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Evaluation Method for Delayed Fracture Susceptibility of Steels and Development of High Tensile Strength Steels with High Delayed Fracture Resistance

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Abstract

This study clarified that by measuring the critical diffusible hydrogen content that causes delayed fracture in steels and the concentration of hydrogen content absorbed from the environment of use, it is possible to establish technology that predicts the delayed fracture susceptibility of steel in its actual service environment. As results of basing this method of evaluation to use hydrogen trapping site to render diffusible hydrogen harmless for 1,300 MPa grade bolts and to promote the improvement of prior austenite grain boundary properties by forming and heat treatment for 1,500 grade PC steel bars were to learn that both developed steel materials have a high critical diffusible hydrogen concentrations. It is considered that these new steels have superior ability to withstand delayed fracture in their actual service environments.

1. Introduction

Delayed fracture is a phenomenon in which a bolt or pre-stressed concrete (PC) steel bar suddenly fails at some time after loading. It results from the hydrogen introduced into the steel by corrosion or plating, for example. As the strength of steel increases, delayed fracture susceptibility also increases. Delayed fracture is thus one of the largest factors that obstructs the strengthening of steels. For example, the F13T class fastener was established in JIS, but the F10T class alone is permitted now due to the problem of delayed fracture.

In recent years, the lightening of weights of automobiles for fuel economy improvement and cost reduction by elimination of some parts or process steps have again called for high strength steels. In many of the evaluation methods for delayed fracture susceptibility which have been proposed to date, however, steels are tested under conditions different from those of their actual use, so performance in their actual service environment cannot be predicted, and they cannot be relatively evaluated as to their delayed fracture susceptibility. In the development of delayed fracture-resistant steels, therefore, it is necessary to establish "a new method for evaluating the delayed fracture susceptibility of steels in their actual service environments" and to develop "delayed fracture-resistant steels" on the basis of the new evaluation method.

This report first describes the development of a new method for evaluating the delayed fracture resistance of steels by taking as an index the concentration of hydrogen that causes delayed fracture. In the development of delayed fracture-resistant steels, a rational approach can be taken in response to the delayed fracture process composed of the entry of hydrogen, the concentration of hydrogen at prior austenite grain boundaries, and the formation of cracks at prior austenite grain boundaries. The proposed approach comprises: (1) preventing the entry of hydrogen; (2) rendering the absorbed hydrogen harmless; and (3) improving grain-boundary properties. The report next describes the development of a 1,300-MPa fastener steel by application of the technology of making the absorbed hydrogen

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harmless by hydrogen trap sites and of a high-strength PC bar steel by improvement in prior austenite grain-boundary properties by thermo-mechanical processing.

2. Method for Evaluating Delayed Fracture Resistance by Diffusible Hydrogen Concentration

2.1 Basic idea of delayed fracture resistance evaluation

Conventional methods evaluate delayed fracture resistance by fracture time or fracture stress ratio in a given acid aqueous solution. The largest problem here is that hydrogen entry characteristics into steel in acid are different from those in an actual service environment[1]. Delayed fracture occurs when hydrogen enters from the environment into the steel and reaches a given concentration. If the concentration of hydrogen absorbed from the actual environment into the steel, $[H_E]$, and the maximum hydrogen concentration at which the steel does not suffer delayed fracture, $[H_C]$, are known, whether or not the steel suffers delayed fracture can be judged. That is, if $[H_C] > [H_E]$, delayed fracture does not occur. A concrete technique for evaluating the $[H_C]$ and $[H_E]$ was studied, and the validity of this thinking was verified.

2.2 Experimental methods

Table 1 gives the chemical composition and tensile strength (TS) after quenching and tempering of test bolt steels. The critical diffusible hydrogen concentration (called $[H_C]$ below) which these steels do not suffer delayed fracture and the maximum concentration of hydrogen (called $[H_E]$ below) that enters from the environment into the steels were evaluated. The bolts were exposure tested in a coastal area in Okinawa to investigate correspondence with laboratory test results.

