

## Visualization of Hydrogen-trapping Sites in Steels by Atom Probe Tomography

Jun Takahashi<sup>1\*</sup> Kazuto Kawakami<sup>2\*</sup> Shinya Teramoto<sup>3</sup>, Yuuji Sakiyama<sup>1</sup> and Tomohiko Omura<sup>1</sup>

<sup>1</sup>. Nippon Steel Corporation, Futtsu-city, Chiba, Japan.

<sup>2</sup>. Nippon Steel Technology Co. Ltd., Futtsu-city, Chiba, Japan.

<sup>3</sup>. Nippon Steel Corporation, Muroran-city, Hokkaido, Japan.

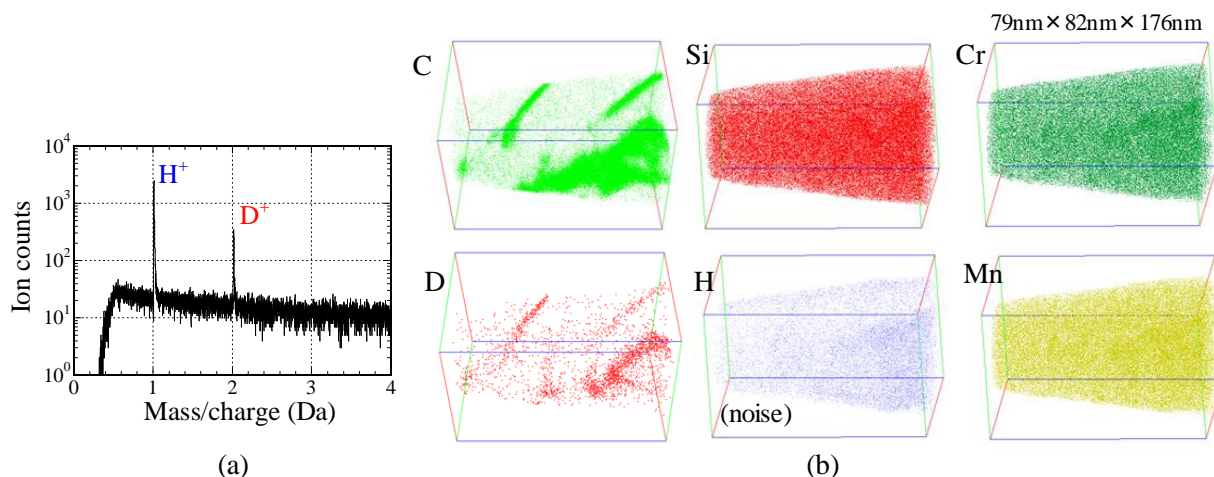
\* Corresponding author: takahashi.3ct.jun@jp.nipponsteel.com

As the tensile strength of steel increases, hydrogen embrittlement becomes more serious. To increase the resistance of high-strength steels against hydrogen embrittlement, dispersion of fine carbide precipitates, such as titanium carbide (TiC) and vanadium carbide (VC), has been proposed [1]. The high number density of precipitates increases the steel strength through a particle-strengthening mechanism, and simultaneously produces several deep trapping sites for hydrogen. However, the origin of hydrogen trapping sites associated with fine precipitates remains unclear because in conventional analysis methods, such as tritium autoradiography, hydrogen microprinting, and secondary ion mass spectrometry (SIMS), the lack of spatial resolution makes it difficult to identify hydrogen trapping sites associated with nano-sized precipitates. Therefore, atomic-scale visualization of hydrogen in steels using atom probe tomography (APT) is essentially required. This paper describes the development of the hydrogen observation technique by APT and its application to steels.

