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Development of Thermal Refining Type High Tensile Bolt

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Abstract

High-tensile fasteners are strongly demanded from the viewpoint of improvement of fuel efficiency by weight-saving bodies of the automobile and improvement of unit performance. However, the hydrogen embrittlement susceptibility of steel increases with strengthening over 1200 MPa. For the application of high-tensile steels, it is necessary to develop high-tensile steel with excellent hydrogen embrittlement resistance and to determine the optimal evaluation methods. This paper describes the high strength steel we developed for heat-treated fasteners, the basic study on hydrogen trapping by nano-sized carbide and methods to evaluate hydrogen embrittlement sensitivity. The hydrogen trapping ability of NaCl-type nano-sized alloyed carbides improves by the combined addition of Mo and V. After direct observation of the hydrogen trapping site of VC by 3DAP (three-dimensional atom probe), it is suggested that C vacancy located on the plate surface of VC is a hydrogen trapping site.

1. Introduction

High-tensile bolts are strongly required from the viewpoint of improvement of fuel efficiency by weight-saving of parts, and enhancing the performance of units. However, when tensile strength is increased and exceeds 1200 MPa, the hydrogen embrittlement susceptibility of steel increases. Hydrogen embrittlement is one of the factors that impede the enhancement of tensile strength.[1] The hydrogen embrittlement of a bolt is known as delayed fracture, and is the phenomenon in which a bolt is abruptly fractured after several days or several years have elapsed after fastening. The delayed fracture is caused by the hydrogen generated by the corrosion of a steel, diffused therein, and is accumulated at stress-concentrated sites. The hydrogen causes the nucleation and propagation of micro cracks and ultimate breakage of components. The difficulty in dealing with this problem is that the lifetime of a steel, including items such as fatigue properties, cannot be predicted.

In the case of the delayed fracture of tempered martensite, cracks are generally generated at the prior-austenite grain boundaries and propagate along the prior-austenite grain boundaries, the phenomenon of which is called intergranular fracture. The grain boundary is considered to be the most vulnerable to the hydrogen embrittlement fracture. In the steel with strengthened grain boundaries where the resistance to hydrogen embrittlement susceptibility is enhanced, the fracture mode transfers to the transgranular fracture mode termed as quasi-cleavage fracture.[2]

Until now, steel manufacturers, bolt manufacturers and automobile companies have tackled this issue focusing on the development of methods to strengthen the prior-austenite grain boundaries and/or to construct an entire drawn pearlite microstructure to eliminate the grain boundaries.[3, 4] This article reports the techniques used to suppress the hydrogen embrittlement and render the hydrogen as harmless in a tempered martensite steel. Reported herein are an evaluation technique for the unpredictable delayed fracture and the delayed fracture prevention concept.

2. Development of Steel and its Concept

2.1 Designing of chemical compositions for development of steel

In the hydrogen embrittlement in tempered martensite, it is crucial to suppress the fracture at the prior-austenite boundaries. **Figure 1** shows the methods for the improvement of hydrogen embrittlement susceptibility pertaining to the prior-austenite grain boundaries. The methods comprise two basic concepts. The first is to strengthen the grain boundaries directly, and the second is to decrease the concentration of hydrogen that exists at the grain boundaries.

To strengthen the grain boundaries, the following techniques are used: (1) reduction of P and S that are segregated at the grain boundaries of prior-austenite and embrittle the grain boundaries, (2) reduction of Mn that promotes the segregation of P at the grain boundaries, (3) strengthening of austenite boundaries by refining the austenite grains with the addition of such elements as Ti, Nb and V forming carbonitrides that act as pinning particles in the austenite

