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Corrosion of metals and alloys — Determination of the critical pitting temperature under potientiostatic control

Corrosion des métaux et alliages — Determination de la température critique de piqûration des aciers inoxydables sous contrôle potentiostatique

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Foreword

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ISO 17864 was prepared by Technical Committee ISO/TC 156, *Corrosion of metals and alloys*.

Introduction

Stainless steel is susceptible to pitting corrosion, crevice corrosion, and stress-corrosion cracking, etc., although it is used as generally a corrosion-resistant material. Pitting phenomenon is generally of a random nature, therefore its measurement requires at least a couple of values. Critical pitting temperature defines the lowest potential-independent temperature, below which pitting does not occur.

The basic methodology was first standardized in ASTM G150, *Standard test method for electrochemical critical pitting temperature testing of stainless steels.*

Corrosion of metals and alloys — Determination of the critical pitting temperature under potientiostatic control

1 Scope

This International Standard describes the procedure for determining the critical pitting temperature for stainless steels (austenitic, ferritic/austenitic, ferritic stainless steel) under potentiostatic control.

The principal advantage of the test is the rapidity with which the critical pitting temperature can be measured in a single test.

The critical pitting temperature, as determined in this International Standard, can be used as a relative index of performance, for example, to compare the relative performance of different grades of stainless steel. The test described in this International Standard is not intended to determine the temperature at which pitting will occur in service.

2 Normative references

The following referenced documents are indispensable for the application 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 8044:1999, *Corrosion of metals and alloys — Basic terms and definitions*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
critical pitting temperature
CPT
lowest temperature on the surface of the specimen at which stable propagating pitting occurs under specified test conditions

3.2
temperature ramp rate
rate at which the temperature of the surface of the specimen is increased during the test

NOTE The temperature ramp rate is expressed in degrees Celsius per second (°C s^{-1}).

4 Principle

4.1 The test involves increasing the temperature of the surface of the specimen at a specified rate, whilst exposing the specimen to a specified environment and maintaining the potential of the specimen at a specified value. The temperature of the surface of the specimen is increased by heating the solution.

4.2 The critical pitting temperature is defined as the temperature of the specimen at which the current density exceeds a specified value for 60 s. A 60 s delay is used in order to ensure that the observed current increase originates from stable propagating pitting, and not short-lived current peaks originating from metastable pitting.

4.3 The specimen holder is designed to ensure that crevice corrosion does not occur at the seal between the specimen and the holder.

4.4 There may be a temperature gradient between the bulk of the solution and the surface of the specimen, the magnitude of which will depend on the geometry and dimensions of the specimen. Guidelines for calibrating the temperature of the surface of the specimen relative to the temperature of the solution are given in Clause 7.

4.5 The temperature ramp rate, environment and applied potential may be varied, depending on the material. Guidelines for selecting the test parameters for austenitic and duplex stainless steels are given in Annex A.

4.6 The critical pitting temperature is specific to the method of testing and should only be used as a comparative measure of performance.

5 Apparatus

5.1 Potentiostat

The potentiostat shall be capable of controlling the electrode potential to within ± 1 mV of a preset value.

5.2 Electrode potential-measuring instrument

The instrument should have a high input impedance of the order of $10^{11}\ \Omega$ to $10^{14}\ \Omega$, to minimize current drawn from the system during measurement. The sensitivity and accuracy of the instrument should be sufficient to detect a change of 1,0 mV.

5.3 Current-measuring instruments

The current in the circuit is evaluated from the potential drop measured across a known resistor. In many potentiostats, this measurement is made internally, but measurements can also be made externally by locating a resistor in the current line from the auxiliary electrode to the auxiliary connection on the potentiostat. The instrument shall be capable of measuring a current to within 2 % of the actual value.

5.4 Temperature controller

The temperature controller shall be capable of increasing the temperature of the surface of the specimen from 0 °C to 100 °C at a controlled rate. This is achieved by heating or cooling the solution. Above 10 °C, the average rate of temperature change of the specimen shall be controlled to within ± 30 % of the desired value, where the average is calculated over a temperature range of 10 °C. Guidelines for calculating the temperature of the specimen relative to the temperature of the solution are given in Clause 7.

