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Corrosion of metals and alloys — Method of measuring the pitting potential for stainless steels by potentiodynamic control in sodium chloride solution

Corrosion des métaux et alliages — Méthode de mesure du potentiel de piqûre des aciers inoxydables par contrôle potentiodynamique en solution de chlorure de sodium

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Foreword

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The committee responsible for this document is ISO/TC 156, *Corrosion of metals and alloys.*

Introduction

Although stainless steel is generally used as a corrosion-resistant material, it is susceptible to pitting corrosion, crevice corrosion, stress corrosion cracking, etc. Among those, pitting corrosion is one of the most common phenomena that occur on stainless steels. A commonly used parameter to evaluate the pitting corrosion resistance of stainless steel, is so-called pitting potential that defines the lowest potential below which stables pits are not considered to grow. Since pitting corrosion generally shows a stochastic nature dependent upon inhomogeneity in terms of size, orientation, alloying components, impurity, inclusions, segregation, surface treatment, history, elapsed time, fluctuation of environment, etc., its measurement requires at least a couple of values.

Corrosion of metals and alloys — Method of measuring the pitting potential for stainless steels by potentiodynamic control in sodium chloride solution

1 Scope

This International Standard describes the procedure for determining the pitting potential for stainless steels (austenitic, ferritic/austenitic, ferritic, martensitic stainless steel) under potentiodynamic control.

The principal advantage compared with other potentiostatic test methods[1][2] is the rapidity of this test method, with which the pitting potential can be measured in a single potential scan.

The pitting potential as determined by this International Standard can be used as a relative index of performance. For example, one can compare the relative performances for different lots of stainless-steel grades and products. The test described in this International Standard is not intended to determine the pitting potential at which actual pitting can occur under real service conditions, or not.

2 Principle

The test involves increasing the anodic potential of the specimen at a specified scan rate while exposing the specimen to a normalized sodium chloride solution at a constant temperature.

The pitting potential (V'_{c10} or V'_{c100}) (see JIS G 0577[3]) is defined as the potential at which the current density exceeds 10 μA/cm^2 or 100 μA/cm^2 for more than 60 s. A 60 s delay is used in order to ensure that the observed current increase originates from stably propagating pitting, since short-lived current peaks originate from metastable pitting.

The specimen holder and the specimen itself are designed to ensure that crevice corrosion does not occur.

3 Apparatus

3.1 Potentiostat

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

3.2 Electrode potential-measuring instrument

The instrument shall have high input impedance sufficient to eliminate potential read error due to current drawn by the instrument during measurement; impedance of the order of 10^{11} Ω to 10^{14} Ω is typical. The sensitivity and accuracy of the instrument should be sufficient to detect a change of 1,0 mV.

3.3 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 may also be made externally by locating a resistor in the current line from the auxiliary electrode to the auxiliary connection of the potentiostat. The instrument shall be capable of measuring a current within 2 % error around the actual value.

3.4 Specimen holder

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

3.4.2 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. Some methods to prevent such crevice attack, using a flushed port cell, or using a flushed specimen holder, are outlined in A.1 and A.2.

3.4.3 If the specimen holder avoiding crevice corrosion cannot be used, the specimen electrode could be treated by the special method as outlined in A.3.

3.5 Test cell

3.5.1 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, a bubbler for de-aeration by inert gas such as N_2 or Ar, and/or a facility for stirring the solution in a repeatable manner.

NOTE This can be achieved by using a mechanical stirring device, or simply by bubbling inert gas through the solution at a controlled rate.

An accuracy of the temperature measuring instrument shall be ±0,4 °C.

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

3.5.3 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.

3.5.4 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.

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

3.6 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, rod, wire, or in the form of gauze supported on a glass frame. The area of the auxiliary electrode shall be at least the area of the specimen.