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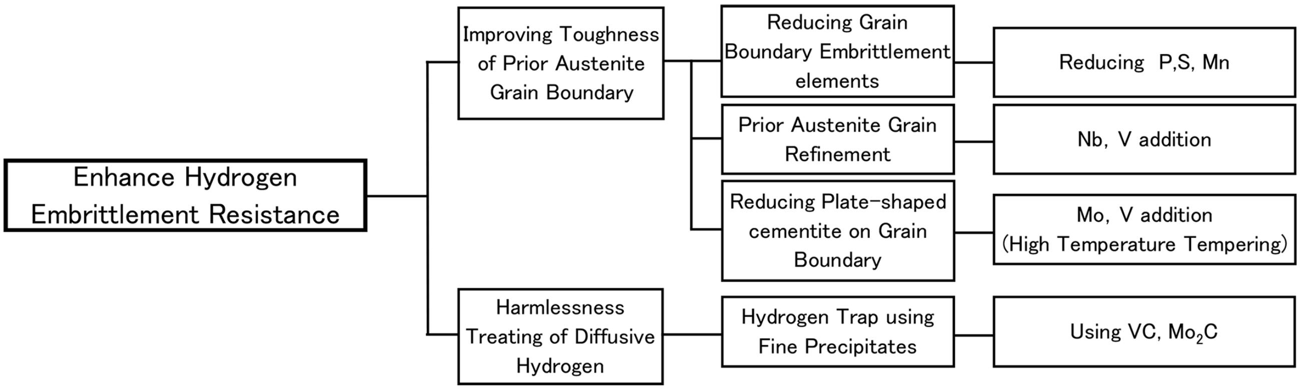

Fig. 1 Methods for improvement of hydrogen embrittlement sensitivity

Table 1 Chemical compositions of high strength steel for fasteners

(mass%)

Steel	Grade	C	Si	Mn	P	S	Cr	Mo	V	Nb
SCM435	10T	0.35	0.20	0.65	<0.03	<0.03	0.95	0.20	-	-
ADS-2	12T	0.35	0.20	0.35	Reduce	Reduce	1.25	0.40	-	Add
MB14	14T	0.40	Reduce	0.50	Reduce	Reduce	1.20	0.70	0.35	-
MB16	16T	0.40	Reduce	0.50	Reduce	Reduce	-	2.00	0.15	-

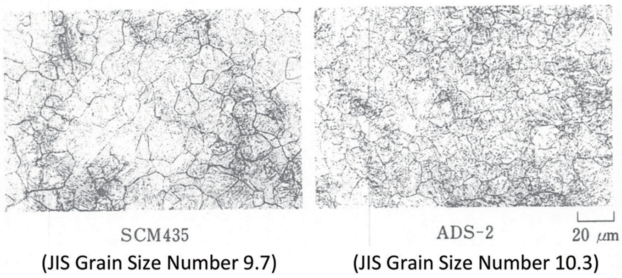

Fig. 2 Comparison of prior austenite grain size between developed steel and conventional steel

region, and (4) application of high temperature tempering to suppress the film type cementite that is formed at the austenite grain boundaries of the prior-austenite and deteriorates the intergranular strength.

In addition to reduce the concentration of the hydrogen existing at the boundaries, the following methods are used: applying high temperature tempering to a steel to which V and/or Mo are added, precipitating nano-sized carbides within the prior-austenite grains, and utilizing such carbides to trap hydrogen so that the intergranular hydrogen is reduced.[5, 6]

2.2 Steel for high tensile bolt

Table 1 shows the steels for high tensile bolts that exceed 1 200 MPa developed by Nippon Steel Corporation based on this concept. Until now, 12T (1 200–1 400 MPa) class, 14T (1 400–1 600 MPa) class and 16T (1 600–1 800) class steels have been developed. Their properties are introduced hereafter.

2.2.1 ADS-2 (Strengthening of prior-austenite grain boundary)[7]

In ADS-2 that focuses on the strengthening of grain boundaries, in addition to the reduction of P, S and Mn contents, austenite grains are refined by adding Nb and utilizing Nb(C,N) as pinning particles in the quenching process. **Figure 2** shows the comparison of the grain size of prior-austenite with that of a conventional steel. Furthermore, by adding more Mo than that added to SCM steel, the tempering temperature is raised and the generation of the film type cementite is suppressed.

