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Standards New Zealand

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Committee representation

This standard was prepared by the P3652 Hydrogen Standards Committee. Membership of the committee was approved by the New Zealand Standards Approval Board and appointed by the New Zealand Standards Executive under the Standards and Accreditation Act 2015.

The committee consisted of representatives of the following nominating organisations:

Coregas

Energy Resources Aotearoa

Fabrum

Fonterra Co-operative Group

Gas Appliance Industry

GasNZ

GNS

Hiringa Energy

HW Richardson Group

HyPotential

Methanex

New Zealand Hydrogen Council

PEC

WorkSafe New Zealand − Energy Safety

Z Energy

Acknowledgement

Standards New Zealand gratefully acknowledges the contribution of time and expertise from all those involved in developing this standard.

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(ISO 11114-4:2017, IDT)

New Zealand Standard

Transportable gas cylinders − Compatibility of cylinder and valve materials with gas contents

Part 4: Test methods for selecting steels resistant to hydrogen embrittlement

Contents

Preface

The government has a legislated 2050 target of net zero greenhouse gas (GHG) emissions, other than from biogenic methane, and a target under the Paris Agreement to reduce net GHG emissions to 50 per cent below gross 2005 levels by 2030.

Hydrogen is set to play a key role in meeting these targets. (New Zealand has considerable renewable energy resources which could be harnessed to sustainably produce hydrogen for use as a next-generation green fuel source and industrial feedstock.)

To enable the safe integration and novel use of hydrogen in all its forms across New Zealand's energy landscape, a suite of hydrogen-related equipment standards is being adopted.

This standard specifies the test methods and the evaluation of results from these tests in order to qualify steels suitable for use in the manufacture of gas cylinders (up to 3000 litres) for hydrogen and hydrogen bearing embrittling gases.

This document only applies to seamless steel gas cylinders.
The requirements of this document are not applicable if at least one of the following conditions for the intended gas service is fulfilled:
(a) The working pressure of the filled embrittling gas is less than 20% of the test pressure of the cylinder;
(b) The partial pressure of the filled embrittling gas of a gas mixture is less than 5 MPa (50 bar) in the case of hydrogen and other embrittling gases, except for hydrogen sulphide and methyl mercaptan (in such cases, the partial pressure shall not exceed 0.25 MPa [2.5 bar]).

NOTE − In such cases, it is possible to design the cylinder as for ordinary (non-embrittling) gases.

The standard was prepared by the P3652 Hydrogen Standards Committee and is identical to and has been reproduced from ISO 11114-4:2017 *Transportable gas cylinders – Compatibility of cylinder and valve materials with gas contents – Part 4: Test methods for selecting steels resistant to hydrogen embrittlement*.

As this standard is reproduced from an international standard, the following applies:
(c) In the source text, 'this International Standard' should read 'this New Zealand standard';
 (d) A full point substitutes for a comma when referring to a decimal marker.

The terms 'normative' and 'informative' have been used in this standard to define the application of the appendix or annex to which they apply. A 'normative' appendix or annex is an integral part of a standard whereas an 'informative' appendix or annex is for information and guidance.

INTERNATIONAL STANDARD

ISO
11114-4

Second edition
2017-04

Transportable gas cylinders — Compatibility of cylinder and valve materials with gas contents —

Part 4:
Test methods for selecting steels resistant to hydrogen embrittlement

Bouteilles à gaz transportables — Compatibilité des matériaux et des robinets avec les contenus gazeux —

Partie 4: Méthodes d'essai pour le choix des aciers résistants à la fragilisation par l'hydrogène

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

The committee responsible for this document is ISO/TC 58, *Gas cylinders*.

This second edition cancels and replaces the first edition (ISO 11114-4:2005), which has been technically revised with the following changes:

— improvement of the procedure corresponding to Method C and adjustment of acceptance criteria;

— light modifications on procedures corresponding to Method A and Method B.

A list of parts in the ISO 11114 series can be found on the ISO website.

Introduction

It is widely recognized that compressed hydrogen and some hydrogen bearing gases can have an embrittling effect on steels. This embrittling effect has resulted in the failure of hydrogen gas cylinders (including some bursts) that has led gas cylinder users and manufacturers to adopt specific measures.

The adoption of these measures has eliminated all known failures of hydrogen cylinders from this embrittlement phenomenon as far has been reported.

The basic recommendation is to limit the tensile strength of the steels (see ISO 11114-1) and eliminate manufacturing defects.

This tensile strength limit of 950 MPa was developed for quenched and tempered gas cylinders of 34 Cr Mo 4 type steels using steelmaking practices, chemistry and manufacturing techniques typical of those used during the early 1980's and successfully used for filling pressures up to 300 bar. This practice has been in widescale use up to the current time. Other higher pressures, although at lower tensile strength limits, have also been used.

In recent years, improvements in steelmaking, e.g. by reducing the sulphur and phosphorus contents, have indicated the possibility of increasing the tensile strength limit of 950 MPa for embrittling gas service. Experimental work has shown that the relevant parameters affecting hydrogen embrittlement are the following:

a) microstructure resulting from the combination of the chemistry and the heat treatment;

b) mechanical properties of the material;

c) applied stress;

d) internal surface imperfections resulting in local stress concentrations;

e) characteristics of the gas contained (composition, quality, pressure, etc.).

When developing this document, only the material aspects, a) and b) and the characteristics of the gas e) above, were considered. Other essential features, c) and d), are covered by the relevant parts of ISO 9809.

Some low alloy steels other than 34 Cr Mo 4 may require tensile strength to be lower than 950 MPa, or may be permitted to be higher than 950 MPa, to be suitable for the manufacture of gas cylinders for embrittling gas service.

This document specifies test methods to identify steels which, when combined with the cylinder manufacturing requirements specified in ISO 9809 (all parts), will result in cylinders suitable for use in embrittling gas service.

These tests have been developed following an extensive world-wide programme which incorporated laboratory and full scale tests. See also AFNOR FD E29-753.

Transportable gas cylinders — Compatibility of cylinder and valve materials with gas contents —

Part 4:
Test methods for selecting steels resistant to hydrogen embrittlement

1 Scope

This document specifies test methods and the evaluation of results from these tests in order to qualify steels suitable for use in the manufacture of gas cylinders (up to 3 000 l) for hydrogen and hydrogen bearing embrittling gases.

This document only applies to seamless steel gas cylinders.

The requirements of this document are not applicable if at least one of the following conditions for the intended gas service is fulfilled:

— the working pressure of the filled embrittling gas is less than 20 % of the test pressure of the cylinder;

— the partial pressure of the filled embrittling gas of a gas mixture is less than 5 MPa (50 bar) in the case of hydrogen and other embrittling gases, with the exception of hydrogen sulphide and methyl mercaptan; in such cases, the partial pressure shall not exceed 0,25 MPa (2,5 bar).

