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Method of measurement of hydrogen permeation and determination of hydrogen uptake and transport in metals by an electrochemical technique

Méthode de mesure de la perméation de l'hydrogène et détermination de l'absorption d'hydrogène et de son transport dans les métaux à l'aide d'une technique électrochimique

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Foreword

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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).

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

This second edition cancels and replaces the first edition (ISO 17081:2004), of which it constitutes a minor revision. Figure 1 has been corrected and Figure 2 made language independent.

Method of measurement of hydrogen permeation and determination of hydrogen uptake and transport in metals by an electrochemical technique

1 Scope

1.1 This International Standard specifies a laboratory method for the measurement of hydrogen permeation and for the determination of hydrogen atom uptake and transport in metals, using an electrochemical technique. The term "metal" as used in this International Standard includes alloys.

1.2 This International Standard describes a method for evaluating hydrogen uptake in metals, based on measurement of steady-state hydrogen flux. It also describes a method for determining effective diffusivity of hydrogen atoms in a metal and for distinguishing reversible and irreversible trapping.

1.3 This International Standard gives requirements for the preparation of specimens, control and monitoring of the environmental variables, test procedures and analysis of results.

1.4 This International Standard may be applied, in principle, to all metals for which hydrogen permeation is measurable and the method can be used to rank the relative aggressivity of different environments in terms of the hydrogen uptake of the exposed metal.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 17475, *Corrosion of metals and alloys — Electrochemical test methods — Guidelines for conducting potentiostatic and potentiodynamic polarization measurements*

3 Terms and definitions

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

3.1
charging
method of introducing atomic hydrogen into the metal by exposure to an aqueous environment under galvanostatic control (constant charging current), potentiostatic control (constant electrode potential), free corrosion or by gaseous exposure

3.2
charging cell
compartment in which hydrogen atoms are generated on the sample surface, including both aqueous and gaseous charging

3.3
decay current
decay of the hydrogen atom oxidation current, after attainment of steady state, following a decrease in charging current

3.4
Fick's second law
second-order differential equation describing, in this case, the concentration of atomic hydrogen in the sample as a function of position and time

Note 1 to entry: The equation is of the form $\partial C(x,t)/t = D\partial^2 C(x,t)/\partial x^2$ for lattice diffusion in one dimension where diffusivity is independent of concentration. See Table 1 for an explanation of the symbols.

3.5
hydrogen flux
amount of hydrogen passing through the metal sample per unit area per unit time

3.6
hydrogen uptake
atomic hydrogen absorbed into the metal as a result of charging

3.7
irreversible trap
microstructural site at which the residence time for a hydrogen atom is infinite or extremely long compared to the time-scale for permeation testing at the relevant temperature

3.8
mobile hydrogen atoms
hydrogen atoms in interstitial sites in the lattice (lattice sites) and reversible trap sites

3.9
oxidation cell
compartment in which hydrogen atoms exiting from the metal sample are oxidized

3.10
permeation current
current measured in oxidation cell associated with oxidation of hydrogen atoms

3.11
permeation flux
hydrogen flux exiting the test sample in the oxidation cell

3.12
permeation transient
variation of the permeation current with time, from commencement of charging to the attainment of steady state, or modification of charging conditions

3.13
recombination poison
chemical within the test environment in the charging cell which enhances hydrogen absorption by retarding the recombination of hydrogen atoms on the metal surface

3.14
reversible trap
microstructural site at which the residence time for a hydrogen atom is greater than that for the lattice site but is small in relation to the time to attain steady-state permeation

4   Symbols

Table 1 gives a list of symbols and their designations.

