



Standard Test Method for Electrochemical Measurement of Diffusible Hydrogen in Steels (Barnacle Electrode)¹

This standard is issued under the fixed designation F 1113; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method describes the procedure for measuring diffusible hydrogen in steels by an electrochemical method.

1.2 This test method is limited to carbon or alloy steels, excluding austenitic stainless steels.

1.3 This test method is limited to flat specimens to which the cell can be attached (see 4.6 and 4.8).

1.4 This test method describes testing on bare or plated steel after the plate has been removed (see 4.4).

1.5 This test method is limited to measurements at room temperature, 20 to 25°C (68 to 77°F).

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

A 165 Specification for Electrodeposited Coatings of Cadmium on Steel²

B 183 Practice for Preparation of Low-Carbon Steel for Electroplating³

B 242 Practice for Preparation of High-Carbon Steel for Electroplating³

D 1193 Specification for Reagent Water⁴

F 519 Test Method for Mechanical Hydrogen Embrittlement Evaluation of Plating Processes and Service Environments⁵

G 3 Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing⁶

3. Summary of Test Method

3.1 A hydrogen-containing part is made the anode in an electrochemical cell. The diffusible (atomic) hydrogen, which

comes to the metal-electrolyte interface, is oxidized to protons (H^+); H^+ combines with hydroxyl ions (OH^-) in the electrolyte to form water. The oxidation current is measured and related to the hydrogen concentration.

4. Significance and Use

4.1 The critical level of hydrogen in steels is that hydrogen which can build up to high concentrations at points of high triaxial stress causing embrittlement of the steel which can lead to catastrophic damage. This hydrogen can enter by various means, such as during pickling and electroplating. Means of reducing this hydrogen during processing are given in Specification A 165 and Practices B 183 and B 242. It is still necessary, however, to know how effective these methods are. Though the ultimate reason for measuring this hydrogen is to relate it to embrittlement, this is not within the scope of this test method. As susceptibility to hydrogen embrittlement is a function of alloy type, heat treatment, intended use, and so forth, the tolerance for hydrogen must be determined by the user according to Method F 519.

4.2 Though the actual hydrogen concentration is not determined in this test method, the current densities have been shown to be useful as an indication of relative hydrogen concentrations (1-3),⁷ and therefore the degree of hydrogen embrittlement (1,2). Thus, measurements can be compared to one another (see 4.1 and 7.1).

4.3 This test method is applicable as a quality control tool for processing (such as to monitor plating and baking) or to measure hydrogen uptake caused by corrosion.

4.4 This test method is nondestructive; however, if there is a coating, it must be removed by a method which has been demonstrated to neither damage the steel nor introduce hydrogen to make the measurement.

4.5 This test method is also applicable to situations producing continuous hydrogen permeation, such as high pressure hydrogen cylinders or corrosion processes. The results, however, would require a different treatment and interpretation (4).

4.6 This test method is also applicable to small parts, such as fasteners. The technique, procedure, and interpretation would, however, have to be altered.

4.7 Use of this test method on austenitic stainless steels and

¹ This test method is under the jurisdiction of ASTM Committee F-7 on Aerospace and Aircraft and is the direct responsibility of Subcommittee F07.04 on Hydrogen Embrittlement.

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² Discontinued in 1988 and replaced by Specification B 766.

³ Annual Book of ASTM Standards, Vol 02.06.

⁴ Annual Book of ASTM Standards, Vol 11.01.

⁵ Annual Book of ASTM Standards, Vol 15.03.

⁶ Annual Book of ASTM Standards, Vol 03.02.

⁷ Boldface numbers in parentheses refer to the list of references at the end of this standard.

other face centered cubic (FCC) alloys would require different measurement times and interpretation of results because of differing kinetics.

4.8 This test method can be used on slightly curved surfaces as long as the gasket defines a reproducible area. The area calculation must, however, be changed.

5. Apparatus

5.1 *Cell*—A photo and drawing of a typical cell, which has been found to be acceptable for hydrogen measurements, are shown in Figs. 1 and 2, respectively.

5.1.1 The cell is made of a nonmetallic material that will not react with or contaminate the solution. The side opening has a recess to accommodate the silicone rubber gasket.

5.1.2 *Gasket*, silicone rubber, shall provide a reproducible solution-contact area with the specimen, preferably 1.0 cm².

5.1.3 *Cell Holder*, a cradle-like C-clamp. Other clamping devices can be used if necessary, such as for larger parts.

