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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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Contents

Page

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 17081 was prepared by Technical Committee ISO/TC 156, *Corrosion of metals and alloys*.

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 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 17475:—1), *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

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1) To be published.

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 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·m^{-3}
C_0	Sub-surface concentration of atomic hydrogen in interstitial lattice sites on the charging side of the sample	mol·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·m^{-3}
D_l	Lattice diffusion coefficient of atomic hydrogen	m^2·s^{-1};
D_{eff}	Effective diffusion coefficient of atomic hydrogen based on elapsed time corresponding to $J(t)/J_{ss} =$ 0,63	m^2·s^{-1};
F	Faraday's constant ($F =$ 96 485 C·mol^{-1})	C·mol^{-1}
$J(t)$	Time-dependent atomic hydrogen permeation flux as measured on the oxidation side of the sample	mol·m^{-2} s^{-1}
J_{ss}	Atomic hydrogen permeation flux at steady-state as measured on the oxidation side of the sample	mol·m^{-2} s^{-1}
$J(t)/J_{ss}$	Normalized flux of atomic hydrogen	1
$I(t)$	Time-dependent atomic hydrogen permeation current	A·m^{-2}
I_{ss}	Steady-state atomic hydrogen permeation current	A·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 depends 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.

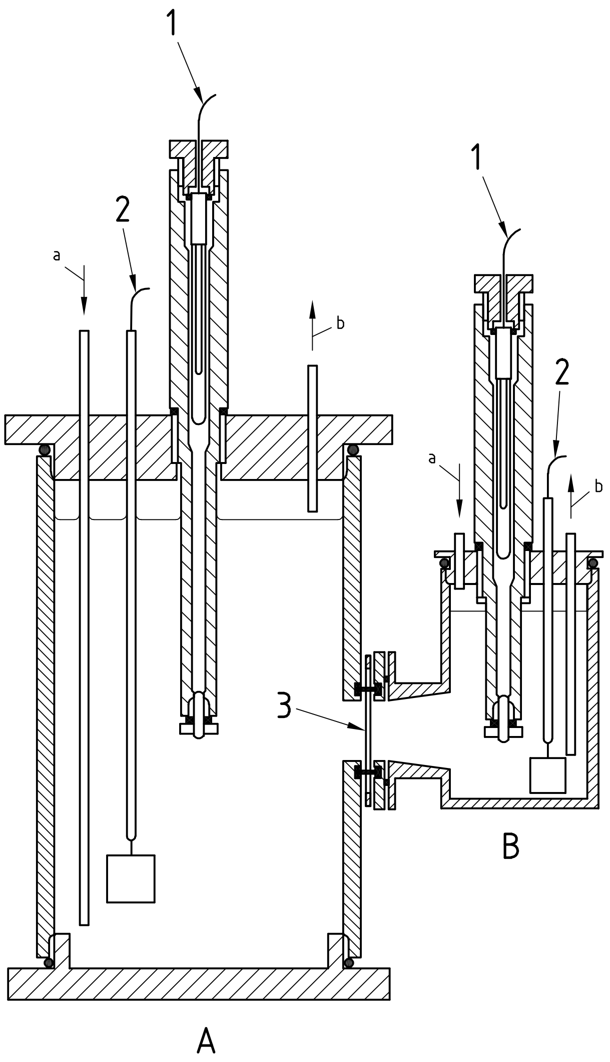
6.2.9 The sample shall be uniquely identified. Stamping or scribing on the sample remote from the active areas is recommended.

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.



Key

A	charging cell
B	oxidation cell
1	reference electrode
2	counter electrode
3	test sample

[a] Gas in.

[b] Gas out.

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

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.

Contamination may be avoided by the use of double junction reference electrodes or by remote monitoring using a solution conductivity bridge arrangement with inert materials.

A standard resistor and a digital voltmeter should be used for recording of oxidation current (and, as appropriate, charging current), or a current monitoring device used for direct measurement, all traceable to appropriate national standards and calibrated on a regular basis, typically once per year. The resistor should be positioned in series in the auxiliary electrode line.

The potentiostats used for each cell shall be configured such that they do not have a common earth.

8 Test environment considerations

8.1 The test environment shall be chosen on the basis of one of the following criteria:

a) relevance to the intended service application;

b) ease and reliability of measurement.

