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Analysis of Hydrogen State in Steel and Trapping Using Thermal Desorption Method

Shingo YAMASAKI* Daisuke HIRAKAMI
Toshiyuki MANABE

Abstract

Hydrogen embrittlement susceptibility of steels rises significantly as the tensile strength increases and the embrittlement susceptibility is influenced by the state of hydrogen in steels. The hydrogen trapping properties in steels were therefore analyzed using thermal desorption method, to establish the solution to improve the hydrogen embrittlement resistance. In hydrogen evolution rate curves of steels, several peaks are observed. Hydrogen trapped at dislocations, MC and epsilon carbides show specific peaks respectively. In relation to hydrogen trapped at dislocation, trap energy and amount was affected by cold-working and fixation of carbon to dislocation. Hydrogen trap capacity of MC carbide depends on the carbide size and the characteristic of carbide/matrix interface. High-strength bolt using hydrogen trap ability with MC carbide was developed by these knowledge.

1. Introduction

There is a strong demand for further strength improvement of steel in the automotive parts market where weight reduction of parts is required for fuel consumption improvement and in the construction industry where cost reduction of the construction period and materials is desired. Amid this, the increase of steel strength has become problematic because it boosts the hydrogen embrittlement susceptibility, hindering steel strength improvement completely.[1] Hydrogen embrittlement is a phenomenon in which a minute amount of hydrogen enters steel when the steel is corroded or plated and diffuses to reach a stress concentration, promoting cracking there and spreading of the crack. There have been several attempts to clarify the hydrogen embrittlement mechanism from various viewpoints; for example, considering hydrogen embrittlement as a brittle fracture on which the lattice embrittlement theory[2] is based, and considering the ductile fracture from which the hydrogen-enhanced localized plasticity (HELP) mechanism[3] and hydrogen-enhanced strain-induced vacancy (HESIV) mechanism[4] are derived. All these approaches have failed to coherently and fully explain hydrogen embrittlement.

One main reason for this is that as hydrogen is the lightest of all elements, it can readily diffuse in steel, and another is that as it only takes a tiny amount of hydrogen to cause the embrittlement, it is difficult to identify the relationship between the state of hydrogen existing in steel and embrittlement.

In this paper, examples of hydrogen state analysis in steel using a thermal desorption method are described.

2. Analysis Technology for Analyzing the State of Hydrogen in Steel

The methods to analyze hydrogen in steel can be roughly classified into two groups: 1) those using technology for visualizing the hydrogen distribution and 2) those involving measurement of the absorbed hydrogen concentration. In the following subsections, typical method types and their characteristics are described for each group.

2.1 Technologies for visualizing the hydrogen distribution

Hydrogen can be trapped in many defects including lattice defects (e.g., atomic vacancies, dislocations, crystal grain boundaries), interfaces of a precipitate or inclusion, and voids. Typical methods for directly associating these metal microstructure defects with local hydrogen distribution include 1) tritium autoradiography[5], 2) hydrogen microprinting[6], 3) secondary ion mass spectrometry[7], and 4) 3D atom probe (3DAP)[8].

2.2 Methods for measuring the hydrogen concentration

Typical methods for measuring the hydrogen concentration in

* General Manager, Head of Div., Ph.D, Bar & Wire Rod Research Lab., Steel Research Laboratories
20-1 Shintomi, Futtsu City, Chiba Pref. 293-8511

steel include the hydrogen permeation method using films[9], the dissolution method using bulk materials, and the thermal desorption method. Using the hydrogen permeation method, the hydrogen ingress behavior that changes over time can be measured but is limited to hydrogen that can move (diffuse). In contrast, the thermal desorption method allows for separate measurement of hydrogen for each existing state in steel including non-diffusible hydrogen, and for measurement of the so-called trap energy as well. The method can be used for either of these purposes.

3. Analysis of Hydrogen State in Steel Using Thermal Desorption Method

As hydrogen that has entered steel can hardly be dissolved in the lattices, such hydrogen is considered to locate in trapping sites such as grain boundaries and lattice defects. In order to determine the mechanism of embrittlement caused by hydrogen ingress, it is important to clarify the state and the amount of hydrogen existing in steel. The thermal deposition is commonly used as a method for measuring the hydrogen amount and analyzing its state in a simple manner.[10] This method heats a test sample containing hydrogen at a constant rate of temperature increase, and detects the emitted hydrogen using a gas chromatograph or quadrupole mass spectrometer. Using this method enables measurement of the relationship between the temperature and hydrogen discharge speed.

