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**Corrosion of metals and alloys —  
Electrochemical test methods —  
Guidelines for conducting potentiostatic  
and potentiodynamic polarization  
measurements**

*Corrosion des métaux et alliages — Méthodes d'essais  
électrochimiques — Lignes directrices pour la réalisation de mesures de  
polarisations potentiostatique et potentiodynamique*



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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 17475 was prepared by Technical Committee ISO/TC 156, *Corrosion of metals and alloys*, in collaboration with the Korea Research Institute of Standards and Science.

## Introduction

Corrosion of metals and alloys in aqueous solutions is generally caused by an electrochemical mechanism. Therefore, one can measure or analyse corrosion phenomena, utilizing a variety of electrochemical techniques. This International Standard, based on ASTM G5<sup>[1]</sup> and ASTM G150<sup>[2]</sup>, defines basic guidelines for potentiostatic potentiodynamic polarization measurements to characterize an electrochemical kinetics of anodic and cathodic reactions.



# Corrosion of metals and alloys — Electrochemical test methods — Guidelines for conducting potentiostatic and potentiodynamic polarization measurements

## 1 Scope

This International Standard applies to corrosion of metals and alloys, and describes the procedure for conducting potentiostatic and potentiodynamic polarization measurements.

The test method can be used to characterise the electrochemical kinetics of anodic and cathodic reactions, the onset of localised corrosion and the repassivation behaviour of a metal.

## 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*

ISO 8407:1991, *Corrosion of metals and alloys — Removal of corrosion products from corrosion test specimens*

ISO 9400:1990, *Nickel-based alloys — Determination of resistance to intergranular corrosion*

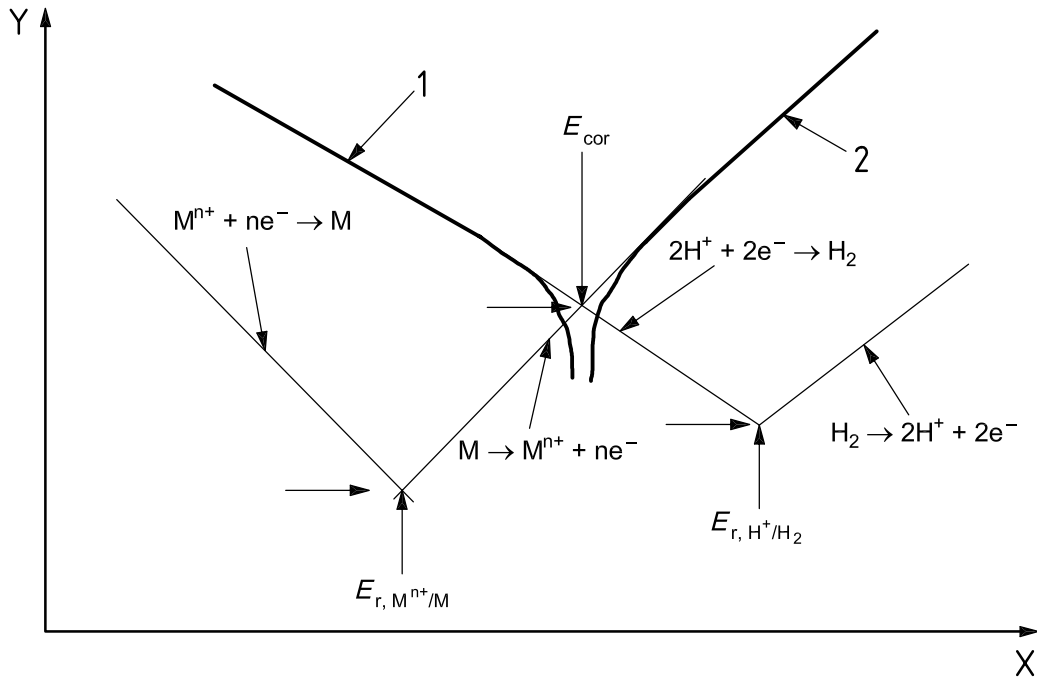
ISO 11463:1995, *Corrosion of metals and alloys — Evaluation of pitting corrosion*

ISO 11846:1995, *Corrosion of metals and alloys — Determination of resistance to intergranular corrosion of solution heat-treatable aluminium alloys*

