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Metallic and other inorganic coatings — Electrochemical measurement of diffusible hydrogen in steels — Barnacle electrode method

Revêtements métalliques et autres revêtements inorganiques — Mesurage électrochimique de l'hydrogène diffusible dans les aciers — Méthode par électrode anatife

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 15724 was prepared by Technical Committee ISO/TC 107, *Metallic and other inorganic coatings*, Subcommittee SC 2, *Test methods*.

Introduction

When atomic hydrogen enters steels and certain other alloys, it can cause loss of ductility or of load-carrying ability, cracking (usually submicroscopic cracks) or catastrophic brittle failure at applied stresses well below the yield strength or even the normal design strength of the alloys. This phenomenon often occurs in alloys that show no significant loss in ductility when measured by conventional tensile tests and is frequently referred to as "hydrogen-induced delayed brittle failure", "hydrogen stress cracking" or "hydrogen embrittlement". The hydrogen can be introduced during fabrication, cleaning, pickling, phosphating, electroplating, autocatalytic processes and in the service environment as a result of cathodic protection reactions or corrosion reactions. Parts that have been machined, ground, cold-formed or cold-straightened subsequent to any heat treatment are especially susceptible to hydrogen embrittlement damage.

Metallic and other inorganic coatings — Electrochemical measurement of diffusible hydrogen in steels — Barnacle electrode method

WARNING — This International Standard does not address any health hazards and safety matters associated with its use. It is the responsibility of the user of this International Standard to establish appropriate health and safety practices and take suitable actions for any national regulations.

1 Scope

This International Standard describes a method that uses an electronic hydrogen detection instrument for measuring relative, diffusible hydrogen concentrations in bare steels or in plated steels after the coating has been removed. It is assumed that the hydrogen is uniformly distributed throughout a part.

The method does not measure actual hydrogen concentration. However, oxidation current densities measured against time provide a useful indication of relative hydrogen concentrations and, therefore, the measurements can be used for comparison purposes. The method may be used as a quality control procedure as it does provide a quick means of measuring the effectiveness of pre- and/or post-plating heat treatments or of monitoring hydrogen uptake during plating or due to corrosion.

It is important to note that the absence of failure in a particular test does not provide confirmation of complete elimination of hydrogen embrittlement because no one test method can provide all the data necessary to evaluate the degree of hydrogen degradation.

For unplated parts the method is non-destructive; however, for plated parts the coating has to be removed prior to measurement by a means proven not to damage the steel or to introduce hydrogen.

This test method is limited to:

— carbon and alloy steels, excluding austenitic stainless steels (see note 1);

— flat specimens to which the cell can be attached (see note 2);

— measurements at room temperature (25 $^\circ$C $\pm$ 1 $^\circ$C).

NOTE 1 If this method is used for austenitic stainless steels and other face centred cubic (FCC) alloys, measurement times and interpretation of results will have to be determined because of the different kinetics involved.

NOTE 2 For slightly curved surfaces it is essential to define an area that is reproducible. The area calculation will be different from that described in this International Standard.

NOTE 3 The method can be applied to small parts, however, this necessitates some modification of the technique, procedure and interpretation of results.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For

undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 9587, *Metallic and other inorganic coatings — Pretreatments of iron or steel to reduce the risk of hydrogen embrittlement*

ISO 9588, *Metallic and other inorganic coatings — Post-coating treatments of iron or steel to reduce the risk of hydrogen embrittlement*

3 Principle

This method is an adaptation of the electrochemical permeation method for hydrogen diffusion.

A hydrogen-containing steel part is made the anode in an electrochemical cell containing an alkaline solution as the electrolyte, with a nickel-nickel oxide (Ni/NiO) electrode forming the cathode. The cell maintains zero hydrogen concentration at the surface of the steel by oxidizing the hydrogen atoms to water. As there is no corrosion reaction taking place at the steel surface, the anodic current measured as a function of time is attributed to the concentration of mobile hydrogen.

In this method, the actual hydrogen concentration is not determined. This is because the calculation of hydrogen concentration requires knowledge of the hydrogen diffusion coefficient in the alloy and knowledge of the decay curve, both of which are not always known, especially at very low hydrogen concentrations. However, comparative current densities can be used to indicate relative hydrogen concentrations.

