fully Martensitic Steels using Atom Probe Tomography

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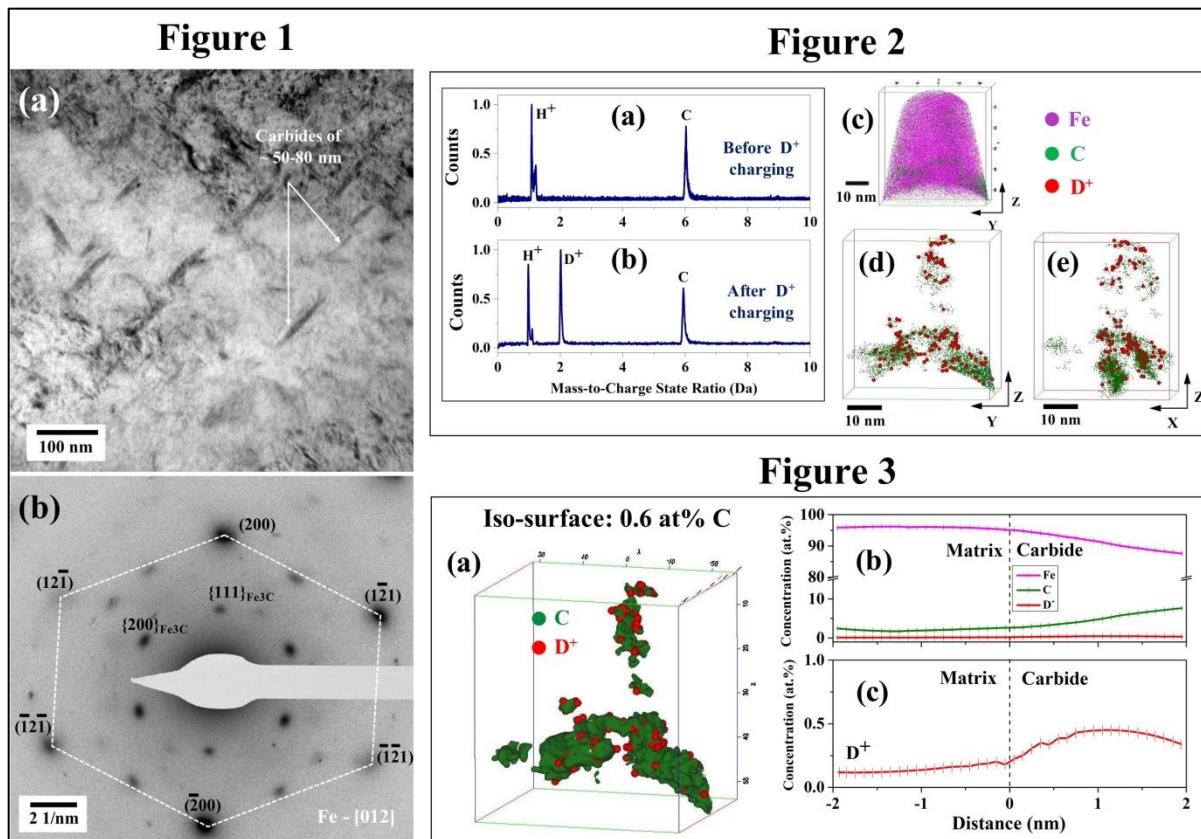
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This paper examines the interaction between deuterium (D) and metal carbides in fully martensitic steel (MS 1500 steel) using atom probe tomography (APT). The presence of hydrogen in advanced high strength steels degrades the mechanical performance, a phenomenon referred to as 'hydrogen embrittlement' (HE) [1]. To prevent such embrittlement, it is critical to understand the adsorption and distribution of hydrogen at the nanoscale interfaces within these steels. For example, Chen *et al.* [2] discussed the distribution of deuterium at dislocations, grain-boundaries (GBs) and precipitates in ferritic and martensitic steels using APT. The use of the deuterium isotope reduces artifact concerns in the identification of hydrogen in APT experiments. They [2] noted that the D atoms are mostly located at the interfaces between NbC precipitates and the ferrite matrix. They also showed that the D atoms are concentrated in the GB regions demonstrating that GBs act as trapping sites in martensitic steel samples. Other researchers have also reported similar findings of D trapping at dislocations, GBs, and near transition metal carbides precipitates [3,4]. Since cementite carbides ( $\text{Fe}_3\text{C}$ ) are commonly formed in steels, in this work, we report the experimental trapping characteristics in this phase.