5.5 Temperature-measurement instrumentation

The temperature-measurement instrumentation shall be capable of measuring the temperature of the test solution with an accuracy of ± 0,4 °C.

5.6 Specimen holder

5.6.1 Any part of the specimen holder coming into contact with the test solution shall be made of an inert material.

5.6.2 The specimen holder shall be designed to ensure that crevice corrosion does not occur at the contact area between the specimen holder and the specimen. A method of preventing such crevice attack, using a flushed-port cell or a flushed specimen holder, is outlined in Annex B.

5.7 Test cell

5.7.1 The test cell shall contain the test specimen, a Luggin capillary probe connected to an external reference electrode for measuring the electrode potential, an auxiliary electrode, a port for insertion of a temperature-measuring device and a facility for stirring the solution in a repeatable manner. This can be achieved using a mechanical stirring device or simply by bubbling gas through the solution at a controlled rate.

5.7.2 A double-walled cell is commonly used to enable the solution to be cooled or heated by recirculating a liquid from an external heating bath to the outer chamber of the cell.

5.7.3 The tip of the Luggin capillary probe shall be positioned so that it is at a distance from the specimen of about, but not closer than, twice the diameter of the tip.

5.7.4 Any part of the test cell or specimen holder that comes into contact with the solution shall be constructed from an inert material. Polycarbonate, glass and polytetrafluoroethylene (PTFE) are suitable materials.

5.7.5 The ratio of the volume of solution in the test cell to the specimen area shall be at least 100 ml/cm^2.

5.8 Auxiliary electrode

The auxiliary electrode is commonly prepared from high-purity platinum. Other materials may be used provided they are inert. The auxiliary electrode may be constructed in the form of sheet or rod, or in the form of a gauze supported on a glass frame. The area of the auxiliary electrode should be at least the area of the specimen.

NOTE Graphite may be used as a auxiliary electrode but care must be taken to avoid contamination; desorption of species retained in the graphite may be necessary prior to use.

5.9 Reference electrode

5.9.1 The reference electrode shall be maintained at ambient temperature external to the test cell and connected to the test cell via a Luggin capillary probe.

5.9.2 Commonly used electrodes include the silver/silver chloride electrode and the saturated calomel electrode. The potentials of these electrodes at 25 °C relative to the standard hydrogen electrode at 25 °C are given in Annex C.

6 Specimens

6.1 Any specimen geometry compatible with the specimen holder may be used.

6.2 A minimum test area of 1 cm^2 shall be used.

6.3 The surface finish shall be reproducible.

7 Calibration of specimen temperature vs. solution temperature

7.1 There may be a temperature gradient between the bulk solution and the surface of the specimen. A test shall be conducted to calibrate the temperature of the specimen relative to the temperature of the solution. The calibration shall be performed using the procedure for the CPT test, given in Clause 8, except that no control or measurement of the electrode potential of the specimen is required.

7.2 The specimen size and geometry, solution volume, stirring rate and temperature ramp rate shall be the same for the calibration test as for the CPT test.

7.3 The specimen temperature shall be measured by installing a suitable temperature-measuring device inside the specimen, as close as possible (< 1 mm) to the surface of the specimen in contact with the solution. The temperature-measuring device shall be located at the centre of the specimen.

7.4 Calibration of the specimen temperature relative to the solution temperature shall be performed by taking measurements of the solution temperature and the corresponding specimen temperature, as the temperature of the bulk solution is increased at the temperature ramp rate. Measurements shall be taken at intervals of not more than 10 °C in the temperature range of interest.

7.5 The specimen-temperature calibration formula shall be calculated, based on a linear-order regression analysis.

7.6 The accuracy of the measurement of the temperature of the specimen based on the calibration data shall be ± 1,0 °C.

8 Procedure

8.1 Preparation of reference electrodes

8.1.1 The difference in potential between the reference electrode and two other, validation, electrodes shall be measured. These electrodes shall be traceable to the standard hydrogen electrode and used and maintained solely for the purpose of validation. If the potential difference is greater than 3 mV, the test electrode shall be rejected.