5.1.4 *Cathode*, a nickel/nickel oxide electrode. It is made by removing the positive plate from a nickel/cadmium battery and attaching a nickel wire or foil. The area of this cathode shall be approximately five times that of the anode.

5.1.5 *Anode*—The anode is the specimen.

5.1.6 The cell is left open to the atmosphere. No purging is used.

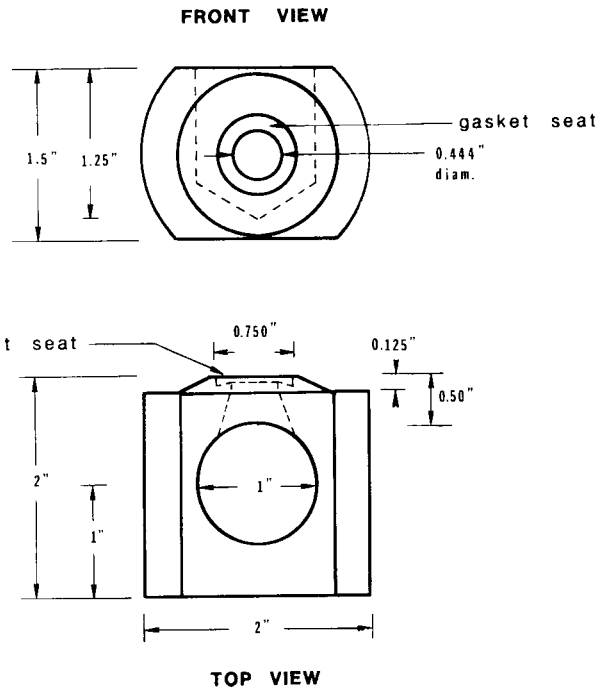


FIG. 2 Engineering Drawing of Cell (3)

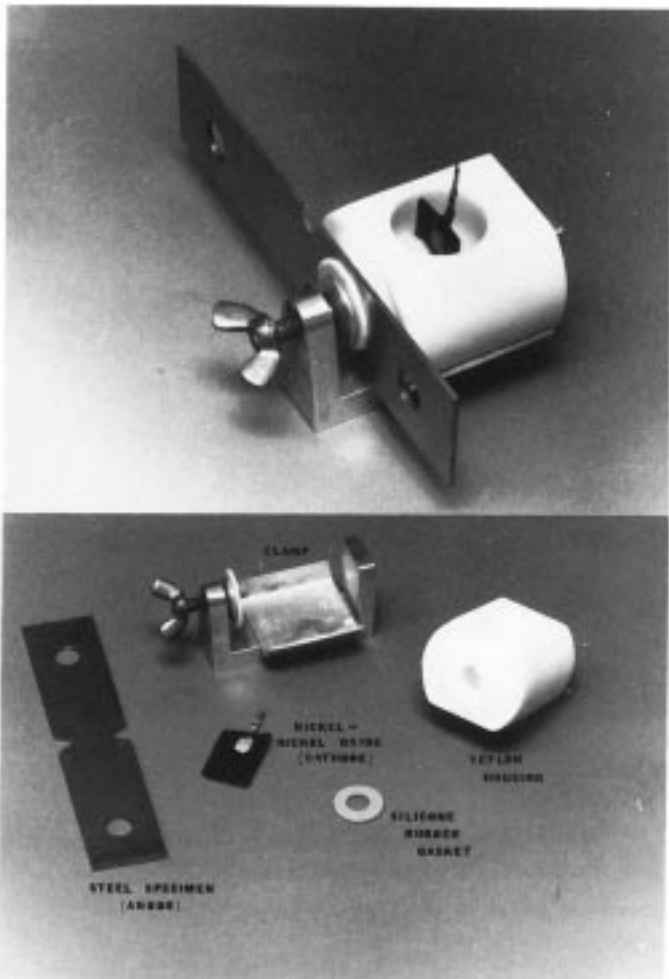


FIG. 1 Photograph of Cell

5.2 *Current Measuring Device*—The current can be measured by any method that will not affect its value. A zero resistance ammeter (5), a current follower (6), and the current measuring system shown in Fig. 3 (1) have been found to be acceptable. The following description refers to Fig. 3.

5.2.1 *Standard Resistor*, connected across the cell through a switch.

5.2.2 *Electrometer*, to determine the current by measuring the voltage drop across the resistor. A 10-kΩ resistor with an electrometer having an input impedance of 10¹² Ω and a 1-mA output has been found to be satisfactory.