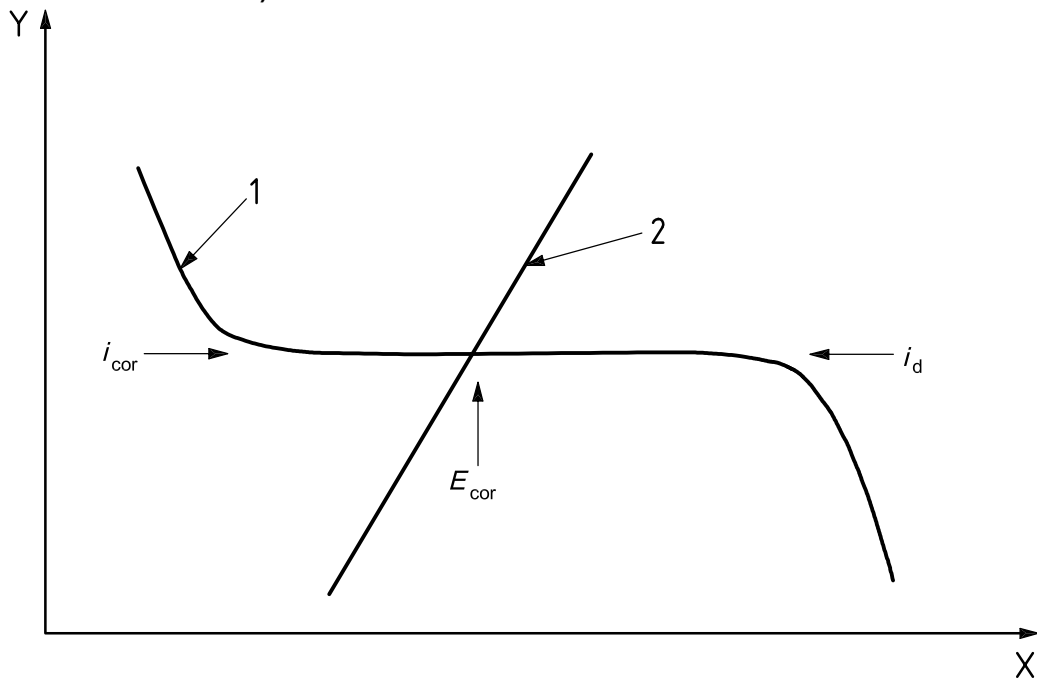
## 3 Principle

**3.1** When a metal is immersed in a solution, the rate of the anodic reaction and that of the cathodic reaction will be in balance at the open-circuit potential (free corrosion potential,  $E_{\text{cor}}$ ). If the electrode potential is displaced from the open-circuit value, the applied current measured will represent the difference between the anodic-reaction current and the cathodic-reaction current. If the displacement of potential is sufficiently large, the net current will be essentially equal to the anodic or cathodic-reaction kinetics, depending on whether the potential is made respectively more positive or more negative with respect to the open-circuit value as shown for a metal in the active state in acid solutions [Figure 1 a)] and in neutral aerated solutions [Figure 1 b)].

**3.2** In certain metal-environment combinations, the metal may be in the passive state (Figure 2). If an aggressive anion is present and the potential is increased (made more positive) with respect to the open-circuit potential, localised breakdown of passivity (e.g. pitting, crevice corrosion, intergranular attack) can result with an attendant increase in the applied current (Figure 2). The potential corresponding to the increase in current can be used as a measure of the resistance of a metal to localised corrosion.