8.1.2 The validation electrodes shall be stored in optimum conditions and regularly compared. If the potential difference between these varies by more than 1 mV, replacement shall be undertaken.

8.2 Preparation of specimen

8.2.1 The specimen shall be prepared to ensure a reproducible surface finish.

The time elapsed between grinding and immersion can have an influence on the subsequent pitting behaviour. The elapsed time selected will depend on the purpose of the test, but should be standardized for a particular set of tests. Little variation in surface film thickness occurs after 24 h, and hence a minimum elapsed time of 1 day is often useful.

8.2.2 The specimen shall be cleaned immediately prior to immersion in the solution by degreasing, rinsing in high-purity water (with a conductivity less than 1 µS·cm), followed by ethanol or a similar solvent, and air drying. After degreasing, care shall be taken not to contaminate the test surface of the specimen.

8.3 Preparation of solution

8.3.1 The solution shall be prepared using reagent-grade chemicals and high-purity water.

8.3.2 Guidance on the selection of the solution for austenitic and other stainless steels is given in Annex A.

8.4 Setting up the test

8.4.1 The exposed surface area of the specimen shall be measured.

8.4.2 For materials with a CPT value < 40 °C or with an unknown CPT value, the temperature ramp shall start at (0 ± 1) °C. In this case, the solution shall be cooled to ⩽ 3 °C prior to filling the test cell. This may be achieved by placing a beaker of the solution in an ice bath. If a double-walled test cell is used, liquid cooled to < 3 °C in a bath should be recirculated to the outer chamber of the test cell before adding the test solution.

8.4.3 For materials with a CPT value > 40 °C, the temperature ramp shall start at < 30 °C.

8.4.4 The specimen, counter electrode and salt bridge shall be placed in the test cell. The test cell shall then be filled with the solution. It is important to ensure that the salt bridge is filled with the test solution and is free of air bubbles, particularly in the restricted space at the tip. A wick, or equivalent device, may be placed in the salt bridge to ensure electric contact, even when small gas bubbles are formed during the test.

8.4.5 The solution shall be stirred continuously throughout the test. This can be achieved using a mechanical stirring device, or simply by bubbling an inert gas through the solution at a controlled rate.

8.4.6 The electrodes shall be connected to the potentiostat and data-recording device, and the connections for temperature measurement and control shall be made. The potential shall not be applied to the specimen until the temperature of the solution has been stable to within ± 1 °C of the desired initial test temperature for a minimum of 600 s.

8.4.7 The open-circuit potential of the test specimen shall be recorded and the desired anodic potential shall than be applied to the specimen. Guidance on the selection of potential is given in Annex A.

8.4.8 When the potential has been applied for 60 s or longer, the temperature of the specimen shall be increased at a controlled rate. The rate of increase of the temperature of the solution that is required to give the desired rate of temperature increase of the specimen can be calculated from the specimen temperature-calibration formula. Guidance on the selection of the temperature ramp rate for austenitic and duplex stainless steels is given in Annex A.

8.4.9 The current and solution temperature shall be monitored throughout the test. The minimum sampling rate shall be 10 readings per minute.

8.4.10 The CPT is defined as the temperature at which the current density reaches 100 $\mu A \cdot cm^{-2}$ and then remains above this level for a minimum of 60 s.

8.5 Ending test

8.5.1 The test shall be terminated when the CPT has been determined.

8.5.2 The specimen shall be removed from the solution and rinsed in water, cleaned with ethanol, rinsed with high-purity water, cleaned with ethanol or a similar solvent and dried in air.

8.5.3 The specimen shall be inspected using an optical microscope at 20 × magnification to determine whether pitting corrosion and crevice corrosion have occurred. Observation of any crevice corrosion on the specimen means that the test is not valid, and the results shall be discarded.

9 Assessment of results

9.1 The CPT is defined as the surface temperature of the specimen at which the current density increases above 100 $\mu A \cdot cm^{-2}$ and then remains above this level for a minimum of 60 s.