NOTE Suggestions for suitable systems for item b) are given in Annex A.

8.2 The environments in the oxidation cell and in the charging cell shall be of sufficient purity for the intended purpose.

8.3 The environment in the oxidation cell shall be prepared using analytical grade chemicals and distilled or deionized water of purity sufficient to avoid unintentional contamination.

8.4 Where the environment in the charging cell is aqueous, the solution shall be either that directly used in service or a laboratory environment prepared with the purity as indicated in 8.3. Gaseous environments shall simulate those for the intended applications.

In some cases for which higher purity of the charging solution is desirable, the solution may be prepared by using appropriate high purity analytical grade chemicals or by pre-electrolysis. Pre-electrolysis may be used to remove certain cationic contaminants by cathodic deposition and usually involves applying a voltage difference between two platinum electrodes in the solution of interest. The area of the cathode should be as large as is reasonable in order to enhance the rate of removal of contaminants.

8.5 The ratio of volume of solution (in millilitres) to metal area (in square centimetres) in the oxidation chamber shall be greater than 20:1.

NOTE A large volume of solution in the oxidation chamber is not necessary as the extent of the reaction is usually relatively small.

8.6 The solution composition in the charging cell shall be maintained constant during the experiment.

The volume of solution in the charging cell depends on the particular choice of environment and the extent of reaction on the specimen. Recombination poisons added to enhance hydrogen entry may be consumed with time. A recirculation system may be necessary in some cases.

NOTE Variations in the pH of the charging solution during a permeation transient can influence the form of the transient, even under constant charging current, because of its influence on surface films.

8.7 Where solution flow is relevant to the intended service application, those flow conditions shall be simulated. In all other cases, testing shall be conducted to enable repeatable conditions whether using stirrers, vigorous purging or slow bubbling.

NOTE Flow of solution in the charging cell can affect the local environment at the surface in some cases.

8.8 The electrode potential of the sample exposed to the oxidation compartment shall be chosen to ensure bulk transport-limited kinetics for oxidation of hydrogen atoms (see 9.12).

8.9 In aqueous solutions the exposure conditions on the charging side of the membrane shall be chosen to represent a particular service application involving corroding conditions, or the conditions shall be selected to maintain constant sub-surface hydrogen concentration.

For characterization of hydrogen transport in the bulk of the material, galvanostatic charging is preferred. For reliable measurement, only minor changes in potential during testing should occur. Significant variations in potential usually indicate a changing surface state and unsteady boundary conditions which can render uncertain the interpretation of the permeation transients.

Potentiostatic charging may also be used provided there are no significant variations in the current.

NOTE Variations immediately following exposure do not necessarily have an important influence on the permeation transient provided the duration is short compared to the overall time of the transient.

8.10 The location of the reference electrode in each compartment shall ensure minimal potential drop between the test sample and the reference electrode (see Clause 7).

8.11 As the temperature of the solution can have a significant effect on hydrogen permeation, the temperature of the solutions in charging and oxidation cells shall be the same and shall be maintained constant to ± 0,5 °C for the period of the experiment. Any variation shall be recorded (see Clause 12).

NOTE This can be achieved using a temperature-controlled room or, in the case of small cells, by immersing the two-compartment cell in a thermostat bath. In the latter case, where the charging compartment is refreshed continuously from a reservoir using a recirculation system, it is necessary for the temperature of the solution in the reservoir to be controlled carefully in order to minimize temperature gradients across the test sample.

9 Test procedure

9.1 Prepare the test sample to the required surface finish and measure the thickness.

9.2 Prepare the solutions and carry out pre-electrolysis where further purification is required (see second paragraph of 8.4).

9.3 Measure the pH of the solutions where appropriate (see 10.1).

9.4 Verify the accuracy of the reference electrodes to 3 mV against two other reference electrodes (see ISO 17475).

The choice of reference electrode is optional but the electrode environment and concentration should be defined.

9.5 Construct the two-compartment cell, using seals as appropriate.

9.6 Add the solution for the oxidation cell to the relevant chamber and commence vigorous purging with a suitable gas to deaerate the solution quickly, if not deaerated previously. Set the potential to the control value.

