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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

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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.

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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.

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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[1] and ASTM G150[2], defines basic guidelines for potentiostatic potentiodynamic polarization measurements to characterize an electrochemical kinetics of anodic and cathodic reactions.

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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_{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.
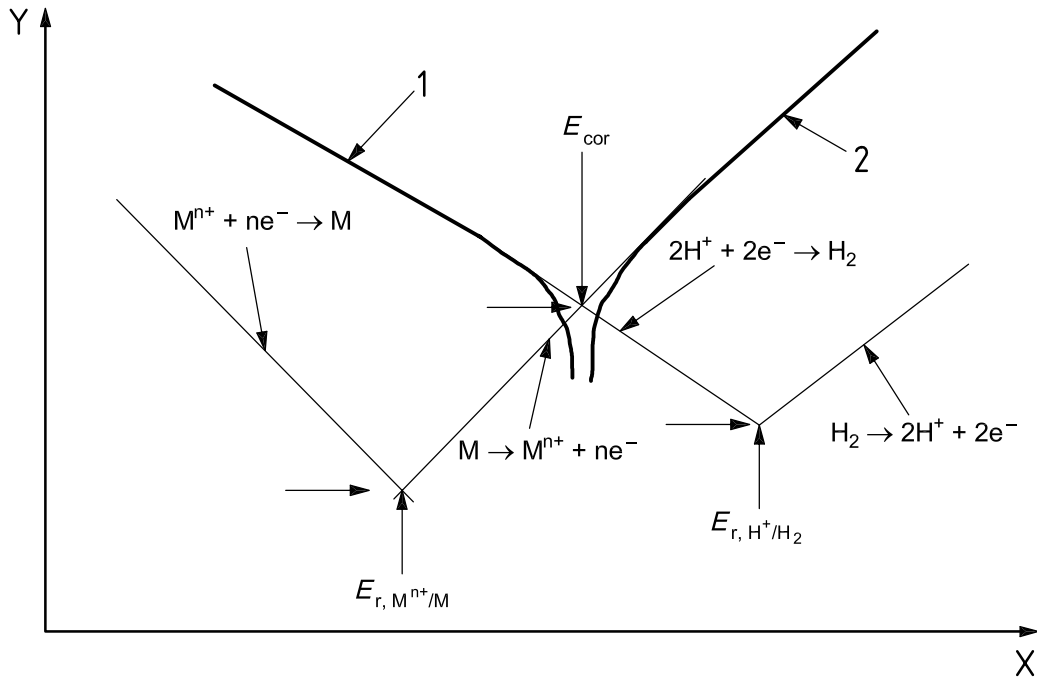
a) **Corrosion rate is under diffusion control**
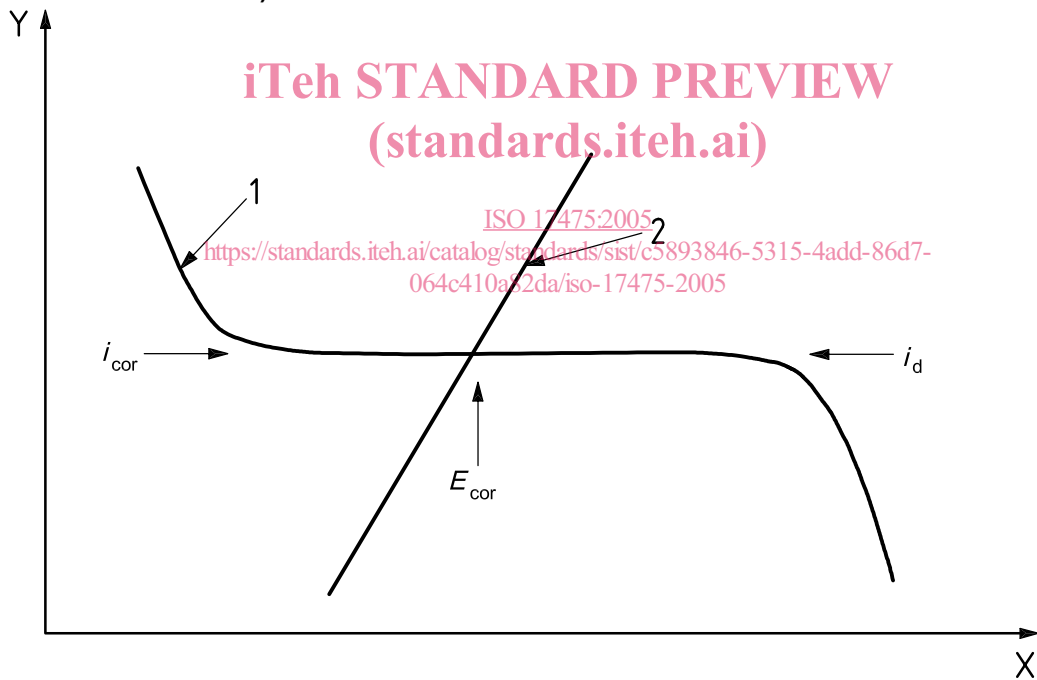
b) **Example by diffusion of oxygen in water**