Table 1 — Symbols and their designations and units

Symbol	Designation	Unit
A	Exposed area of sample in the oxidation cell	m^2
$C(x, t)$	Lattice concentration of hydrogen as a function of position and time	$mol \cdot m^{-3}$
C_0	Sub-surface concentration of atomic hydrogen in interstitial lattice sites on the charging side of the sample	$mol \cdot m^{-3}$
C_{0R}	Summation of the sub-surface concentration of hydrogen in interstitial lattice sites and reversible trap sites on the charging side of the sample	$mol \cdot m^{-3}$
D_l	Lattice diffusion coefficient of atomic hydrogen	$m^2 \cdot s^{-1}$
D_{eff}	Effective diffusion coefficient of atomic hydrogen based on elapsed time corresponding to $J(t)/J_{ss} = 0{,}63$	$m^2 \cdot s^{-1}$
F	Faraday's constant ($F = 96\ 485\ C \cdot mol^{-1}$)	$C \cdot mol^{-1}$
$J(t)$	Time-dependent atomic hydrogen permeation flux as measured on the oxidation side of the sample	$mol \cdot m^{-2}\ s^{-1}$
J_{ss}	Atomic hydrogen permeation flux at steady-state as measured on the oxidation side of the sample	$mol \cdot m^{-2}\ s^{-1}$
$J(t)/J_{ss}$	Normalized flux of atomic hydrogen	1
$I(t)$	Time-dependent atomic hydrogen permeation current	$A \cdot m^{-2}$
I_{ss}	Steady-state atomic hydrogen permeation current	$A \cdot m^{-2}$
L	Sample thickness	m
t	Time elapsed from commencement of hydrogen charging	s
t_b	Elapsed time measured by extrapolating the linear portion of the rising permeation current transient	s
t_{lag}	Time to achieve a value of $J(t)/J_{ss} = 0{,}63$	s
x	Distance in sample measured in the thickness direction	m
τ	Normalized time ($D_l t/L^2$)	1
τ_{lag}	Normalized time to achieve a value of $J(t)/J_{ss} = 0{,}63$	1

5 Principle

5.1 The technique involves locating the metal sample of interest between the charging and oxidation cells, where the charging cell contains the environment of interest. Hydrogen atoms are generated on the sample surface exposed to this environment.

5.2 In gaseous environments, the hydrogen atoms are generated by adsorption and dissociation of the gaseous species. In aqueous environments, hydrogen atoms are produced by electrochemical reactions. In both cases, some of the hydrogen atoms diffuse through the metal sample and are then oxidized to hydrogen cations on exiting from the other side of the metal in the oxidation cell.

A palladium coating is sometimes applied to one or both sides of the membrane following initial removal of oxide films. A palladium coating on the charging face of the membrane affects the sub-surface hydrogen concentration in the substrate and the measured permeation current. It is important to verify that the calculated diffusivity is not influenced by the coating. Palladium coating is particularly useful for gaseous charging.

5.3 The environment and the electrode potential on the oxidation side of the membrane are selected so that the metal is either passive or immune to corrosion. The background current established prior to hydrogen transport is steady, and small compared to the hydrogen atom oxidation current.

5.4 The electrode potential of the sample in the oxidation cell is controlled at a value sufficiently positive to ensure that the kinetics of oxidation of hydrogen atoms are limited by the flux of hydrogen atoms, i.e. the hydrogen atom oxidation current density is transport limited.

NOTE   Palladium coating of the oxidation side of the sample can enhance the rate of oxidation and thereby enable attainment of transport-limited oxidation of hydrogen atoms at less positive potentials than for the uncoated sample.

5.5 The oxidation current is monitored as a function of time. The total oxidation current comprises the background current and the permeation current.

5.6 The thickness of the sample, L, is usually selected to ensure that the measured flux reflects volume (bulk) controlled hydrogen atom transport.

NOTE   Thin specimens may be used for evaluation of the effect of surface processes on hydrogen entry (absorption kinetics or transport in oxide films).

5.7 In reasonably pure metals with a sufficiently low density of microstructural trap sites, atomic hydrogen transport through the material is controlled by lattice diffusion.

5.8 The effect of alloying and of microstructural features such as dislocations, grain boundaries, inclusions, and precipitate particles is to introduce traps for hydrogen atoms, which retard hydrogen transport.

The rate of hydrogen atom transport through the metal during a first permeation test can be affected by both irreversible and reversible trapping. At steady-state, all of the irreversible traps are occupied. If the mobile hydrogen atoms are then removed and a subsequent permeation test conducted on the sample, the difference between the first and second permeation transients may be used to evaluate the influence of irreversible trapping on transport.

For some environments the conditions on the charging side of the sample may be suitably altered to induce a decay of the oxidation current after attainment of steady-state. The rate of decay is determined by diffusion and reversible trapping only and hence can also be used to evaluate the effect of irreversible trapping on transport during the first transient.

NOTE 1   Reversible and irreversible traps can both be present in a particular metal.

NOTE 2   Comparison of repeated permeation transients with those obtained for the pure metal can be used, in principle, to evaluate the effect of reversible trapping on atomic hydrogen transport.

NOTE 3   The technique is suitable for systems in which hydrogen atoms are generated uniformly over the charging surface of the sample. It is not usually applicable to corroding systems in which pitting attack occurs, unless the charging cell environment is designed to simulate the localized pit environment and the entire metal surface is active.