Hydrogen in steel is diffused through the lattices during temperature increase, moving to the surface where it is discharged. During that time, hydrogen in the lattices is diffused by its own movements of repeated capture and release from trapping sites, or of being released from the trapped state. This means that the temperature-hydrogen discharge speed curve contains the information of binding energy involving hydrogen trapping at various lattice defects, and useful information of the state of hydrogen in the steel can be obtained. In general, if the binding energy between hydrogen and a trapping site is small, and the hydrogen discharge is dominated by the diffusion degree, the peak temperature is changed, influenced by the size of the test sample. If the binding force between hydrogen and the trapping site is strong, and the hydrogen discharge is dominated by the dissociation degree, the peak temperature is not susceptible to the test sample size. Thus, in the thermal desorption method, the information on the hydrogen trapping site and binding energy between hydrogen and the defect can be obtained by using thin film-test samples.

Figure 1 shows the measurement results of samples all charged with hydrogen, as typical examples of hydrogen discharge curves obtained using the thermal desorption method. The samples were taken from monocrystalline ferrite steel, tempered martensite structure of carbon steel and V-added steel, and a drawn wire of pearlite steel. The peak at 100°C, which is formed by diffusible hydrogen, can be seen in many cases. The other peaks, which are formed by hydrogen trapped at precipitates and dislocations, may vary depending on the steel material composition, heat treatment, processing conditions, etc. The state of hydrogen existing in steel and behavior of hydrogen being trapped indicated by these peaks are described in detail.

4. Hydrogen Trapping at Dislocations

Hydrogen embrittlement is affected by the interaction of dislocations and hydrogen.[3] In order to clarify the hydrogen embrittlement mechanism, it is necessary to reveal the trapped state of hydrogen at dislocations. As shown by the measurement results of the thermal desorption method in Fig. 1, the plastic formed pearlite steel had a hydrogen discharge peak around 300°C in addition to one around 100°C.[11] Hydrogen that formed this 300°C peak appeared to have been trapped at dislocations originated from the plastic forming process.

For drawn pearlite steel containing carbon at 0.82 mass% cathodically charged with hydrogen (**Fig. 2**) and the same steel tempered after being heated at 950°C for an hour and then cathodically charged with hydrogen (**Fig. 3**), thermal desorption analysis was conducted twice immediately after the hydrogen charge and after retention at room temperature for a month.[12] As a result of the measurement after one-month retention at room temperature, both samples were found to have hydrogen that formed the 100°C peak smaller in amount than the measurement result just after the hydrogen charge. The drawn pearlite steel had hydrogen that formed the 300°C peak showing little change in amount after the one-month retention. The tempered steel had hydrogen that formed the 300°C peak decrease after the one-month retention, in addition to the decrease in hydrogen that formed the 100°C peak.

Obata, et al. examined the hydrogen behavior of being trapped in steel samples with different C contents that were heated in a hy-

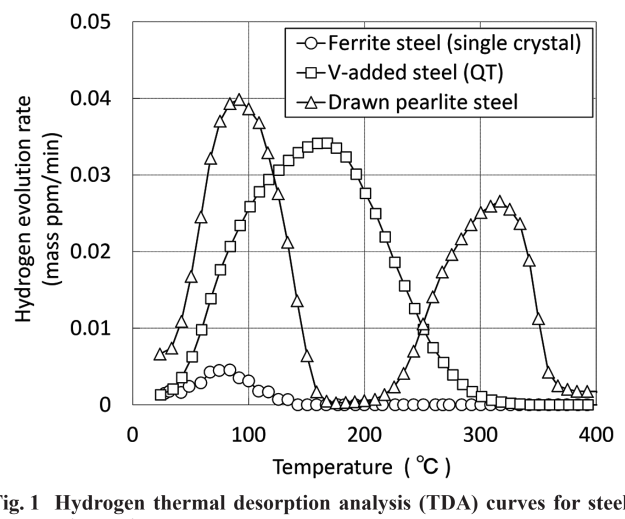

Fig. 1 Hydrogen thermal desorption analysis (TDA) curves for steels with various hydrogen trap

