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Direct observation of hydrogen-trapping sites in vanadium carbide precipitation steel by atom probe tomography

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Atomic-scale direct observation of hydrogen-trapping sites in vanadium carbide (VC) precipitation steel was performed using a three-dimensional atom probe (3DAP) with a deuterium-charging method. Most of the deuterium (D) atoms were observed at larger VC platelets, while such trapping of D atoms was not observed at smaller VC platelets. 3DAP analysis showed that these platelets had the chemical composition V_4C_3. The results suggest that the misfit dislocation cores on semicoherent platelets are deep trapping sites for hydrogen.

Keywords: Atom probe tomography; Deuterium; Hydrogen trapping site; Vanadium carbide; Steel

Hydrogen embrittlement is an especially serious problem in high-strength steels. To increase resistance against hydrogen embrittlement, dispersion of fine carbide precipitates, such as titanium carbide (TiC), vanadium carbide (VC) and niobium carbide (NbC), has been proposed. A high number density of precipitates increases the tensile strength through the precipitation-strengthening mechanism and simultaneously produces a number of deep trapping sites for hydrogen [1,2]. Many studies on hydrogen trapping in steels containing fine carbide precipitates have been carried out [1–5]. However, hydrogen-trapping sites associated with fine precipitates have still not been fully elucidated, although some trapping sites, e.g. the strain field surrounding a coherent particle, the coherent interface, the incoherent interface and the inside of the particle, have been proposed. The lack of spatial resolution has made it difficult to determine the hydrogen-trapping sites associated with nanosized carbide precipitates. In order to predict the behaviour of hydrogen in the steel and to solve the embrittlement problem, the real trapping sites associated with fine precipitates must be understood.

It has been suggested that atom probe tomography (APT) should be an excellent tool for nanoscale visualization of the hydrogen distribution in steel due to its high spatial resolution and low specimen temperature [6]. The quantitative performance of APT for hydrogen analysis was confirmed through the investigation of a stable titanium hydride with an well-known composition [7], and a direct atomic-sale observation technique for hydrogen-trapping sites was developed by a modified three-dimensional atom probe (3DAP) with a "deuterium charge cell" [8].

In this study, atomic-scale observation of hydrogen-trapping sites in VC precipitation steel was carried out. VC precipitates are used in many high tensile steels to increase the tensile strength. It has been reported that VC precipitation improves the performance of resistance against hydrogen embrittlement [2], and that hydrogen desorption peaks associated with VC precipitates appeared at 140 and 200 °C during thermal differential analysis [4,5]. VC precipitate is known to have an NaCl-type crystal structure (face-centred cubic) with the chemical composition V_4C_3 [9], which indicates that the precipitates contain a high number density of carbon vacancies under thermal equilibrium conditions. Epicier et al. [10], however, using diffraction analysis by transmission electron microscopy (TEM), reported that the precipitates have the monoclinic structure of V_6C_5. Recently, Oba et al. suggested, based on small-angle X-ray and neutron scattering analyses, that the composition of VC_x ($x = 0.9$–1.0) varies with the holding temperature [11]. The chemical composition of VC precipitates, therefore, remains unclear. Herein, we discuss the hydrogen-trapping sites of VC precipitates based on

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the results of direct observation and chemical composition analysis.

In an APT analysis chamber, residual hydrogen gas (H_2) is absorbed on the needle tip surface of the steel and then field-evaporated. This background hydrogen interferes with observation of the dissolved and trapped hydrogen in the steel. Deuterium-charging enables separation of the deuterium charged into the steel from the background hydrogen [8,12]. Deuterium has a sufficiently lower natural abundance (0.015%) and its chemical properties are almost the same as those of hydrogen, although the diffusion coefficient of deuterium in steel is slightly smaller than that of hydrogen because of its larger mass. The calculated de-trapping time and diffusion distance suggest that solute hydrogen (H) atoms in ferritic steel can sufficiently diffuse even at low temperature [8], but H atoms at trapping sites with even small trapping energy ($\sim$20 kJ mol^{-1}) are never released in the temperature range of the atom probe measurement (50–70 K). Therefore, the deuterium (D) atoms at the trapping sites should be visualizable when the charged deuterium is prevented from escaping from the needle tip surface after deuterium charging. The "deuterium charge cell" attached to the storage chamber of the 3DAP enables the heating of a needle tip in a deuterium atmosphere of up to 1 atm for charging, and then rapid cooling of the needle tip to prevent the charged deuterium from escaping.