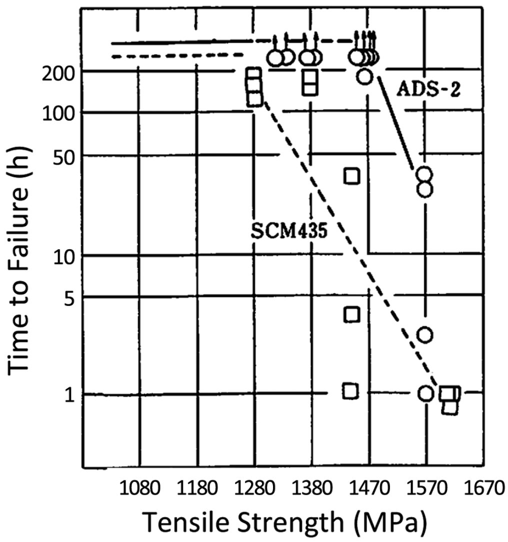

Fig. 3 Evaluation of developed steel related to hydrogen embrittlement sensitivity

Figure 3 shows the result of the constant loading test conducted for the developed steel having various tensile strengths obtained by changing the tempering temperature. The test was conducted for the strength level of each steel, charging hydrogen continuously in the Walpole's buffer solution of pH2±0.5 at 25°C,under a constant loading condition. The test piece is a round bar 6 mm in diameter having an annular notch of 1 mm in depth (4 mm in the bottom diameter), and the loaded tensile stress condition is 1/2 that of the tensile strength of the notched portion. As compared with the conventional steel SCM435, above 1 300 MPa, the time of failure is improved and the developed steel is excellent in hydrogen embrittlement susceptibility.

2.2.2 MB series (Hydrogen trapping by nano-sized carbide)[8]

This steel, in addition to the aforementioned reduction of P and S, is added with V and Mo compositely and used after high temperature tempering. With this, the developed steel exploits the refining of the austenite grains pinned by the V(C,N) particles, intergranular strengthening by high temperature tempering, and the hydrogen trapping by the nano-sized V, Mo carbides precipitated during the high temperature tempering. The effect of the high temperature tempering is that the grain boundaries are strengthened by suppressing the film type cementite. As an example, **Fig. 4** shows the effect of high temperature tempering on 0.4%C-2.0%Mo-0.1%V steel as suggested by Kubota et al., and the comparison of its hydrogen embrittlement susceptibility with that of the conventional steel, respectively.

The constant loading test was conducted wherein various loads are applied to the round bar test piece having an annular notch under the test condition of being charged with cathodic electrolytic hydrogen in a H_2SO_4 solution of pH3. The plotted data in the figure shows the ratio of the stress that does not develop fracture at 200 h with hydrogen charging vs. the delayed fracture stress without hydrogen charging. As compared with SCM435, the developed steel is excellent in hydrogen embrittlement susceptibility, and in addition, hydrogen embrittlement susceptibility at the tempering temperature of 823K is further enhanced at 873K and 903K. **Figure 5** shows the transmission electron microscope (TEM) images of the microstructures tempered at 823K and 903K. In the 823K image, the precipitation of the film type cementite is observed at the grain boundaries. On the other hand, in the 903K image, the cementite is granularized, and the grain boundaries are considered to have been strengthened by the high temperature tempering.

2.3 Hydrogen trapping by nano-sized carbide

By adding V, Mo and the like, nano-sized carbides are precipitated during tempering, which trap the hydrogen diffused in the steel, and reduce its concentration at the grain boundaries. Thus, the intergranular embrittlement by hydrogen is suppressed.