9.2 The CPT shall be calculated from the temperature of the solution at which the current density increases above 100 µA·cm^{-2} and then remains above this level for a minimum of 60 s, using the specimen temperature-calibration formula.

9.3 For materials that exhibit a very high passive-current density, for example some nickel-based alloys, a higher critical-current density may be chosen. This shall be noted in the test report. The CPT should not be compared with values obtained using a different critical-current density.

10 Test report

The test report shall include the following information:

a) a full description of the test material from which the specimens were taken, including composition and structural condition, type of product and section thickness;

b) orientation, geometry and size of test specimens;

c) surface finish of specimens, including the storage time between carrying out the final surface finish and testing;

d) test area of specimen;

e) type of test cell and volume of test solution;

f) test environment and electrode potential;

g) temperature ramp rate;

h) description of the specimen surface after testing; if no pits were observed, this shall be noted explicitly;

i) critical pitting temperature (CPT), CPTs below 10 °C shall only be reported as $<$ 10 °C;

j) formula for conversion of test-solution temperature to specimen temperature.

Annex A
(informative)

Guidelines for selecting the test parameters

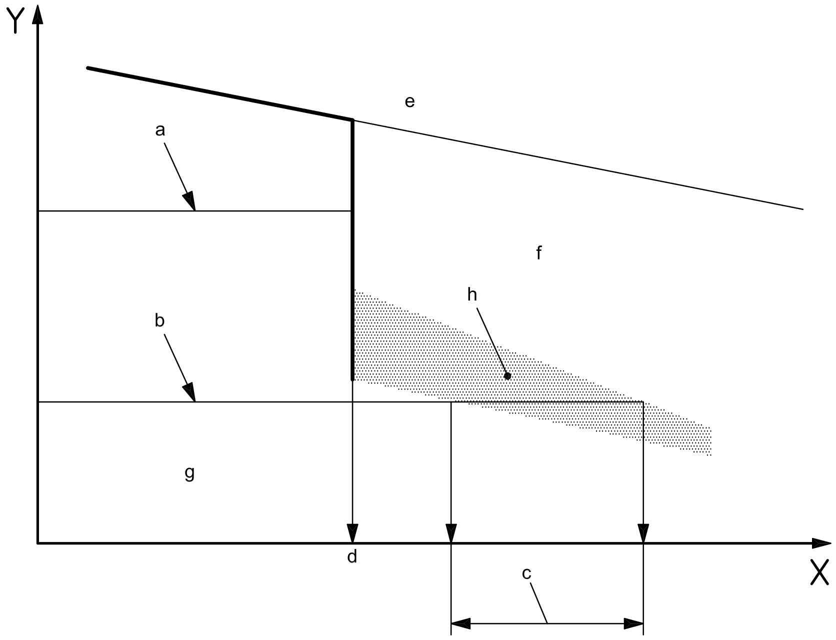
This annex explains the relationship between pitting potential and critical pitting temperature, and the guidelines for selecting the test parameters for austenitic and other stainless steels.

A.1 Pitting-potential range

The measured pitting potential at a given temperature varies because of the random nature of the pitting initiation process. Therefore, the characteristic pitting potential is best described as a range. Generally, the pitting potential will decrease with increasing temperature. The occurrence of pitting on stainless steels, as a function of temperature and potential, is shown in Figure A.1.

A.2 Potential-independent CPT

Below a certain temperature, only passive or transpassive corrosion occurs on a stainless steel. This temperature limit signifies the potential-independent CPT, see also Figure A.1.



Key

X temperature

Y potential

[a] High potential.

[b] Low potential.

[c] Potential-dependent.

[d] Potential-independent.

[e] Transpassive corrosion.

[f] Pitting.

[g] No pitting.

[h] Pitting potential range.

Figure A.1 — Principle of the potential and temperature effects on the pitting corrosion of stainless steels

A.3 Potential-dependent CPT

At temperatures above the potential-independent CPT, pitting may occur depending on the potential; see also Figure A.1. Figure A.1 depicts the potential-dependent CPT range for a specific low potential. Principally, the low temperature limit of the potential-dependent CPT is the potential-independent CPT.