2.3 Experimental results

To identify the $[H_C]$ of the test steels, circumferentially notched specimens were prepared from bolts and tested for delayed fracture. The circumferential notch was shaped to provide a stress concentration factor of 3.5 to simulate the threads on the bolts. The specimens were cathodically charged with hydrogen and plated with cadmium to prevent the effusion of hydrogen from them. They were then left to stand at room temperature for 24 hours to ensure a uniform hydrogen concentration, tested in tension at a constant load, and measured for the time to fracture. The applied stress was 0.9 of the tensile strength of smooth specimens.

After the delayed fracture test, the cadmium plating was removed, and the specimens were thermally analyzed with a quadrupole mass spectrometer. The analytical results of the tempered martensite SCM440 steel are shown in **Fig. 1**. The peak hatched in the vicinity of 100°C indicates the hydrogen introduced by the cathodic charge. This peak is of diffusible hydrogen that can move in the steel by diffusion at room temperature. The integrated area of the peak is taken as the diffusible hydrogen concentration. For the details of the test, refer to Reference[2].

Based on the above-mentioned results, the maximum hydrogen concentration below which the delayed fracture test specimens do not fail is defined as $[H_C]$ (refer to **Fig. 2**). The $[H_C]$ and exposure test results of the test steels are shown in **Fig. 3**. The $[H_C]$ can be obtained as a value characteristic of each steel that depends on the composition, hardness, and other properties of the steel. The $[H_C]$ data do not always agree with the exposure test results, however.

The hydrogen concentration required for crack initiation and propagation is separately analyzed[3]. The $[H_C]$ is confirmed to be the same as the average hydrogen concentration required for cracking as the process that governs delayed fracture.

The amount of hydrogen entering from the environment is so small that it rarely has been measured to date. This study has succeeded in measuring this hydrogen with a high-sensitivity mass spectrometer. Because the exposure test site is a coastal area in Okinawa, the cyclic corrosion test (CCT) with a 5% salt solution spray had been conducted for 30 days by considering the effect of seal salt particles. The concentration of diffusible hydrogen introduced into the steel due to corrosion, $[H_E]$, was measured by thermal analysis. The corrosion test was conducted under no load, and sampling for hydrogen analysis was performed after the end of the salt spray test during which the corrosion of the specimens is considered to advance most.

The $[H_E]$ data and exposure test results are shown in **Fig. 4**. The $[H_E]$ greatly varies with the type of steel. A comparison with Fig. 3 indicates that the steels C, D and E are higher in $[H_E]$ than $[H_C]$. This points to the need for evaluating both of the hydrogen embrittlement resistance of steels as represented by the $[H_C]$ and the hydrogen entry

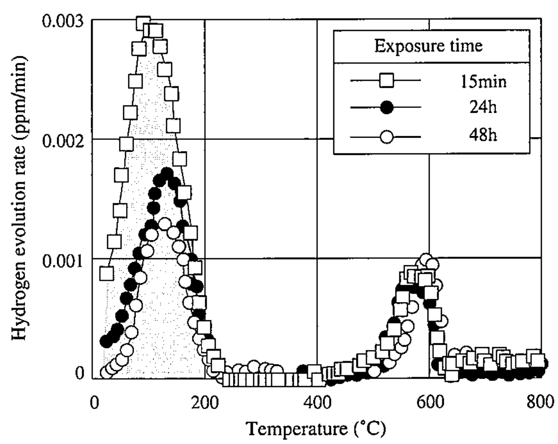


Fig. 1 Effect of exposure time in air at room temperature after hydrogen charge on hydrogen evolution curves as obtained by thermal analysis of hydrogen-charged specimens

Table 1 Chemical compositions (wt%) and mechanical properties of test steels

Steel	C	Si	Mn	Cr	Mo	V	Al	B	Temper(°C)	TS (MPa)
A	0.21	0.14	0.76	0.64	—	—	0.074	0.0010	440	1,078
B	0.21	0.14	0.76	0.64	—	—	0.074	0.0010	350	1,303
C	0.35	0.05	0.25	1.20	0.80	—	—	—	430	1,568
D	0.30	0.98	0.51	1.99	Addition		—	—	510	1,537
E	0.30	0.98	0.51	1.99	Addition		—	—	430	1,627
F	0.41	0.07	0.51	1.20	Addition		—	—	590	1,450