NOTE A potential of + 544 mV vs SHE is typical for several metals exposed to 0,1 mol/l NaOH (see 9.10). The magnitude of the oxidation (passive) current depends on the system but values lower than 0,1 μA cm^{-2} are usually readily attainable.

9.7 Once the oxidation current has achieved a steady, low value, add the environment to the charging cell.

In some cases, aqueous solution may be added to the charging cell prior to establishment of the steady-state oxidation current provided that exposure does not generate significant hydrogen, e.g. a passivating system with a very low passive current.

When testing at an elevated temperature, minimize the thermal shock by slowly adding the preheated solution to the charging side, as this can sometimes result in significant perturbation of the passive current in the oxidation cell.

If the charging solution is to be deaerated, either carry this out prior to addition of the solution to the charging cell or else by vigorous purging on addition of the solution to the charging cell, to remove oxygen quickly. Continue deaeration during the test.

9.8 Switch on the stirring motors, where used. For non-passivating systems, commence galvanostatic charging or potentiostatic charging on exposure of the test sample.

9.9 Monitor the total oxidation current (comprising background passive current and atomic hydrogen oxidation current) until steady state is achieved.

9.10 In order to define the control potential for the system, conduct a preliminary test, preferably under the test conditions, for which the oxidation current is largest. Increase the control potential on the oxidation side and monitor the current. If the steady current at the new potential is significantly higher, then increase the electrode potential progressively until the steady current at each potential becomes independent of potential.

An initial increase in current is obtained but for transport-limited kinetics this should subsequently decrease to a steady-state value equivalent to that obtained prior to the change in potential. The potential should not be raised too high, in order to prevent an increase in current due to oxidation of hydroxyl ions.

9.11 To distinguish the effects of irreversible and reversible trapping on hydrogen transport, reduce the charging current to zero. Allow sufficient time for hydrogen atoms in interstitial lattice sites and reversible trap sites to exit. Then repeat the charging procedure.

NOTE 1 Monitoring of the permeation current indicates when all the mobile hydrogen has been removed. If the charging current is not reduced to zero and consequently a permeation current remains, a residual concentration gradient exists and this complicates interpretation of subsequent increasing permeation transients. This consideration applies also to tests in which step increases in charging current are made (see 11.3.6). Irreversible trapping is not detected using this procedure if the traps are already full (e.g. from material processing) prior to the first permeation study.

NOTE 2 The charging current can be reduced by increasing the potential or by changing the environment.

If the intention is to analyse the decay current, the requirement for a defined boundary condition in utilizing mathematical solutions of transport equations means that the conditions on the charging side shall be such as to oxidize or recombine the hydrogen at its transport limited rate.

Repetitive permeation transients can also be generated for some systems by withdrawing the test sample after attainment of steady-state permeation and allowing the hydrogen atoms to diffuse out. Elevated temperatures may be used to accelerate removal provided there are no microstructural changes. The specimen surface may then be repolished, cleaned and the permeation procedure repeated.

9.12 Unless the thickness of the specimen represents a particular service application, repeat tests with test samples of twice the thickness of the original test sample.

NOTE With increasing thickness of specimen the significance of surface processes on the rate of transport is diminished with respect to transport through the bulk of the material. These tests indicate the relative extent to which the transport of hydrogen is controlled by transport through the bulk of the material, or by surface processes, e.g., absorption kinetics or transport through an oxide film.

9.13 Measure the final pH of the solutions, where appropriate (see 10.1).

9.14 Where significant corrosion has occurred, measure the final thickness of the sample.

9.15 Conduct replicate tests to determine the repeatability of the method of measurement.

10 Control and monitoring of test environment

10.1 In near-neutral unbuffered solutions, pH changes can occur and the pH shall be measured before and after a test.

NOTE For galvanostatic/potentiostatic cathodic polarisation tests in very acid or very alkaline solutions (0,1 mol/l), environmental variations during a test are often negligible.

10.2 For reliable interpretation of hydrogen permeation transients, the surface condition in the charging cell shall remain constant during the test.

For this reason, monitoring of the electrode potential is useful even in galvanostatic tests because it gives an indication of changing surface state. Similarly, monitoring of the current is important in potentiostatic tests.

10.3 In some applications, corrosion products or films may develop and influence hydrogen absorption. Simple analysis of the hydrogen permeation transient is then not readily possible.