A.3.1 At potentials within the pitting-potential range, pitting will occur if the temperature is sufficiently high. In this case, the critical pitting temperature will depend on the specific potential and on the variation in the pitting potential.

A.3.2 At a potential above the pitting-potential range and below the transpassive potential, pitting will occur virtually instantaneously.

A.3.3 At potentials below the pitting-potential range, no pitting will occur.

A.4 General information

This International Standard defines a fast potentiostatic method to determine the potential-independent CPT by using a high potential of 944 mV versus standard hydrogen electrode (SHE). This generally will correspond to a potential above the pitting-potential range.

A.5 Simple CPT determination

If uncertainties exist in the correct choice of potential to determine the potential-independent CPT, a simple CPT determination at a potential 100 mV above will indicate whether the CPT determined is truly potential independent. Any conclusions based on such a test should take into account the expected repeatability of the method, the homogeneity of the test material and the level of the transpassive potential range.

From Figure A.1, it can be concluded that the best precision in the CPT determination will be achieved if a potential slightly below the onset of transpassive corrosion is selected. In this case, some variation of the potential will not affect the CPT measure.

The following test parameters are suitable for determining the CPT of austenitic stainless steels, ferritic/austenitic stainless steels and even ferritic stainless steels with a corrosion resistance ranging from solution-annealed X5CrNiMo17-12-2 (Type 316 stainless steel) to solution-annealed X1CrNiMoCuN 20-18-7 (high-Mo stainless steel).

Table A.1 — Recommended test parameters for stainless steels

Solution	1,0 Mol/l NaCl
Temperature ramp rate	$(1,7 \times 10^{-2} \pm 5 \times 10^{-3})$ °C s^{-1}
Applied potential	+ 944 mV_{SHE}

Annex B
(informative)

Method of preventing a crevice attack

B.1 Flushed-port cell for plate specimen (see Figure B.1)

B.1.1 The flushed-port cell consists of a cylindrical double-walled chamber, as shown in Figure B.1. The solution can be cooled or heated by recirculating a liquid from an external heating bath to the outer chamber of the cell.

B.1.2 The auxiliary electrode, the Luggin capillary probe, the temperature-measurement device and the stirring device are mounted inside the cell.

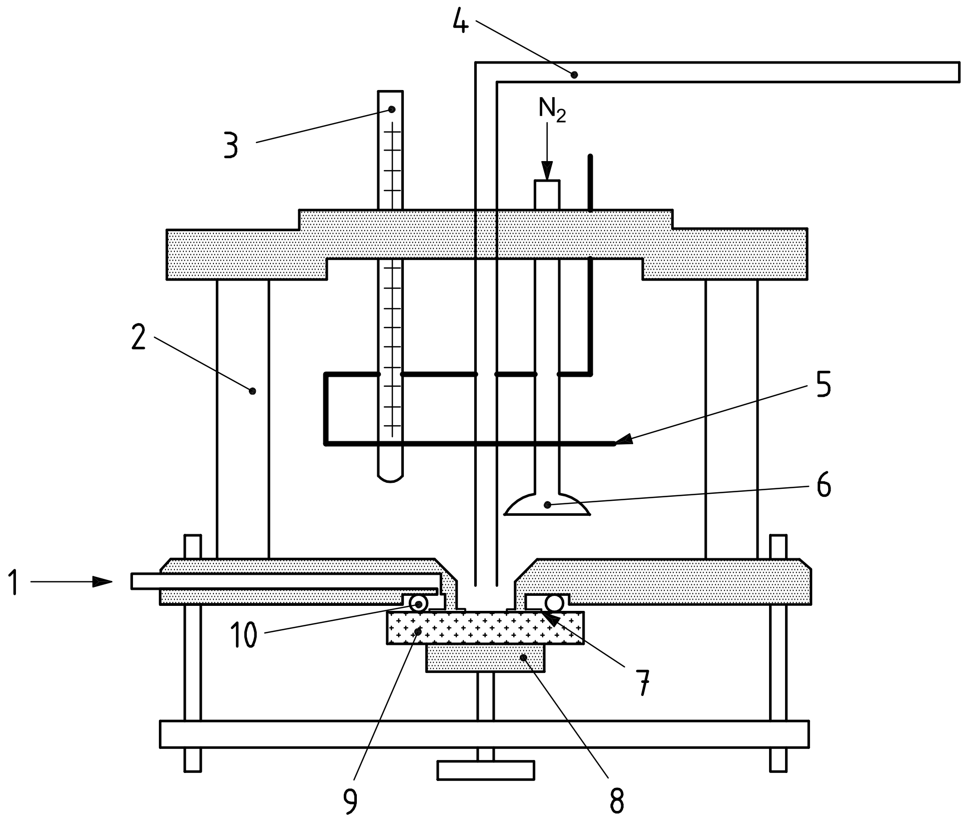
B.1.3 The key feature of the cell is the seal between the specimen and the cell. The specimen holder is incorporated in the base of the cell, with the specimen mounted outside the cell. Elimination of crevice corrosion at the contact point between the specimen and the cell is achieved by continuously pumping a small volume of high-purity water into the contact region. This prevents build-up of chloride ions in the crevice region. The flow rate of high-purity water, necessary to avoid the crevice corrosion, is typically in the range of $1{,}1 \times 10^{-6} \cdot \mathrm{s}^{-1}$ to $1{,}4 \times 10^{-6}\ \mathrm{L} \cdot \mathrm{s}^{-1}$ for a 1 cm^2 port opening.