NOTE   In such cases, it is possible to design the cylinder as for ordinary (non-embrittling) gases.

2   Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 7539-1, *Corrosion of metals and alloys — Stress corrosion testing — Part 1: General guidance on testing procedures*

ISO 7539-6:2011, *Corrosion of metals and alloys — Stress corrosion testing — Part 6: Preparation and use of precracked specimens for tests under constant load or constant displacement*

ISO 9809-1, *Gas cylinders — Refillable seamless steel gas cylinders — Design, construction and testing — Part 1: Quenched and tempered steel cylinders with tensile strength less than 1 100 MPa*

ISO 9809-2, *Gas cylinders — Refillable seamless steel gas cylinders — Design, construction and testing — Part 2: Quenched and tempered steel cylinders with tensile strength greater than or equal to 1 100 MPa*

ISO 11114-1:2012, *Gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 1: Metallic materials*

ISO 11120, *Gas cylinders — Refillable seamless steel tubes of water capacity between 150 l and 3000 l — Design, construction and testing*

3   Terms, definitions, symbols and abbreviated terms

3.1   Terms and definitions

For the purposes of this document, the following terms and definitions apply. Some of the definitions used are based upon those in ISO 7539-1 and ISO 7539-6.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/

- ISO Online browsing platform: available at http://www.iso.org/obp

3.1.1
embrittling gases
gases which can cause cracking of metal due to the combined action of stress and hydrogen atoms

Note 1 to entry: Embrittling gases are listed as groups 2 and 11 in ISO 11114-1:2012, A.4.

3.1.2
hydrogen rupture pressure
P_{H2}
maximum pressure recorded during the hydrogen rupture pressure test

3.1.3
helium rupture pressure
P_{He}
maximum pressure recorded during the helium rupture pressure test

3.1.4
hydrogen embrittlement index
maximum value of the ratio P_{He}/P_{H2} as a function of the pressure rise rate

3.1.5
environmentally-assisted cracking
synergistic effect on a metal caused by the simultaneous action of a particular environment and a nominally static tensile stress, which results in the formation of cracking

3.1.6
threshold stress
stress above which a crack will initiate and grow, for the specified test conditions

3.1.7
plane strain stress intensity factor
K_1

function of applied load, crack length and specimen geometry having dimensions of stress $\times \sqrt{\text{length}}$ which uniquely define the elastic-stress field intensification at the tip of a crack subjected to opening mode displacements (mode I)

Note 1 to entry: K_1 uniquely defines the elastic stress field intensification at the tip of a crack subjected to opening mode displacements.

3.1.8
threshold stress intensity factor for susceptibility to environmentally-assisted cracking
K_{1H}
stress intensity factor above which an environmentally-assisted crack will initiate and grow, for the specified test conditions under conditions of high constraint to plastic deformation, i.e. under essentially plane strain conditions

3.2 Symbols and abbreviated terms

a effective crack length measured from the crack tip to the loading plane

a_0 average value of a

B specimen thickness

e_m mean disc thickness

E modulus of elasticity

K_{IAPP} applied elastic stress-intensity factor

K_{1H} threshold stress intensity factor

m elastic displacement per unit load

P applied load

P_r actual rupture pressure

P_r' corrected rupture pressure

$P_r'_{H2}$ corrected hydrogen rupture pressure

$P_r'_{He}$ theoretical helium rupture pressure corresponding to the same pressure rise rate as for the hydrogen test, calculated by regression from the corrected helium rupture pressure

R_m actual value of tensile strength

V crack-mouth opening displacement (CMOD) defined as the mode 1 (also called opening-mode) component of crack displacement due to elastic and plastic deformation, measured at the location on a crack surface that has the greatest elastic displacement per unit load, m

W effective width of a compact specimen, measured from the back face to the loading plane

Y stress intensity factor coefficient derived from the stress analysis for a particular specimen geometry, which relates the stress intensity factor for a given crack length to the load and specimen dimensions

HAC   hydrogen assisted cracking

4 General requirements

The test methods as described in Clause 5 are valid for all designed working pressures. The test shall be performed at room temperature at not less than the designed working pressure. All tests shall be conducted to evaluate the hydrogen embrittlement taking into account conditions that will be found in the intended application. The composition of the tested gas shall have a concentration of embrittling gas not less than the maximum concentration in the intended application. The tests shall be performed for selecting steels for hydrogen/embrittling gases and mixtures cylinders. Chromium-molybdenum steels, quenched and tempered with a guaranteed maximum actual ultimate tensile strength of 950 MPa, do not need to be tested and can safely be used for the construction of hydrogen/embrittling gases cylinders; however, H_2S mixtures at more than 100 bar working pressure need to be tested. For carbon-manganese steels, different limits on ultimate tensile strength apply (as described in ISO 9809-1).

The tests described in Clause 5 are "qualification tests" for a given steel composition and heat treatment. This means that the tests need not be repeated for each type, as defined in ISO 9809 (all parts), of cylinder once a steel has been qualified for a specific design strength level.

The test samples shall be taken from a representative cylinder or from a piece of tube (for long cylinders, according to ISO 11120), representative of the relevant manufacturing process including heat treatment.

The test samples shall have a mechanical strength not lower than the maximum intended tensile strength to be used for the cylinders to be manufactured. If it is intended later to increase the maximum strength of the steel, a new qualification test shall be performed.

With respect to the possible variation of the chemical composition, the chemistry of the steel tested shall be recorded in the qualification test report and the difference in chemistry for the steels actually used for the cylinders shall not exceed the "permissible difference" according to ISO 9809-2. In addition, for sulphur and phosphorus, these permissible differences are limited to 0,005 % and 0,010 %, respectively. In no case shall the phosphorus content of either the qualification or the production cylinders exceed 0,015 %.

With respect to the heat treatment, the manufacturer shall specify the relevant temperatures and times, and the quenching conditions (if relevant). Any modification to the heat treatment needing a new type approval according to ISO 9809-2 requires a new qualification test.

For the qualification of a given steel for the manufacturing of gas cylinders, method A, B, or C can be used (see 5.1, 5.2 and 5.3, respectively). Additionally, tensile tests shall be carried out (see 5.4).

5   Test methods

5.1   Disc test (method A)

5.1.1   Principle of test

A mounted test piece in the shape of a disc is subjected to an increasing gas pressure at constant rate to burst or to crack. The embrittling effect of hydrogen (or other embrittling gas) is evidenced by comparing the hydrogen rupture pressures, P_{H2}, with the helium rupture pressures, P_{He}, helium being chosen as a reference gas.

The ratio P_{He}/P_{H2} shall be determined.

