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Steel — Measurement method for the evaluation of hydrogen embrittlement resistance of high strength steels

Acier — Méthode de mesure pour l'évaluation de la résistance à la fragilisation par l'hydrogène des aciers à haute résistance

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Foreword

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The committee responsible for this document is ISO/TC 17, *Steel*, Subcommittee SC 7, *Methods of testing (other than mechanical tests and chemical analysis)*.

Introduction

The mechanical properties of high strength steels, such as tensile strength, elongation and reduction of area, would be degraded by the effect of hydrogen, known as hydrogen embrittlement, and the susceptibility of hydrogen embrittlement becomes greater with increasing the strength level of steels. This International Standard suggests a standardized test method for the evaluation of hydrogen embrittlement resistance of high strength steels.

Steel — Measurement method for the evaluation of hydrogen embrittlement resistance of high strength steels

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard provides a method for the evaluation of the resistance to hydrogen embrittlement (i.e. hydrogen delayed fracture) using constant loading test with hydrogen pre-charged specimens. The amount of hydrogen content absorbed in the specimens is analysed quantitatively by thermal desorption analysis such as gas chromatography, mass spectrometry and so on. In the case of hydrogen continuous charging such as hydrogen absorption in aqueous solution at free corrosion potential, hydrogen absorption in atmospheric corrosion environments and hydrogen absorption in high pressure hydrogen gas, the evaluation method is also briefly described. This method is mainly applicable to the evaluation of hydrogen embrittlement resistance of high strength steel bolts.

2 Principle

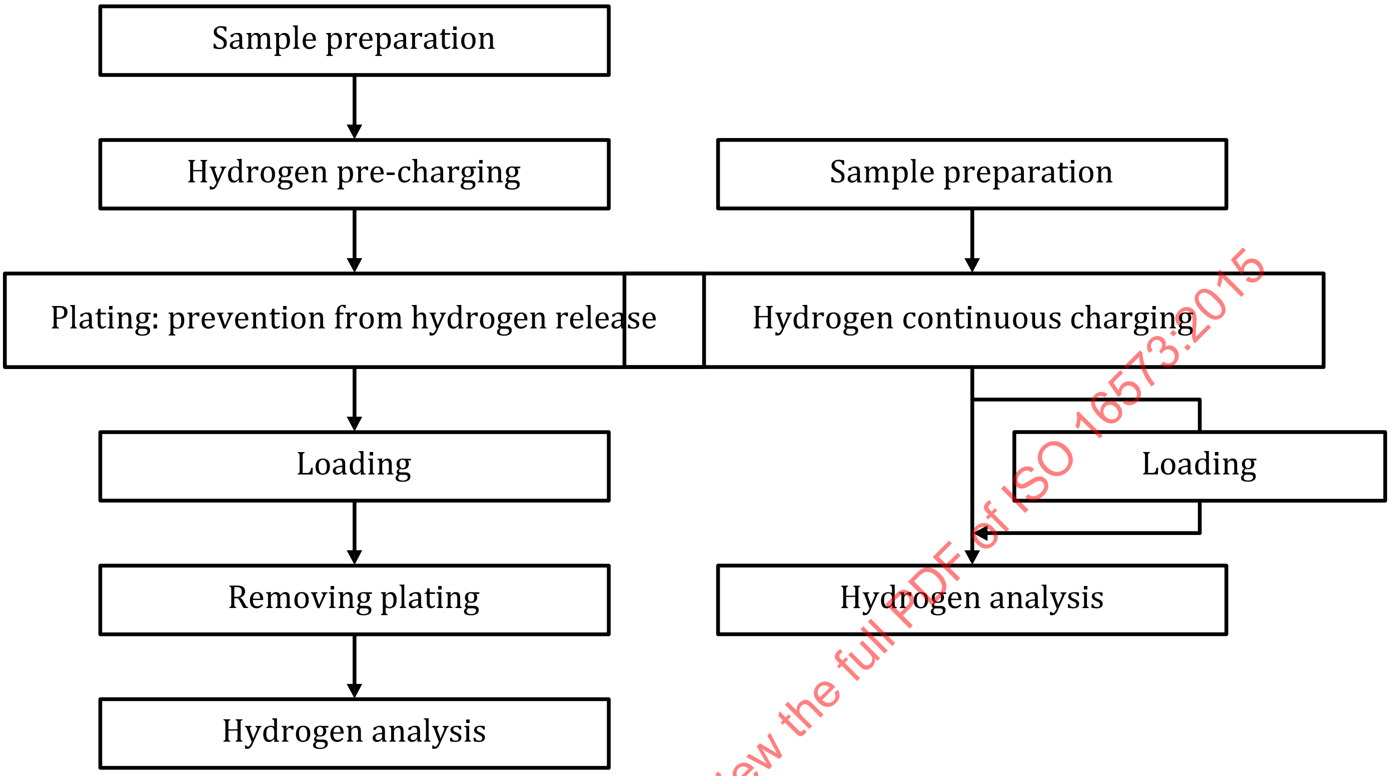
This test method is used to evaluate material resistance to hydrogen embrittlement. Figure 1 shows schematic sequences for a) hydrogen pre-charging method and b) hydrogen continuous charging method. For the hydrogen pre-charging method [see Figure 1 a)], prepare a test specimen which has a higher hydrogen level by forcibly charging hydrogen into the specimen. Apply constant load to the hydrogen charged test specimen and measure the time to failure. By testing specimens containing various contents of diffusible hydrogen, which is mainly responsible for hydrogen embrittlement, the relationship between diffusible hydrogen content and times to failure can be obtained. Diffusible hydrogen content can be measured by thermal desorption analysis using the test specimen after failure. This method can provide at least qualitative comparison of the resistance to hydrogen embrittlement among several high strength steels having different microstructures or compositions. For the hydrogen continuous charging method [see Figure 1 b)], a test specimen is loaded in one of the following three conditions:

a) in aqueous solution at free corrosion potential;

b) in atmospheric corrosion environments;

c) in high pressure hydrogen gas.

Then, hydrogen analysis is carried out after failure of the specimen. If specimens do not fail up to 100 h (up to 200 h, if necessary), qualitative comparison of the resistance to hydrogen embrittlement can be made by hydrogen analysis of unbroken specimens.

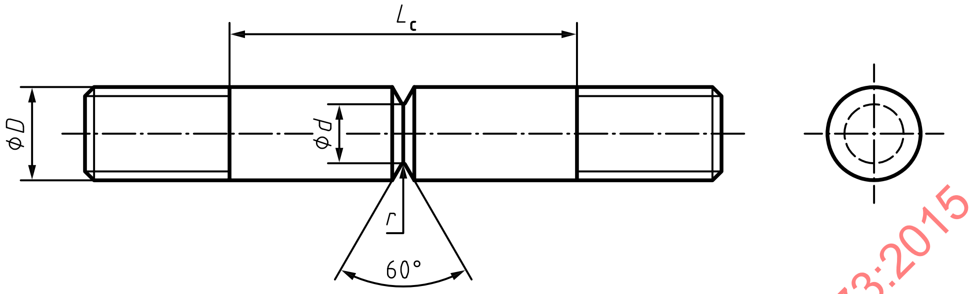


a) Hydrogen pre-charging method **b) Hydrogen continuous charging method**

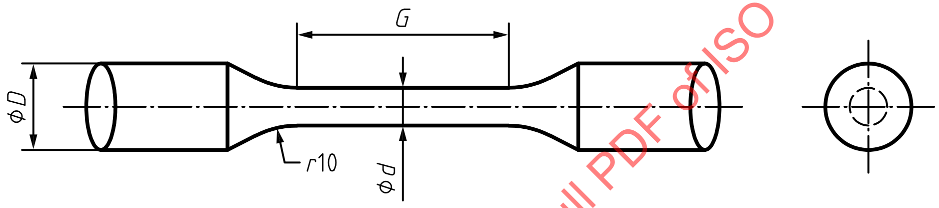
Figure 1 — Flow chart illustrating the test methods

3 Specimen preparation

The dimensions of the specimens are shown in Figure 2, and other configurations of the test specimen may be applied. It is recommended to use specimens of 10 mm in diameter as a standard size. For samples with smaller diameter (i.e. D = 5 mm), r/D = 0,02 may be applied.[1][2]



a) Notched specimen



b) Smooth specimen

d/D	0,6
r/D	0,01 or 0,02
L_c/D	7
G/D	5

Figure 2 — Dimensions and shape of specimens

4 Hydrogen charging methods

4.1 General

There are four hydrogen charging methods, such as cathodic charging, hydrogen absorption in aqueous solution at free corrosion potential, hydrogen absorption in atmospheric corrosion environments and hydrogen absorption in high pressure hydrogen gas. The examples of the condition of each method are as follows.