In this method, it is assumed that the hydrogen is uniformly distributed throughout the steel part and that hydrogen is not appreciably lost due to diffusion during the course of the measurement. Furthermore, as the measurement is relatively rapid, it is probable that trapped hydrogen that is not easily released without stress but that could contribute to delayed failure, will not be detected.

This method is based on measurement of current that decays over a fixed period, in this case for 30 min. The current density will depend on the material as well as on the hydrogen concentration. Each material will have a background current density (see 7.4). A measurement higher than background indicates the presence of hydrogen. Higher current densities indicate higher hydrogen concentrations; the higher the current densities the higher the likelihood of hydrogen embrittlement. A background correction of the actual measurement, however, is not made (see note to 7.4).

4 Reagents

Reagent grade chemicals of sufficiently high purity to ensure the accuracy of the determination shall be used in all tests.
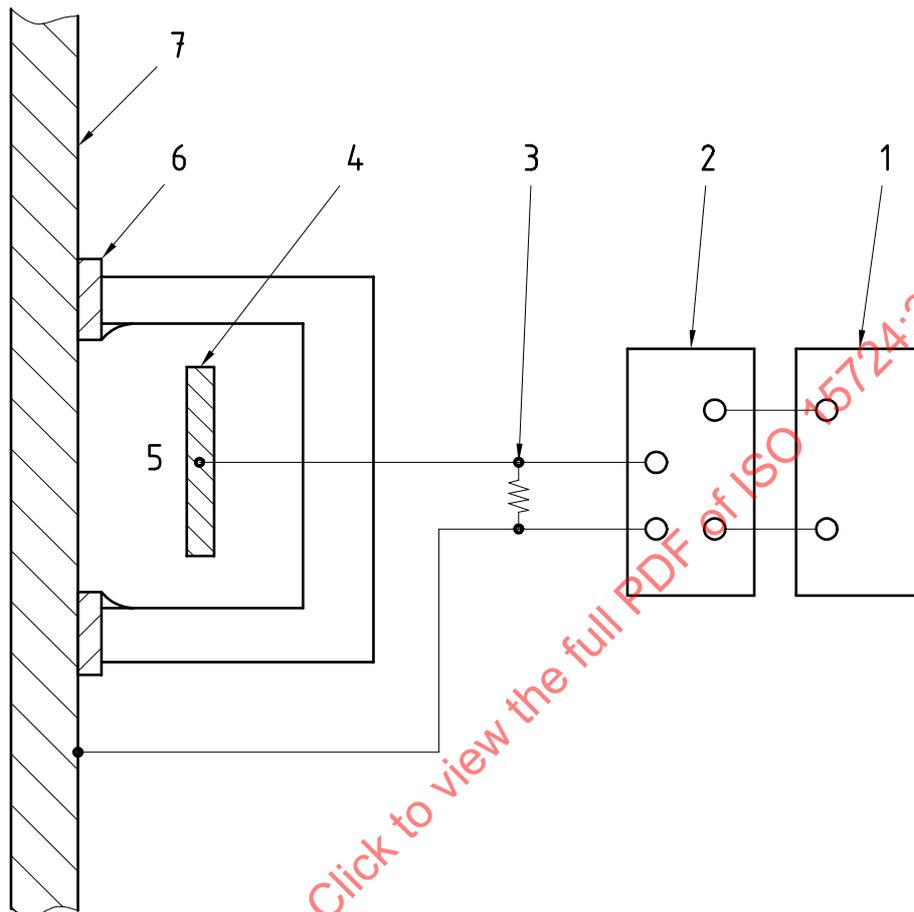
4.1 Electrolyte (0,2 M sodium hydroxide solution), dissolve 8 g of sodium hydroxide (NaOH) pellets in distilled or de-ionized water and dilute to 1 l.

4.2 Methyl alcohol (CH_3OH).

4.3 Ethyl alcohol (C_2H_5OH).

5 Apparatus

See Figures 1 and 2.