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

3.7 Reference electrode

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

3.7.2 Commonly used electrode is the saturated silver/silver chloride electrode (sat.SSCE). The potentials of these electrodes relative to the standard hydrogen electrode at 25 °C are given in ISO 17474.[4]

If the saturated calomel electrode (SCE) is used, strict control to handle mercury and mercury containing substances in terms of health and environmental issues shall be taken. The use of saturated calomel electrode shall follow nation’s rules and regulations.

4 Specimens

4.1 The specimen shall be taken from a test material such that the test area is minimum 1,0 cm^2. Different surfaces are permitted, if they are used in actual application: e.g. different heat treatments, and different surface finish.

4.2 The specimen may be taken by sawing, cutting, grinding, etc. The depth affected by machining shall be removed by progressive grinding so that the traces of machining may not affect the test results.

NOTE If relevant parties agree, any surface finishes different from the above recommendation may apply as far as they are reproducible.

5 Procedure

5.1 Preparation of reference electrodes

5.1.1 The difference in potential among the reference electrode and two other validation electrodes shall be measured. The latter electrodes shall be traceable to the standard hydrogen electrode, and shall be maintained solely for the purpose of validation. If the potential is different by greater than 3 mV, the electrode shall be rejected.

5.1.2 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.

5.2 Preparation of specimen

5.2.1 The final grinding of the specimen may be dry or wet. Before measurement, the specimen is recommended to be ground with 600 grit paper, and shall then be thoroughly cleaned.

NOTE 1 After grinding, it takes time for the air formed film to achieve a quasi-steady condition. The most rapid change in filming occurs in the first period with progressive stabilization at longer periods.

NOTE 2 A minimum time period of 24 h is recommended. However, a shorter period may be adopted depending on the purpose of the test. Nevertheless, the time period in a set of tests should be consistent.

NOTE 3 If relevant parties agree, surface finishes different from the above recommendation may apply as far as they are reproducible.

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

5.3 Preparation of solution

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

5.3.2 The test solution should reflect the intended application; otherwise 1 M (k mol m^{-3}) sodium chloride aqueous solution may be used.

NOTE The recommended test solution of 1 M sodium chloride aqueous solution can be prepared by dissolving 58,44 g of reagent-grade sodium chloride into 1 000 mL of distilled or ion-exchange water.

5.4 Setting up test

5.4.1 The exposed surface area of the test specimen shall be measured.

5.4.2 The standard temperature of the test solution shall be (30 ± 1) °C.

The tests may be performed at a different temperature depending on the purpose, but the same temperature for a particular set of tests shall be applied.

5.4.3 For anodic polarization, completely immerse the test surface area in the de-aerated test solution; leave it to stand there to stabilize temperature and corrosion potential for at least 1 min. Then, start potential sweeping at the rate of 10 mV/min from corrosion potential until the anodic current density reaches more than 500 μA/cm^2 and less than 1 000 μA/cm^2. In case statistical analysis of the potential data was intended, the sweep rate of 20 mV/min may be used. If these sweep rates are not available by reason of the apparatus or other, a sweep rate close to it may be used.

Regardless of the type of test assembly (see Annex A), deaeration of the solution shall be undertaken prior to immersion. A deaeration period of 1 h per litre of test solution is usually sufficient at typical gas flow rates of 0,1 L/min of e.g. N_2 or Ar.

5.4.4 The pitting potential shall be expressed by the value of the potential for which pitting becomes stable; i.e. current density increases continuously with potential as shown in Figure 1. The pitting potential is defined as the potential corresponding to the anodic current density of 10 μA/cm^2 or 100 μA/cm^2 of the stable pitting region. The pitting potentials shall be denoted as V'_{C10} or V'_{C100}, respectively. Figure 1 shows an example of the measurement.

5.4.5 For each test, use a fresh specimen and a fresh test solution.

5.5 Recording

The value of pitting potential measurement shall be recorded in volts (V), down to three decimal places. Also, the sweep rate and grinding condition prior to the test, the reference electrode, time elapsed between grinding and immersion, and the test temperature shall be noted (see Clause 7).