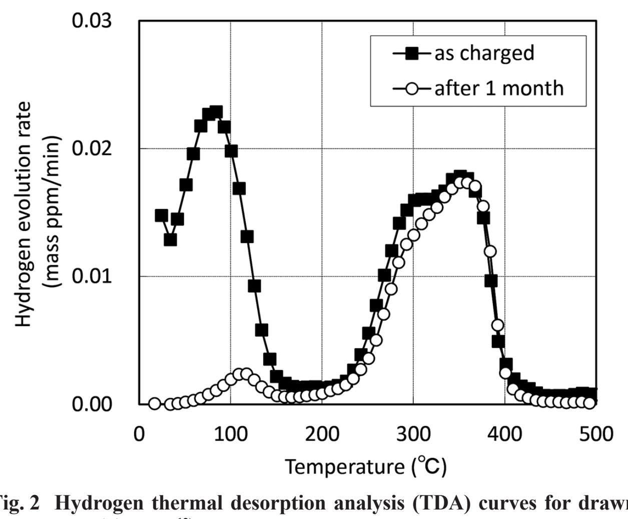

Fig. 2 Hydrogen thermal desorption analysis (TDA) curves for drawn pearlitic steel[12]

drogen atmosphere at 950°C in 1 atm and then were tempered. According to the report, along with the increase of the C content, in other words, along with the decrease of the martensitic transformation temperature M_S, the amount of hydrogen that formed the 100°C peak reduced, while hydrogen that formed the 300°C peak increased (**Fig. 4**[11)]). They also examined the diffusion time of the dissolved hydrogen and dissolved carbon to the dislocation core during the time period from the start of martensitic transformation in the test samples to when the samples had been cooled to room temperature. The research revealed that whereas C reaches the dislocation followed by H in low C steel with high M_S, H may reach the dislocation first in steel with a larger C content, which means lower M_S (**Fig. 5**[12)]).

Figure 6 shows the change in hardness of the as-tempered 0.82 mass% C steel retained at room temperature.[12)] Hardness was increased over time retained at room temperature, showing age hardening behavior. From these results, it appeared that in the 0.82 mass% C steel, hydrogen was trapped before carbon at the dislocation core formed during tempering, and then was replaced by carbon existing in the steel during the retention at room temperature, thus causing the decrease of hydrogen that formed the 300°C peak.

Hydrogen that caused the second peak at the higher temperature than the first one is likely to have been trapped at a strain field at the interface between ferrite and cementite, in addition to the possibility of having been trapped at a dislocation core. **Figure 7** shows the thermal desorption curves of hydrogen in round bar samples (5 mm in diameter × 300 mm in length) of ultra-low carbon steel, which would not form cementite, cathodically charged with hydrogen. One of the samples underwent the hydrogen measurement immediately after the hydrogen charge, and the other was subjected to the hydrogen measurement after it was twisted five times using a torsion tester.[13)] The measurement results of low and medium carbon steel samples are also shown.

The measurement results of the samples immediately after the hydrogen charge show only the discharge of trapped hydrogen that peaked at around 100°C. The measurement results obtained after the torsion test show only the second peaks at temperatures higher than those of the first peaks around 100°C. It appears that this was because hydrogen locating in the stress fields of dislocations, etc., was trapped at dislocation cores newly formed by twisting the samples.

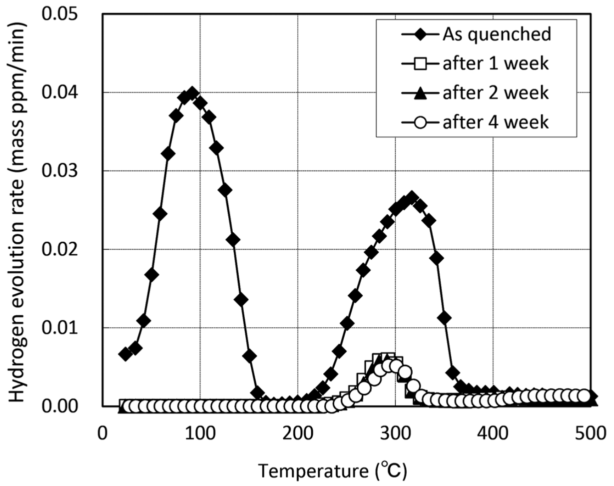

Fig. 3 Changes in TDA curves with aging at room temperature of 0.82 mass%C steel annealed in hydrogen atmosphere followed by quenching[12)]