B.1.4 The specimen is separated from the cell port by one or more filter-paper rings, creating a diffusion barrier for the high-purity water. This ensures that the high-purity water flows around the entire crevice region.

B.1.5 The ingress of high-purity water into the seal dilutes the test solution. The extent of dilution will depend on the volume of test solution used. To counteract the dilution, a solution with a concentration of ions twice that of the test solution should be pumped into the test cell at the same flow rate as the high-purity water.

B.1.6 Pumping high-purity water into the crevice region should not dilute the test solution close to the surface of the specimen, except at the extremities of the exposed area of the specimen. As the test solution is denser than the high-purity water, the high-purity water flows upwards, away from the specimen surface. Furthermore, the stirring caused by gas purging, or by a mechanical stirrer, mixes the high-purity water with the test solution.

B.1.7 As the specimen is partly outside the cell, there will be a difference in temperature between the solution and the specimen. This can be reduced by ensuring good mixing of the test solution using gas purging and mechanical stirring, by insulating the part of the specimen external to the cell and by minimising the area of the specimen that is external to the cell.



Key

1 purified water
2 double-walled glass chamber
3 thermometer
4 luggin capillary
5 counter electrode
6 gas disposer
7 filter paper
8 mounting screw
9 specimen
10 o-ring

Figure B.1 — Design principles of the flushed-port cell

B.2 Flushed electrode holder for plate specimen (see Figure B.2)