a) Corrosion rate is under diffusion control



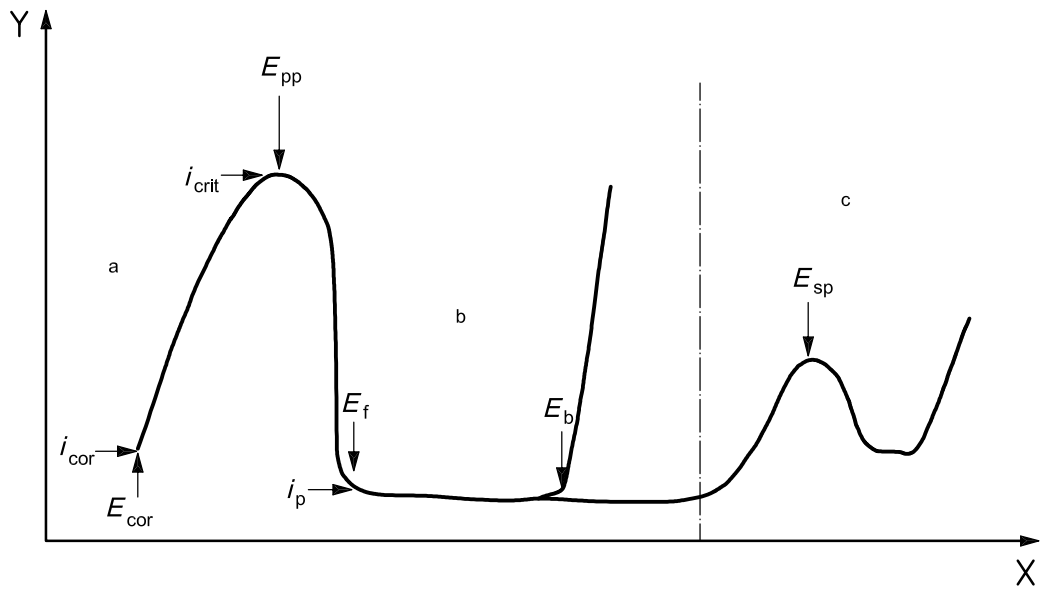
b) Example by diffusion of oxygen in water

**Key**

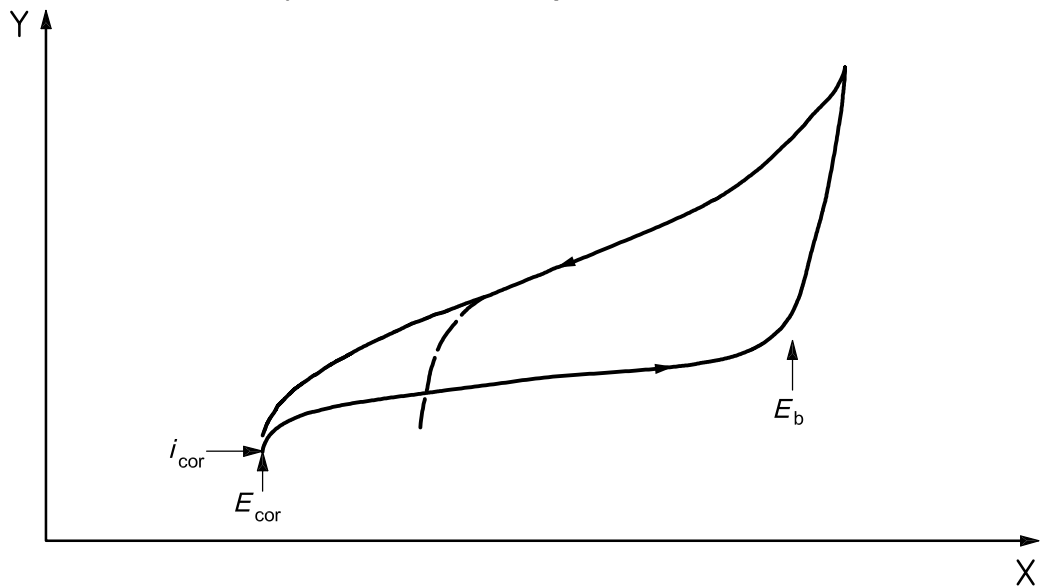
- X potential
- Y log current density
- 1 cathodic
- 2 anodic
- $E_{cor}$  corrosion potential
- $i_{cor}$  corrosion current density
- $E_r$  reversible electrode potential
- $i_o$  exchange current density
- $i_d$  limiting diffusion current density, which corresponds to the maximum diffusion rate of oxygen in the solution

**Figure 1 — Schematic anodic and cathodic polarization curves for metals corroding in a system where the cathodic reaction is reduction of protons**





a) Metals with active-passive transition



b) Metals without active-passive transition

**Key**

- X potential
- Y log current density
- $E_{cor}$  corrosion potential
- $i_{cor}$  corrosion current density
- $E_{pp}$  passivation potential
- $i_{crit}$  critical current density for passivation
- $i_p$  passive current density
- $E_f$  flade potential
- $E_b$  breakdown potential
- $E_{sp}$  secondary passivation potential
- a Active.
- b Passive.
- c Transpassive.

**Figure 2 — Schematic anodic polarization curves**

**3.3** If the potential is subsequently decreased after the onset of localised corrosion, the potential at which repassivation occurs (when the applied current returns to approximately the same value as the passive current) can be considered to be indicative of the resistance of the metal to propagation of localised corrosion; the more noble the potential, the greater the resistance.

