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

Reference number
ISO 11114-4:2017(E)

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

Page

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 × $\sqrt{\text{length}}$ 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 $0{,}5^{0{,}25}_{-0{,}05}\,\text{mm}$.

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 retrodifusion).

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).