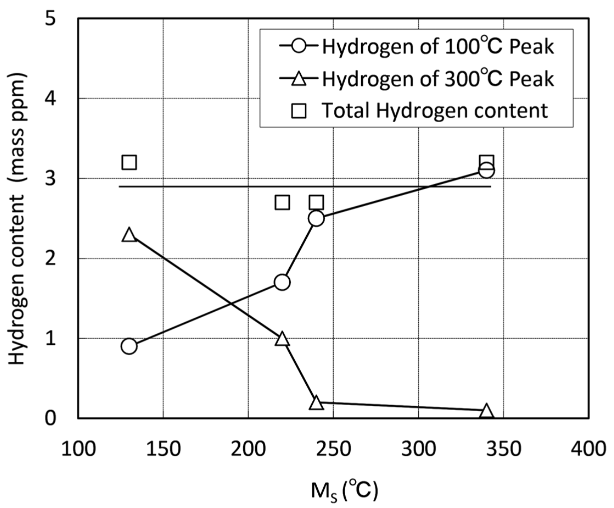

Fig. 4 Effect of carbon content on the amount of hydrogen in steel that annealed in hydrogen atmosphere followed by quenching[11)]

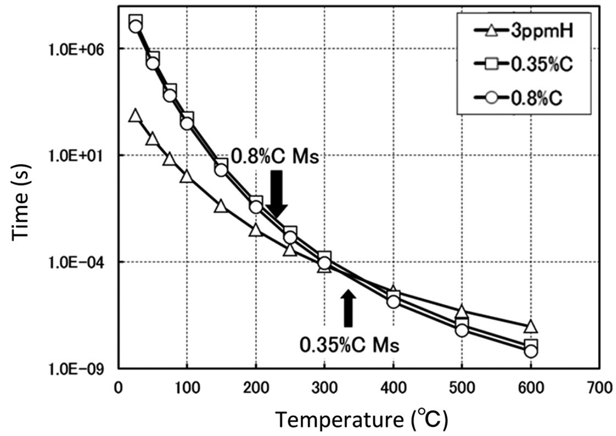

Fig. 5 Conditions for diffusion of hydrogen and carbon to reach dislocation in terms of temperature and time[12)]

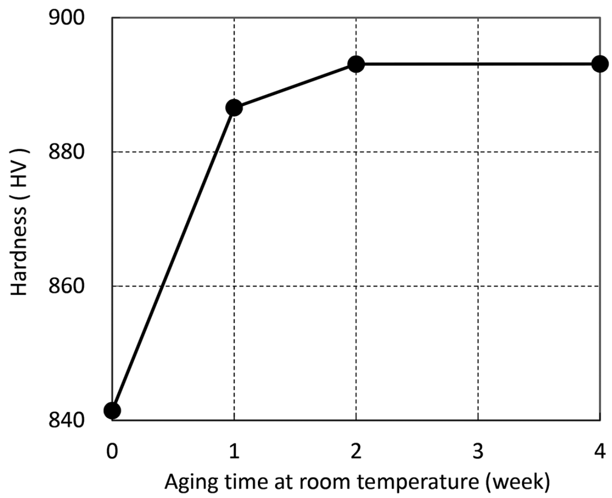

Fig. 6 Changes in Vickers hardness with aging at room temperature of 0.82 mass%C steel annealed in hydrogen atmosphere followed by quenching[12)]

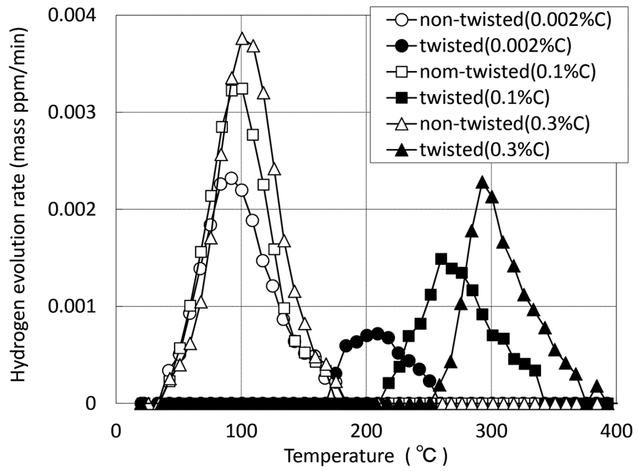

Fig. 7 Changes in TDA curve of low carbon steel by torsion processing [13)]

The second peak temperatures that differ depending on the C amount are considered to have occurred due to different dislocation density, i.e., trapping site density, since work-hardening properties also differ depending on the C amount.

