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Technical Review

Approaches for Fundamental Principles 1: Evaluation Method of Hydrogen Embrittlement and Improvement Techniques of Delayed Fracture

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1. Introduction

As represented by lighter, higher-function automotive parts, the need for stronger steel materials has become greater than ever before. One of the factors that impede further enhancement in the strength of steel materials is hydrogen embrittlement, which is caused by the entry of extremely minute amounts of hydrogen into the steel from the environment as a result of corrosion, etc. The higher the steel strength and the larger the applied stress, the greater the susceptibility of the steel to hydrogen embrittlement.[1] With the aim of overcoming hydrogen embrittlement of high-strength steel, various approaches are taken from the standpoint of controlling the steel microstructure. In addition, in view of the fact that there are no established techniques to estimate or evaluate the susceptibility of steel to hydrogen embrittlement in the actual environment, activities aimed at standardizing techniques to evaluate hydrogen embrittlement have been carried out energetically. In this technical review, we describe the progress of techniques to evaluate the hydrogen embrittlement (delayed fracture) of steel and to improve the resistance to delayed fracture using high-strength bolts as an example.

2. Technology for Evaluating Delayed Fractures

As conventional methods for evaluating delayed fractures, there are: 1) measuring the critical delayed fracture stress or fracture time using a constant-load test, 2) obtaining the fracture stress and ductility parameters, such as elongation, using the Slow Strain Rate Technique (SSRT), and 3) obtaining fracture mechanics parameters using previously cracked test pieces.[2] Even today, many different methods of evaluation are used since the mode of applied stress, the shape of the test piece, and the conditions for hydrogen charging differ widely. The problem in those evaluation methods is that the correspondence between the results of an accelerated test and the delayed fracture characteristic of steel in the actual environment has not been verified. In any of the conventional evaluation methods cited above, the results of conventional evaluation tests do not agree with the results of measurements in the actual environment. The major reason for this is considered to be that the mode of entry of hydrogen into the steel specimen in an acid solution is entirely different from that in the actual environment.

Although the mechanism by which a delayed fracture occurs has yet to be clarified, it is generally considered that a delayed fracture of steel occurs in the process in which a crack occurs in the steel material and starts propagating when the amount of the hydrogen having entered and accumulated in the steel reaches a certain level. From that standpoint, attention has been paid to the delayed fracture evaluation method based on the hydrogen concentration in steel, proposed by Suzuki et al.[3] and modified by Yamasaki et al.[4] The basic concept of the above evaluation method is as follows. First, measure both: (1) the maximum amount of diffusible hydrogen that does not cause any delayed fracture of steel material (critical diffusible hydrogen content [Hc]), and (2) the amount of diffusible hydrogen that enters the steel material from the environment (absorbed hydrogen content [He]). Then, if [Hc] is larger than [He], it is judged that the steel material is free from delayed fractures. Since a delayed fracture is induced by diffusible hydrogen, the above evaluation method based on the amount of hydrogen is very rational. It has been confirmed that the results of delayed fracture evaluation using the method based on the amount of hydrogen agree with the results of an exposure test of steel bolts. Therefore, it is considered that this evaluation method can be used to predict the delayed fracture characteristics of steel materials in the actual environment.[4]

Evaluating the delayed fracture characteristics of steel materials on the basis of the hydrogen amount has been made possible largely by establishment of the know-how of hydrogen charging and hydrogen analysis, as well as development of the gas chromatograph and quadrupole mass spectrometer that permit measuring extremely small amounts of hydrogen contained in steel with an accuracy of 0.01 ppm. In addition, hydrogen thermal desorption spectroscopy using those hydrogen analyzers has made it possible to separate non-diffusible hydrogen from diffusible hydrogen in steel and estimate the existence state of hydrogen in steel.

Fig. 1 shows the hydrogen evolution rate curves obtained by hydrogen thermal desorption spectroscopy by charging hydrogen into tempered martensitic structures of carbon steel and alloy steel and into pearlitic steel drawn into a high-carbon steel wire. It can be seen that the peak temperature for hydrogen evolution rate differs according to the method of strengthening of the steel material, that is, the type and density of lattice defects. The equilibrium hydrogen concentration in α-iron at room temperature is estimated to be 0.001 mass ppm in 0.1-MPa hydrogen. Therefore, it is considered that the

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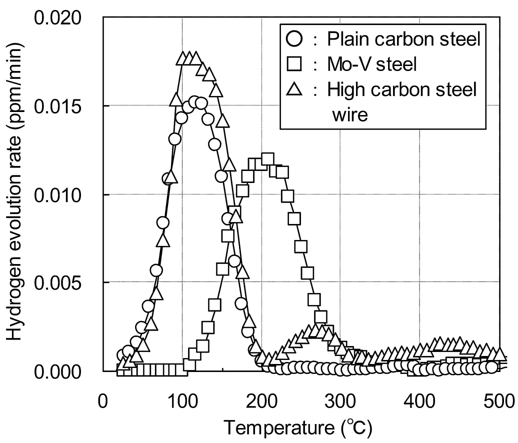

Fig. 1 Hydrogen evolution rate curves

hydrogen that entered the steel material has mostly been trapped in dislocations, grain boundaries, vacancies, and precipitates, etc. From Fig. 1, it can be seen that the hydrogen trapped in various types of lattice defects is either diffusible or non-diffusible and that the influence of trapped hydrogen on hydrogen embrittlement can be clarified. Thus, the hydrogen evolution rate curves provide useful information in developing new steel materials and deepening the understanding of hydrogen embrittlement.