5.2.3 *Strip Chart Recorder*, to monitor the electrometer output. A recorder having an input resistance of 100 kΩ has been found to be satisfactory.

5.2.4 *Timer*, accurate to within 10 s in a 30-min run.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

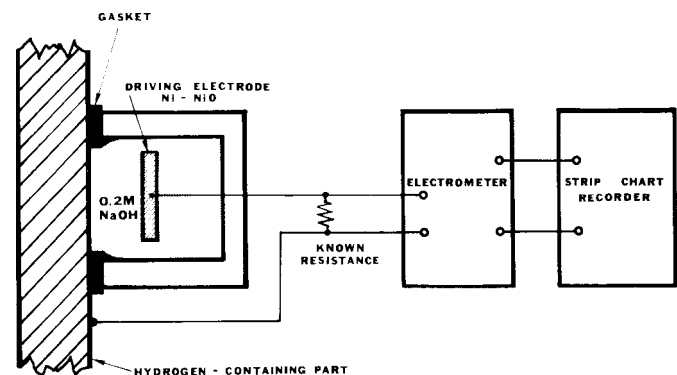


FIG. 3 Schematic of Measuring Apparatus (1)

all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁸ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Distilled or deionized water conforming to Specification D 1193, Type IV, shall be used to prepare all solutions.

6.3 *Sodium Hydroxide Solution (0.2M)*— Dissolve 8 g of sodium hydroxide (NaOH) pellets in water and dilute to 1 L.

6.4 *Ammonium Nitrate Solution (120 g/L)*—Dissolve 120 g of ammonium nitrate (NH₄NO₃) in water and dilute to 1 L.

6.5 *Methyl Alcohol (CH₃OH)*.

6.6 *Ethyl Alcohol (C₂H₅OH)*.

7. Test Specimens

7.1 The test specimen can be a coupon of 1- to 6-mm thickness or an actual part. If it is a coupon, it shall be of the same alloy, form, temper/condition, and surface finish as the part. The specimen shall be of sufficient size to accommodate the cell and of sufficient smoothness and flatness to prevent leaking of the electrolyte under the gasket (see 8.2). If possible, specimens shall be of sufficient size for a duplicate measurement to be made (see 9.4).

8. Calibration and Standardization

8.1 Calibrate the nickel/nickel oxide (Ni/NiO) electrode against a saturated calomel electrode (SCE) in 0.2M NaOH. A freshly charged Ni/NiO electrode will be at least 350 mV positive to the SCE when measured according to Practice G 3. It shall be recharged when its potential is less than 300 mV positive to the SCE.

NOTE 1—Repeated use of the Ni/NiO electrode will cause a temporary drain of the charge. To prevent this from happening, alternate two electrodes during a series of measurements.

8.1.1 Charge the Ni/NiO electrode in a 0.2M NaOH solution for ½ h at a current density of 5 to 10 mA/cm².

8.1.2 The Ni/NiO electrode is made the anode, that is, connected to the positive terminal of the charging source. Any conductor that will not react with the solution, such as platinum, graphite, or steel, may be used as the cathode.

8.2 Determine the specimen contact area which is outlined by the gasket.

8.2.1 Assemble the cell with a smooth piece of aluminum sheet or foil, at least 0.04 mm thick, between a specimen and the gasket. The Ni/NiO electrode is not needed.

8.2.2 Fill the cell with 0.2M NaOH solution and allow the aluminum to be etched by the alkaline solution for about 20 min.

8.2.3 Dismantle the cell and rinse well. A properly assembled cell will produce a sharply defined, circular etch (see Fig. 4).

⁸ Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see Analar Standards for Laboratory Chemicals, BDH Ltd., Poole, Dorset, U.K., and the United States Pharmacopeia and National Formulary, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.



FIG. 4 Etched Areas (NaOH on Al) Showing (A) Good Gasket Fit and (B) Poor Fit Showing Undercutting of Gasket as a Result of Undertightening or Worn Gasket

8.2.4 Measure the diameter of the etched circle under a microscope (10×), and calculate the area (see 10.2).

8.2.5 A poor gasket or improper tightening of the cell will be detected by this procedure. Overtightening will produce a deformation of the gasket, resulting in an out-of-round etch. Undertightening, or a worn-out gasket, will cause crevices, resulting in etching under the gasket (see Fig. 4).