5.9 The method may be used for stressed and unstressed samples but testing of stressed samples requires loading procedures to be taken into consideration.

6   Samples

6.1   Dimensions

Samples shall be in the form of plate or pipe. The dimensions shall be such as to enable analysis of the permeation transient based on one-dimensional diffusion, e.g. for plates with a circular exposed area, the radius exposed to the solution should be sufficiently large relative to thickness.

A ratio of radius to thickness of 10:1 or greater is recommended. This condition may be made less stringent if the exposed area on the oxidation side is smaller than that on the charging side. A ratio of

radius to thickness of 5:1 or greater is recommended if the radius of the exposed area on the oxidation side is reduced to 90 % of the area of the charging side.

For pipes, the ratio of the outer radius to the inner radius shall be less than 1,1:1 if the experimental results are to be analysed based on planar one-dimensional diffusion.

6.2 Preparation

6.2.1 As hydrogen atom permeation can be influenced by microstructural orientation, the form of the original material shall be recorded (e.g. bar) as well as the location and orientation of the sample relative to that of the original material (see Clause 12).

6.2.2 Samples shall be prepared using one of the following methods:

a) electrochemical discharge machining (EDM) plus final machining;

b) mechanical cutting.

EDM is particularly useful for preparing thin sheets of material but can introduce hydrogen into the metal. Although hydrogen atoms dissolved in lattice sites or reversible trap sites are gradually lost subsequent to EDM, hydrogen atoms can be retained in irreversible trap sites. The amount of hydrogen generated and the extent of ingress into the metal depend on the details of the EDM process and the material characteristics but sufficient material should be removed by subsequent machining to ensure that all residual hydrogen atoms are removed.

NOTE 1 Careful consideration should be given to the method of manufacture of sheet samples.

NOTE 2 The preferred method for the preparation of thin sheets of material is fine mechanical cutting.

6.2.3 Sheet samples shall be machined to the required thickness. Care shall be taken in machining to minimize surface damage.

6.2.4 The thickness of the sample in the region of interest shall be as uniform as possible with a maximum variation no greater than ± 5 %.

6.2.5 The oxidation side of the sample shall be mechanically ground or polished to a repeatable finish. The charging side may be similarly treated or used as for an intended service application.

NOTE Electropolishing of samples may also be employed in appropriate cases.

6.2.6 After polishing, traces of polishing chemicals shall be removed by an appropriate cleaning procedure.

NOTE Rinsing with distilled water, followed by alcohol and a non-chlorinated solvent, is adequate for most cases.

6.2.7 The final thickness shall be measured in at least five locations in the exposed region of the membrane. The sample shall then be degreased and the specimen stored in a dry environment.

Palladium coating of the sample may be undertaken at this stage. Electrochemical methods of forming the coating can introduce hydrogen atoms into the material and can influence the subsequent permeation measurements. Argon etching of the surface followed by sputter coating with palladium can avoid this problem.

6.2.8 A suitable electrical connection shall be made to the sample remote from the active areas.

6.2.9   The sample shall be uniquely identified. Stamping or scribing on the sample remote from the active areas is recommended.

7   Apparatus

Two-compartmental environmental cell consisting of separate charging and oxidation cells (e.g. as shown in Figure 1) constructed from inert materials, with reference electrodes and auxiliary electrodes (usually platinum).

Sealed oxidation cells, in which an additional membrane (usually palladium) is clamped against the test sample and the flux exiting this additional membrane is measured, may be used provided that it is demonstrated that the introduction of this additional interface has no effect on the calculated diffusivity.

A Luggin capillary should be used for more accurate measurement of potential where the current is large. In order to avoid shielding effects, the tip of the Luggin should be no closer to the surface than twice the diameter of the tip. Typically the distance is 2 mm to 3 mm.

Non-metallic materials are recommended for cell construction.

At temperatures above 50 °C leaching from the cell material (e.g. silica dissolution from glass) can modify the solution chemistry and may influence hydrogen permeation. Polytetrafluoroethylene is an example of a suitable material for elevated temperatures up to about 90 °C.

Where metallic chambers are necessary, the materials chosen shall have a very low passive current to ensure minimal effect on the solution composition, and shall be electrically isolated from the membrane.

When testing at elevated temperatures the O-ring material shall be selected to minimize possible degradation products from the seals and contamination of the solution.