**3.4** The displacement in potential can be stepwise, with the magnitude of the potential step and the time at a specific potential selected according to the application and purpose of the experiment. This type of testing is known as potentiostatic.

**3.5** When the potential is displaced in a continuous mode at a controlled scan (displacement) rate, the test is described as potentiodynamic.

**3.6** The kinetics of the electrochemical processes occurring on the surface can be time dependent, for example due to film formation, and hence the time that the potential is held at a specific potential in potentiostatic testing or the potential scan rate in potentiodynamic testing can be critical. For example, too high a rate of change may lead to overestimation of the breakdown potential for localised attack. For this reason, the interpretation of polarization data shall be considered carefully, particularly when applied to service conditions.

**3.7** The measurement of the electrode potential can be influenced by ohmic drop in the solution. For solutions of low conductivity, a correction shall be made.

## 4 Apparatus

### 4.1 Potentiostat

The potentiostat should be capable of controlling the electrode potential to within  $\pm 1$  mV of a preset value. A scanning potentiostat is used for potentiodynamic measurements. For such measurements, the potentiostat shall be capable of automatically scanning the potential at a constant rate between preset potentials.

### 4.2 Electrode potential-measuring instruments

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.

### 4.3 Current-measuring instruments

Use appropriate current-measuring instruments with maximum error 0,5 %.

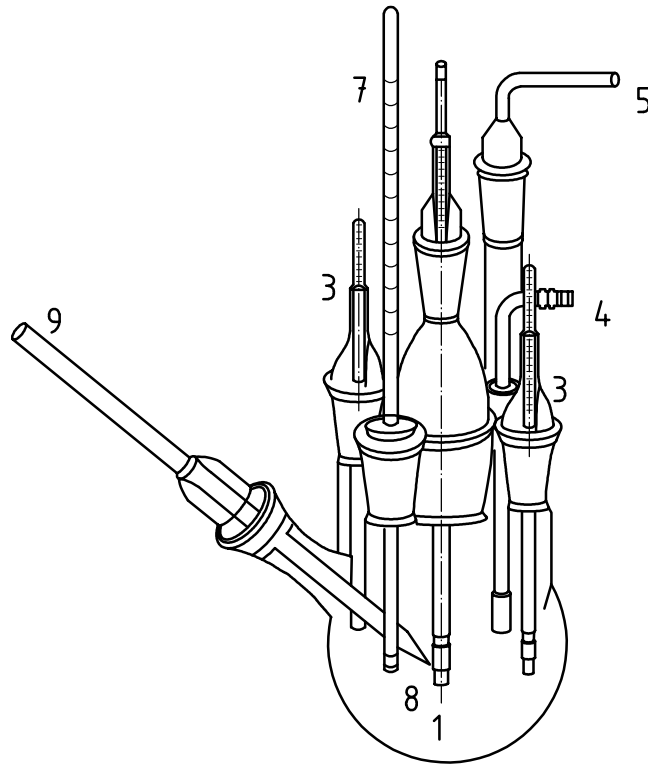
### 4.4 Test cell

**4.4.1** The test cell should contain the working electrode (the metal to be polarized), a reference electrode for measuring the electrode potential, and one or two auxiliary electrodes. The test cell should incorporate inlet and outlet gas ports and a port for insertion of a temperature-measuring device.

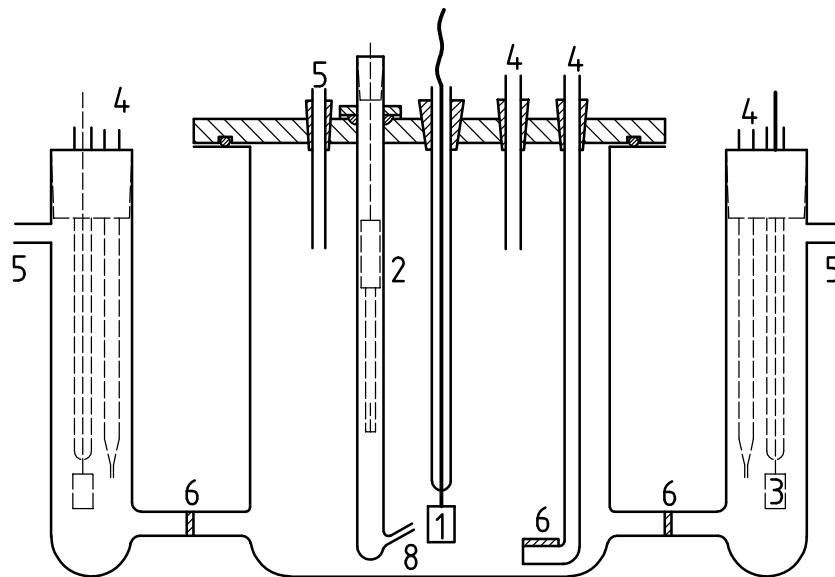
NOTE The term auxiliary electrode is synonymous with counter electrode.