These carbides are of the NaCl-type MC system. **Figure 6** shows the hydrogen evolution curves according to Yamasaki et al.[9] obtained by the hydrogen analysis using the thermal desorption analysis method (TDA) for the hydrogen-charged ferrite steel and the steel with precipitated MC carbides. As the MC carbides have the peak evolution rate at a temperature higher than that of the ferrite steel, the MC carbides trap hydrogen with higher energy. Furthermore, Yamasaki et al. studied the effects of the chemical compositions of the MC carbides and the precipitation condition thereof on the hydrogen trapping capacity using various 0.1%C-based steels wherein V and Mo are added so that only the MC-system carbides are precipitated therein.

Figure 7 shows the hydrogen trapping capacities of the various steels for various tempering times.[10] The hydrogen trapping capacity is defined as the mass of the hydrogen evolved under 400°C

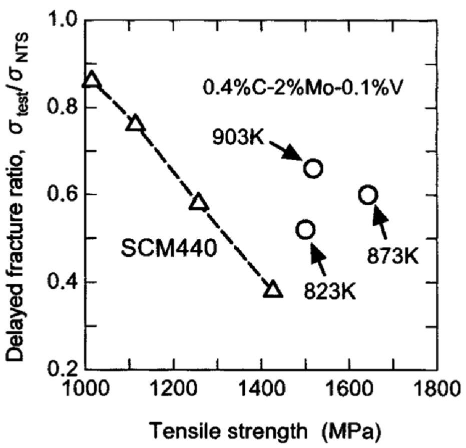

Fig. 4 Evaluation of developed steel related to hydrogen embrittlement sensitivity

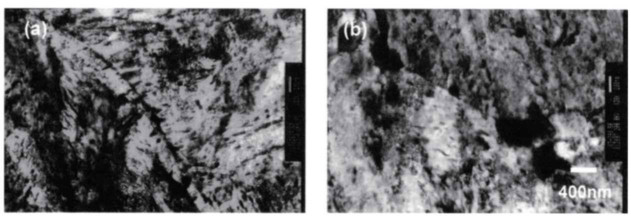

Fig. 5 TEM micrographs of pre-austenite grain boundaries (a) 823 K tempered, (b) 903 K tempered

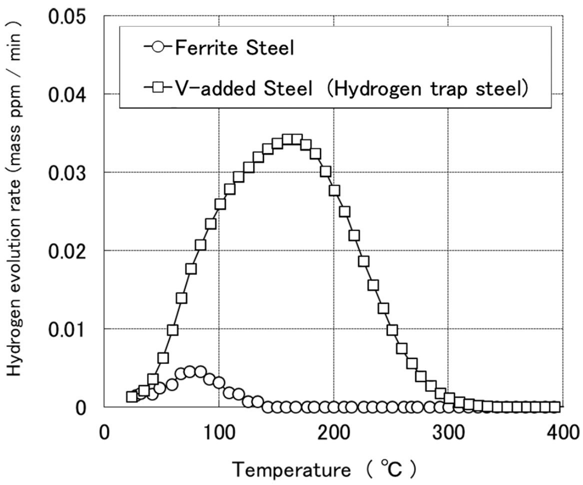

Fig. 6 Hydrogen thermal desorption analysis (TDA) curves for hydrogen trap steel

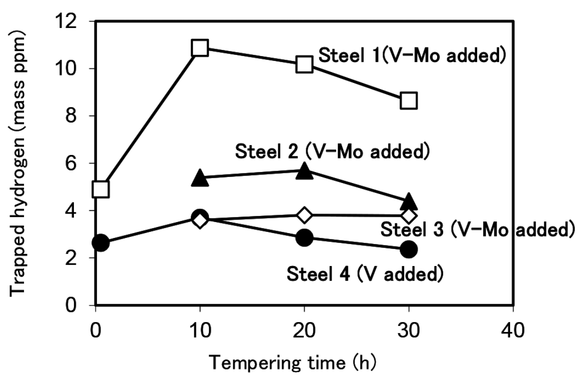

Fig. 7 Hydrogen trapping capacity of V-Mo added steels for various tempering time