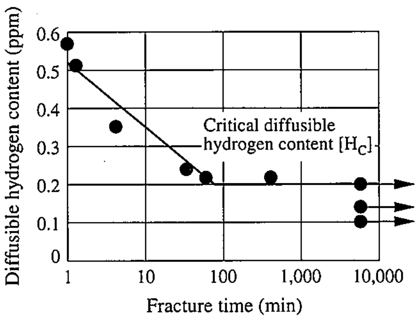


Fig. 2 Typical measurement of critical diffusible hydrogen concentration (SCM435, 1,450 MPa)

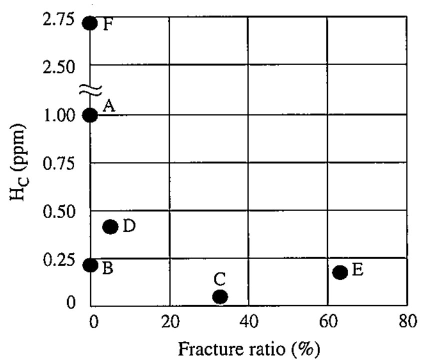


Fig. 3 Relationship between delayed fracture probability in exposure test and critical diffusible hydrogen concentration (H_C)

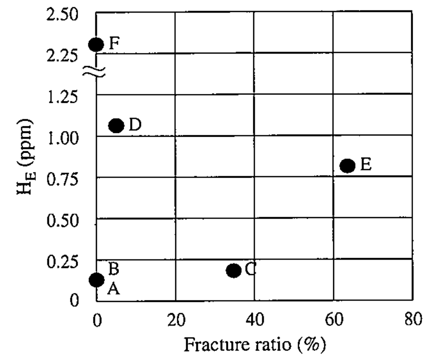


Fig. 4 Relationship between delayed fracture probability in exposure test and absorbed hydrogen concentration (H_C) in cyclic corrosion test

characteristics in the operating environment as represented by the $[H_E]$ when determining the delayed fracture susceptibility of steels.

2.4 Proposal of method for evaluating delayed fracture susceptibility in actual environment

The parameter given by the following equation is proposed as an index for evaluating the delayed fracture susceptibility of steels in the actual environment:

$$([H_C] - [H_E]) / [H_C] \quad \cdots\cdots (1)$$

The smaller the value of the parameter, the lower the delayed fracture resistance the steel should have. If the delayed fracture test conditions or CCT conditions simulate the service conditions, delayed fracture is expected not to occur as long as the value of the parameter is positive.

The relationship between the parameter of Eq. (1) and the exposure test results is shown in **Fig. 5**. A good correlation is observed. This means that the parameter reflects the delayed fracture susceptibility of steels in their service environment with considerable accuracy. There are still many unknown points about the entry characteristics of hydrogen into steels. The proposed method is one attempt to clarify the entry of hydrogen into steels. Evaluation by reference to the critical diffusible hydrogen concentration and introduced hydrogen concentration of steels is becoming mainstream[4, 5]. Judgment of the delayed fracture susceptibility of steels according to these hydrogen concentrations is considered feasible.

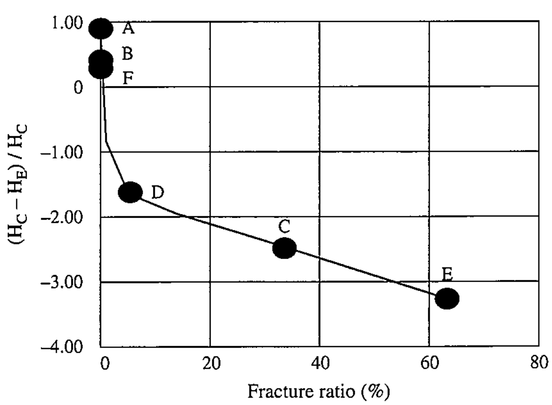


Fig. 5 Relationship between delayed fracture probability in exposure test and parameter $[(H_C - H_E) / H_C]$

3. High Strength Bolt Steel

The development of high strength bolts capable of reducing their own weight and accomplishing the size and weight reduction of parts to be fastened is an important issue from the standpoints of automobile fuel economy improvement and performance enhancement. High strength bolts for civil engineering and building applications are greatly effective in achieving construction labor savings because the required number of bolts can be reduced. This chapter describes the steel developed by Nippon Steel for high strength bolts (12 to 14T classes) against this background.