4.2 Cathodic charge method

4.2.1 Hydrogen charging solution

To estimate the effect of hydrogen on the mechanical properties of steels, the hydrogen is forced to diffuse into the specimens by the cathodic charging method. For hydrogen pre-charging, the charging solution should be prepared and the chemical compositions of the solutions are listed in Table 1.

Two kinds of solutions may be used for hydrogen pre-charging. Solution 1 may be used for introducing a relatively large amount of hydrogen to the specimens and Solution 2 may be used for introducing a small amount of hydrogen.

Table 1 — Chemical composition of the solutions for hydrogen charging

Charging solution	Element	Content g /L	Mark
Solution 1	NaCl	30	Large amount of hydrogen
	NH_4SCN	3	
Solution 2	NaOH	4	Small amount of hydrogen

4.2.2 Hydrogen charging conditions

The electro-chemical cell for hydrogen pre-charging may be placed in a 200 ml to 1 000 ml beaker. It is recommended that the anode of the electrochemical cell be made of platinum wire of spiral type of 0,5 mm in diameter and 2 m in length (counter electrode), and the specimen works as the cathode (working electrode). After the Pt wire and the specimen are placed in the cell, apply the constant current of its current density in the range of 0 A/m^2 ~20 A/m^2 by using potentio/galvanostat for 48 h. A charging time of 48 h is recommended, but other charging times are also optional as long as a total time of 72 h is reached for hydrogen charging and the homogenization treatment by room temperature exposure after cadmium (Cd) plating. For materials with low hydrogen diffusion coefficient, the hydrogen charging time and the total time may be increased. The specimen's surface area should be calculated for proper current supply. The pre-charged hydrogen amount may be changed by varying the current density or pre-charging time. However, it is recommended to use fixed pre-charging time and current density to get reproducible test results.

4.3 Hydrogen absorption in aqueous solution at free corrosion potential

For hydrogen charging by corrosion in acid, HCl solutions or HCl with CH_3COOH/CH_3COONa buffered solutions are often used. For example, specimen shall be immersed in 5 % HCl solution at room temperature. Immersion time shall be determined based on the specimen size and hydrogen diffusion coefficient of the tested material.

4.4 Hydrogen absorption in atmospheric corrosion environments

For hydrogen charging by atmospheric corrosion, the salt spray test (SST) or cyclic corrosion tests (CCT) including salt spraying, drying and humidifying are carried out. As an example, desirable CCT processes are listed in Table 2.

Table 2 — Example of CCT processes

Process	Conditions	Time
Salt spray	5 % NaCl, 35 °C	2 h
Dry	20 % to 30 % humidity, 60 °C	4 h
Wet	≥95 % humidity, 50 °C	2 h

4.5 Hydrogen absorption in high pressure hydrogen gas

For hydrogen charging by hydrogen gas, the specimens shall be exposed directly to gaseous hydrogen up to 140 MPa at above room temperature. Exposure time shall be determined based on the specimen size and hydrogen diffusion coefficient of the tested material. However, extreme care is necessary and it is not recommended due to the danger of experiment.

5 Preparation of electroplating solution and electroplating condition

5.1 General

The plating process is applied for the hydrogen pre-charging method in order to prevent hydrogen release during the loading test.

5.2 Electroplating solution

After hydrogen pre-charging, Cd plating should be conducted to prevent the release of hydrogen from the specimens during constant loading test. Cd is a well-known toxic material but the hydrogen diffusivity in Cd is known to be nearly zero. Instead of using toxic Cd, other appropriate plating materials, for example Zn, may be applied. The elements for Cd plating solution and the amounts of each element are listed in Table 3. The pH of the solution should be 3 pH to 5 pH. To adjust the pH of the solution, one can add H_3BO_4 or ammonium solution. (Please make reference to the recommended Zn plating solution in Table 3).

Table 3 — Elements for Cd and Zn plating solutions and the amounts of each element

Solution	Element	Type	Amount
Cd plating solution	$Cd(BF_4)_2$	solution [(C) = 50 %]	427 g
	NH_4BF_4	solute	48 g
	H_3BO_4	solute	21,6 g
	H_2O (distilled)	solvent	460 ml
	pH	-	3 to 5
Zn plating solution	$ZnCl_2$	solute	45 g
	KCl	solute	234 g
	H_3BO_4	solute	21,6 g
	Sodium Dodecyl Sulfate	solute	0,5 g
	H_2O (distilled)	solvent	700 ml
	pH	-	5 to 6

5.3 Electroplating conditions

An electrochemical reaction is used for Cd plating. Immerse the metal platinum (Pt) anode into the prepared Cd solution, and immerse the specimen in order for it to work as a cathode. After hydrogen pre-charging, clean the specimens by mechanical grinding (polishing) or with 0,1 N HCl and 0,1 N NaOH by ultrasonic cleaner for 30 s, respectively. Then, immerse the specimens in Cd plating solution and apply a constant current of 0,5A for 300 s. Other conditions of current and time may also be used for Cd plating. Using the potential difference, Cd is adhered to the surface of the specimen.