The lower the ratio, the less susceptible the steel will be to embrittlement. This ratio is dependent on the pressure rise rate, which shall remain constant during the whole test.

NOTE   Hydrogen/embrittling gases rupture pressures also depend on the hydrogen purity. Oxygen or traces of water vapour can partially inhibit the hydrogen embrittlement effect.

5.1.2   Test conditions and procedure

5.1.2.1   Sample disc

The sample disc shall be flat and ground (or machined to an equivalent surface finish), and shall have the following characteristics.

Dimensions:

— diameter: $58\,^{0}_{-0,05}$ mm;

— thickness: 0,75 mm ± 0,01 mm;

— flatness: less than 1/10 mm deflection.

NOTE 1   The hydrogen rupture pressures are in the range of 300 bar. If it is intended to evaluate the steel for higher working pressure, thickness higher than 0,75 mm can be used.

NOTE 2   For gases intended to be used at maximum working pressure less than 100 bar, the test results could be conservative. In such case, the test could be repeated with disk at thickness such that the failure pressure is no more than service pressure.

Surface condition (both sides):

— roughness: Ra value (see ISO 4287) less than 0,001 mm; the roughness of the samples used for both H_2 and He tests shall be equivalent;

— no visible oxides.

The following operations shall be performed to verify the sample quality.

— Immediately after the final preparation and prior to the testing, store the samples in a dry atmosphere, i.e. a desiccator.

— Degrease the sample and check thickness at 4 points taken 90° apart to define a mean thickness.

— Determine the disc's hardness (e.g. Vickers) over its outer circumference (outside the O-ring zone) to verify that machining has not altered the original material properties.

5.1.2.2   Cell and other apparatus

The cell (see Figure 2) is composed of two stainless steel flanges embedding the disc. A volume of approximately 5 cm^3 is provided below the disc. Above the disc, a high-strength steel ring is mounted ($R_m \geq 1\,100$ MPa). The internal diameter is 25,5 mm and the ring curvature radius where it meets the disc is $0,5^{0,25}_{-0,05}$ mm.

Gas discharges can occur after disc bursting either through the lower flange or upper flange discharge port to the atmosphere. This permits the evacuation of the installation and a check of the hydrogen purity and freedom from either oxygen ($O_2 < 1$ µl/l) or water vapour ($H_2O < 3$ µl/l). It also permits regulation of the gas flow and adjustment of the pressure rise rate.

NOTE   1 µl/l= 1 ppm. The use of ppm is deprecated.

The sealing device shall be an elastomer O-ring for helium testing, and for hydrogen testing at rates of more than 10 bar/min. For hydrogen testing at rates not exceeding 10 bar/min, indium O-rings shall be used (to eliminate oxygen retrodiffusion).

For the flange assembly, ten high-strength steel bolts should be used, size M10 or equivalent. The tightening torque shall be 30 Nm for elastomer O-rings and 100 Nm for indium O-rings.

Hydrogen and helium shall be stored in high-pressure containers connected to the test cells. A flow control valve between the high-pressure container and the cell shall be used to adjust the pressure rise rate.

5.1.2.3   Test procedure

For a satisfactory outcome of the test performances, operations in the following sequences shall be carried out.

— Evacuation of the cell by pumping to eliminate any traces of air or moisture absorbed by the walls. Purging with the gas to be used, followed by vacuum pumping, can also be used to improve the cleaning efficiency.

— Check the purity of the gas flowing out of the cell before testing to ensure absence of trace of air or moisture absorbed by the walls and the gas specification has been met.

— Adjustment of the gas flow to achieve the appropriate pressure rise rate (if necessary).

— Isolation of the cell (at the start of pressure rise).
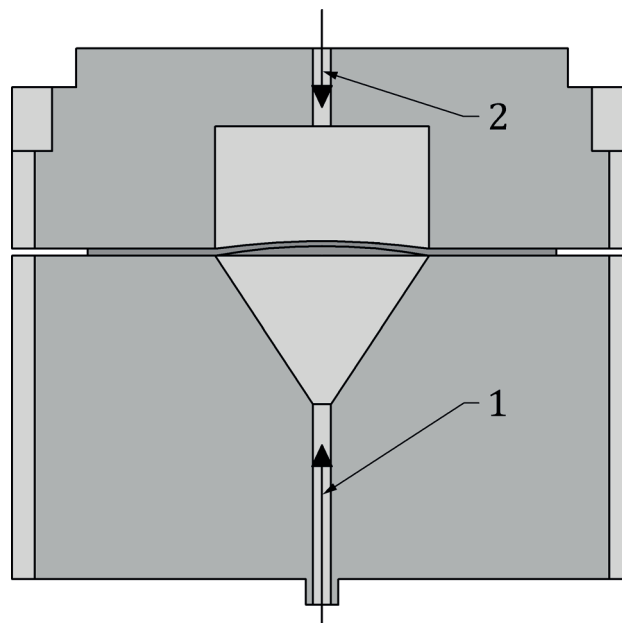
Key

1   disc is subjected to P_{H2} on the lower side

2   disc is subjected to P_{N2} on the upper side

NOTE   The disc is loaded with $\Delta P = P_{H2} - P_{N2}$.

Figure 1 — Compensating pressure disc test principle

The rate of pressure rise shall be regular and kept as constant as possible, neglecting the gas compressibility factor with pressure.

To evaluate the behaviour of steels at pressure higher than 300 bar, either a thicker disc shall be used (see 5.1.2.1) or a compensating pressure of inert gas (see Figure 1) shall be introduced progressively in the upper part of the disc cell at the same rate and pressure as hydrogen (e.g. up to 400 bar). Then, the hydrogen pressure is further increased as indicated in 5.1.1 at a constant rate to burst or to crack (e.g. at 700 bar) to evaluate the behaviour of the steel at about 700 bar).

The rupture pressures shall be noted from the recorded readings at the end of the test. The pressure gauge shall be accurate to ±2 % for the intended measured rupture pressure.

The tests shall be carried out with hydrogen (for quality, see 5.2.2.3) and with helium (H_2O < 3 µl/l) for a range of pressure rise rates evenly distributed between 0,1 bar/min and 1 000 bar/min. Once a range of pressure rise rates showing maximum hydrogen sensitivity has been established, three additional tests shall be conducted within this area, in order to establish the minimum value for the rupture pressure (see Figure 3). Six helium tests and nine hydrogen tests (i.e. 15 tests in total) are enough for a thorough material evaluation.

5.1.3   Treatment and interpretation of test results

5.1.3.1   Disc thickness

Rupture pressure P_r shall be systematically corrected for deviation from the "ideal" value corresponding to the test of a standard thickness disc.