The hydrogen embrittlement resistance properties of drawn pearlite steel change due to aging. Given this, the interaction state between the dislocation and hydrogen is considered to have been changed. In order to clarify the hydrogen embrittlement behavior going forward, it will be necessary to analyze in more detail the influence of the two discharge peaks of hydrogen emanating from dislocations as found through thermal desorption.

5. Hydrogen Trapping Using Fine Precipitates

The use of fine precipitates is one of the techniques to render hydrogen that has entered steel due to corrosion, etc., benign. Among those used for this purpose, MC carbides are popular. In practice, steel added with V alone or that with more additives such as Mo, Nb, Ti in addition to V in a combined manner is tempered at high temperature near 600°C and used in the method in many cases. Some examples are described below.

5.1 MC carbide

Steel with NaCl-structured MC carbide precipitates discharges hydrogen at a higher temperature than the temperature at which so-called diffusive hydrogen is discharged as shown in Fig. 1. This indicates that hydrogen exists in steel in a more stable manner (with higher trapping energy) than diffusive hydrogen does.[14)] **Figure 8** shows the hydrogen trapping capacity of samples taken from steel containing 0.1 mass% C and 2.0 mass% Mn in which V and Mo additives were used so that MC carbide precipitation alone could occur at equilibrium. These samples were quenched, and tempered at 600°C for various durations to measure the hydrogen trapping capacity for each sample.[15)] The trapped hydrogen amount was the value obtained by measuring the amount of discharged hydrogen at temperatures not exceeding 400°C from the samples heated at a rate of temperature increase of 100°C/h after hydrogen was made to enter the samples by 48-hour cathodic charge and then diffusible hydrogen was discharged in the 20°C atmosphere. While the amount of the MC carbide was increased over time during the tempering, the hydrogen trapping capacity was likely to show a peak in 10 to 20 hours from the start of tempering.

Furthermore, although the amount of an MC carbide that precipitates in steel at equilibrium does not largely change depending on the steel type, the maximum value of the hydrogen trapping capacity does significantly. **Figure 9** shows the influence of the Mo fraction in an M site in an MC carbide that existed in steel tempered for 10 hours on the hydrogen trapping capacity per MC carbide particle.[15)] As seen from the figure, the Mo amount in the MC carbide depended on the steel composition, and along with the increase of Mo in the carbide, the hydrogen trapping capacity per carbide particle was increased.

Kosaka, et al. studied the influence of the MC carbide composition on the hydrogen trapping capacity, using two types of samples: one was taken from steel containing 0.1 mass% C to which Nb, Ti, and V were added such that the stoichiometric composition of an MC carbide was achieved; and the other was taken from steel containing 0.1 mass% C to which combined additives of Ti-V and V-Mo were added.[16)] **Figure 10** shows the relationship between the tempering temperature and hydrogen trapping capacity of steel tempered at various temperatures with the tempering duration fixed to one hour. A peak of the hydrogen trapping capacity can be seen around 600°C. In addition, the hydrogen trapping capacity varies depending on the added elements (MC carbide composition).

From the examination results as described above indicating that the hydrogen trapping capacity is dependent on the MC carbide composition and that over-aging causes the hydrogen trapping ca-

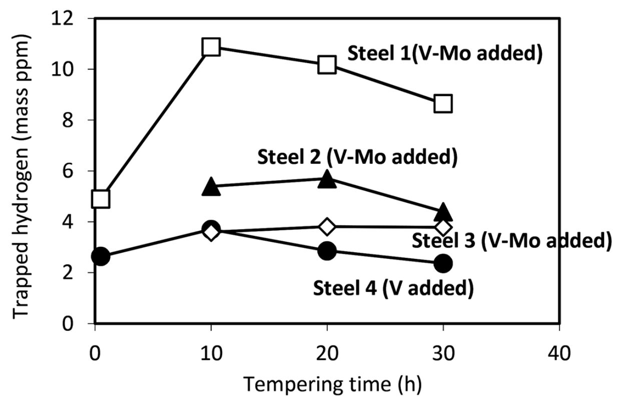

Fig. 8 Hydrogen trapping capacity of V-Mo added steels for various tempering time [15)]