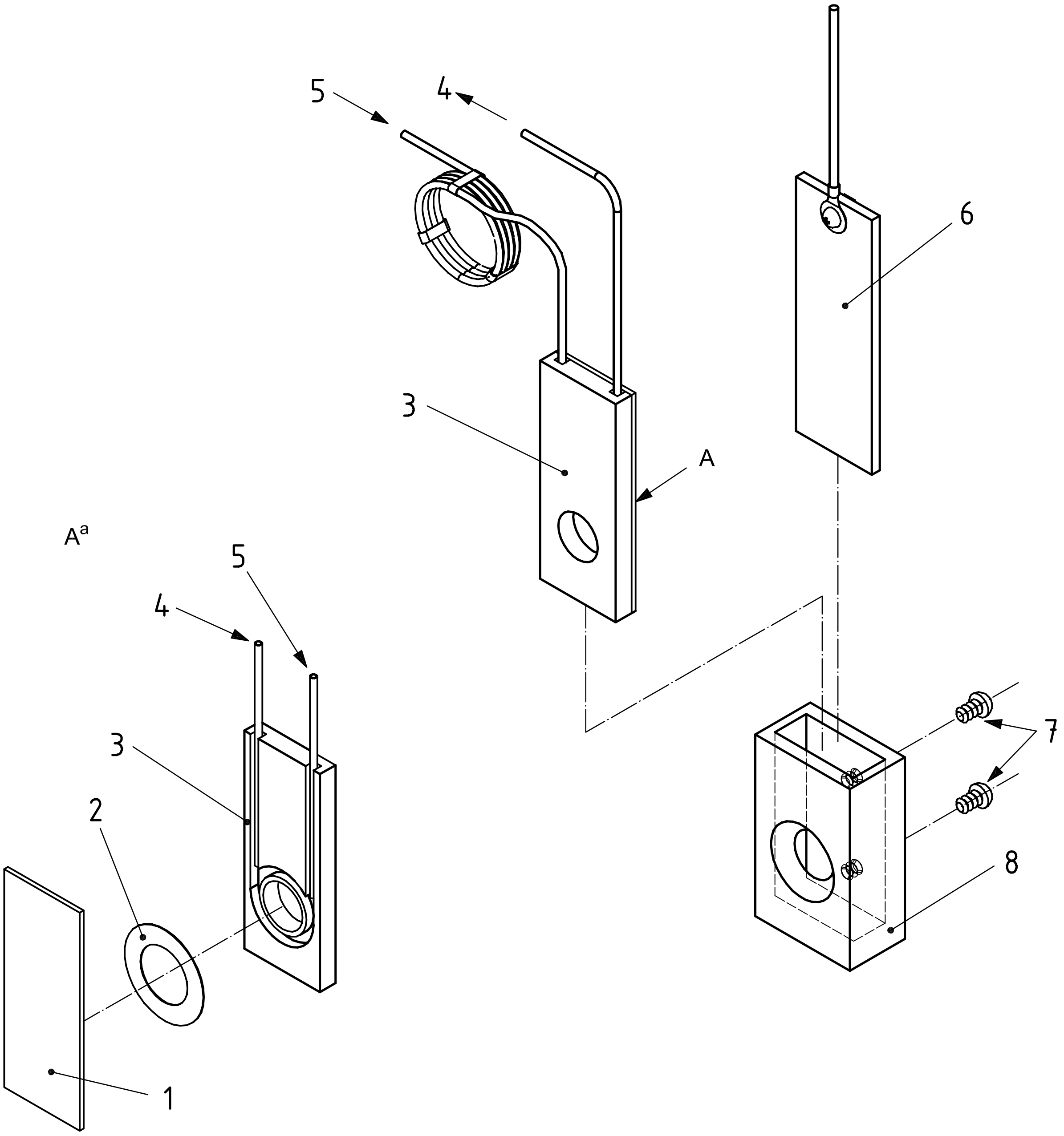
B.2.1 The electrode-holder system is designed to prevent crevice corrosion by inserting filter paper between the rubber gasket and the electrode surface, and is flushed with high-purity water coming through fine PTFE tube by siphon from the outside storage flask.

B.2.2 The system preventing crevice corrosion consists of a main frame of the box-type holder made of transparent acrylic resin, a gasket made of fluorine-containing rubber, filter paper, a fine PTFE tube for introducing high-purity water, a stainless-steel thin plate for backup and the thin-plate specimen electrode.

B.2.3 A bundle of looped PTFE tube was immersed with the electrode holder in the test solution, so that the temperature of high-purity water could be maintained as close as possible to the test solution temperature.

B.2.4 In Figure B.2, the shape and dimension of the holder and rubber gasket, and the assembling procedure of the electrode system preventing crevice corrosion, are shown. At the centre of the filter paper, an open circle of 11 mm diameter is cut by a punch. The centre of the front side of the holder and the rubber gasket have a circular hole of 11,3 mm diameter, providing a 1 cm^2 circle area exposed to the test solution. The inner and outer diameter of the PTFE tube is, for example, 1,56 mm and 0,96 mm.

B.2.5 The flow rate of high-purity water through the PTFE tube is usually controlled at around $2{,}8 \times 10^{-5}\, L{\cdot}s^{-1}$, and the flushing rate through filter paper is approximately 2 % to 6 % of the water flow, for example, $8{,}3 \times 10^{-7}\, L{\cdot}s^{-1}$.