Key

1   Strip chart recorder
2   Electrometer
3   Known resistance
4   Driving electrode, Ni/NiO
5   0,2 M NaOH
6   Gasket
7   Hydrogen-containing part

Figure 1 — Schematic diagram of a barnacle electrode system

5.1   The barnacle electrode system.

This consists of

5.1.1   cell, left open to the atmosphere without any purging (see Figure 2), and made of a non-metallic inert material that will not react with or contaminate the electrolyte, and the side opening of which has a recess to accommodate a silicon rubber gasket.

5.1.2   gasket, made of silicon rubber, that shall provide a reproducible contact area between the solution and the specimen, preferably 1 cm^2.

5.1.3   cell holder, a cradle-like C-clamp.

Dimensions in millimetres
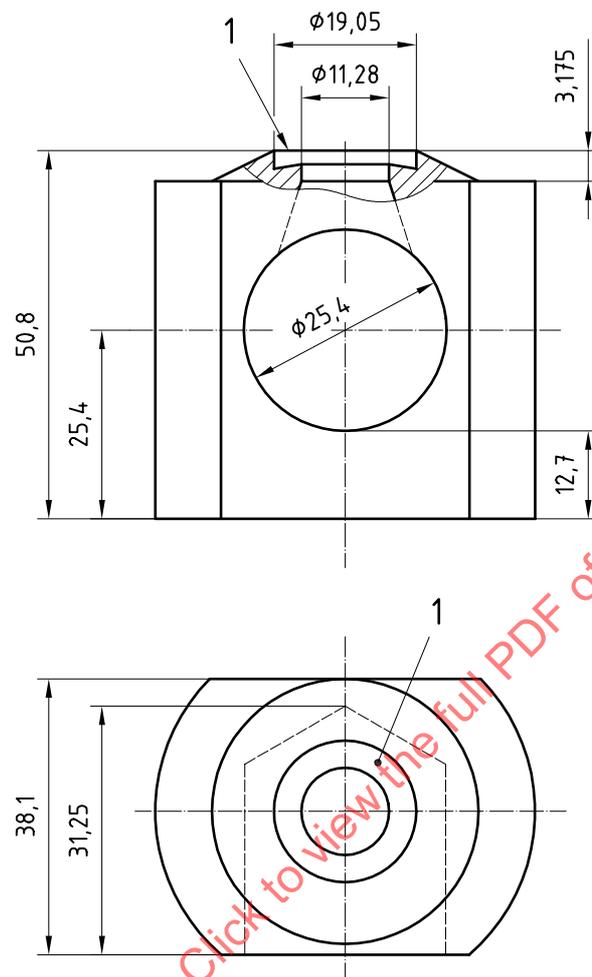
Key

1   Gasket seat

Figure 2 — Barnacle electrode cell

5.1.4   anode (i.e. the specimen to be tested).

5.1.5   cathode, a Ni/NiO electrode (e.g. from a nickel-cadmium battery), the area of which shall be approximately five times that of the anode.

5.1.6   a current measuring device.

NOTE   The current can be measured by any method that will not adversely affect the system; e.g., in this International Standard, the device consists of:

a)   a standard resistance connected across the two electrodes via a switch;

b)   an electrometer to determine the current by measuring the voltage drop across the resistance (a 10 kΩ resistor with an electrometer having an input impedance of 10^{12} Ω has been found to be satisfactory);

c)   a strip chart recorder to monitor the electrometer measurements (an input resistance of 100 kΩ has been found to be satisfactory);

d)   a timer accurate to within 10 s in a 30 min run.

5.2 Microscope.

5.3 Nylon cleaning pad, impregnated with aluminium oxide.

6 Test specimens

The specimen can be an actual part or a coupon 1 mm to 6 mm thick. If a coupon is used, it shall be of the same material and form, and have the same heat treatment and surface finish as the part, in order to depict the same hydrogen parameters, such as hydrogen uptake during processing, mobile versus trapped hydrogen and surface finish. The specimen shall be sufficiently large to accommodate the cell and for a duplicate measurement to be made (see 8.3.6). It shall also be sufficiently flat and smooth to prevent leakage of the electrolyte under the gasket.