(termed as diffusible hydrogen) that is measured by TDA after cathodic electrolytic hydrogen charging under a common charging condition and holding at room temperature. The hydrogen trapping capacity shows its peak at the tempering time of 10–20 h, and although the amount of the balanced precipitation of MC carbides is almost equal, the maximum value of the trapping capacity differs greatly depending on the type of steel. Furthermore, as **Fig. 8** shows, in the steel tempered for 10 h, along with the increase of the Mo ratio at M sites of MC carbide particles, the hydrogen trapping capacity per particle of the carbides increases.

In the ferrite, the MC carbide maintains the Baker-Nutting relationship with respect to the ferrite matrix, and is a plate-shaped precipitate having its plane on $(001)_{VC}$ and the orientation relationship of $(001)_{VC}/(001)_{\alpha}$. There is still room for further discussion as to where the hydrogen is trapped on the interface between the MC carbide and the ferrite matrix. However, the coherent interface and the coherency strain field on the interface of the carbide and Fe matrix, inside of the carbide, misfit dislocation, C vacancy in the MC carbide and the like are considered as possible sites.[11–15)]

In order to directly observe the state of the hydrogen trapped by the nano-sized carbide, Takahashi et al. charged deuterium to steels having various types of VC precipitated under various aging conditions, and conducted observation by a three-dimensional atom probe (3DAP).[16–18)] Takahashi et al. focused on the existent locations of the deuterium under the VC-precipitating sub-aging and the peak aging conditions, and found that in the peak aging and the over-aging, the deuterium is trapped on the $(001)_{VC}$ plane, but not thereon in the sub-aging, and that the hydrogen trapping energy of the steel in the peak aging and the over-aging is higher than that in the sub-aging. Furthermore, as a result of the observation by a high-resolution transmission electron microscope (TEM), the misfit dislocation exists only partially, and during the transition from the sub-aging to the peak aging, the C/V atom ratio of the VC carbide changes from 0.9–1.0 to 0.7–0.8. Therefore, they assumed that the hydrogen trap site is not the misfit dislocation, but the C vacancy on the plane of the VC carbide.

Kosaka et al.[12)] report that, in the study of compositely adding carbide precipitating elements, the coherency-strain increasing element (addition of Mo to VC) increases the hydrogen trapping content, and the addition of the element (V to TiC) that decreases the coherency-strain decreases the hydrogen trapping content. The relationship between the change of the coherency strain by the composite addition of MC precipitating elements and the C vacancy density remains a subject for future study.

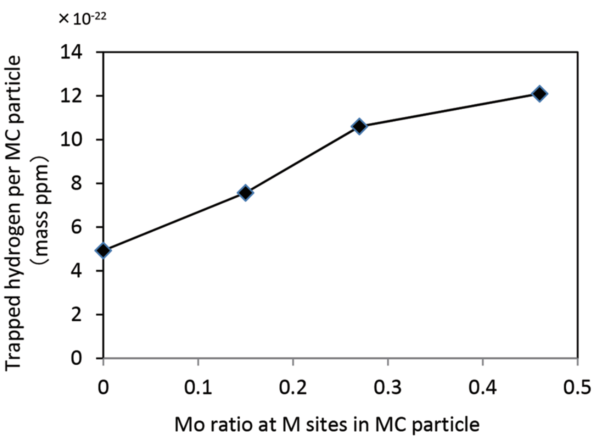

Fig. 8 Relationship between fraction of Mo in 'M' of MC and hydrogen trapping capacity per MC particle in V-Mo added 0.1%C-2.0%Mn steels[16)]