For these studies, a commercially available MS1500 steel with a nominal chemical composition of 0.20-0.22 wt.% C, 0.60-0.62 wt.% Mn and 0.01-0.03 wt.% Si was used. All other solute additions were at a level of < 0.05 wt.%. The atom probe specimens were prepared by an electropolishing method using a two-electrode (platinum as cathode and  $0.8 \times 0.8 \times 20 \text{ mm}^3$  dimension steel sample as anode) cell setup with an applied voltage of 10-15 V. Electrolyte of 10% perchloric acid in acetic acid followed by 2% perchloric acid in butoxy ethanol was used to prepare the APT specimen. After the preparation of final needle-shaped APT specimen (~ 80 nm), an electrolytic deuterium charging experiment was performed with an applied voltage of 2.2 V and a charging time of 30 sec at room temperature in a 0.1M NaOD in  $\text{D}_2\text{O}$  solution. To suppress the deuterium diffusion within the charged sample, the APT specimen (loaded onto an APT puck holder-carousel) was transferred into a cryogenic liquid nitrogen setup immediately following charging and the rapidly transferred into the LEAP-5000XS instrument where it was loaded into a cryogenic cooling condition. APT experiments were performed in voltage-pulse mode with 60 K temperature, 0.5% detection rate, 20% pulse fraction and 200 kHz pulse frequency. APT data was reconstructed using IVASE 3.8.8 software package.

Microstructural examination using TEM confirmed the presence of nanoscale cementite phase in the fully martensitic microstructure.  $\text{Fe}_3\text{C}$  is observed as the needle-like features in the matrix region with size range of ~ 50-80 nm (Fig. 1(a)). Selected area diffraction (SAED) pattern (Fig. 1(b)) shows the two sets of diffraction spots. One set is from [012]  $\alpha\text{-Fe}$  zone axis and the other set corresponds to  $\text{Fe}_3\text{C}$ . The specimen (before and after D charging, Fig. 2(a) and (b), respectively) showed the hydrogen (H) peak at 1 Da which is expected because of the residual gas from the analysis chamber; the clear 2 Da peak confirms the charging. The reconstructed APT data (Fig. 2(c)) displayed the distribution of Fe, C and D atoms within the sample. The other alloying elements were found to be distributed uniformly within the sample and are not presented to enable visual clarity. The spatial location of D atoms and their spatial correlation with C atomic regions are shown in the reconstructed APT data, Fig. 2(d) and (e), respectively in Y-Z and X-Z directions. Based on the 0.6 at% C iso-concentration surface, C partitioning revealed the distribution of D atoms in and around the carbide ( $\text{Fe}_3\text{C}$ ) phase regions, Fig. 3(a). From the

proximity histogram, Fig. 3(b) and (c), the D is observed to increase within the carbide. While cementite is a line-compound, its orthorhombic structure offers potential opportunities for interior trapping [5]. The implications of trapping differences between different carbides found in steels as well as between interfaces and interior sites will be discussed [6].



**Figure 1.** (a) TEM bright field image showing the microstructure of carbides ( $\text{Fe}_3\text{C}$ ) distribution in fully martensitic (MS1500) microstructure. (b) The corresponding diffraction pattern of the  $\text{Fe}_3\text{C}$  with the surrounding  $\alpha\text{-Fe}$  matrix.

**Figure 2.** The mass spectrum data showing (a) before and (b) after deuterium charging. 3D reconstructed APT data showing (c) the distribution of Fe, C and D atoms within the sample, the localized position of D and C atomic positions (d) Y-Z direction and (e) X-Z direction.

**Figure 3.** (a) APT 3D reconstruction showing 0.6 at% C iso-concentration surface value (b) and (c) Proximity histogram obtained from 0.6 at% C iso-concentration surface value.

#### References:

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