The corrected rupture pressure, P_r', shall be given by Formula (1):

$$P_r' = \frac{P_r \times 0,75}{e_m} \tag{1}$$

where

e_m is the mean disc thickness.

5.1.3.2 Presentation and interpretation of test results

Rupture pressures, corrected as indicated in 5.1.3.1, shall be plotted against the pressure rise rate (actual rupture pressure divided by the test duration) expressed in bar/min (see Figure 3).

For each hydrogen test, calculate the ratio given in Formula (2):

$$P_r'_{He} \big/ P_r'_{H2} \tag{2}$$

where

$P_r'_{He}$ is the theoretical helium rupture pressure corresponding to the same pressure rise rate as for the hydrogen test, calculated by regression from the corrected helium rupture pressure;

$P_r'_{H2}$ is the corrected hydrogen rupture pressure.

Ratios of $P_r'_{He}/P_r'_{H2}$ shall be plotted against the pressure rise rate (see Figure 4).

The embrittlement index of a material is the maximum value of the above-mentioned ratio. The material shall be considered as suitable for compressed hydrogen/embrittling gas cylinders if the index is less than or equal to two.

5.1.4 Failure in conducting test

If it is found that a failure occurred during the conduction of a test (e.g. inappropriate surface condition, abnormal hardness, irregular pressure rise), the test shall be repeated.

5.1.5 Test report

The detailed test conditions (gas purity, rupture pressure, hardness of the specimen, ratio $P_r'_{He}/P_r'_{H2}$, embrittlement index) and the cylinder design drawing including the material properties, chemical composition and heat treatment conditions of the tested cylinder shall be reported.
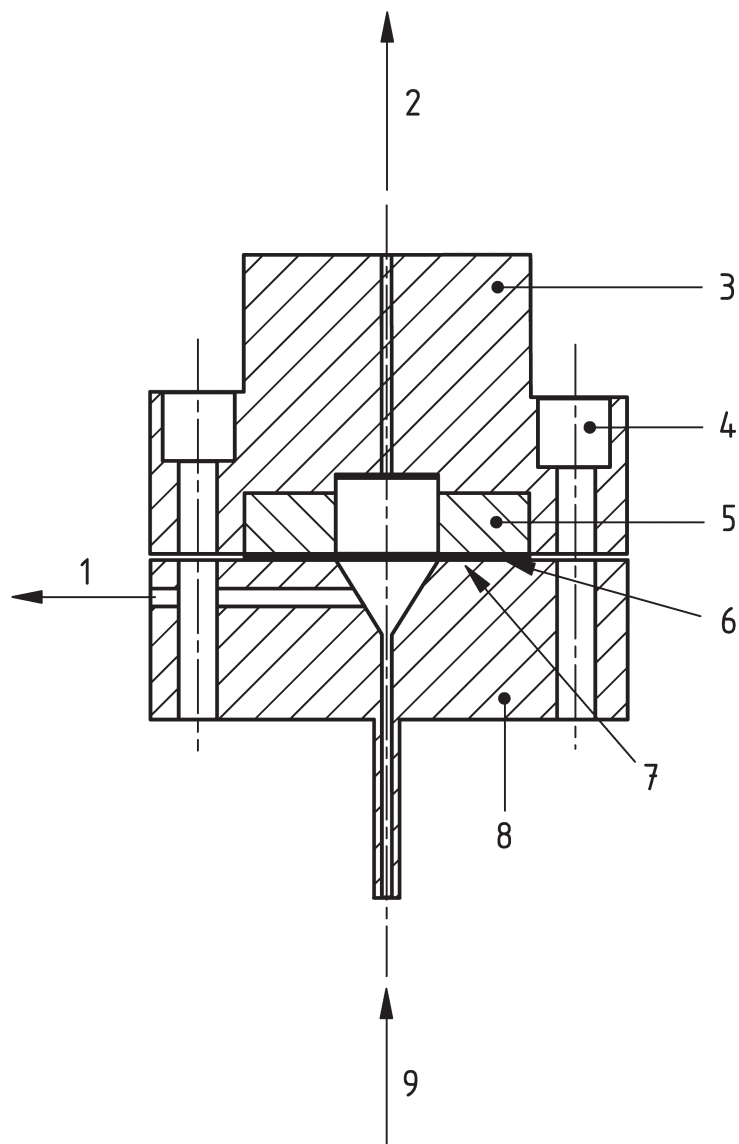
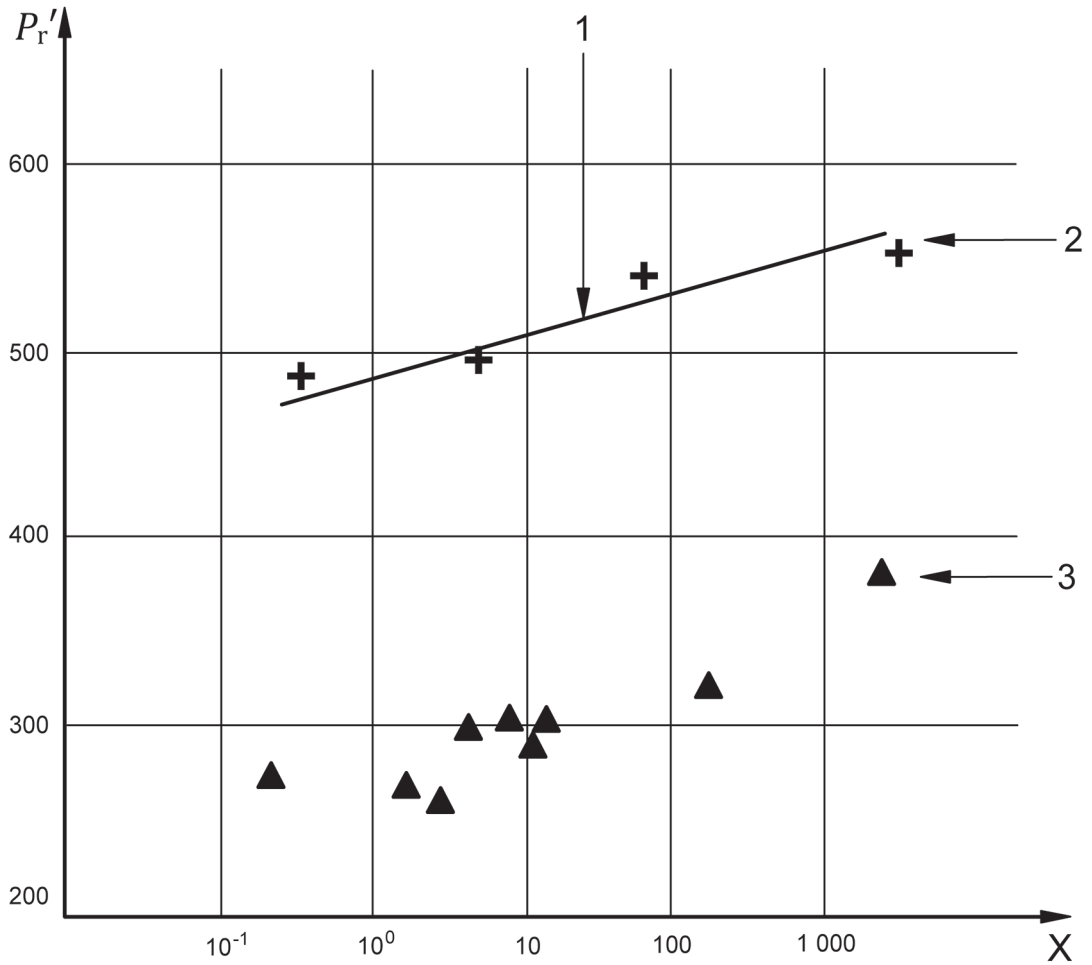**Key**