**4.4.2** The detailed construction of the test cell depends on the application. Examples commonly used are shown in Figure 3. The important distinction of Figure 3 b) is that the auxiliary electrodes are separated from the main cell of the working electrode by a fritted disc, in order to limit contamination of the main cell by reaction products generated at the auxiliary electrodes.

**4.4.3** The auxiliary electrodes should be positioned so that the current distribution about the specimen is symmetrical.



a) Auxiliary electrode included in the main cell



b) Auxiliary electrode separated from the main cell

**Key**

- |                        |   |
|------------------------|---|
| 1 specimen             | 6 fritted disc  |
| 2 reference electrode  | 7 thermometer   |
| 3 auxiliary electrodes | 8 probe here corresponds to Luggin capillary                    |
| 4 reference electrode  | 9 salt-bridge connection to the reference electrode (not shown) |
| 5 gas inlet            |   |

**Figure 3 — Schematic diagram of electrochemical polarization cells with auxiliary electrode**

**4.4.4** The reference electrode may be inserted directly into the main cell. Precautions should be taken to ensure that it is maintained in the proper condition. To avoid mutual contamination, a double-junction reference electrode may be used or the reference electrode located in a separate chamber and linked to the main cell by a salt bridge. To minimise the potential drop between the reference electrode and the working electrode, a Luggin capillary should be used as shown in Figure 3 a) and Figure 3 b). The tip of the capillary probe shall be positioned so that it is at a distance from the working electrode of about, but not closer than, 2 times the diameter of the tip.

**4.4.5** The test cell should be constructed of a material which is inert in the environment at the temperature of testing.

**4.4.6** The volume of solution in the test cell shall be such as to reduce to insignificance any change in the solution chemistry as a consequence of the reaction processes.

NOTE In most cases, a solution volume greater than 100 ml/cm<sup>2</sup> of specimen surface is considered to be adequate.

**4.4.7** To assess the effect of flow on the electrode kinetics, a magnetic stirrer may be used but, where more defined control is required, the use of a rotating disc or rotating-cylinder assembly is recommended.

## **4.5 Electrode holder**

The auxiliary and working electrodes shall be mounted in such a way that the holder and mounting material have no influence on the measurement. An example of an electrode-mounting assembly is shown in Figure 4. For steels with a protective oxide film, the seal of the test specimen to the holder can sometimes lead to undesired crevice attack of the steel at the interface. A method of preventing such crevice attack for certain applications, using a flushed port cell or a flushed specimen holder, is outlined in Annex A, although the method is not suitable for studies of rotating electrodes.

## **4.6 Electrode material**

The working electrode is prepared from the test material of interest, usually in the form of a rod or sheet. 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 a sheet or rod, or in the form of a gauze supported on a glass frame with the test specimen located centrally. The area of the auxiliary electrode should be at least the area of the working electrode.

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

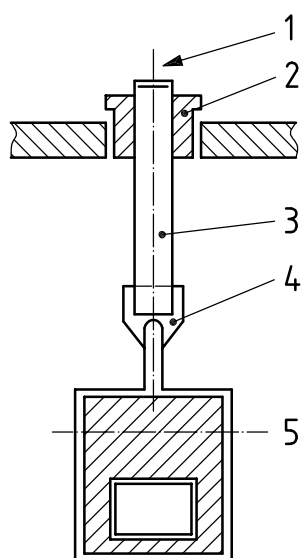
## **4.7 Reference electrode**

The type of reference electrode used will depend on the application, e.g. temperature and environment. Commonly used electrodes include the saturated calomel electrode and silver/silver chloride electrode. The potential of these electrodes at 25 °C, relative to the standard hydrogen electrode at 25 °C, is given in Annex B.