3. Technology for Improving Resistance to Delayed Fracture of High-Strength Bolts

High-strength bolts have a tempered martensitic structure and the strength at which the occurrence of a delayed fracture in a natural environment becomes a problem is 12 T (tensile strength 1,200-1,400 MPa) or more. Since the prevailing mode of delayed fracture of high-strength bolts is intergranular fractures along prior γ-grain boundaries, efforts have been made to reduce impurities (P, S) and refine prior γ grains. From the standpoint of improving the delayed fracture characteristic, it is most effective to spheroidize the intergranular carbides by high temperature tempering.[5] However, when high temperature tempering around 600℃ is implemented, the steel strength declines markedly, although [Hc] improves. Therefore, technology to control the steel microstructure that permits increasing the strength of steel and improving the resistance to delayed fracture of steel at the same time becomes important. Besides, since bolts are formed by cold forging, it is necessary to limit the carbon concentration of steel from the standpoint of securing the desired cold forgeability.

As a means of strengthening bolts which contain 0.4mass% C and which are to be tempered at 600℃, it is realistic to utilize precipitation strengthening by alloy carbides of Mo, V, and Nb, etc. In order to calculate the degree of precipitation strengthening τ_p (cutting mechanism) by fine precipitates of tens of nm, the following Equation (1) of Gerold-Harberkorn has been proposed.

$$\tau_p = G\,\varepsilon^{3/2}\,(fr/b)^{1/2} \quad (1)$$

Where, G denotes the modulus of rigidity; ε is the coherent strain; f is precipitate volume fraction; r is precipitate radius; and b is the Burgers vector. The degree of precipitation strengthening in Equation (1) above is proportional not only to the precipitate size and volume fraction, but also to the coherent strain to the power of 3/2. The implication is that coherent strain influences precipitation strengthening significantly.

Therefore, we studied the influences on precipitation strengthening of each of the alloy carbides of Mo, V, Ti and Nb, and combinations of those alloy carbides when the steel was tempered at 600℃. As a result, it was found that: (1) The size of every alloy carbide was in the order of 10 nm, (2) The larger the coherent strain of the alloy carbide, the greater became the degree of precipitation strengthening, and (3) Any of the combinations of alloy carbides (e.g., V_4C_3 and $(V, Mo)_4C_3$) that increased the coherent strain caused the degree of precipitation strengthening to increase, whereas any of the combinations of alloy carbides (e.g., TiC and (T,V)C) that decreased the coherent strain caused the degree of precipitation strengthening to decrease.[6] It has been confirmed that the experimental degrees of precipitation strengthening almost coincide with the calculated degrees obtained by using Equation (1) above.

On the other hand, alloy carbides having a fine and coherent stain field help trap hydrogen. Takahashi et al. charged deuterium into steel material containing fine TiC precipitates and analyzed the condition of the hydrogen in the steel using a three-dimensional atom probe (3DAP). As a result, they found that the hydrogen atoms existed in the neighborhood of the TiC-matrix interfaces as shown in **Fig. 2**.[7] In addition, they suggested that the coherent strain field or the site of C in TiC should be a site that traps hydrogen atoms. Since the amount of hydrogen trapped by alloy carbides influences the delayed fracture characteristic, we studied the relationship between the amount of precipitation strengthening and the trapped hydrogen

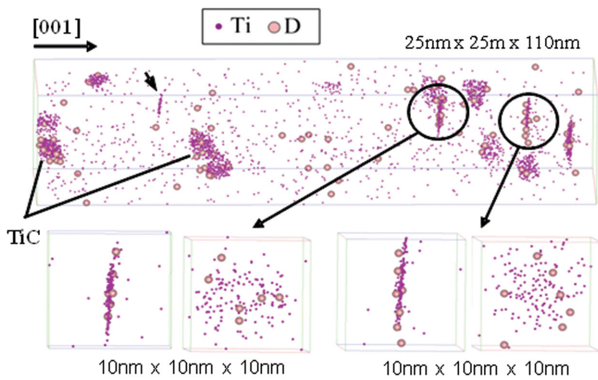

Fig. 2 3D elemental maps of deuterium–charged specimens of TiC steel

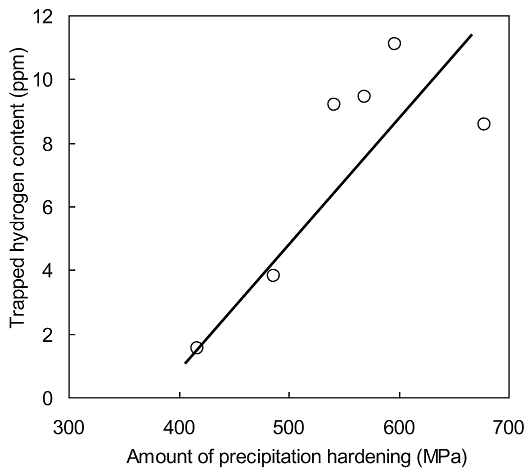

Fig. 3 Relationship between trapped hydrogen content and amount of precipitation hardening