3.1 Features of developed steel

Delayed fracture in quenched and tempered steels often occurs at prior austenite grain boundaries. Improvement in delayed fracture resistance thus calls for strengthening the prior austenite grain boundaries. Among the grain-boundary strengthening methods reported to date are: (1) reduction in grain-boundary segregation elements such as phosphorus and sulfur[6]; (2) grain refinement by addition of niobium, titanium and vanadium, and reduction in grain-boundary segregation elements[7]; and (3) prevention of film-like cementite precipitation at the prior austenite grain boundaries by high-temperature tempering[8].

A method is proposed whereby hydrogen traps are transgranularly dispersed to trap introduced hydrogen, thereby lowering the grain-boundary hydrogen concentration and preventing grain-boundary fracture. Vanadium carbonitrides that precipitate on tempering are effective hydrogen traps[9].

The chemical composition of a new high strength bolt steel developed by making use of the above-mentioned grain-boundary strengthening and hydrogen trapping techniques is given in **Table 2**. Vanadium is a hydrogen trapping element and is also effective in refining the grain size and raising the tempering temperature by secondary hardening on tempering. For these reasons, vanadium is uti-

Table 2 Chemical composition of new steel (wt%)

	C	Si	Mn	P	S	Cr	Mo	V
New steel	0.40	0.05	0.50	< 0.010	< 0.010	1.20	Addition	
SCM440	0.40	0.20	0.80	0.015	0.015	1.10	0.20	—

lized as basic element in the new steel. The new steel is provided with a higher tensile strength than that of the SCM440 at the same tempering temperature by secondary hardening due to the precipitation of molybdenum and vanadium carbonitrides. It can be tempered at elevated temperatures above 600°C to obtain a strength of the 13T class (tensile strength of 1,300 to 1,500 MPa). The prior austenite grains in the new steel are markedly refined by the addition of vanadium and are 10 μm or less as compared with usually about 20 to 30 μm for the conventional bolt steel SCM440. Given the reduction in cold forgability by the addition of molybdenum and vanadium, cold forgability is improved by lowering the silicon content to ensure the fabricability of bolts. The cold forgability of the new steel after spheroidize annealing is equivalent to that of the SCM440. This means that bolts can be made from the new steel without raising the cold forging cost.

3.2 Delayed fracture susceptibility of new steel

The delayed fracture test results of the new steel which is quenched and tempered to the 13T class are shown in **Fig. 6**. The test method was based on the critical diffusible hydrogen concentration[2]. The specimen was cathodically charged with hydrogen and loaded in air with a constant stress of 90% of the tensile strength. The hydrogen content of the specimen was changed by changing the hydrogen charging time, and the critical diffusible hydrogen concentration [H_C] was then determined. The new steel is much higher in the [H_C] than the SCM440, and it exhibits excellent delayed fracture resistance. Namely, the new steel is less likely to suffer delayed fracture when charged with a large amount of hydrogen.

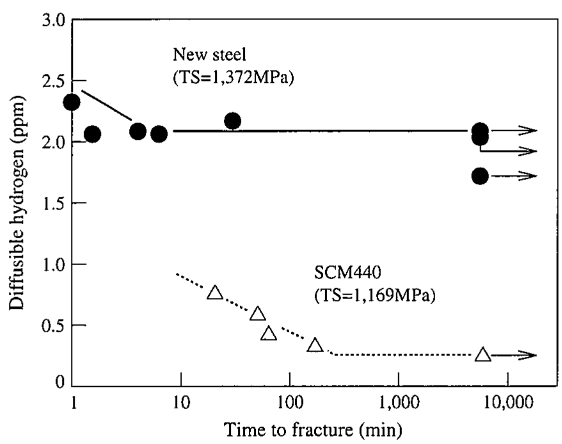


Fig. 6 Delayed fracture test results by critical diffusible hydrogen concentration method

To confirm its delayed fracture susceptibility in an environment where hydrogen continuously enters into the new steel from outside, it was delayed fracture tested by a method of applying stress while charging with hydrogen. This test method has also confirmed that the new steel exhibits higher delayed fracture resistance than does SCM440.

Fracture surfaces after the delayed fracture test are shown in **Photo 1**. While the SCM440 (a) reveals a clear-cut grain-boundary fracture surface, the new steel (b) presents a transgranular quasi-cleavage fracture surface, not an intergranular fracture surface.