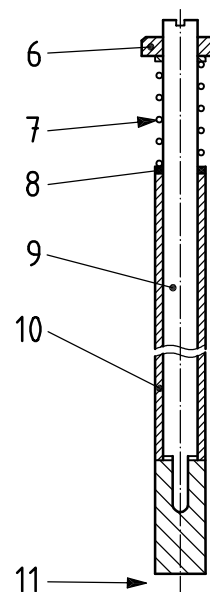
## **4.8 Specimen preparation**

**4.8.1** The specimen should be prepared with a well-defined surface finish according to the application. In most cases, a *R<sub>a</sub>* value less than 1 µm is desirable to limit the possibility of enhanced reaction in grooves induced by grinding.

**4.8.2** The time elapsed between grinding and immersion can have an influence on the subsequent polarization 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. The specimens should be cleaned and degreased (e.g. using alcohol or acetone) and stored in a desiccated cabinet.



a) Painted test pieces



b) Bar-shaped test pieces

**Key**

- 1 lead wire
- 2 rubber cap
- 3 resin tube
- 4 resin seal
- 5 immersion line
- 6 nut
- 7 spring
- 8 washer
- 9 stainless shaft
- 10 PTFE
- 11 test piece

**Figure 4 — Examples of electrode holders****4.9 Auxiliary electrode preparation**

The auxiliary electrode shall be free of any product that would contaminate the solution.

NOTE Dipping of platinum electrodes in concentrated HCl and thoroughly rinsing in high-purity water (with a conductivity less than  $1 \mu\text{S}\cdot\text{cm}$ ) is usually sufficient.

**4.10 Solution preparation**

The solutions shall be prepared from analytical reagent-grade chemicals and high-purity water (with a conductivity less than  $1 \mu\text{S}\cdot\text{cm}$ ), unless testing takes place in the actual service fluid.

**5 Procedure**

The test procedure adopted depends critically on the type of cell used, with respect to whether the specimen is added to the cell after prior conditioning of the solution or whether, as in one type of flushed port cell, the specimen is incorporated into the cell and the solution then added.

**5.1** Measure the difference in potential between the reference electrode and two other validation electrodes. These electrodes should be traceable to the standard hydrogen electrode and used and maintained solely for the purpose of validation. If the potential is different by greater than 3 mV, the test electrode should be rejected.

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

**5.3** Measure the exposed surface area of the specimen. The accuracy of this measurement will depend on the purpose of the test.

**5.4** Assemble the cell with the auxiliary electrode, monitoring probes and Luggin capillary.

**5.5** Add the specimen after pre-conditioning of the solution.

**5.5.1** Add the test solution to the cell.

**5.5.2** When testing in aerated solutions, either an air pump or a cylinder of compressed air can be used to ensure constancy of conditions. When purging with gas, the solution should be purged with the appropriate gas for a sufficient time to achieve equilibrium.

**NOTE** The time to purge the cell will depend on the sensitivity of the test system to low levels of oxygen. The extent of de-aeration in non-acidic environments at ambient temperatures can be assessed by polarising a small platinum probe in the initially aerated solution, at a potential in the transport-limited regime for oxygen reduction (e.g. about  $-0,4$  V SCE at ambient temperature) and monitoring the decay of current with time. Since the water reduction current is very low, the decrease in current reflects the extent of de-aeration.

When testing in  $H_2S$  solutions, the solution shall be de-aerated prior to bubbling with  $H_2S$  gas.

**WARNING —  $H_2S$  gas is poisonous. Appropriate precautions shall be taken.**

**5.5.3** Control the temperature to  $\pm 1$  °C by immersing the test cell in a controlled-temperature water bath or by other convenient means (e.g. double-walled vessel with circulation of fluid from a temperature-controlled reservoir).

**5.5.4** Mount the specimen on the electrode holder.

**5.5.5** Transfer the specimen to the test cell and adjust the Luggin probe tip so that it is at a distance from the working electrode of about, but not closer than, 2 times the diameter of the tip.

## **5.6 Flushed port cell**

Add the solution to the cell and follow procedures 5.5.2 and 5.5.3.

**5.7** Record the open-circuit specimen potential, i.e. the free corrosion potential, with time after immersion. The period of exposure at open circuit prior to polarization will depend on the purpose of the experiment. In some applications, it can be useful to allow the open-circuit potential to attain a steady value. Otherwise, a period of 1 h should be allowed.

**NOTE** When a specimen is immersed in a solution, the initial surface film will be characteristic of that formed in air and this film may break down or change its properties with time upon immersion, thus inducing a change in potential.