The choice of reference electrode depends on the particular exposure conditions. Saturated calomel electrodes (SCE) or silver/silver chloride electrodes are often used, although use of the former is no longer permitted in some countries because of environmental concerns. The chloride concentration in the latter shall be specified. The solution contained in the reference electrode shall not contaminate the test solution.
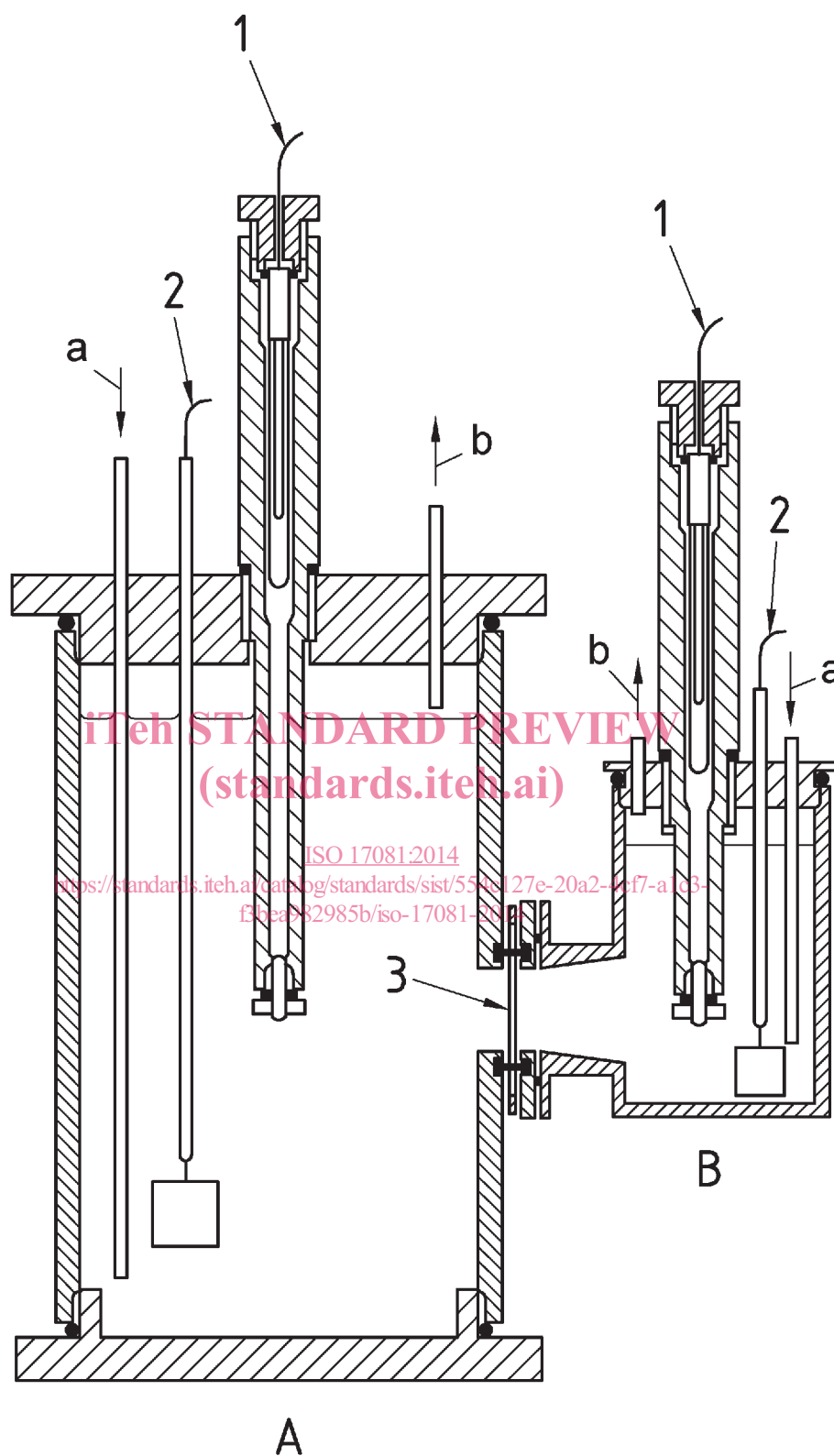
Key

A	charging cell	1	reference electrode	a	Gas in.
B	oxidation cell	2	counter electrode	b	Gas out.
		3	test sample		

Figure 1 — Hydrogen permeation cell (constructed of polytetrafluoroethylene) with double junction electrodes