The thickness of Cd plating should be at least 15 µm or higher to prevent hydrogen release. Extreme care is needed to handle the solutions containing Cd during the entire Cd plating procedures.

6 Constant loading test

6.1 Constant loading test procedures

The suggested methods for the constant loading test are the following.

a) Use adequate jig to apply uniaxial loading to the specimens.

b) Specimens containing various diffusible hydrogen content should be used to measure the time to failure. In the case of hydrogen continuous charging, various current densities should be applied to measure the time to failure of a specimen.

c) Stress ratio (applied stress/tensile stress) should be in the range of between 0,3 and 0,9.

NOTE Tensile strength is measured in evaluated type of specimen without hydrogen charge in advance.

d) If the specimens are not fractured after up to 100 h (up to 200 h, if necessary), one can conclude that these specimens do not fracture under these conditions and discontinue the test.

e) To ensure recurrence, it is recommended that at least three specimens be tested at the same stress ratio.

f) After the constant loading test, diffusible hydrogen contents of the specimen should be immediately measured. If it is impossible to measure diffusible hydrogen content immediately following the test, specimens shall be preserved below –30 °C, preferably in liquid nitrogen, to prevent hydrogen release from the fractured surface.

6.2 Presentation of the results

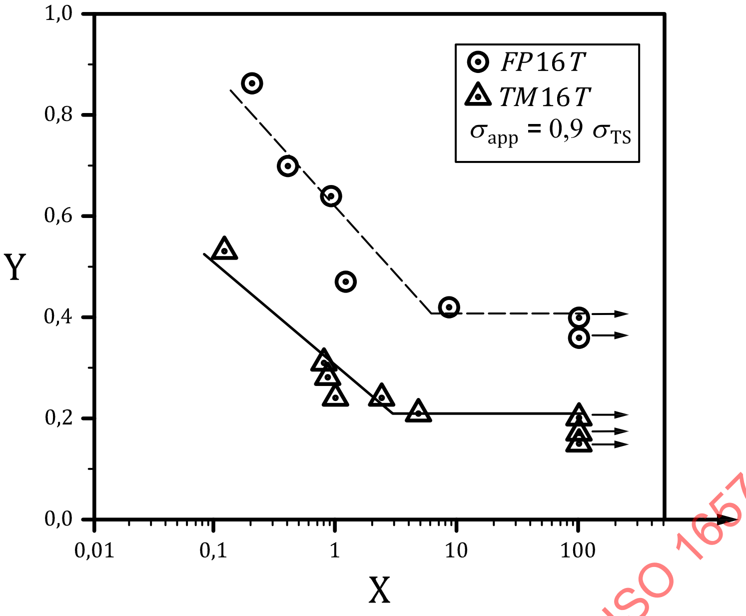
a) Figure 3 shows an example of the results of the constant loading test.

b) The abscissa indicates the time-to-failure of the specimens and the ordinate represents the diffusible hydrogen content or the applied stress ratio (applied stress/notch tensile stress).

c) The critical hydrogen content below which the fracture does not occur is defined as the amount of hydrogen of the specimen which is not fractured up to 100 h (see Figure 3).

d) It may be concluded that the susceptibility to hydrogen embrittlement is greater if time-to failure is shorter when tested at the same stress ratio and comparable hydrogen content.

As an additional evaluation method, local hydrogen concentration and local stress may be calculated by numerical method for comparing the results of specimens with different stress concentration factors.[3]