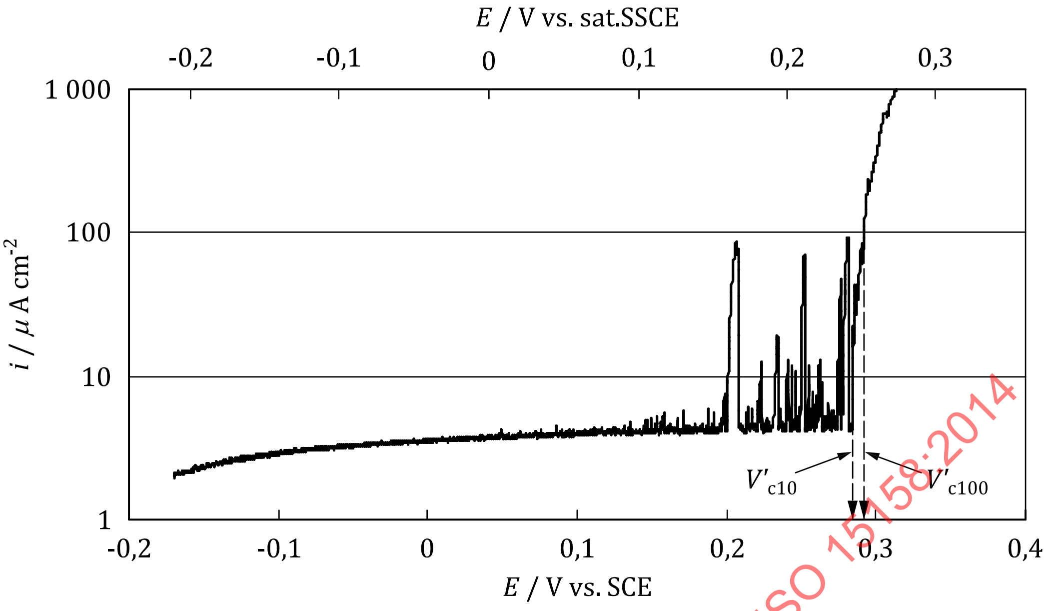


Figure 1 — Example of anodic polarization curve of 4301-304-00-I stainless steel at 30 °C with respect to potential *E* and current density *i*, where the test was performed in deaerated 1 M NaCl solution with sweep rate of 10 mV/min, just after dry grinding followed by cleaning

5.6 Ending test

5.6.1 The test shall be terminated when the pitting potential has been determined.

5.6.2 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.

5.6.3 Using a magnifier with a capacity of 20 times or more, observation of the measured specimen shall be conducted, to confirm the pitting occurred, and to ensure any crevice corrosion had not occurred. If corroded crevice is found, exclude this test from the results.

6 Statistical analysis of pitting potential data

6.1 Pitting corrosion of stainless steels shows statistical nature, thus the number of experiments for a given condition should be considered among relevant parties to obtain the reliable average and standard deviation values. At least two experiments for a condition are required for statistical analysis. Since the total area of the specimen is one of factors in determining the probability of finding the weakest site, the number of repeats should reflect the specimen area. For the 1 cm^2 area as recommended in this International Standard, five repeats or more are recommended.

6.2 The average value of pitting potential data shall be calculated. To show results for a condition, an example of statistical analysis of pitting potentials is shown in Annex B. For more details on statistical analyses, the literature[5] in the Bibliography can be consulted.

7 Test report

The test report shall include the following information:

a) reference to this International Standard, i.e. ISO 15158:2014;

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

c) orientation, geometry and size of test specimens;

d) surface finish of specimen including the storage time between carrying out the final surface finish and testing;

e) test area of specimen;

f) type of test cell, type of reference electrode, specimen holder and volume of test solution;

g) test environment in terms of chloride concentration, temperature, pH, the kind and purity of gas inserted in the test solution, and gas specification regarding remained oxygen if necessary;

h) corrosion potential, and sweep rate;

i) description of the specimen surface after testing, magnification used for checking pitting and crevice corrosion under microscope;

j) pitting potential data to an accuracy of 1 mV expressed with respect to the standard hydrogen electrode, preferably statistical analysis, and typical polarization curves in the original.