**5.8** Commence the potential scan or potential stepping in either an anodic or a cathodic direction, beginning at the corrosion potential ( $E_{cor}$ ) or any other potential, depending on the purpose of the test, and record the current variation with time.

**NOTE 1** In some applications in which the air-formed film on the metal is readily reduced, it may be desirable to initiate anodic polarization after holding at a cathodic potential for a period.

NOTE 2 The choice of scan rate, or rate of potential stepping, depends on the purpose of the test (see also 3.6). A scan rate of  $0,17 \text{ mVs}^{-1}$  can be useful for determining general trends and for comparing different materials. For potential stepping, a step size of  $0,05 \text{ V}$  with  $300 \text{ s}$  hold-time is similarly useful. However, for quasi-steady-state conditions, the hold-time should be sufficient to allow the current to attain a steady value at each potential. Similarly, there is value in conducting scanning tests at progressively lower scan rates, until no difference in polarization behaviour is observed.

**5.9** For pitting and repassivation studies, the potential is usually scanned or stepped gradually until it is above the breakdown potential and then subsequently decreased to the open-circuit value.

**5.10** For tests of long duration, the pH of the solution shall be measured after the test as a measure of constancy of the solution chemistry.

## 6 Test report

The test report shall include the following information:

- a) a reference to this International Standard;
- b) a full description of the test material from which the specimens were taken, composition, heat treatment, type of product;
- c) method of manufacture of the specimens and details of the surface preparation;
- d) the solution composition, pH, volume and temperature, and any variations with time;
- e) area of the specimen exposed to the test solution;
- f) description of cell and electrodes used;
- g) time of immersion prior to polarization;
- h) open-circuit potential, and whether this was steady, and end potential;
- i) the potential shall be quoted with respect to the standard hydrogen electrode;
- j) potential step height and hold time, or scan rate;
- k) plot of applied current density versus applied potential. including an indication of any correction for solution potential drop and its method of evaluation.

## Annex A (informative)

### Method of preventing a crevice attack for certain applications

#### A.1 Flushed port cell

**A.1.1** The flushed port cell consists [see Figure A.1 a)] of a circular double-walled glass chamber to facilitate heating by an external recirculating heating bath and various inlets, connections for temperature measurement, electrodes and gas purging.

**A.1.2** The bottom of the cell incorporates the specimen holder. The specimen is mounted outside the cell. Elimination of crevice corrosion at the contact point of the specimen and the cell port is achieved by continuously pumping a small volume of high-purity water into the contact area of the cell port.

**A.1.3** The specimen is separated from the cell port by one or more filter-paper rings, creating a diffusion barrier between the purified water, the specimen and the test solution. The high-purity water pumped into this region displaces any electrolyte that would otherwise be in the crevice-like region. The water flow is typically in the range of 4 ml/h to 5 ml/h for a 1 cm<sup>2</sup> port opening. The cell shall be large enough to ensure sufficient test-solution volume to minimize the dilution effect from the purified water within the timeframe of the test. Where necessary, the dilution of the test solution should be balanced by addition of appropriately concentrated test solution at the same rate.

**A.1.4** The test area exposed to the electrolyte is not isolated from the test solution by the high-purity water because the difference in density between the high-purity water and the test solution makes the high-purity water flow upwards just on the port sides. Furthermore, stirring of the solution will cause effective mixing.