10.4 For tests in which H_2S gas is bubbled through the solution, the dissolved H_2S content of the solution shall be sampled and measured. Sufficient time shall be allowed for equilibrium to be obtained prior to exposure of the test sample.

10.5 For tests using other recombination poisons, it is recommended that sampling of the charging solution be carried out before and after testing, at least once for the particular experimental conditions to determine the extent of depletion of the recombination poison, if any, during the test.

11 Analysis of results

11.1 General

Prior to analysis of both steady-state and transient permeation currents, subtract the background current, usually associated with the passive current of the oxidation cell, from the measured oxidation current.

11.2 Analysis of steady-state current

To calculate the sub-surface concentration of hydrogen in the lattice sites at the charging surface, from the steady-state permeation current, use the following equation:

$$J_{\mathrm{ss}} = \frac{I_{\mathrm{ss}}/A}{F} = \frac{D_{\mathrm{l}} C_0}{L} \qquad (1)$$

A plot of J_{ss} against reciprocal thickness should be linear for volume controlled transport although this requires that the C_0 value in the separate experiments be identical.

For highly alloyed metals and for multiphase metals, Equation (1) may be inadequate. In highly alloyed metals, the lattice diffusion coefficient may not be that of the primary element, e.g. iron in corrosion-resistant steels. In multiphase materials diffusion path tortuosity and alternative diffusion paths through the material need to be considered.

When only reversible trapping is important and the permeation transient for this case can be represented by Fick's second law, the sub-surface concentration of hydrogen atoms in lattice and reversible trap sites can be calculated from the following equation:

$$J_{\mathrm{ss}} = \frac{D_{\mathrm{eff}} C_{\mathrm{0R}}}{L} \qquad (2)$$

NOTE For some systems a peak in the transient may be observed and a steady current may not be attained. This can be due to the development of voids in the material and/or due to changes in surface film (e.g., build up of corrosion products) on the charging side of the sample.

11.3 Analysis of permeation transient

11.3.1 To calculate the effective diffusion coefficient based on the elapsed time for $J(t)/J_{\mathrm{ss}} =$ 0,63, use the following equation:

$$D_{\text{eff}} = \frac{L^2}{6t_{\text{lag}}} \tag{3}$$

A value for the effective diffusivity may also be calculated using:

$$D_{\text{eff}} = \frac{L^2}{15{,}3t_{\text{b}}} \tag{4}$$

11.3.2 The values for D_{eff} calculated by the two methods shall be in agreement if Fick's second law is applicable.

11.3.3 To verify the applicability of Fick's second law to the permeation transient, plot the permeation transient in the form of normalized flux [$J(t)/J_{\text{ss}}$] against the logarithm of normalized time τ where $J(t)$ is calculated as follows:

$$J(t) = \frac{I(t)/A}{F} \tag{5}$$

Compare the normalized permeation transient with that derived from Fick's second law which, for rising transients, is given by:

$$\frac{J(\text{t})}{J_{\text{ss}}} = 1 + \sum_{n=1}^{\infty}(-1)^n \exp(-n^2\pi^2\tau) \tag{6}$$

Sample data are given in Table 2.

Table 2 — Normalized flux as a function of normalized time based on solution of Fick's law for a rising permeation transient

τ	$J(t)/J_{\text{ss}}$
$3{,}0 \times 10^{-2}$	$1{,}57 \times 10^{-3}$
$4{,}0 \times 10^{-2}$	$1{,}09 \times 10^{-2}$
$5{,}0 \times 10^{-2}$	$3{,}40 \times 10^{-2}$
$6{,}0 \times 10^{-2}$	$7{,}14 \times 10^{-2}$
$7{,}0 \times 10^{-2}$	$1{,}20 \times 10^{-1}$
$8{,}0 \times 10^{-2}$	$1{,}75 \times 10^{-1}$
$9{,}0 \times 10^{-2}$	$2{,}34 \times 10^{-1}$
$1{,}0 \times 10^{-1}$	$2{,}93 \times 10^{-1}$
$1{,}2 \times 10^{-1}$	$4{,}06 \times 10^{-1}$
$1{,}6 \times 10^{-1}$	$5{,}91 \times 10^{-1}$
$2{,}0 \times 10^{-1}$	$7{,}23 \times 10^{-1}$
$2{,}4 \times 10^{-1}$	$8{,}13 \times 10^{-1}$
$2{,}8 \times 10^{-1}$	$8{,}74 \times 10^{-1}$
$3{,}5 \times 10^{-1}$	$9{,}37 \times 10^{-1}$
$4{,}5 \times 10^{-1}$	$9{,}76 \times 10^{-1}$
$5{,}5 \times 10^{-1}$	$9{,}91 \times 10^{-1}$
$7{,}0 \times 10^{-1}$	$9{,}98 \times 10^{-1}$
$9{,}0 \times 10^{-1}$	1,0