Key

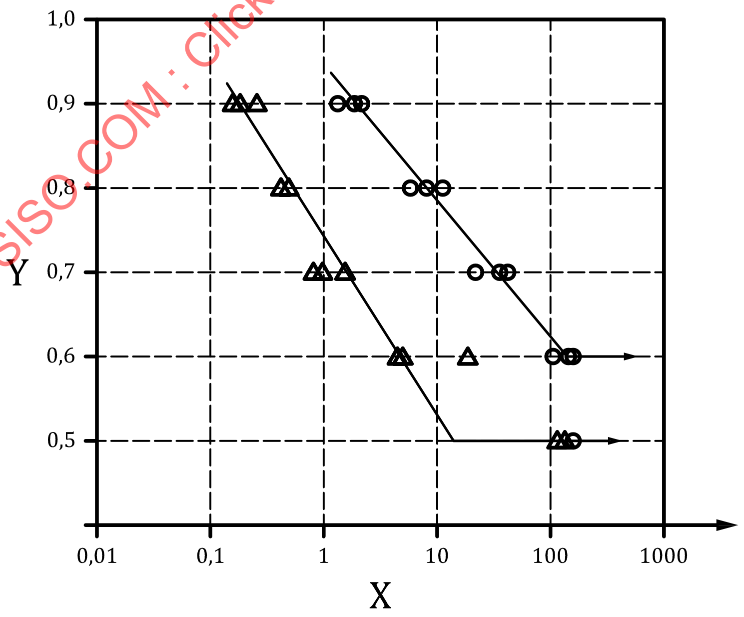
X time to failure, h

Y diffusible hydrogen content, % (mass fraction or mass ppm[a])

[a] 0,01 % (volume fraction) is the equivalent of 100 ppm; ppm is a deprecated unit.

FP16T and TM16T denote full pearlite microstructure and tempered martensite microstructure, respectively, having the same tensile strength of 1 600 MPa.[4]

Figure 3 — Example of the results of the constant loading test (time to failure vs diffusible hydrogen content)



Key

X time to failure, h

Y stress ratio, σ_{ap}/σ_{nb}

Stress ratio (σ_{ap}/σ_{nb}) represents applied stress/notch tensile stress.

Figure 4 — Example of the results of the constant loading test

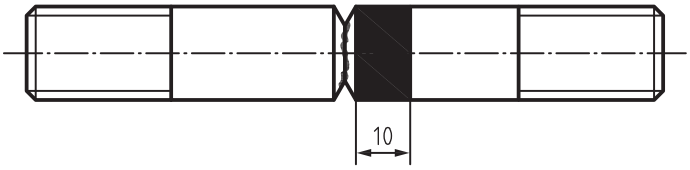
7 Post-test specimen treatment

After specimens are fractured, the following process shall be applied.

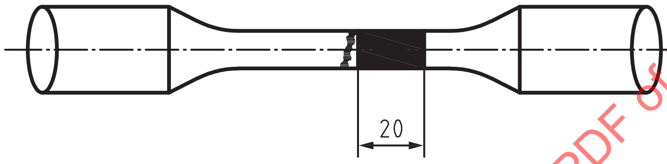
a) Keep fractured specimens in liquid nitrogen to prevent hydrogen desorption.

b) Cut fractured specimens for the hydrogen analysis from the nearest point to the fractured surface toward the thread (see Figure 5).

Dimensions in millimetres



a) Notched specimen



b) Smooth specimen

The shaded area represents the part taken for hydrogen content analysis.

Figure 5 — Hydrogen content analysis

c) For the Cd-coated specimens (pre-charged condition), removing the Cd layer is necessary before analysing diffusible hydrogen content. To remove the Cd layer, the cut specimen is immersed into Cd plating solution and the electrodes are connected in a reverse way of the Cd plating, i.e. the anode is the specimen and the cathode is the platinum (Pt). A constant current of 1,2 A is applied for 5 min to remove the Cd layer completely. After the electrochemical process, the specimens should be cleaned with ethanol by ultrasonic cleaner for 30 s. After removing the Cd layer, the specimen shall be kept in liquid nitrogen again before performing hydrogen thermal desorption analysis. (Removing the Zn layer is same as removing the Cd layer.) This procedure should not be applied for the continuous charging method.

8 Hydrogen thermal desorption analysis

8.1 General

In general, diffusible hydrogen is calculated by integrating the first peak of the curve of thermal desorption analysis. When several peaks are observed at low temperature (i.e. below 400 °C), diffusible hydrogen may be calculated by integrating peaks below 400 °C of the curve of thermal desorption analysis. Since the heating rate does not have a significant influence on test results, high heating rate such as 100 °C/h is recommended. The heating rate should be reported.

8.2 Experimental apparatus (gas chromatograph)

The equipment for thermal desorption analysis consists of 3 parts: heating, gas sampling, and detecting. When the specimens are heated, hydrogen inside of the specimens diffuses out and flows into the gas chromatography column with carrier gas (high purity Ar or He gas). The heating rate is fixed at 100 °C/h