As discussed above, the new steel yields better delayed fracture properties than the conventional steel SCM440 when tested by either of the methods described. Actual bolts have been under exposure test. The new steel is confirmed to have no fracture at two and a half years after the start of the exposure test.

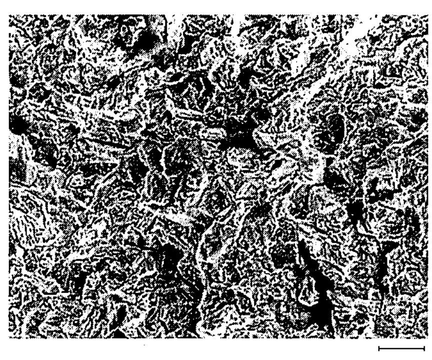
The TEM micrograph of the new steel is shown in **Photo 2**. The new steel has grain-boundary cementite spheroidized because its tempering temperature is high. It was also confirmed that fine vanadium carbonitrides are precipitated in the matrix.

3.3 Hydrogen evolution behavior of new steel

The thermal hydrogen analysis results of the new steel are shown in **Fig. 7**. In the as-quenched condition (a), the new steel exhibits almost the same hydrogen evolution profile as the SCM440. When tempered at high temperatures (b), the new steel exhibits a peak in the vicinity of 200°C. This is a phenomenon peculiar to vanadium-microalloyed steels and it suggests that the formation of hydrogen traps concerns with the precipitation of vanadium carbonitrides during the tempering treatment[9]. Since these vanadium carbonitrides are considered to precipitate, both intergranularly and transgranularly, during tempering and the trapping of hydrogen by the vanadium carbonitrides is considered to have lowered the intergranular hydrogen concentration and raised the delayed fracture resistance of the new steel.

The above results suggest the following probable reasons for the excellent delayed fracture resistance of the new steel: (1) The increase in the number of hydrogen traps produced by the precipitation of vanadium carbonitrides during tempering lowered the intergranular hydrogen concentration. (2) The grain boundaries were cleaned by the reduction in phosphorus and sulfur contents and by grain refinement. (3) The high-temperature tempering treatment spheroidized grain-boundary cementite and improved the grain-boundary binding force. It is presumed that these effects combined to prevent the grain-boundary fracture of the new steel.

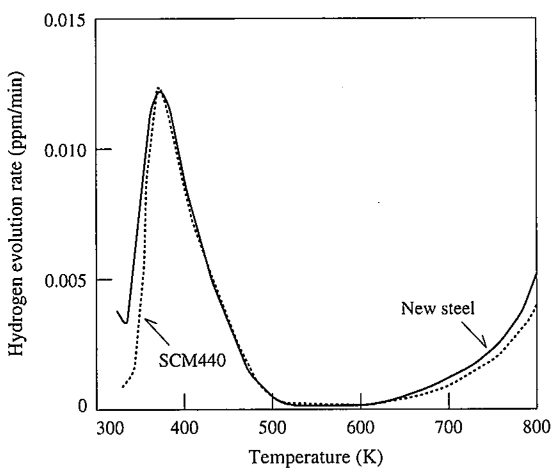
(a) SCM440



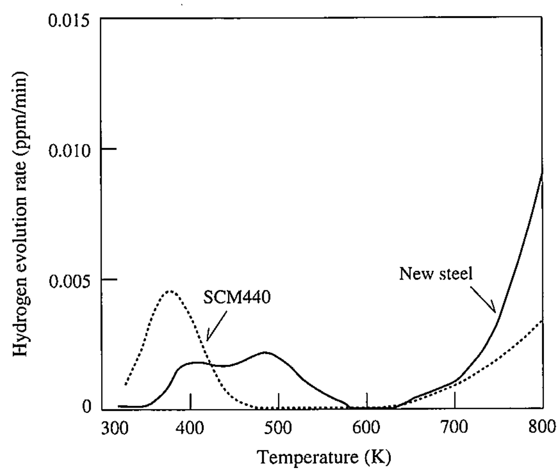
(b) New steel

Photo 1 Delayed fracture surfaces

Photo 2 Precipitates observed in new steel



(a) As quenched



(b) Tempered at 973K

Fig. 7 Hydrogen evolution phenomenon of new steel

4. Improvement in Delayed Fracture Resistance of PC Bar Steel by Thermo-mechanical Processing

Pre-stressed concrete (PC) steels used in PC members like poles and piles are available as PC steel wires strengthened by the drawing of eutectic pearlite steel and as PC steel bars with the tempered martensite microstructure of medium-carbon steel. The PC steel bars are advantageous in that they can be spot welded, but are reported to be lower in delayed fracture resistance than the PC steel wires. This section describes the results of laboratory study conducted from the standpoint of thermo-mechanical processing to improve the delayed fracture resistance of a 1,420-MPa PC bar steel.