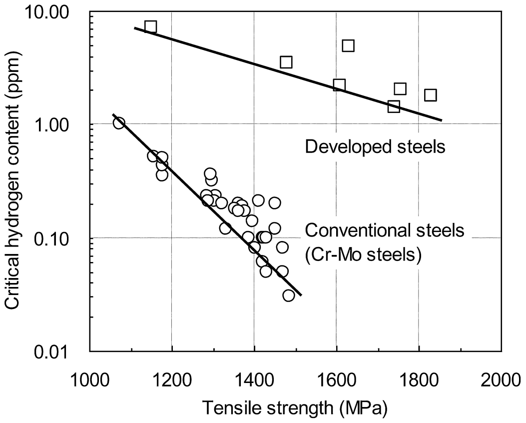

Fig. 4 Relationship between critical hydrogen content of developed steels and tensile strength

content using various types of alloy carbides. The study results are shown in **Fig. 3**.[6] From the figure, it can be seen that: (1) With the increase in the amount of precipitation strengthening, or with the increase in coherent strain, the trapped hydrogen content increases, and (2) The trapped hydrogen content increases when the steel has any of the combinations of alloy carbides added that cause the coherent strain to increase, whereas it decreases when the steel has any of the combinations added that cause the coherent strain to decrease.

As shown in Fig. 1, the emission temperature for hydrogen trapped in Mo-V steel with fine alloy carbides is higher than in ordinary carbon steel. The reason for this is that the diffusion coefficient of hydrogen decreases owing to the trap effect. It has been clarified that the hydrogen that was trapped in alloy carbides was diffusible hydrogen having significant influence on delayed fracture, although its diffusion coefficient is small. Kubota et al.[5] and Yamazaki et al.[4] studied the influence of hydrogen trapped in alloy carbides on the delayed fracture characteristic using various types of steel of the same strength. On the basis of the study results, they report that the [Hc] and resistance to delayed fracture, or delayed fracture strength ratio, of the steel with trapped hydrogen were better than those of ordinary tempered martensitic steels and that the mode of delayed fracture was quasi-cleavage fractures. The transition from intergranular fractures to quasi-cleavage fractures is considered due to the spheroidization of carbides in grain boundaries by high temperature tempering, or the increase in grain boundary strength, and to the decrease in the amount of hydrogen in the grain boundaries caused by hydrogen trapping of alloy carbides in the grains.[5]

On the basis of the above study results and taking into consideration the improved efficiency of cold forging, heat treatment and other manufacturing processes, Nippon Steel Corporation developed new 12-16 T high-strength bolt steels containing Mo and V.[5,8] **Fig. 4** shows the relationship between strength and [Hc] of the newly developed steels. It can be seen that the new steels have better delayed fracture characteristics than conventional steel. From exposure tests on actual bolts carried out in Okinawa, it has been confirmed that they display strong resistance to delayed fracture in the actual environment as well.[8] Those steels for bolts have already been put to practical use in the fields of automobiles and civil engineering/construction.

4. Conclusion

The need for stronger steel materials is ever increasing. In order to meet the need, it is indispensable to cope with the hydrogen embrittlement of steel. It is being clarified that internal fatigue fractures and rolling fatigue fractures of high-strength steels are the result of hydrogen embrittlement. By further enhancing our technical innovativeness in research on hydrogen embrittlement, we would like to help improve the strength of steel materials.

References

1) Nagumo, M.: Fundamentals of Hydrogen Embrittlement. First Edition. Tokyo, Uchida Rokakuho, 2008, p.219
2) Tarui, T., Yamasaki, S.: Tetsu-to-Hagané. 88, 612 (2002)
3) Suzuki, S., Ishii, N., Miyagawa, T., Harada, H.: Tetsu-to-Hagané. 79, 227 (1993)
4) Yamasaki, S., Takahashi, T.: Tetsu-to-Hagané. 83, 454 (1997)
5) Kubota, M., Tarui, T., Yamasaki, S., Ochi, T.: Shinnittetsu Giho. (381), 57 (2004)
6) Kosaka, M., Yoshida, S., Tarui, T.: CAMP-ISIJ. 17, 1371 (2004)
7) Takahashi, J., Kawakami, K., Kobayashi, Y., Tarui, T.: Scripta Mater. 63, 261 (2010)
8) Uno, K., Kubota, M., Nagata, M., Tarui, T., Kanisawa, H., Yamasaki, S., Azuma, S., Miyagawa, T.: Shinnittetsu Giho. (387), 85 (2007)

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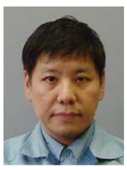

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