A summation from $n = 1$ to 6 is sufficiently accurate.

If the normalized permeation transient is steeper than predicted from Fick's second law, this indicates that trap occupancy is significant. An effective diffusion coefficient may be calculated for this case using Equation (3) but it has no theoretical basis since the steepness of the permeation transient indicates a changing effective diffusivity with time. Hence, values based on t_{lag} and t_{b} will differ. For comparative purposes it is recommended that the calculation based on t_{lag} be quoted.

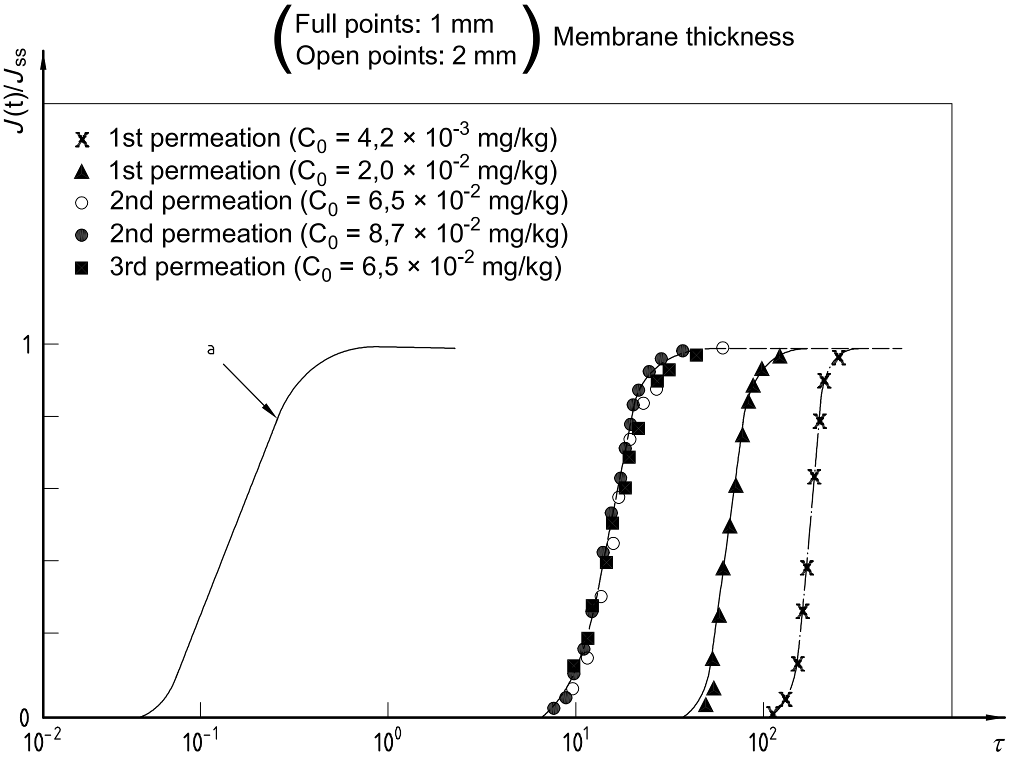
NOTE A permeation transient which is less steep than predicted from Fick's second law is often an indication of unsteady surface conditions.

When peaks in the transients are observed (see Note in 11.2), this implies the value of the effective diffusivity is also varying with time and analysis is uncertain, but Equation (3) may be used as an empirical estimate for $J(t)/J_{\text{ss}} = 0{,}63$.

11.3.4 If volume-controlled transport is of primary interest, 11.3.2 and 11.3.3 shall be repeated for a test sample with increased thickness. Consistency of values of D_{eff} for constant C_0 will confirm the dominance of volume-controlled transport.