1	port for evacuation and flow adjustment	6	disc
2	discharge port	7	O-ring
3	upper flange	8	lower flange
4	bolt hole	9	gas inlet
5	high-strength steel ring		

NOTE   This figure is not to scale. See dimensions in 5.1.2.1 and 5.1.2.2.

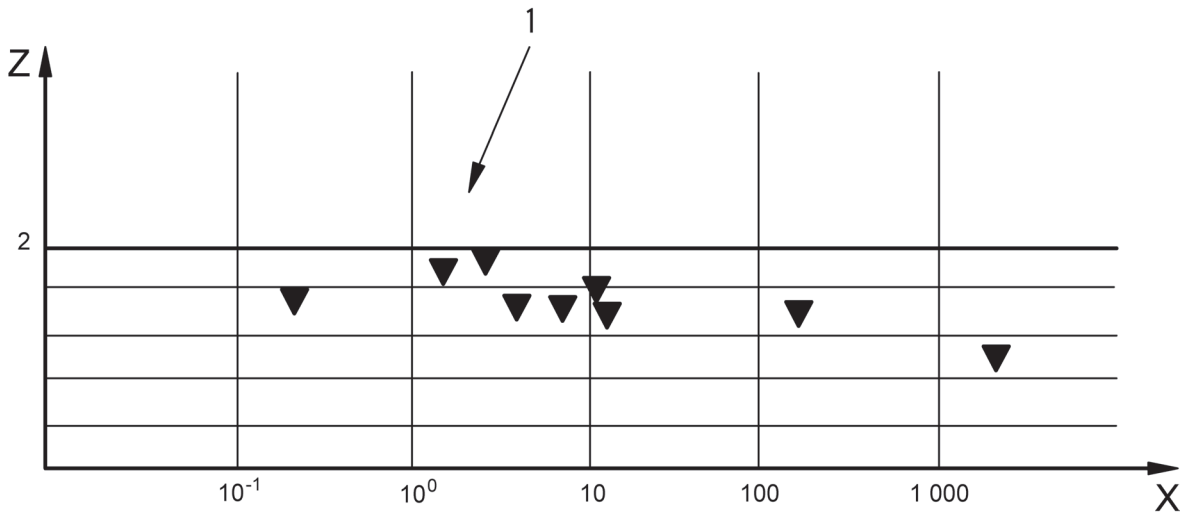**Figure 2 — Schematic test installation (test cell)**

Key

1   regression curve

2   helium corrected rupture pressures ($P_{r}'_{He}$)

3   hydrogen corrected rupture pressures ($P_{r}'_{H2}$)

X   pressure rise rate (bar/min)

P_{r}' corrected rupture pressure (bar)

Figure 3 — Examples of hydrogen and helium corrected rupture pressures as a function of the pressure rise rate

Key

1   hydrogen embrittlement index

X   pressure rise rate (bar/min)

Z $P_r'_{He}/P_r'_{H2}$

Figure 4 — Examples of the ratio $P_r'_{He}/P_r'_{H2}$ as a function of the pressure rise rate

5.2   Fracture mechanics test (method B)

5.2.1   Principle of the test method

This specifies a method for the determination of the threshold stress intensity factor (K_{1H}) for susceptibility to cracking of metallic materials in gaseous hydrogen (or other embritlling gases).

The procedure covers the use of machined compact tension test pieces, as described in ISO 7539-6, for the determination of the threshold stress intensity factor, as described in ISO 7539-1.

The test involves a specimen containing a machined notch. This notch is extended by fatigue cracking and then subjected to an incrementally increasing tensile load during exposure to a pressurised, gaseous hydrogen environment. The objective is to quantify the conditions under which environmentally-assisted crack propagation can occur.

If the specimens pass the test requirements, then the material is characterized as suitable for gas cylinders filled with compressed hydrogen.

NOTE   The test can be carried out with any other embrittling gas or gas mixture (e.g. H_2S, hydrides). The acceptance criteria of the considered gas will then be defined similarly.

5.2.2   Test procedure

5.2.2.1   Specimen type

The test involves the use of a compact tension (CT) type specimen, according to the geometry given in Figure 5 (ISO 7539-6:2011, Figure 3), with a *W* dimension of 26 mm and *B* equal to the greatest thickness allowed by the cylinder wall curvature and thickness, but not less than 85 % of the design thickness of the cylinder being qualified. The specimen orientation (Y-X) relative to the cylinder axis is shown in Figure 6.

At least three specimens taken 120° apart from the cylindrical wall shall be tested. Flattening of specimen blanks is not allowed. If the test specimen thickness cannot meet the validity requirements of ISO 7539-6, then the thickest possible specimen as specified above shall be tested.