Annex A
(informative)

Specimen holder

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

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

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

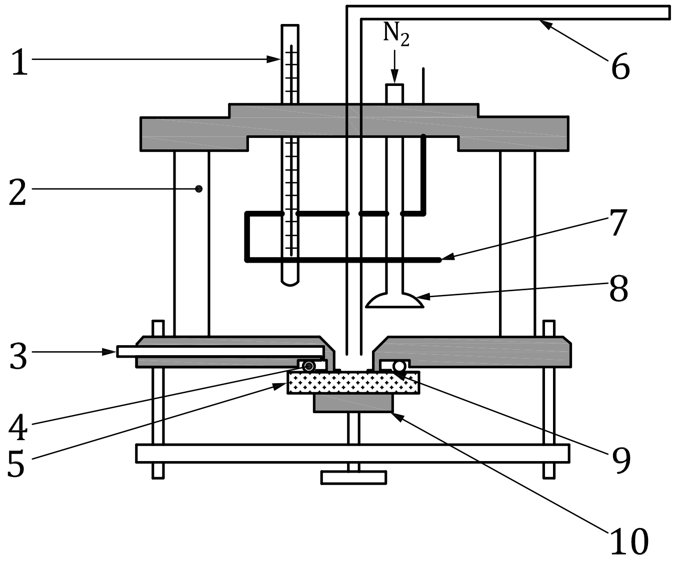
A.1.3 The key feature of the cell is the seal between the specimen and the cell. The specimen holder is incorporated in the base of the cell, with the specimen mounted outside the cell. Elimination of crevice corrosion at the contact point between the specimen and the cell is achieved by continuously 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 $1,1 \times 10^{-6}$ L/s to $1,4 \times 10^{-6}$ L/s for a 1 cm^2 port opening.

A.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.

A.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.

A.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.

A.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 minimizing the area of the specimen that is external to the cell.



Key

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

Figure A.1 — Design principles of the flushed port cell

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

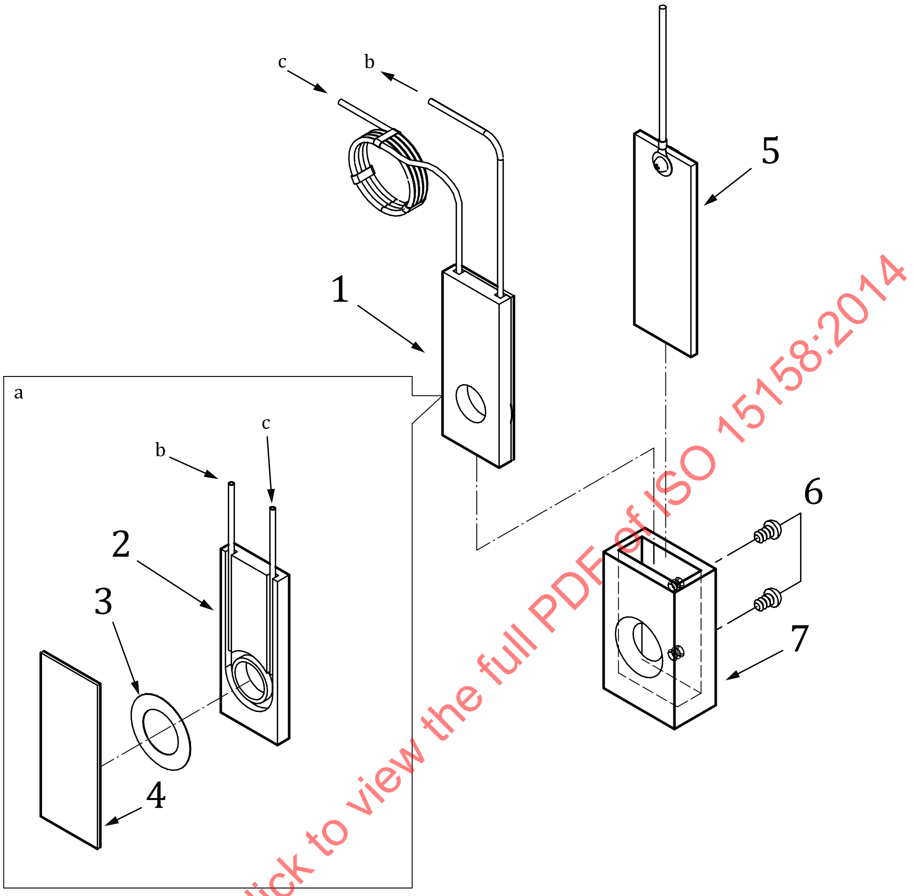
A.2.1 The electrode holder system is designed to prevent crevice corrosion by inserting filter paper between the rubber gasket and the electrode surface and flushed with high purity water coming through fine PTFE tube by siphon from the outside storage flask.