3. Method for Evaluating Hydrogen Embrittlement Susceptibility

To evaluate the hydrogen embrittlement susceptibility, the conventional constant loading test method defines the fracture time and the limit stress under a fixed hydrogen charging condition as shown in Clause 2.2, while the slow strain rate tensile test method based on the slow strain rate technique (SSRT) defines the fracture stress under a similar fixed hydrogen charging condition. Several research organizations have conducted comparison and evaluation studies on various steels using these methods. A number of suggestions concerning the mechanism of the hydrogen embrittlement have been proposed, and as a general mechanism of fracture, it is considered that hydrogen is accumulated at the stress concentrated site, and when the hydrogen concentration reaches a certain level, a crack is generated, propagates and causes fracture.

Then, Suzuki et al.[19)] suggested a delayed fracture evaluation method on the basis of hydrogen content as a standard wherein an up-to-100 h constant loading test is conducted, using a round bar test specimen having an annular notch. Furthermore, Yamasaki et al.[20)] introduced a method of enclosing hydrogen in the steel after hydrogen charging by applying Cd plating. Furthermore, the method was improved so as to disperse the hydrogen evenly in the steel by holding the test piece for 24 h at room temperature after the coating. With this improvement, the average hydrogen concentration in the steel can be captured with the analysis result of the hydrogen content after the test. In the evaluation method concept suggested by Yamasaki et al., the upper limit of diffusible hydrogen content [Hc] (diffusible hydrogen mass upper threshold) that does not trigger delayed fracture in steel, and the diffusible hydrogen intrusive to steel in the environment [He] (intrusive hydrogen content) are measured, and if [Hc] is larger than [He], delayed fracture is judged not to occur. This fracture evaluation method based on the hydrogen content corresponds to the result of the bolt exposure test.

This evaluation method is significant in that the diffusible hydrogen content upper threshold can be expressed by the average hydrogen concentration. Conventionally, the local hydrogen content H^* at the stress-concentrated sites can be expressed as the following formula shows, using partial molar volume V_m, local maximum hydrostatic-pressure stress σ^*_m and the average hydrogen content H. The local hydrogen content can be discussed based on the average hydrogen content.[21)]

$$H^* = H exp\left[\frac{V_m \sigma^*_m}{RT}\right] \quad (R\text{: gas constant, } T\text{: absolute temperature})$$

In order to verify the validity of the evaluation developed by the said method, a study has been made on the process of fracture due to hydrogen embrittlement. Yamasaki et al.[22)] conducted a study to capture by acoustic emission (AE) the generation of the hydrogen-induced crack and the propagation thereof during the test by the said method. After capturing the initial stage crack generation by AE, the test specimen was dehydrogenated, tensile-strength-tested, and the fracture surface was observed by a scanning electron microscope. As a result, it was revealed that the crack is the intergranular crack at the position 200 μm below the notch bottom, the size of which agrees with that obtained by the AE wave form analysis (**Fig. 9**).