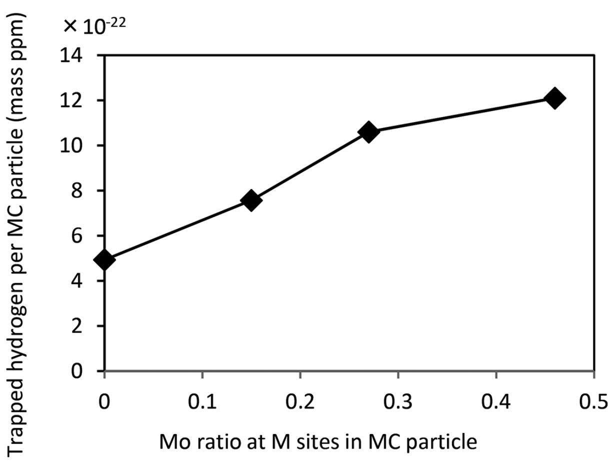

Fig. 9 Relationship between fraction of Mo in 'M' of MC and hydrogen trapping capacity per MC particle in V-Mo added 0.1%C-2.0%Mn steels [15)]

pacity to decrease, it is considered that the interface between the carbide and steel matrix has a significant influence on the hydrogen trapping as described later.

5.2 ε-carbide

Teramoto, et al.[17] examined steel containing 0.6 mass% C added with Si and Cr. The steel was tempered at various temperatures. Teramoto, et al. found a behavior of hydrogen being trapped in the steel similar to that seen in V-added steel. **Figure 11**[17] shows the hydrogen discharge curve. **Figure 12** shows the relationship between the tempering temperature and hydrogen trapping capacity. The hydrogen trapping capacity of the steel in this study differs from that of steel in which MC carbide precipitates described above in that the peak temperature is lower, around 400°C. This appears to be because ε-carbide, which is a carbide in a state of non-equilibrium, disappeared along with the formation of cementite during high temperature tempering.

5.3 Consideration on hydrogen trapping sites

The MC carbide data as obtained indicates that the hydrogen trapping capacity depends on the carbide composition, and also that the hydrogen trapping capacity decreases due to over-aging; in view of this, it is considered that the interface of the carbide and steel matrix significantly influences the behavior of hydrogen being trapped rather than the carbide itself.

Takahashi, et al. conducted an analysis of the state in which hydrogen exists in steel with fine TiC precipitated in it. The steel was charged with deuterium, and the state of hydrogen in steel was examined using a 3DAP (three-dimensional atom probe). As shown in **Fig. 13**[18], they found deuterium atoms present in the vicinity of the interface between the platy TiC precipitate surface and steel matrix, and proposed misfit dislocations as sites where hydrogen atoms are trapped.

Meanwhile, Kosaka, et al. assumed that hydrogen is trapped in a matched strain field between an MC carbide and steel matrix. They reported that the value obtained with a formula for calculating the amount of precipitation strengthening using a matched strain field showed good correlation with the measurement value, and that the amount of precipitation strengthening showed a correlation with the amount of trapped hydrogen.[16] In another research, Kawakami, et al. proposed theories that vacancies in an MC carbide are the sites where hydrogen atoms are trapped, and that the concentration of vacancies in C, i.e., trapping capacity, varies depending on the MC carbide composition.[19]

Examining the hydrogen discharge curve in detail, the peak temperature range tends to shift to a temperature range higher by approx. 20°C (in other words, the trap energy becomes high) by increasing the number of additives from just one to several additives, for example, from V to V + Mo, and in the case of steel to which V and Mo have been added in a combined manner, by being tempered for a long time, the hydrogen discharge peak temperature tends to be shifted to a temperature range even higher. Within steel in which