7 Calibration

7.1 Calibrate the Ni/NiO electrode (5.1.5) against a saturated calomel electrode (SCE) in 0,2 M NaOH solution (4.1). A freshly charged Ni/NiO electrode will be at least 300 mV more noble (i.e. positive) than the SCE. It shall be recharged when its potential drops to less than 300 mV more noble (i.e. positive) than SCE.

7.2 Charge the Ni/NiO electrode using a platinum, or similar, inert electrode as the cathode and the Ni/NiO electrode as the anode in 0,2 M NaOH solution for 30 min at a current density of 5 mA/cm^2 to 10 mA/cm^2.

NOTE To prevent a temporary drain of the charge due to repeated use of the Ni/NiO electrodes, alternate two electrodes during a series of measurements.

7.3 Calculate the cell contact area outlined by the gasket as follows.

Using the cell holder (5.1.3) assemble the cell (5.1.1) on a flat specimen with a smooth piece of aluminium foil or sheet, at least 0,04 mm thick, between the specimen (5.1.4) and the gasket (5.1.2). The Ni/NiO electrode is not needed.

Fill the cell with 0,2 M NaOH solution and allow the aluminium to be etched for about 20 min.

Dismantle the cell and rinse the aluminium sample thoroughly.

NOTE 1 A properly assembled cell will produce a sharply defined circular etched area.

Measure the diameter of the circle using a microscope (5.2), see 9.2.

NOTE 2 A poor gasket or improper tightening of the cell can be detected by this procedure. Overtightening will produce a deformation of the gasket, resulting in an out-of-round etch. Undertightening, or a worn gasket, will cause crevices, resulting in etching under the gasket.

7.4 Measure the background current density by using uncoated specimens containing no hydrogen, or specimens that have been subjected to heat treatment (see ISO 9587), prepared in accordance with clause 6. Keep these coupons in a desiccator for at least 1 week before measuring in order to ensure that no hydrogen is produced due to corrosion.

NOTE The background measurement is used as a reference to indicate the presence or absence of hydrogen. It is not used in any calculation.

8 Procedure

8.1 Specimen preparation

8.1.1 The procedure for preparation of the specimen for testing depends on whether it is plated (see 8.1.3) or not (see 8.1.2). Preparation of the specimen shall take no longer than 5 min.

8.1.2 For unplated specimens, abrade the surface lightly with an aluminium oxide impregnated nylon cleaning pad (5.3) to remove surface contamination and to provide a reproducible surface finish. Wipe clean with a tissue soaked in methyl alcohol (4.2) or ethyl alcohol (4.3).

8.1.3 For plated specimens with post-plating heat treatment (see ISO 9588), remove the coating from an area on one side of the specimen large enough to accommodate the cell (approximately 40 mm $\times$ 40 mm), using an appropriate method or reagents that will not introduce hydrogen into the specimen. Rinse with water and dry. Prepare the bare surface in accordance with 8.1.2.

8.2 Cell assembly

8.2.1 The time to assemble the cell and the commencement of measurement shall take no longer than 5 min. The total time from the beginning of the specimen preparation to completion of the cell assembly shall be no longer than 10 min.

8.2.2 Clamp the cell to the specimen just tightly enough to prevent leakage (see note 2 to 7.3).

8.2.3 Insert the Ni/NiO electrode in the centre of the cell cavity. Ensure that there is no direct contact between this electrode and the specimen.

8.2.4 Connect the resistance and the switch between the Ni/NiO electrode and the specimen (see Figure 1).

8.2.5 Connect the electrometer across the resistance so that the Ni/NiO electrode will measure positive and the steel negative when the cell is activated.

8.2.6 Connect the recorder (5.1.6) to the electrometer output.

8.2.7 Fill the cell with 0,2 M NaOH, ensuring that the Ni/NiO electrode and the measurement area are completely covered with the solution.

8.3 Current measurement

8.3.1 Measurement of the current shall commence within 1 min of filling the cell. The measurement shall always be made for the same length of time so that the current densities, correlated with susceptibility to hydrogen embrittlement, as measured, e.g., by the inclined wedge method described in ISO 10587, can be compared. In this International Standard a measurement time of 30 min has been chosen for high-strength low-alloy steels. As diffusion is temperature-dependent, all measurements shall be made at room temperature (25 $^\circ$C $\pm$ 1 $^\circ$C) so that comparison can be made with other data.