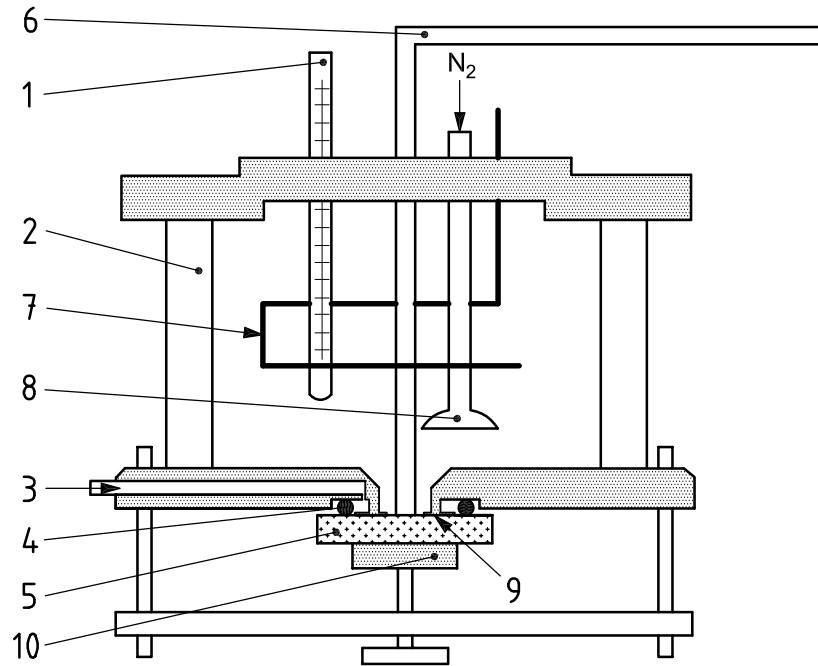
**A.1.5** Because the specimen is mounted outside the cell, there can be a difference in temperature between the electrolyte and the specimen when testing at elevated temperatures. This can be minimized by stirring, and by a combination of insulation and minimising the volume of the metal to reduce its effectiveness as a heat sink.

#### A.2 Flushed electrode holder [Figure A.1 b)]

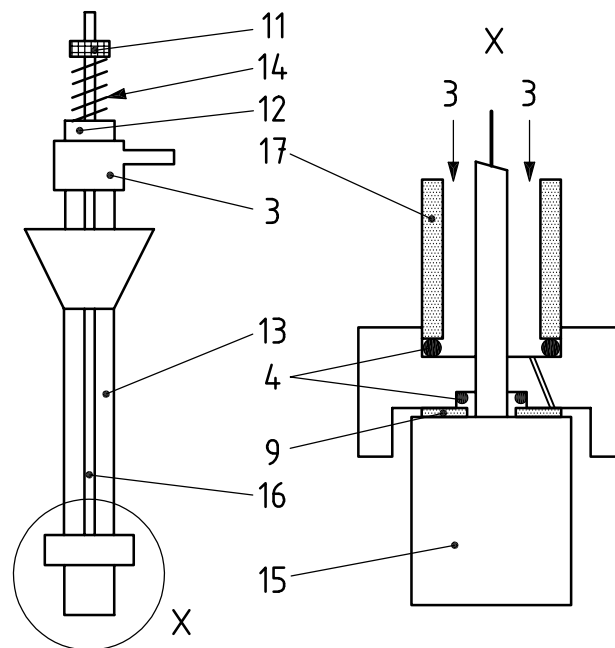
**A.2.1** High-purity water is fed through a glass tube sealed with O-rings to the PTFE mount at the bottom. The water is distributed through the filter paper on top of the specimen. The stainless-steel connecting rod, on which the specimen is mounted, is painted to avoid electrical contact with the high-purity water. A typical flow rate is about 1,5 ml/h for a cylindrical specimen of 10 mm diameter.

**A.2.2** See A.1.4.





a) Design principles of the flushed port cell



b) Modified cylindrical specimen holder using the flushed-port-cell principle

**Key**

- |                               |                         |                           |
|-------------------------------|-------------------------|---------------------------|
| 1 thermometer                 | 7 counter electrode     | 13 glass tube             |
| 2 double-walled glass chamber | 8 gas disposer          | 14 spring                 |
| 3 purified water              | 9 filter paper          | 15 cylindrical specimen   |
| 4 o-ring                      | 10 mounting screw       | 16 painted connecting rod |
| 5 specimen                    | 11 screw                | 17 glass tube             |
| 6 Luggin capillary            | 12 PTFE disc and o-ring |                           |

**Figure A.1 — Sketch of flushed port cell and electrode holder**

**Annex B**  
(informative)**Potential of selected reference electrodes at 25 °C with respect to the standard hydrogen electrode (SHE)**

| <b>Reference electrode</b>                        | <b>Potential with respect to SHE, V</b> |
|---|---|
| Saturated calomel electrode                       | + 0,244                                 |
| 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                                 |

## Bibliography

- [1] ASTM G5:1994, *Standard reference test method for making potentiostatic and potentiodynamic anodic polarization measurements*
- [2] ASTM G150:1999, *Standard test method for electrochemical critical pitting temperature testing of stainless steels*
- [3] European Federation Corrosion Publication No. 2:1996, *A working party report on practical corrosion principles*
- [4] JIS G 0579:1983, *Method for making anodic polarization measurement for stainless steels*