In addition, **Fig. 10** shows the relationship between the diffus-

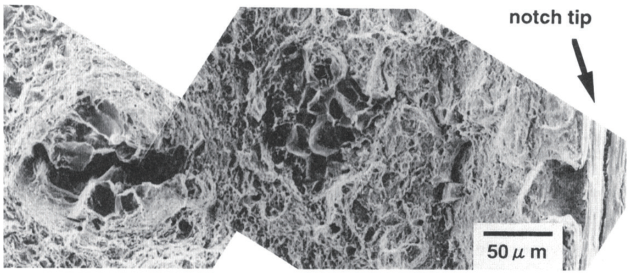

Fig. 9 Initial crack of round notch specimen due to hydrogen embrittlement

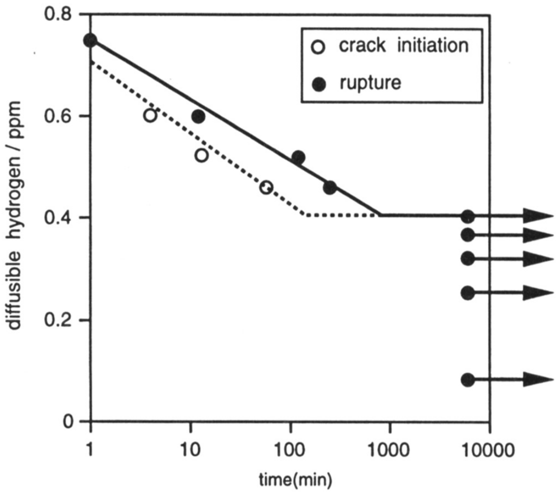

Fig. 10 Relationship between initial crack and rupture time in the test of Hc evaluation

ible hydrogen content and the crack initiation time and the rupture time. Above the diffusible hydrogen content upper threshold [Hc], a crack is initiated after a latent time, and within several hundred minutes, the crack propagates discontinuously, and generates rupture, while below [Hc], such cracks are not generated. Therefore, in the steel that endures 100 h, the possibility of crack occurrence is low. Furthermore, it has been revealed that when an initial crack is noticed in the constant loading test with the hydrogen charging up to above [Hc], the constant loading test is stopped and suspended until the restart of the constant loading test under a revised condition of dehydrogenation and the subsequent hydrogen charging to below [Hc]. The said initial crack then propagates after a latent period and develops fracture in the restarted loading test. Namely, the initial crack is considered to be dominant in the process of fracture due to hydrogen embrittlement.

In order to visually capture the processes of the initial crack generation and the propagation thereof, Yamasaki et al.[23] conducted a hypothetical study on the process based on both an actual delayed fracture surface of a bolt and a fracture surface of a constant-loading test piece by fracture surface tomography analysis (FRASTA). Similarly to the AE study result, in both cases of the delayed-fractured bolt and the loading test specimen, the crack origin in the [Hc] state is located in the neighborhood of the maximum point of the triaxial stress on the inside of the bottom of the notch, and takes the form of a discontinuous crack propagation wherein a new crack is generated ahead of the crack. This evaluation method is considered as valid from the viewpoints of the generation of the initial crack and the formation process of the fracture surface.

As for [He], hydrogen analysis is generally conducted for the sample exposed to a corrosive environment, and furthermore, a detailed study on the hydrogen intrusion is also conducted. Omura et al.[24] conducted a study on the factors that promote the hydrogen intrusion under an atmospheric air environment and their action mechanisms by using the electrochemical hydrogen permeation method. In the measurement under an atmospheric air environment, a large mass of hydrogen intrusion was suggested in summer and/or in the areas where there is an abundance of airborne salinity. The result of measurement in a cyclic corrosion test (CCT) shows that, although depending on the equilibrium state of the corrosion rate, Cl^- ions enriched and the Fe ionized through hydrolysis in a water film, the hydrogen intrusion exhibits its maximum value when the relative air humidity is 50–60%.

The evaluation of [He] under various automobile operation surroundings based on this concept and the evaluation method is thus considered to become increasingly important in future.

4. Conclusion

The quenching and tempering type bolt steel that exceeds 1 200 MPa, a fundamental study on the hydrogen trapping steel and the hydrogen embrittlement evaluation method based on the hydrogen content threshold in Nippon Steel have been described.

(1) The hydrogen trapping capacity of the NaCl type carbide is improved by the composite addition of Mo and V, and from the result of the observation by a three-dimensional atom probe (3DAP), the possibility of the hydrogen being trapped in the C vacancy of the VC is suggested.

(2) As for the hydrogen embrittlement evaluation method, the evaluation method based on the average hydrogen content facilitates the assumption of the local hydrogen concentration, and is judged as appropriate from the viewpoint of the results of the observation of the processes of the occurrence of the initial crack and the propagation thereof.

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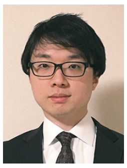

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