8.3.2 Turn on the cell switch and activate the timer simultaneously.

During measurement the oxidation current will decrease with time by a few orders of magnitude. Therefore, for the first 5 min, set the recorder at an appropriately high setting to prevent overload. The final readings will be in the microampere range. Adjust the electrometer and the recorder accordingly.

**8.3.3** Record the current for 30 min.

8.3.4 Turn off the switch.

8.3.5 Dismantle the cell, rinse and dry.

8.3.6 Repeat the measurement (8.3.2 to 8.3.5), if required, on the same specimen, either on a nearby area without overlap or on the opposite side of the specimen. The time taken to prepare the specimen in accordance with 8.1, shall not exceed 10 min after completion of the previous measurement (see 8.3.1 to 8.3.5).

8.3.7 If a series of measurements is to be made during the day, alternate Ni/NiO electrodes and gaskets to ensure recovery between the runs.

NOTE   Examples of recorder tracings showing good measurement, acceptable measurement and poor measurement are shown in Figure 3.
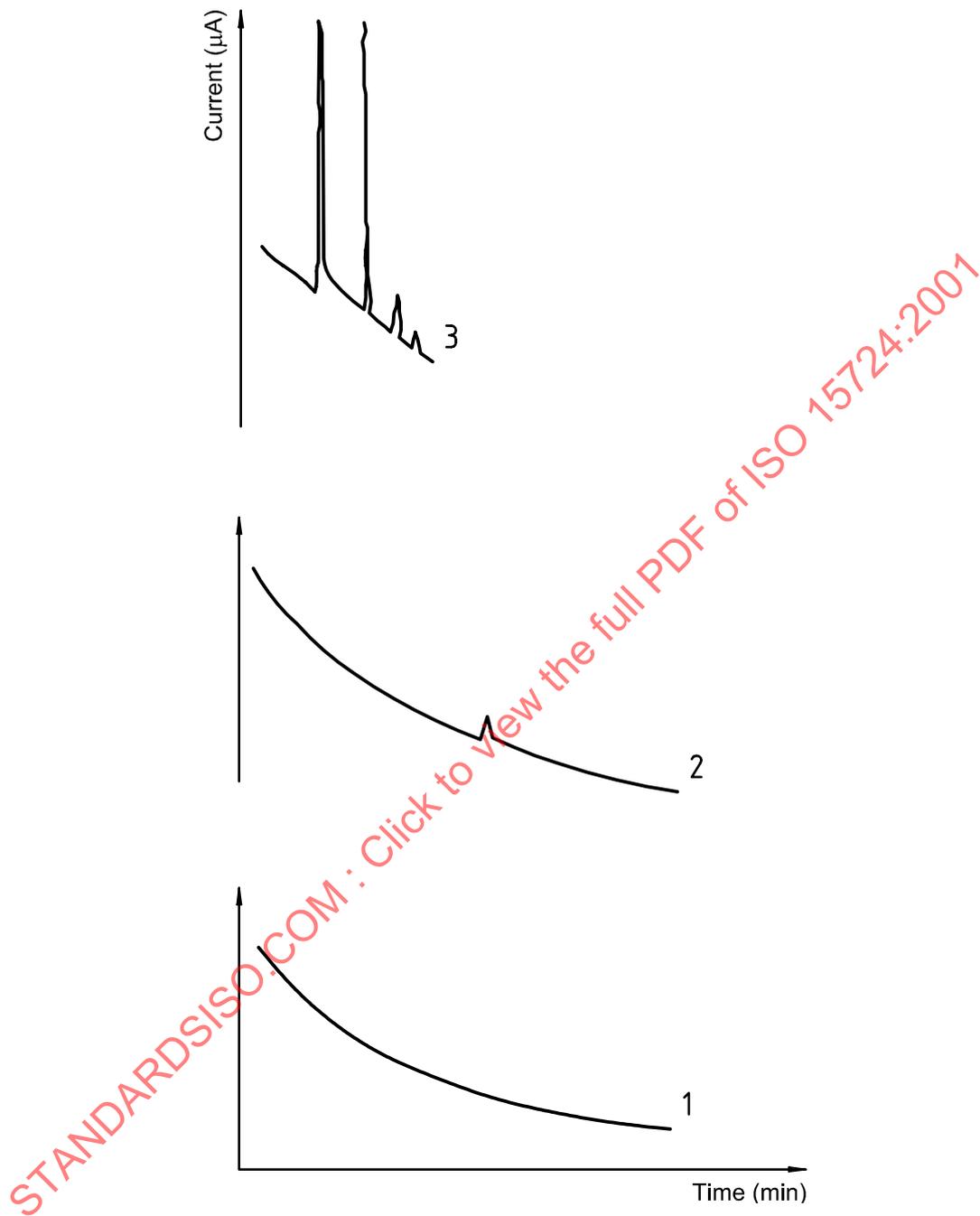
Key