Dimensions in millimetres
Surface roughness values in micrometres
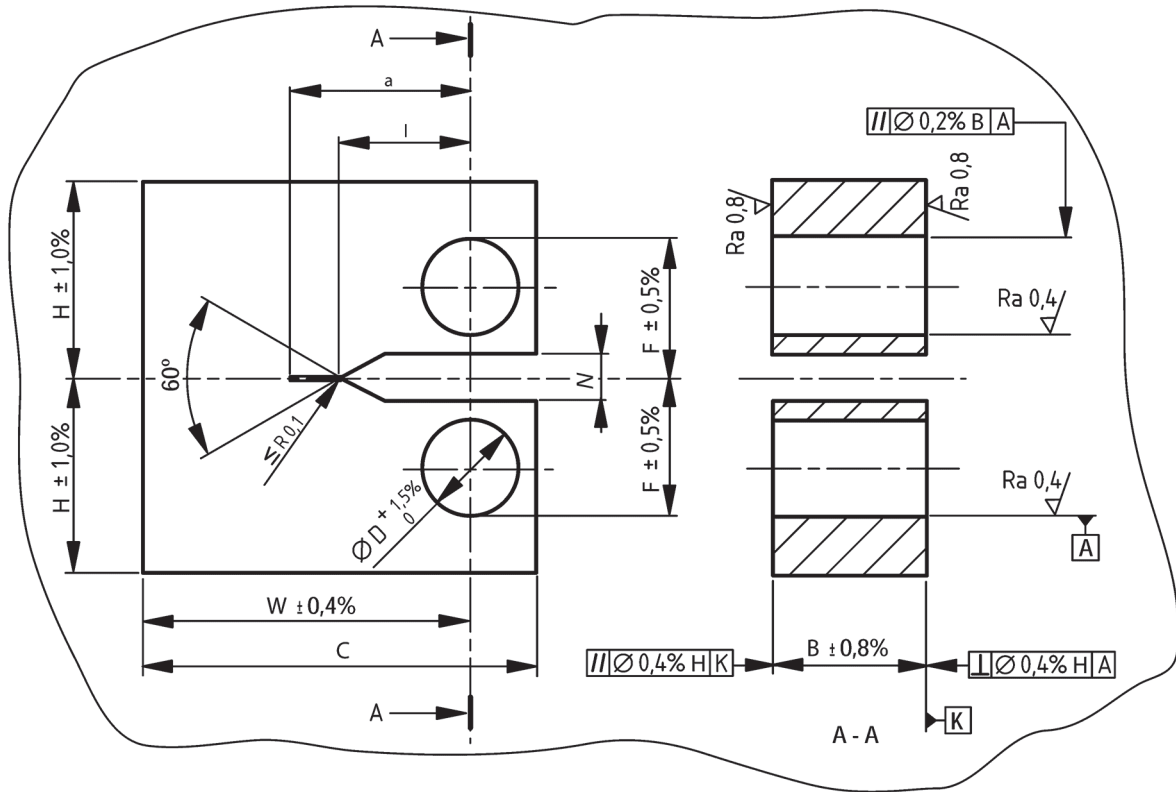
Key

W   net width

C   total width, 1,25 W minimum

B   thickness, 0,5 W

H   half height, 0,6 W

D   hole diameter, 0,25 W

F   half distance between hole outer edges, 1,6 D

N   notch width, 0,065 W maximum

l   effective notch length, 0,25 W to 0,40 W

a   effective crack length, 0,45 W to 0,55 W

Figure 5 — Proportional dimensions and tolerances for compact tension test pieces
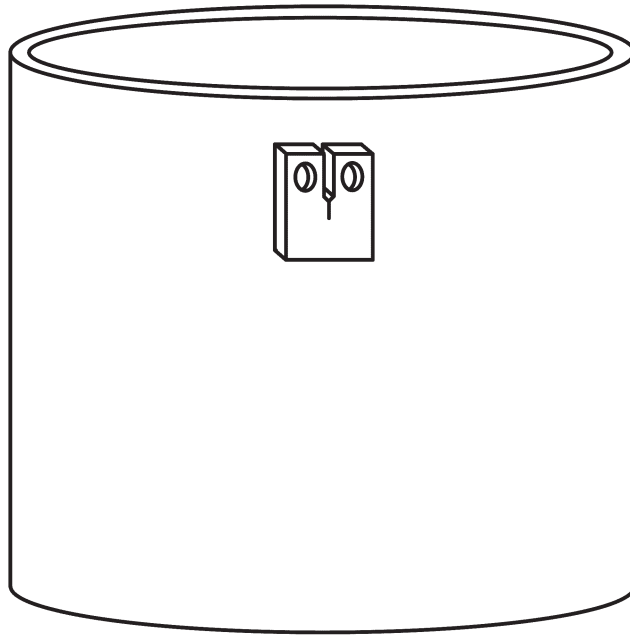
Figure 6 — Test piece: type and orientation

5.2.2.2 Specimen preparation

Prior to fatigue pre-cracking, all necessary electrical contacts and wires required for crack monitoring shall be attached to the specimen. The specimen shall be thoroughly degreased, with particular attention paid to the notch tip region.

During all subsequent operations, especially the fatigue pre-crack, the specimen shall not be contaminated in order to ensure a clean crack front.

Fatigue pre-cracking shall be conducted to meet the general requirements detailed in ISO 7539-6:2011, Clause 6 for the initiation and propagation of fatigue cracks. The final maximum pre-cracking load shall give a final maximum stress intensity lower than the initial stress intensity required for the test.

On completion of fatigue pre-cracking, the specimen shall be measured as detailed in ISO 7539-6:2011, Clause 7 to determine the thickness, B, width, W, and average length of the fatigue pre-crack on the specimen surfaces. The last of these values shall be used in assessing the load necessary to produce the required initial stress intensity.

To prevent oxidation of the crack tip, the specimen shall now be put on test. If, for any reason, this is not possible, the specimen shall be stored in a clean, desiccated environment until ready for testing.

5.2.2.3 Gas purity and pressure

The gas pressure in the test chamber shall be not less than the working pressure at which the cylinder needs to be evaluated. In the case of hydrogen, a purity of at least 99,999 5 %, and $O_2 \leq 1$ µl/l and $H_2O \leq 3$ µl/l. For other gases, the purity shall be equivalent to that of the gas being used. This gas shall be covered by a batch certificate of conformity. As an alternative, gas with a 99,999 9 % purity ($O_2 \leq 0,1$ µl/l and $H_2O \leq 0,5$ µl/l) and covered by an individual certificate of conformity may be used.