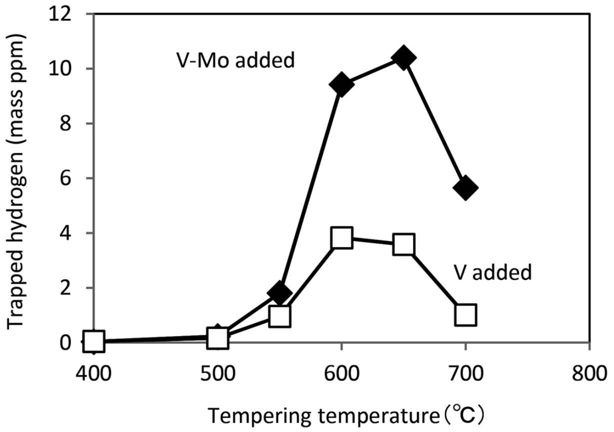

Fig. 10 Hydrogen trapping capacity of V-Mo added 0.1%C-2.0%Mn steels tempered at various temperatures

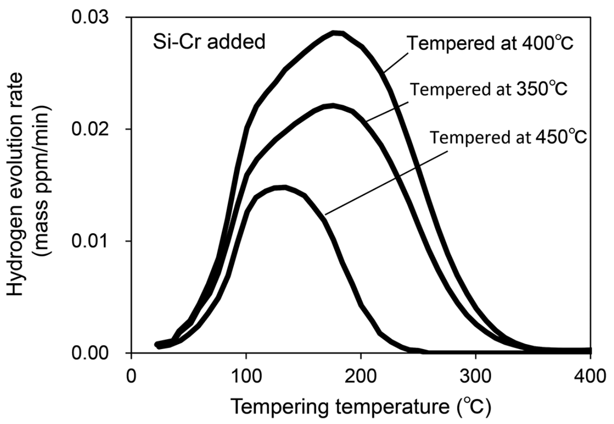

Fig. 11 Hydrogen evolution rate curves of Si-Cr added 0.6%C steel tempered at various temperatures[17]

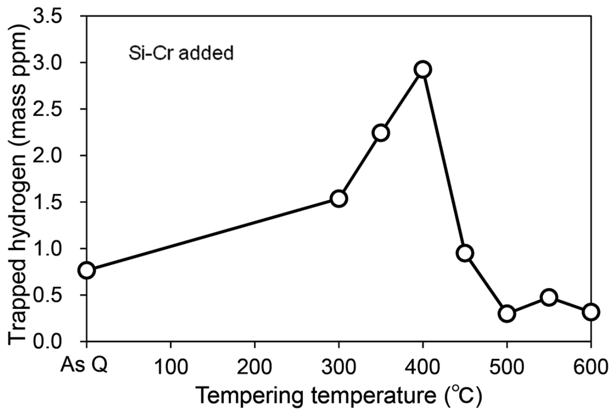

Fig. 12 Hydrogen trapping capacity of Si-Cr added 0.6%C steels tempered at various temperatures

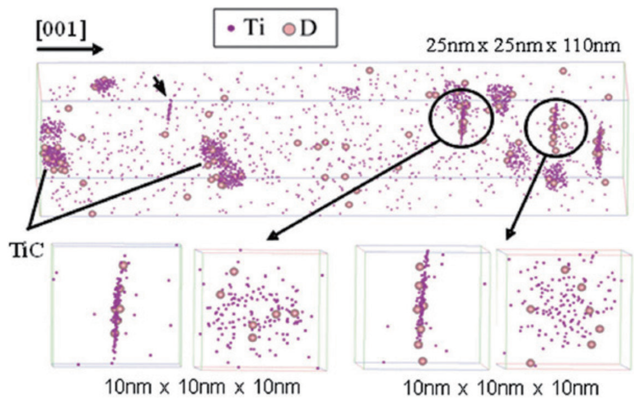

Fig. 13 3-demensional mapping of deuterium-charged steel[18] multiple additives are used, the carbide composition (amounts of matched strain and vacancies in C), misfit dislocation density, etc. are considered to change over time during tempering, affecting the hydrogen trapping capacity. Going forward, it will be necessary to analyze the phenomenon more microscopically.

Based on this research, we developed steel with combined additives of V and Mo for manufacturing high strength bolts exceeding 12T.[20] This steel has already been used for bolts in the automobile, civil engineering, and construction fields.

6. Conclusion

We examined the state of hydrogen existing in steel using the thermal desorption method, and that of the hydrogen trapping capacity of fine precipitates, the results of which are summarized as follows.