4.1 Philosophy for improvement in delayed fracture resistance of PC steel bars

Strengthening the prior austenite grain boundaries is proposed as one method for improving the delayed fracture resistance of 1,500-MPa high-strength steels[10, 11]. Generally, alloying elements are added to improve the delayed fracture resistance of these high-strength steels. The PC wire steels are of simple composition, but have excellent delayed fracture resistance. One of the probable reasons advanced is that the fibrous structure produced by the drawing operation resists the propagation of the delayed fracture crack. While many of the conventional tempered martensite microstructures fail by grain-boundary fracture, the steel wire fails by transgranular fracture (or quasi-cleavage fracture). This suggests that if the prior austenite grain boundaries are elongated as observed in the steel wire, the tempered martensite steel can be also improved in delayed fracture resistance. A thermo-mechanical control process composed of unrecrystallized region rolling and direct quenching is effective in accomplishing the elongation of the prior austenite grain boundaries[12].

4.2 High-strength PC steel bars with excellent delayed fracture resistance

The relationship between the rolling temperature and critical diffusible hydrogen concentration [H_C] of a 0.29C-0.20 Si-0.75Mn-B steel is shown in **Fig. 8**. The test steel was hot rolled at a finish rolling temperature of 770 to 910°C, immediately quenched in water, and induction tempered to a strength of about 1,470 MPa. The steel is recrystallized at 910°C, partially recrystallized at 800°C, and unrecrystallized at 770°C. The [H_C] of the steel rolled in the unrecrystallized region is 0.90 ppm and extremely high as compared with 0.15 ppm for conventional induction quenched and tempered steels. Despite simple composition, the test steel is markedly improved in delayed fracture resistance.

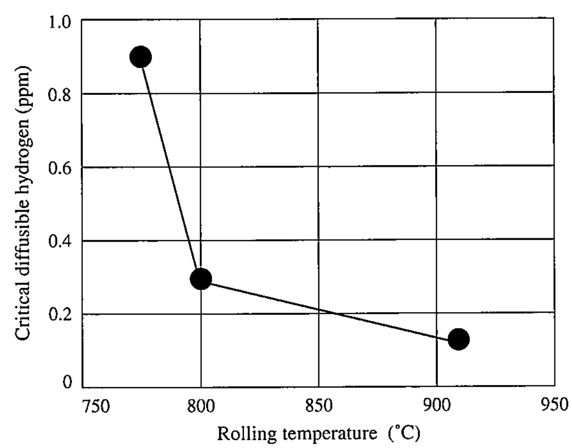


Fig. 8 Effect of rolling temperature on critical diffusible hydrogen concentration

The delayed fracture of the recrystallization region rolled and induction quenched and tempered steel is a typical grain-boundary fracture. When the steel is rolled in the partial recrystallization region, its delayed fracture is a mixture of grain-boundary fracture and quasi-cleavage fracture. When the steel is rolled in the unrecrystal-lization region, its delayed fracture is mostly quasi-cleavage cracking. Rolling in the unrecrystallization region significantly increases the [H_C], probably because the delayed fracture changed from grain-boundary fracture to quasi-cleavage fracture grain-boundary fracture.

The diffusible hydrogen concentration [H_E] of the steel in the cyclic corrosion test in which the steel is sprayed with a 5% salt solution to accelerate its corrosion is about 0.1 ppm, irrespective of the rolling conditions, and it is much lower than the [H_C] of 0.9 ppm for the steel rolled in the unrecrystallized region. Therefore, the steel manufactured by the process consisting of unrecrystallization region rolling, direct quenching, and induction tempering is thought to offer excellent resistance to delayed fracture in the service environment.