5.2.2.4 Test apparatus

The tests shall be conducted in a stainless steel chamber such as shown together with the loading bars and specimen in Figure 7, and installed on a servo-hydraulic test machine (Figure 8).
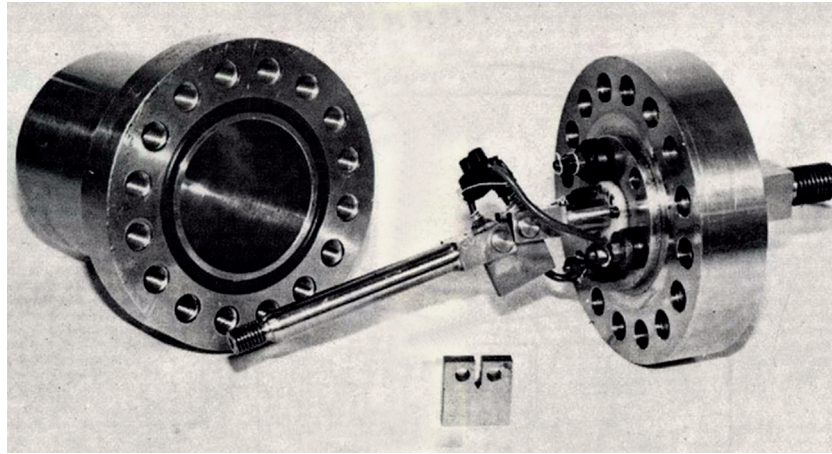
Figure 7 — Stainless steel chamber, showing loading bars and specimen
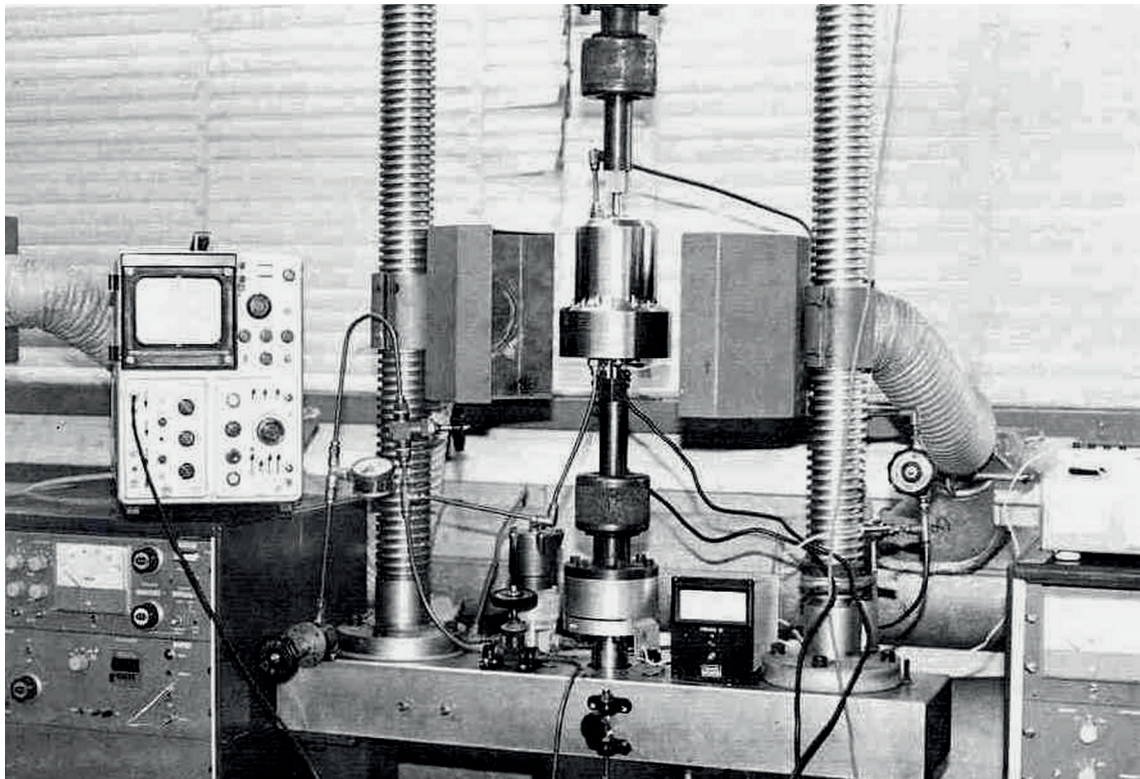
Figure 8 — Servo-hydraulic test machine

After installation of the specimen, it is recommended that the test chamber be evacuated to a pressure of <130 Pa prior to the introduction of gaseous hydrogen. The purity of the gaseous environment in the test chamber shall be as specified in 5.2.2.3.

Crack initiation and any subsequent growth shall be detected and monitored using a direct current potential drop (DCPD) method.

5.2.2.5   Test method

If there is no prior knowledge of the material's threshold stress intensity factor, then the test shall be started using a load which produces a stress intensity factor of 1 MPa·m^{0,5} at the crack tip (for

calculation of the load, see ISO 7539-6). Otherwise, the test may be started at a stress intensity factor equivalent to, but not exceeding, 50 % of the stress intensity factor derived from previous work.

The applied load shall be recorded continuously. The specimen shall be held at the initial load for a period of at least 20 min to allow for crack growth at room temperature. If no crack growth is detected by the end of the hold period, as evidenced by a plateau in the potential drop curve, the load shall be increased at a controlled rate in a step equivalent to a crack tip stress intensity factor increase of 1 MPa·m^{0,5}, and held for a further 20 min. This procedure shall be continued until failure occurs, with the appropriate load being recorded on the test data sheet.

The load shall be increased at the end of a hold period, by means of a servo-controller, at a constant rate of 2×10^{-3} kN·s^{-1}, until attainment of the crack tip stress intensity required for the subsequent hold period. This would result in a controlled crack tip stress intensity factor increase totalling 1 MPa·m^{0,5} over a time interval of approximately 1 min, assuming a test piece of thickness 7 mm and with an a/W of 0,5.

5.2.2.6 Specimen measurement

After the test, the specimen shall be inspected in accordance with ISO 7539-6, with the appropriate measurements to ±0,01 mm being made using a travelling microscope.

5.2.3 Test results

5.2.3.1 Analysis and acceptance criteria

Calculation of the test result shall be as stated in ISO 7539-6, through a relationship of the form as given by Formula (3):

$$K_{1H} = YP/BW^{0,5} \qquad\qquad (3)$$

The load, P, used in the calculation is that applied to the specimen before the final increment that caused failure.

Provided that the K_{1H} values of both CT specimens are greater than or equal to $(60/950) \times R_m$ (MPa·m^{0,5}), then the material is qualified for a maximum tensile strength (R_m) equal to the average of the two tensile strength values obtained in 5.4. If the constraint validity requirement of 5.2.2.1 is not met, then the material is suitable up to the design thickness of the cylinder tested.

5.2.3.2 Failure in conducting test

If it is found that a failure occurred during the conduction of a test (e.g. inappropriate surface condition, abnormal hardness, irregular pressure rise), the test shall be repeated.

5.2.3.3 Test report

The detailed test conditions [gas purity and pressure, record of the direct current potential drop (DCPD) measurements, location and dimension of the specimen, K_{1H} and R_m (see 5.4) and the cylinder design drawing], including the material properties and chemical composition and the heat treatment conditions of the tested cylinder, shall be reported.

5.3 Test method to determine the resistance to hydrogen assisted cracking of steel cylinders (method C)

5.3.1 General

A fatigue precracked specimen is loaded by a constant displacement method to a stress intensity K_{IAPP} in pressurized hydrogen gas or other embrittling gas at room temperature. After the test period, the specimen is examined to assess whether the initial fatigue crack did or did not grow. To determine the

extent of crack propagation, calculate the K value at arrest condition. If the test specimen exhibits less than or equal to a specified amount of crack growth at a K_{arrest} value that is less than the acceptable threshold, then the material is characterized as suitable for gas cylinders with respect to the hydrogen assisted cracking (HAC) resistance requirement.