Key

1 specimen

2 filter paper

3 fluoro-rubber gasket

4 H_2O outlet

5 H_2O inlet

6 support plate

7 acrylic plastic screw

8 acrylic plastic holder

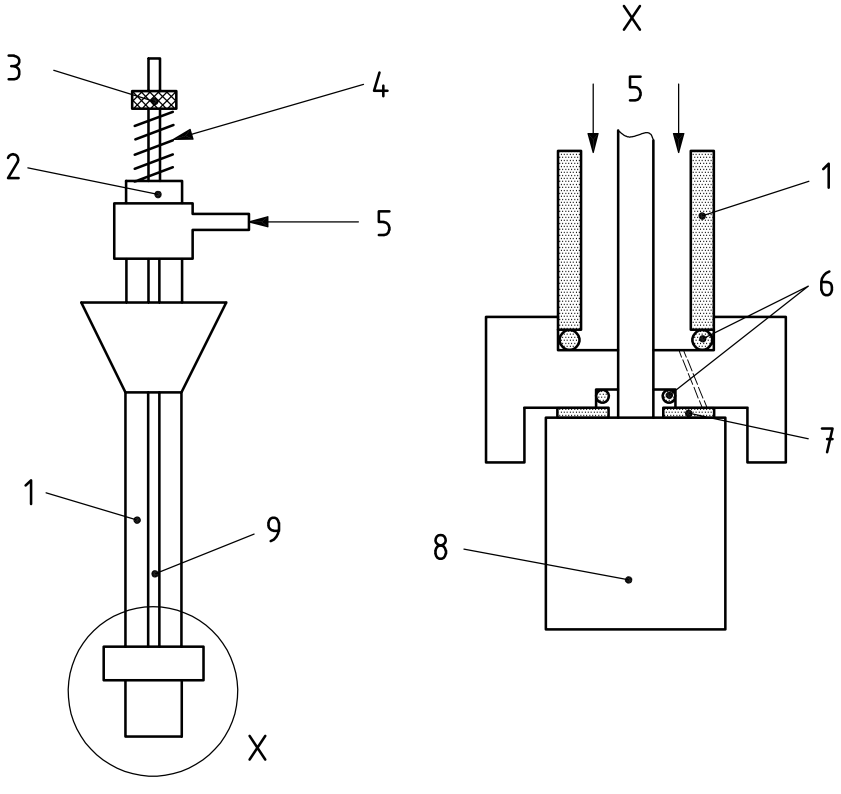
[a] Reverse side.

Figure B.2 — Flushed electrode holder for plate specimen

B.3 Flushed electrode holder for cylindrical specimen (see Figure B.3)

B.3.1 High-purity water is fed through a glass tube sealed with O-rings to the PTFE mount at the bottom. The water is distributed through the filter paper on top of the specimen. The stainless-steel connecting rod, on which the specimen is mounted, is painted to avoid electrical contact with the high-purity water. A typical flow rate is about 4×10^{-4} ml·s^{-1} for a 10 mm diameter cylindrical specimen.

B.3.2 Pumping high-purity water into the crevice region should not dilute the test solution, except at the extremities of the exposed area of the specimen. As the test solution is denser than the high-purity water, the high-purity water flows upwards, away from the specimen surface. Furthermore, the stirring caused by gas purging, or by a mechanical stirrer, mixes the high-purity water with the test solution as soon as it enters the cell chamber.



Key

1 glass tube
2 PTFE disc and o-ring
3 screw
4 spring
5 purified water
6 o-ring
7 filter paper
8 cylindrical specimen
9 painted connecting rod

Figure B.3 — Modified ASTM G5-type specimen holder using the flushed-port-cell principle

Annex C
(informative)

Potential difference of selected reference electrodes at 25 °C with respect to the standard hydrogen electrode (SHE)

Reference electrode	**Potential difference with respect to SHE**, V
Silver/silver chloride electrode in saturated KCl	0,196
Silver/silver chloride electrode in 1 molar KCl	0,222
Silver/silver chloride electrode in 0,1 molar KCl	0,288
Saturated calomel electrode	0,244

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