1   Good measurement

2   Acceptable measurement

3   Poor measurement

Figure 3 — Typical examples of recorder tracings showing good (1), acceptable (2) and poor (3) measurements

9 Results

9.1 Calculate the current from the voltage drop across the standard resistance using Ohm's Law, $E = IR$, where I is the current, E is the voltage drop and R is the resistance. For example, if the full-scale voltage on the strip chart recorder is 10 mV and the resistance is 10 kΩ, then the full scale current is 1 µA.

9.2 Calculate the contact area from the diameter of the etched surface area (see 7.3). Measure the diameter, D, in two directions and take the average value. If the contact area is round the area, A is given by:

$$A = \pi \left(D/2 \right)^2$$

e.g., if the average diameter is found to be 1,2 cm, the area, $A \left[= \pi \left(1{,}2/2 \right)^2 \right]$, is 1,1 cm^2.

9.3 Calculate the current density; e.g., if the 30 min current is 0,55 µA, and the contact area is 1,1 cm^2, then the current density, I_d, is $\left(= 0{,}55/1{,}1 \right)$ 0,5 µA/cm^2.

10 Interpretation of results

10.1 Irregular recorder tracings (Figure 3) indicate scratches, pits, crevices or gas bubbles. If the cell is constructed and filled with the solution properly, gas bubbles should not form. A light tap on the cell should dislodge any bubbles. If the problem persists, i.e. the recorder trace is still poor, terminate the measurement and start a new test in accordance with 8.1. Visually inspect the specimen for any deep scratches or pits. Crevices can be a problem if the cell is not tightened properly. Undertightening will allow the solution to run under the gasket producing an enlarged contact area and leading to crevice corrosion. Overtightening will cause the gasket to deform thus changing the area. Corrosion in a pit or crevice, or an enlarged contact area will all lead to excess measured current. If difficulties persist, they are more probably due to the gasket. Test the cell tightening procedure in accordance with 7.3.

10.2 A measurement higher than the background current density indicates the presence of hydrogen; a high level of hydrogen is an indication of a probable hydrogen embrittlement problem. The absence of hydrogen or a low hydrogen concentration does not, however, prove that hydrogen embrittlement has not occurred. It is possible that a high level of hydrogen introduced during processing, such as pickling or electroplating may have caused local damage before any diffusion. A background correction of the actual measurement shall not be made (see note to 7.4).

10.3 Care shall be taken in inferring hydrogen levels over the whole part from limited measurements, especially if the part has a variable geometry or possible local metallurgical variations. For example, measurements on thin sections of a part will show a higher hydrogen concentration due to a higher surface to volume ratio than on thick sections showing a low hydrogen level. Therefore, stresses on thin sections will have a more damaging effect than stresses on the bulk.

10.4 As the measurement is relatively rapid, it measures hydrogen that diffuses easily. It is, therefore, probable that trapped hydrogen that is not easily released without stress, but that could contribute to delayed failure, would not be detected.

11 Test report

The test report shall include the following:

a) reference to this International Standard, i.e. ISO 15724;

b) the 30 min current reading for each measurement and the calculated mean;

c) the area and the calculated mean current density;

d) the type of specimen; coupon or actual part, part number, lot, steel grade, strength, temper/metallurgical condition, plating applied and time and temperature of stress- or embrittlement-relief treatment;