11.3.5 To evaluate the extent of reversible and irreversible trapping, compare the first and second permeation transients.

If the first permeation transient takes longer than the second permeation transient, i.e., the normalized permeation curves are displaced to longer times (see Figure 2), it can be deduced that irreversible traps exist and affect permeation.



[a] Lattice diffusion.

NOTE Results show irreversible trapping (first transient) and dependency on charging conditions (C_0 value). Note the time delay and steepening of the curves relative to lattice diffusion (Fick's second law), the similarity of the second and third transients and the independence of thickness.

Figure 2 — Rising permeation transients for BS 970 410S21 (EN 10088-3) stainless steel in acidified NaCl at 77 °C

11.3.6 In the absence of void formation, second and subsequent transients shall concur provided the C_0 values are similar.

NOTE Analysis of second and subsequent transients which are steeper than predicted by Fick's second law can be carried out to quantify the binding energy and the density of reversible trap sites. However, the analysis is non-trivial and involves numerical solution of mass conservation equations incorporating diffusion and reversible trapping with the trap occupancy term incorporated.

Analysis of first permeation transients which are steeper than Fick's second law should account for both reversible and irreversible traps and this also necessitates numerical analysis.

In analysing the results from step-charging experiments the initial hydrogen flux shall be accounted for (a simple subtraction may not be valid).

12 Test report

The test report shall include the following information:

a) reference to this International Standard, i.e., ISO 17081;

b) test material characterization in terms of specification, product form, chemical composition and heat treatment;

c) orientation and location of the test sample relative to parent product;

d) method of sample preparation;

e) average thickness of sample and exposed area in charging and oxidation cells and average thickness of sample after test, if changed.

   If the distribution of the thickness (see 6.2.4 and 6.2.7) is outside the recommended range, the individual measured values should be reported.

f) description of the environment chamber and the volume of solution in the charging and oxidation cells; for gaseous charging, the pressure of the gas in the charging compartment and the purity of the gas;

g) initial solution composition and purity of solvent and chemicals in both compartments, the degree of aeration, flow conditions, temperature, pH where appropriate (see 10.1) and final values of these variables; for tests in aqueous solutions containing H_2S, the initial and final concentrations;

h) controlling electrode potential in the oxidation cell in terms of a standard electrode (standard hydrogen electrode); the potential may be quoted in terms of the other reference electrode types such as saturated calomel electrode (SCE) or silver/silver chloride at 25 °C provided the electrode solution and concentration are specified;

i) electrochemical conditions in the charging cell and any variation during the test, e.g., significant variation in electrode potential during galvanostatic charging;

j) method of obtaining repeat transients;

k) appearance of the surfaces of the test sample after testing if changed significantly from the initial condition;

l) data output including the background current density and the steady-state permeation current density or the C_0 value;

m) shape of the transient relative to the prediction from Fick's law and observation of any peak in the transient.

The lattice diffusivity used in Equation (1) to calculate C_0 shall be defined.

The effective diffusion coefficient may also be reported, quoting its method of determination and including the variability of the results and a representative example of $J(t)/J_{ss}$ or $I(t)/I_{ss}$ versus t or τ.

Annex A
(informative)

Recommended test environments for specific alloys

A.1 General

This annex gives examples of test conditions suitable for measurement of hydrogen diffusivity and trapping within the volume of the material for alloy systems for which a reliable range of data and testing experience are available.

A.2 Stainless steels

A.2.1 Martensitic stainless steel

The environment in both cells should be 0,1 mol/l NaOH. The potential in the oxidation cell should be set at about $+$ 544 mV vs SHE. Cathodic polarization with charging currents of approximately 1 mA cm^{-2} may be used to generate hydrogen. On attainment of steady state, the potential of the charging surface should be set to $+$ 544 mV vs SHE. The permeation current then decays to the passive current and the cathodic charging current should then be reapplied to generate a second permeation transient.

An alternative approach to the cathodic polarization which generates much higher C_0 values and permeation currents involves using acidified 0,5 mol/l NaCl in the charging cell. At a pH value of about 2,6 the oxide film is rapidly dissolved and charging is induced by the corrosion current. Subsequent transients can be obtained by removal of the test sample and baking out the mobile hydrogen overnight at about 80 °C before retesting.