4.3 Factors responsible for improvement in delayed fracture resistance of unrecrystallization region rolled steel

In the grain-boundary fracture of the steel rolled in the recrystallization region or quenched and tempered, once the initial crack of delayed fracture occurs at a prior austenite grain boundary, it easily propagates along the prior austenite grain boundaries. The initiation of an initial crack, about 50 μm in diameter, is considered as a process governing the delayed fracture of the steel[3]. The [H_C] at which grain-boundary fracture occurs is reported to be the hydrogen concentration required for the initiation of an initial crack[3].

In the unrecrystallization region rolled steel with elongated austenite grains, the initiation origin is presumably the prior austenite grain boundary. When stress is applied in parallel with the elongated austenite grains, a large stress does not act at the grain boundaries. Since the crack must propagate through the austenite grains with high delayed fracture resistance, quasi-cleavage cracking occurs. As a result, the [H_C] is considered to increase. The prior austenite grains in the unrecrystallization region rolled steel are not linear but irregular in many portions, and the microscopic geometrical shape effect of the grain boundaries is considered to contribute to the control of grain-boundary cracking. That is, the high-strength steel produced by the above process is expected to increase in both the hydrogen content required for the initiation of an initial crack and the hydrogen content required for the propagation of the initial crack.

In the steels that suffer grain-boundary fracture, the [H_C] is known to improve with increasing tempering temperature. The effect of the tempering conditions on the [H_C] of the steel rolled in the unrecrystallization region and adjusted to a strength of about 1,470 MPa is shown in **Fig. 9**. The 0.29C-0.20 Si-0.75 Mn-B steel greatly changes in [H_C] with the tempering conditions. When the steel is induction heated at the highest tempering temperature, it has the highest [H_C]. The delayed fracture mode is a fracture surface mainly composed of quasi-cleavage cracking under each set of tempering conditions. This result indicates that when the delayed fracture is mainly composed of quasi-cleavage cracks, the delayed fracture resistance depends on the tempering temperature, and suggests that the shape

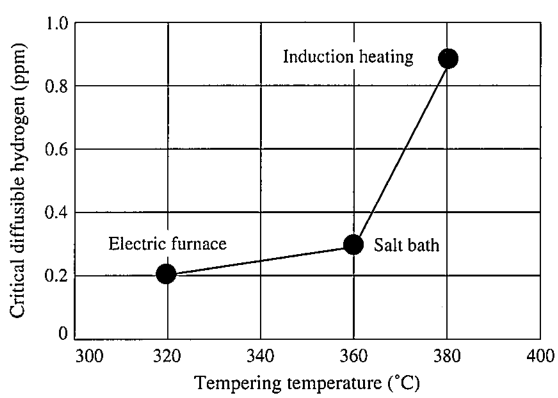


Fig. 9 Relationship between tempering temperature and critical diffusible hydrogen concentration of steels suffering quasi-cleavage cracking

of transgranular carbides exerts an effect in addition to intergranular segregation and intergranular carbide morphology.

The hardness of the steel directly water quenched after hot rolling increases with decreasing finish rolling temperature, irrespective of whether the steel is rolled in the recrystallization or unrecrystallization region. This means that the dislocations in the work-hardened austenite grains are inherited by the martensite. As a result, the lower the temperature at which the steel is rolled, the higher the temper softening resistance and the tempering temperature the steel has. In the process composed of unrecrystallization region rolling, direct quenching, and induction heating, besides the above-mentioned geometrical shape effect of the prior austenite grain boundaries, the ability to perform high-temperature tempering is considered to raise the [H_C].

5. Conclusions

An attempt has been made to evaluate delayed fracture susceptibility by using the hydrogen concentration as an index. It has been clarified that the delayed fracture critical diffusible hydrogen concentration [H_C] and the corrosion-introduced hydrogen concentration [H_E] vary from steel to steel and that the possibility of the steels not suffering delayed fracture in their service environments can be increased by making the [H_C] larger than the [H_E].

The utilization of vanadium carbonitrides as hydrogen traps and the improvement in the properties of prior austenite grains by thermo-mechanical processing have been found to be very effective techniques for improving the [H_C]. Both methods retard prior austenite grain-boundary fracture in the delayed fracture test, assure a very high [H_C] of about 1 ppm or more, and are expected to provide excellent delayed fracture resistance.

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