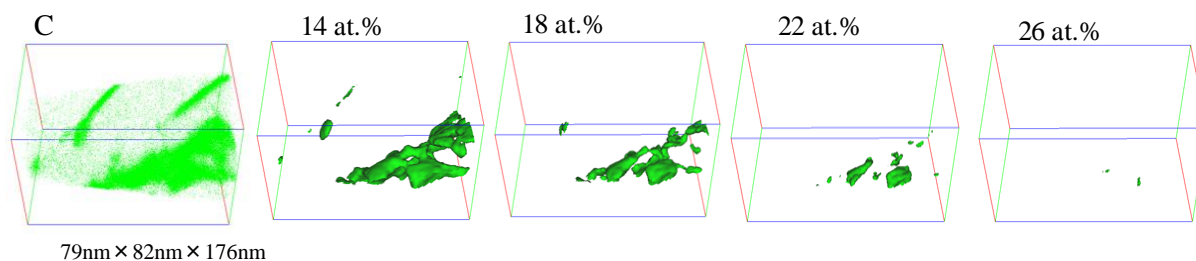
Although the effectiveness of APT in hydrogen analysis was demonstrated through the measurements of titanium hydride [2], APT had some problems in direct observation of hydrogen within steel. The residual hydrogen gas (H<sub>2</sub>) in the analysis chamber was absorbed on the specimen tip surface, and the absorbed hydrogen atoms were field-evaporated like constituent atoms [3]. Such hydrogen noise hindered the observation of the actual hydrogen within the steel, even under the ultra-high vacuum condition. To separate the hydrogen within the steel from the hydrogen noise, the charge of deuterium (natural abundance: 0.015%) was adopted [4,5]. However, the charged deuterium was easily detrapped from the trapping sites and escaped from the surface in a very short time at room temperature. We designed a “deuterium charge cell” attached to the storage chamber of a three-dimensional atom probe, which enabled local heating of a specimen tip in a deuterium atmosphere for charging and, subsequently, rapid cooling of the specimen tip [5]. Based on the equipment, the deuterium atoms at trapping sites associated with fine carbide precipitates in steels were successfully visualized for the first time, and the origin of the deep trapped sites as carbon vacancies in the coherent interface was proposed [6,7].

The analysis techniques have been further improved and applied to various steels. For instance, hydrogen observation in the tempered martensite steel with high silicon content (Fe-0.6C-2Si-1Mn-1mass%Cr) is reported. Tempering at 400 °C significantly increased the amount of trapped hydrogen, and the trap energy was approximately 31 kJ/mol, by thermal desorption analysis [8]. Transmission electron microscopy (TEM) diffraction analysis indicated a large amount of  $\epsilon$ -carbide precipitates in the steel [8]. Fig. 1 shows the APT analysis result of the deuterium-charged specimen tip of the tempered steel. Deuterium atoms are definitely observed in fine carbon-enriched regions, where other metallic atoms are hardly enriched. Fig. 2 shows the isoconcentration maps of carbon. The carbon concentrations are less than 25 at.%, which is lower than the stoichiometric composition (Fe<sub>2</sub>C) of  $\epsilon$ -carbide. The carbon-enriched regions were considered to be fine  $\epsilon$ -carbide precipitates with carbon vacancies. First

principles calculation indicated that the O-sites of carbon vacancies with a small number of neighboring carbon atoms in  $\epsilon$ -carbide have hydrogen trap energies in the range of 34–52 kJ/mol but the diffusion barriers are considerably high (17–117 kJ/mol) [9]. It implied that the diffusion pathways with low diffusion barriers increase with high number density of carbon vacancies and, consequently, hydrogen atoms reach the inner region of fine  $\epsilon$ -carbide precipitates. The origin of hydrogen trapping sites in the tempered martensite steel was considered to be the O-sites of carbon vacancies in  $\epsilon$ -carbide precipitates [9].



**Figure 1.** APT analysis result of the deuterium charged specimen tip of 400°C-tempered high-Si martensite steel: (a) mass spectrum and (b) 3D elemental maps.



**Figure 2.** Carbon isoconcentration maps of the deuterium charged specimen tip.

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