(1) Regarding the hydrogen discharge peak near 300°C, it can be seen only in the cases of cold-worked steel and quenched high-carbon steel, and in the case of steel containing dissolved carbon (e.g., as-quenched martensite steel), its height is lowered by aging at room temperature. Given this, hydrogen that forms the peak near 300°C is considered to be hydrogen strongly trapped at the dislocation core while competing with carbon atoms. The hydrogen desorption peak near 100°C is highly likely to have been formed by hydrogen trapped at the elastic stress field.

(2) The discharge peak at 200°C is formed by hydrogen trapped by MC carbide particles or ε-carbide particles. As the hydrogen trapping capacity of an MC carbide varies depending on the alloy composition and aging time, i.e., the size of the precipitate, the hydrogen trapping capacity of an MC carbide is considered to be strongly influenced by the characteristics of the matched interface between the precipitate and matrix.

Today, the demand for strength improvement of steel for various purposes is much stronger than before. In order to attain progress in improving the strength of steel, hydrogen embrittlement must be overcome. We will strive to deepen our technology for controlling the state of hydrogen in steel and contribute to the prevalence of steel with a higher level of strength.

References

1) Matsuyama, S.: Delayed Fracture. Nikkan Kogyo Shimbun, 1989
2) Oriani, R.A., Josephic, H.: Acta Metall. 22, 1064 (1974)
3) Tabata, T., Birnbaum, H.K.: Scr. Metall. 18, 231 (1984)
4) Nagumo, M., Nakamura, M., Takai, K.: Metall. Mater. Trans. A. 32A, 339 (2001)
5) Saito, H., Miyazawa, K., Ishida, Y.: J. Japan Inst. Met. Mater. 55, 366 (1991)
6) Kanno, M., Kuramoto, S.: Latest Hydrogen Detection Method and Hydrogen Embrittlement Prevention Method. The Japan Institute of Metals and Materials, 23 (1999)
7) Someno, M., Kobayashi, M., Saito, H.: Journal of the Mass Spectrometry Society of Japan. 25, 263 (1975)
8) Takahashi, J., Kawakami, K., Kobayashi, Y., Yamada, J.: Shinnittetsu Giho. (390), 20 (2010)
9) Yoshizawa, S., Tsuruta, T., Yamakawa, K.: Corros. Eng. 4, 511 (1975)
10) Suzuki, N., Ishii, N., Miyagawa, T., Harada, H.: Tetsu-to-Hagané, 79, 227 (1993)
11) Obata, T., Hirakami, D., Yamasaki, S., Tarui, T.: CAMP-ISIJ. 13, 1384 (2000)
12) Hirakami, D., Yamasaki, S., Tarui, T., Ushioda, K.: Tetsu-to-Hagané, 100, 142 (2014)
13) Hirakami, D., Obata, T., Tarui, T.: CAMP-ISIJ. 14, 1301 (2001)
14) Yamasaki, S., Takahashi, T.: Tetsu-to-Hagané, 83, 454 (1997)
15) Yamasaki, S., Bhadeshia, H.K.D.H.: Proc. 17th IFHTSE Congress. 2008, p. 434
16) Kosaka, M., Yoshida, S., Tarui, T.: CAMP-ISIJ. 17, 1371 (2004)
17) Teramoto, S., Kubota, M., Miyamoto, G.: Proceedings of JSSE Conference on Springs and Restitution Effect. Japan Society of Spring Engineers, 2012, p. 5
18) Takahashi, J., Kawakami, K., Kobayashi, K., Tarui, T.: Scripta Mater. 63, 261 (2010)
19) Kawakami, K.: ISIJ-Int. 52, 1693 (2012)
20) Kubota, M., Tarui, T., Yamasaki, S., Ochi, T.: Shinnittetsu Giho. (381), 57 (2004)

Shingo YAMASAKI
General Manager, Head of Div., Ph.D
Bar & Wire Rod Research Lab.
Steel Research Laboratories
20-1 Shintomi, Futtsu City, Chiba Pref. 293-8511

Toshiyuki MANABE
Senior Researcher
Bar & Wire Rod Research Lab.
Steel Research Laboratories

Daisuke HIRAKAMI
Chief Researcher, Ph.D in Engineering
Bar & Wire Rod Research Lab.
Steel Research Laboratories