Since the steel is ferritic, diffusivities are relatively high and sample thicknesses of approximately 250 µm or greater at 20 °C and approximately 1 mm at 80 °C are recommended.

A.2.2 Duplex ferritic austenitic stainless steel

The environment in both cells should be 0,1 mol/l NaOH and the potential of the sample in the oxidation cell should be $+$ 544 mV vs SHE. Cathodic polarization with charging currents of approximately 1 mA cm^{-2} may be used to generate hydrogen atoms. Subsequent transients may be generated by polarizing the charging surface to $+$ 544 mV vs SHE before reapplying cathodic charging.

The sample thickness should be approximately 100 µm at 20 °C and approximately 200 µm or greater at 80 °C.

A.2.3 Austenitic stainless steel

The test conditions should be those for duplex ferritic austenitic stainless steel (see A.2.2). Since the diffusivity of hydrogen in austenitic stainless steel is very low, testing at a temperature of approximately 80 °C is recommended. The acceptable test sample thickness depends on the temperature, and specific recommendations for this alloy type are not possible because of lack of data. Nevertheless, the values of thickness recommended for the duplex stainless steel would probably be more than adequate for austenitic stainless steels and could be adopted initially.

A.3 Nickel alloys

The test conditions should be those for duplex ferritic austenitic stainless steels (see A.2.2).

The diffusivity of these face-centred cubic alloys will be small compared to body-centred cubic systems. Accordingly, testing at elevated temperatures (e.g. 80 °C) may be preferred. Sample thicknesses of 200 µm or greater are recommended for pure nickel and 100 µm or greater for alloys 600, X-750 and 718 at 80 °C.

A.4 Carbon, carbon-manganese and low alloy steels

0,1 mol/l to 1 mol/l NaOH is recommended for the environment in the oxidation cell with the electrode potential set to + 300 mV vs SCE.

When not simulating specific service conditions, cathodic polarization in near neutral solution has been found to provide effective charging conditions for the determination of diffusivity and trapping parameters, in a repeatable fashion. Charging in other environments such as 0,1 mol/l NaOH has been observed to lead to a transient surface state with permeation transients that are usually shallower than Fick's law and not very repeatable. The transients can be very prolonged with a slow drift to steady state. Testing in acid solution can lead to the development of voids and a peak in the current transient which makes analysis difficult.

Palladium coating of the charging surface prior to cathodic charging in 0,1 mol/l NaOH can minimize variations in surface conditions during the permeation transient and yield repeatable transients provided the sample thickness is adequate.

The effective diffusivity of low alloy steels can vary by orders of magnitude depending on the material composition and microstructure, and general recommendations for the thickness of the sample cannot be made. For tests at 20 °C the sample thickness can range from 1,0 mm to the order of centimetres.

Aqueous charging of low alloy steels in H_2S environments may give rise to high values of the hydrogen permeation current. Depending on the thickness of sample, palladium coating of the oxidation surface may provide more repeatable data because of the increased efficiency of the hydrogen atom oxidation reaction.

Examples of effective testing conditions for several steels are as follows.

EXAMPLE 1 3,5 % Ni-Cr-Mo-V:

— deaerated 3,5 % NaCl;

— charging current = 0,06 mA cm^{-2};

— thickness of specimens 1 mm and 2 mm.

EXAMPLE 2 BS 4360 50D:

— deaerated 3,5 % NaCl;

— charging current = 0,06 mA cm^{-2};

— 4 mm thick membrane.

Also:

— deaerated 0,1 mol/l NaOH;

— charging current= 0,5 mA cm^{-2};

— thickness of specimens 2 mm and 3 mm (palladium coated on charging side).

EXAMPLE 3 AISI 4340:

— deaerated 0,1 mol/l NaOH;

— charging current = 1,0 mA cm^{-2};

— thickness of specimens 1 mm and 2 mm (palladium coated on charging side).

The varying thickness for the different materials reflects the variations in effective diffusivity, the thicker specimens being most appropriate for the steel with the higher values. For a specific material, the charging conditions can also affect the required thickness.

Bibliography

[1] ISO 8044, *Corrosion of metals and alloys — Basic terms and definitions*

[2] EN 10088-3, *Stainless steels — Part 3: Technical delivery conditions for semi-finished products, bars, rods and sections for general purposes*

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