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
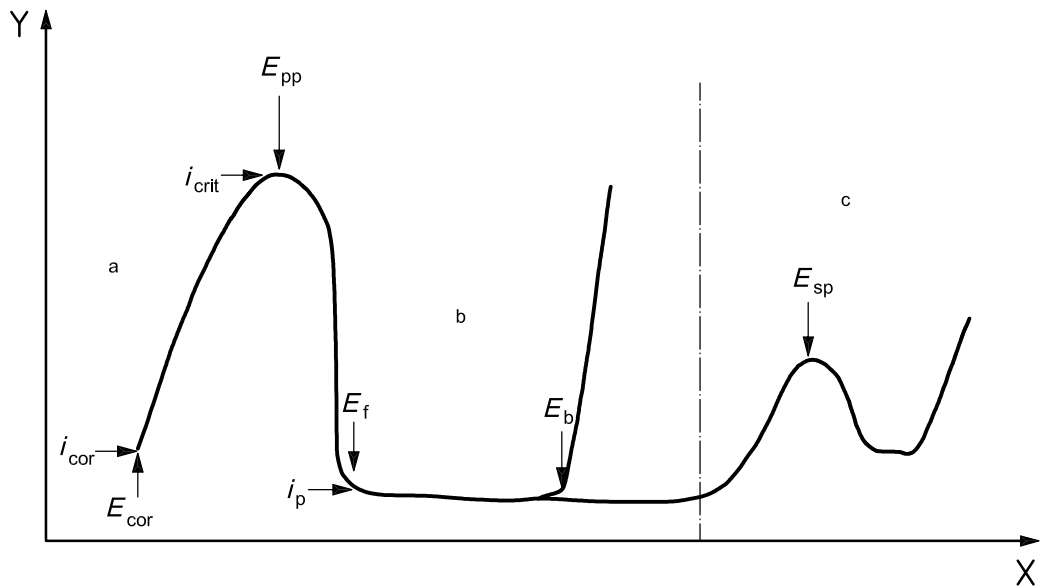
a) Metals with active-passive transition
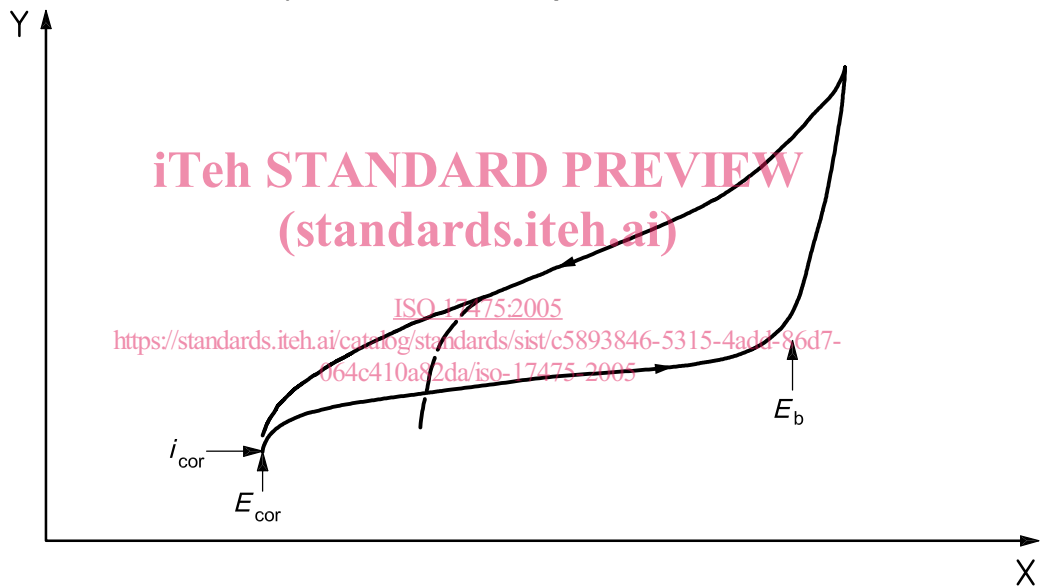
b) Metals without active-passive transition