Precipitation-strengthened steel containing a high number density of fine VC precipitates was produced for this experiment. Round bars of a V-containing low-carbon steel (Fe–0.087C–0.1Mn–3.0Al–0.35 V mass%) were heated at 1250 °C for 10 min followed by quenching into water. Most of the material retained the ferrite (body-centred cubic) structure even at 1250 °C due to the Al addition. The steel was composed mainly of sub-millimeter-sized ferrite grains with very low density dislocations, which is advantageous for reducing the frequency of tip rupture during the atom probe measurement and separating the trapping sites associated with precipitates from those associated with dislocations. VC precipitation was then achieved by annealing the samples in an argon atmosphere at 580 °C for various aging times. Under-aged (2 h) and peak-aged (16 h) steel samples were used for this study. The increment in yield strength by annealing was about 100 and 350 MPa for the under-aged and peak-aged samples, respectively, which suggests that a high number density of nanosized VC particles precipitated in the samples. A Hitachi H8000 transmission electron microscope operated at 200 kV was used for the characterization of the precipitates in the samples. Electropolishing was used to prepare the thin films for TEM analysis.

Figure 1 shows a TEM bright-field image and a selected-area diffraction pattern (500 nm diameter aperture) of the peak-aged sample. A high density of short line images parallel to the [1 0 0] and [0 1 0] directions was observed under an incident electron beam parallel to the [0 0 1] direction. The diffraction pattern represents definite streaks elongating in the [1 0 0] and [0 1 0] directions, suggesting that the VC precipitates have a thin plate shape on the {0 0 1} plane. It is known that VC precipitates have an NaCl-type crystal structure that

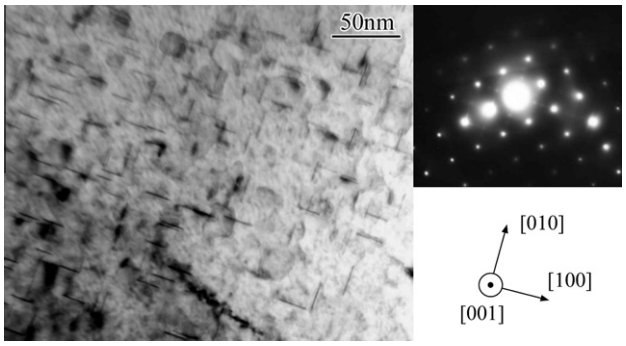

Figure 1. TEM bright-field micrograph and selected-area diffraction image of the peak-aged steel sample.

maintains the Baker–Nutting orientation with a ferrite matrix, i.e. $(0\,0\,1)_{VC}//(0\,0\,1)_{\alpha}$ and $[1\,1\,0]_{VC}//[1\,0\,0]_{\alpha}$, with a broad interface on the (0 0 1) plane [9]. The edge length of the platelets was in the range of 10–20 nm, and their thickness was about 1 nm. In the under-aged sample, however, definite precipitates were not observed, which implies that the VC precipitates and/or clusters that contributed to the precipitation strengthening were very fine.

An energy-compensated 3DAP with a large-angle reflectron (Oxford Nanoscience Ltd.) was used in this experiment. Needle specimen tips were produced using a standard electropolishing method. In the charge cell under high vacuum ($<8 \times 10^{-4}$ Pa), the needle specimen with the sample holder was cooled (<-150 °C) with liquid nitrogen, and then deuterium gas of high purity (99.9998%) was introduced. Only the tip position of the needle specimen was heated by the special heater in the deuterium atmosphere ($\sim$0.8 atm). Deuterium was charged into the specimen tip at 200–300 °C for 5 min. The heater was then removed from the tip position and the deuterium gas was pumped out. The specimen tip rapidly cooled down within a few seconds by thermal conduction to the sample holder with a large heat capacity. The specimen tip, maintained at much lower than -100 °C, was transferred to the analysis chamber and placed on a sample stage maintained at <70 K. The atom probe measurements were carried out in an ultra-high vacuum ($<4 \times 10^{-9}$ Pa) with the specimen temperature at 50–65 K, the total probing voltage in the range of 7–14 kV, the pulse fraction at 20–25% and a pulse frequency of 20 kHz.

The atomic data sets from 3DAP measurements were analyzed using IVAS software (Cameca, version 3.6.0.). A peak at 2 amu in the mass spectrum was assigned to deuterium ions (D^+) [8], and its mass width was set to be less than 0.03 amu. A peak at 25.5 amu was assigned to vanadium ions (V^{2+}). Peaks at 6, 6.5, 12, 13, 18 and 24 amu were assigned to carbon ions. A peak at 24.5 ($^{12}C_3{}^{13}C^{2+}$) was not observed, indicating that no tetramer ion (C_4^{2+}) appeared as a result of the field evaporation of the VC. Therefore, the peak at 24 amu was assigned only to the dimer ion (C_2^+) [13].

Figure 2 shows 3D elemental maps of the peak-aged sample with deuterium-charging. Two datasets of different measurements are presented (Fig. 2a and b). The measurement direction, which was nearly along the [0 0 1], is indicated by the bold arrow. The crystallo-