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

A.2.3 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 the test solution temperature.

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

A.2.5 The flow rate of high purity water through the PTFE tube is usually controlled at around 2,8 × 10^{-5} L/s and the flushing rate through filter paper is approximately 2 % to 6 % of the water flow, as an example, 8,3 × 10^{-7} L/s.



Key

1	fluoro-rubber gasket
2	fluoro-rubber gasket
3	filter paper
4	specimen
5	support plate
6	acrylic resin screws
7	acrylic resin holder
a	Reverse side.
b	H_2O outlet.
c	H_2O inlet.

Figure A.2 — Flushed electrode holder for plate specimen

A.3 The specimen electrode avoiding crevice corrosion

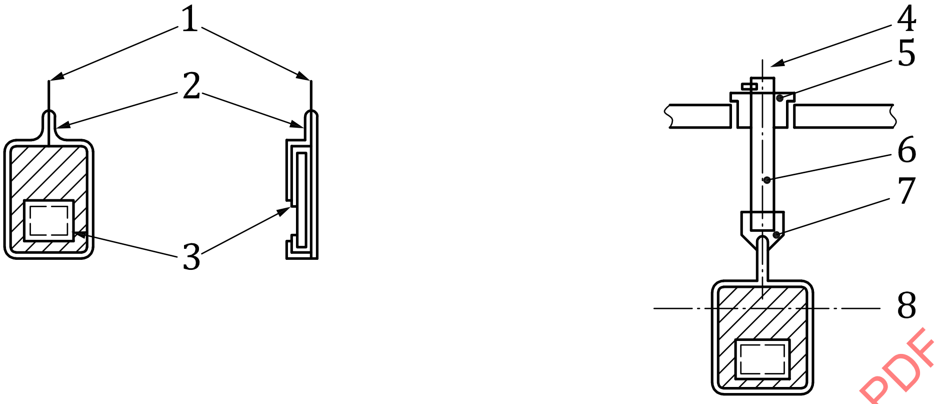
A.3.1 The test area of the specimen electrode should be preferably passivated (by immersion in nitric acid solution, mass fraction of 20 % to 30 %, at 50 °C, for not less than 1 h) to prevent the occurrence of crevice corrosion.

A.3.2 The leads shall be soldered or spot-welded to one end of the specimen.

A.3.3 For insulation of the specimen, a final 11 mm × 11 mm area of the specimen unaffected by soldering or spot-welding shall be left exposed, while the remaining area of the specimen and the leads shall be covered with epoxy resin, vinyl resin, silicone resin, or other insulator, either laid over or laid to fill up the surface.

A.3.4 Examples of specimen electrodes are shown in Figure A.3. The area surrounded by the dotted line is ground. The area underneath the insulator is kept passivated to avoid crevice corrosion.

A.3.5 The test area of the specimen thus prepared shall be considered 1 cm^2.



a)

b)

Key

1 lead wire
2 insulative sealing paint
3 passive film
4 lead wire
5 rubber cap
6 resin tube
7 resin seal
8 immersion line

Figure A.3 — An example of the specimen electrode