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.
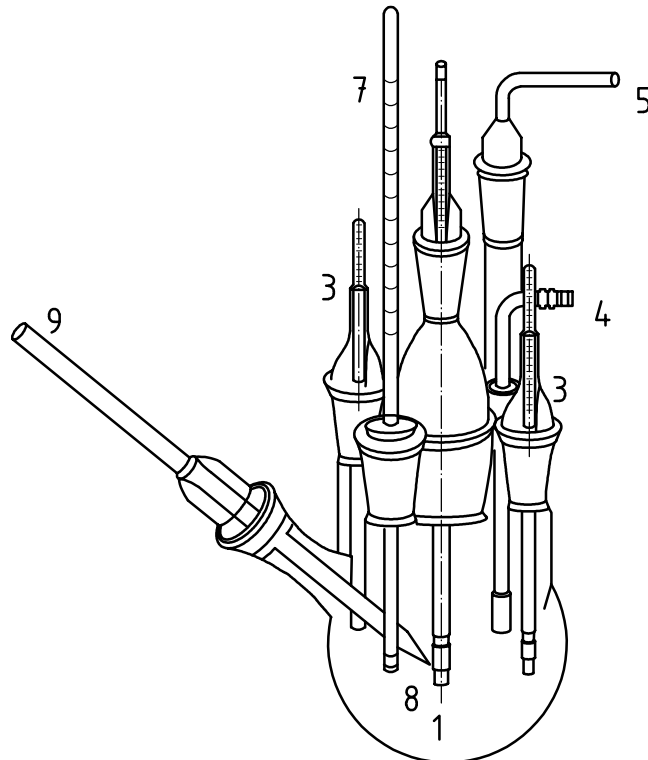
a) Auxiliary electrode included in the main cell
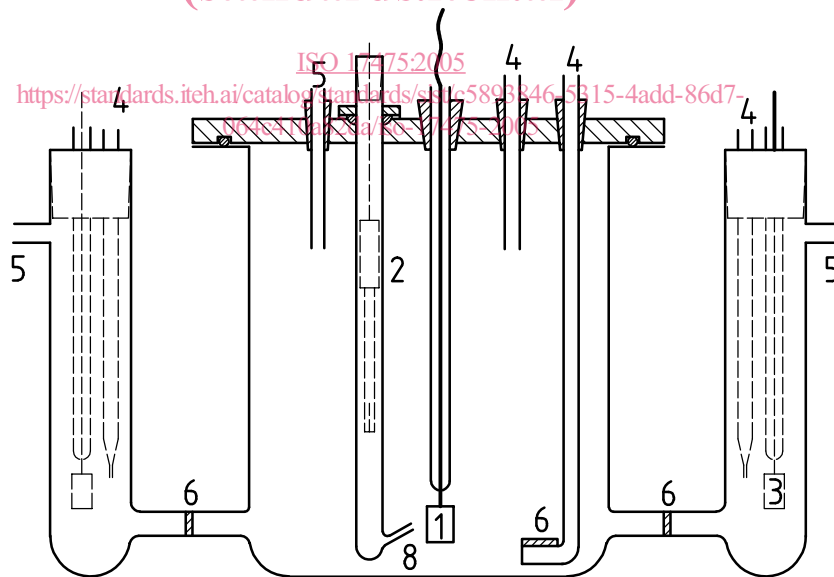
b) Auxiliary electrode separated from the main cell

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