Testing shall be conducted using applicable rules of ISO 7539-6 and additional rules specified in this document. Rules provided in ISO 7539-6 on corrosive environment need not be satisfied. Some symbols used in this method are to be found in ISO 7539-6:2011, Clause 3.

NOTE   The test can be carried out with any other embrittling gas or gas mixture (e.g. H_2S, hydrides). The acceptance criteria of the considered gas will then be defined similarly.

5.3.2   Specimen configurations and numbers of tests

5.3.2.1   Fracture specimens

5.3.2.1.1   The compact tension (CT) specimen geometry given in Figure 5 (ISO 7539-6:2011, Figure 3) shall be used. The specimen thickness shall not be less than 85 % of the design thickness of the cylinder which is being qualified.

5.3.2.1.2   Specimen orientation shall be Y-X in ISO 7539-6:2011, Figure 15, for rectangular section.

5.3.2.1.3   At least three specimens taken 120° apart from the cylindrical wall shall be tested. Flattening of specimen blanks is not allowed.

5.3.2.1.4   If test specimen thickness cannot be obtained from the specified location or locations to meet the validity requirements of 5.3.4.5, then the thickest possible specimen shall be tested.

5.3.2.2   Tensile specimens

Three longitudinal tensile specimens taken adjacent to the CT specimens from the cylindrical wall area shall be used according to ISO 9809-1.

5.3.3   Fatigue precracking

All rules provided in ISO 7539-6:2011, Clause 6 shall be met.

5.3.4   Specimen testing procedure

5.3.4.1   All rules in ISO 7539-6:2011, Clause 7 shall be satisfied, except for those in ISO 7539-6:2011, 7.2.2, 7.2.6, 7.5.1, 7.5.2, 7.5.4, and 7.5.5.

5.3.4.2   Load the fatigue-precracked specimens to a stress-intensity K_{IAPP} determined from Formula (4):

$$K_{IAPP} = 1,5 \left(60\right) \times \left(R_m / 950\right) \tag{4}$$

Specimens may be loaded by a suitable constant displacement method.

5.3.4.3 Constant displacement loading

For testing of CT specimens at a constant displacement loading, use Formula (5):

$$V = \frac{(K_{IAPP})\sqrt{w}}{E\left[f(x)\right]\left(\sqrt{B/B_N}\right)} \tag{5}$$

where

$f(x) = (1 - x)^{0,5}\,(0,748 - 2,176\,x + 3,56\,x^2 - 2,55\,x^3 + 0,62\,x^4)$

$$x = \frac{a}{w}$$

5.3.4.4 For specimens loaded by constant displacement method, the loading shall be determined by the following method.

a) At the end of the test, record the crack mouth opening displacement (CMOD) before unloading.

b) Unload the specimen.

c) Reload the specimen up to the measured CMOD in a device suitable for load measurement. Record the load and use this load in the K_{IAPP} calculations. This calculated K_{IAPP} shall be equal to or greater than the calculated K_{IAPP} value from 5.3.4.2.

5.3.4.5 All specimens shall meet the validity requirements specified in ISO 7539-6:2011, 7.6.6 e), except as exempted in 5.3.4.1 above.

5.3.5 Test procedure

5.3.5.1 Place the test specimens in a high-pressure test chamber.

NOTE   Extended periods of time after loading and before exposure to hydrogen gas can affect the final results.

For a satisfactory outcome of the test performances, the following operations shall be carried out.

— Evacuation of the cell by pumping to eliminate any traces of air or moisture absorbed by the walls. Purging with the gas to be used, followed by vacuum pumping, can also be used to improve the cleaning efficiency.

— Check the purity of the gas flowing out of the cell before testing to ensure absence of trace of air or moisture absorbed by the walls and the gas specification has been met.

— The O_2 content in the hydrogen gas shall not exceed 1 µl/l and H_2O content shall not exceed 3 µl/l. Pressurize the test chamber with hydrogen gas to the pressure at which the steel needs to be evaluated.

5.3.5.2 The specimens shall be tested for at least 1 000 h at room temperature.

5.3.6 Crack growth examination

5.3.6.1 After the specified test period, unload the specimen and mark the HAC advance using one of the following methods.

a) Heat tinting the specimen at about 300 °C for 30 min.

b) Fatigue cycling at maximum stress-intensity factor not exceeding 0,6 K_{IAPP}. Advance the crack by at least 1 mm.

followed by:

c) Fracturing the specimen at very low temperature such as that of liquid nitrogen.

5.3.6.2   Measure the crack growth, using a scanning electron microscope. Measurements shall be taken at locations perpendicular to the pre-crack at 25 %, 50 % and 75 % of *B*. Calculate the average of these three values.

5.3.6.3   If the average measured crack growth does not exceed 0,25 mm**,** the specimen passes the tests. If the measured values exceed 0,25 mm, calculate the new K_{I}. If this new K_{I} is greater or equal to (60) × (Rm/950), the specimen will also pass the test.

5.3.7   Cylinder material qualification

5.3.7.1   If all specimens pass, the material is qualified for maximum tensile strength equal to the average of the three tensile strength values obtained in 5.3.2.2.

5.3.7.2   If the constraint validity requirement of 5.3.4.5 is not met, then the material is suitable up to the design thickness of the cylinder wall.

5.3.8   Failure in conducting test

If it is found that a failure occurred during the conduction of a test (e.g. inappropriate surface condition, abnormal hardness, irregular pressure rise), the test shall be repeated.

5.3.9   Test report

The information described in ISO 7539-6:2011, Clause 8, with the exception of 8 e), shall be reported. The report shall indicate if the validity criteria are met or not and shall include scanning electron microscope micrographs. The report should be kept on file permanently as a record that the cylinder material has been tested and found acceptable.

5.4   Tensile tests

Two longitudinal tensile specimens taken adjacent to the CT specimens (if applicable) from the cylindrical wall area shall be tested in accordance with test procedures of the ISO 9809 series.

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[1]   ISO 4287, *Geometrical Product Specifications (GPS) — Surface texture: Profile method — Terms, definitions and surface texture parameters*

[2]   ISO 9809-3, *Gas cylinders — Refillable seamless steel gas cylinders — Design, construction and testing — Part 3: Normalized steel cylinders*

[3]   ISO 9809-4, *Gas cylinders — Refillable seamless steel gas cylinders — Design, construction and testing — Part 4: Stainless steel cylinders with an Rm value of less than 1 100 MPa*

[4]   AFNOR FD E29-753, *Gas cylinders — Hydrogen compatibility testing for metals*

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