8.3 Measure uncoated coupons, prepared in accordance with 7.1, to determine the background current density. Keep these coupons desiccated for at least one week before measuring, to assure that no hydrogen, as a result of corrosion, is produced, and to allow any hydrogen in the specimens to escape.

NOTE 2—The background measurement is used only as a reference to indicate the presence or absence of hydrogen. It is not used in any calculation.

9. Procedure

NOTE 3—This procedure pertains to cadmium-plated specimens. Any other plating must be removable by a method that will neither damage the steel nor introduce hydrogen.

9.1 Specimen Preparation:

NOTE 4—The time to prepare the specimen must take no longer than 5 min.

9.1.1 Remove any cadmium plate from an area on one side of the specimen large enough to accommodate the cell (approximately 40 by 40 mm) by swabbing with ammonium nitrate solution. Rinse with water and dry. Swabs made of polyurethane foam or cotton have been found to be satisfactory.

9.1.2 Abrade the surface lightly with an aluminum oxide-impregnated nylon cleaning pad to remove surface contamination and to provide a reproducible surface finish. Wipe clean using a tissue wet with methyl or ethyl alcohol.

9.2 Cell Assembly:

NOTE 5—The time to assemble the cell and start the measurement must take no longer than 5 min. The total time from the start of 9.1.1-9.3.1 must take no longer than 10 min.

9.2.1 Clamp the Cell to the Specimen.

NOTE 6—The cell should be clamped only tight enough to prevent leakage. Overtightening will cause deformation of the gasket. Proper tightening can be determined by following the procedure in 8.2.

9.2.2 Clamp the Ni/NiO electrode in the center of the cell cavity using the cell dimensions of Fig. 1. For other cell designs, the distance between the electrodes shall be 25 mm.

9.2.3 Connect the resistor and switch between the Ni/NiO electrode and the specimen.

9.2.4 Connect the electrometer across the resistor so that the Ni/NiO electrode will measure positive and the steel negative.

9.2.5 Connect the recorder to the electrometer output.

9.2.6 Fill the cell with 0.2M NaOH, making sure that the Ni/NiO electrode and the specimen measurement area are completely covered with solution.

9.3 Making the Measurement:

NOTE 7—The measurement must be started within 1 min of filling the cell.

9.3.1 Simultaneously turn on the cell switch and the timer.

NOTE 8—The oxidation current decreases with time. During the measurement, it will change by a few orders of magnitude. Therefore, for the first 5 min, set the recorder at an appropriate high setting to prevent overload. The final readings will be in the microampere range. Adjust the electrometer and recorder accordingly.

9.3.2 Record the current at the end of 30 min. This shall be referred to as the 30-min reading.

NOTE 9—The current measurement must always be made for the same length of time. In this test method, 30 min has been chosen. The reasons for this are given in references (1,3).

9.3.3 Turn off the switch.

9.3.4 Dismantle the cell, rinse, and dry.

9.4 Repeat Measurements:

NOTE 10—If the recorder tracing is poor (see Fig. 5), a repeat measurement must be made.

9.4.1 If cadmium-plated coupons or parts are of sufficient size, make duplicate measurements on the same specimen, either alongside or opposite to the first in accordance with 9.1. If alongside, the newly swabbed area shall not overlap the first. The specimen preparation procedure in 9.1.1 must be started no more than 10 min after completion of the previous measurement taken in 9.3.2.

9.4.2 If a series of measurements are to be made during the day, alternate Ni/NiO electrodes and gaskets must be used. Allow at least 45 min between runs using the same ones.

10. Calculation

10.1 Calculate the current from the voltage drop across the standard resistor using Ohm's law, $I = E/R$. 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.

10.2 Calculate the contact area from the diameter of the etched surface (see 8.2). The diameter, D, should be measured in two directions and averaged. If it has been established that the contact area is essentially round, the area, A, is given by: $A = \pi (D/2)^2$. For example, if the average diameter is found to be 1.2 cm, the area is $3.14 (1.2/2)^2$ or 1.10 cm².

10.3 Current density is the current per unit area. For example, if the 30-min current is 0.66 μA, and the exposed area is 1.1 cm², then the current density is 0.66/1.1 or 0.60 μA/cm².

11. Interpretation of Results

11.1 The 30-min current density will depend on the material as well as the hydrogen concentration. Each material will have a background current density (see 8.3) as a result of passivation reactions. A measurement higher than background indicates the

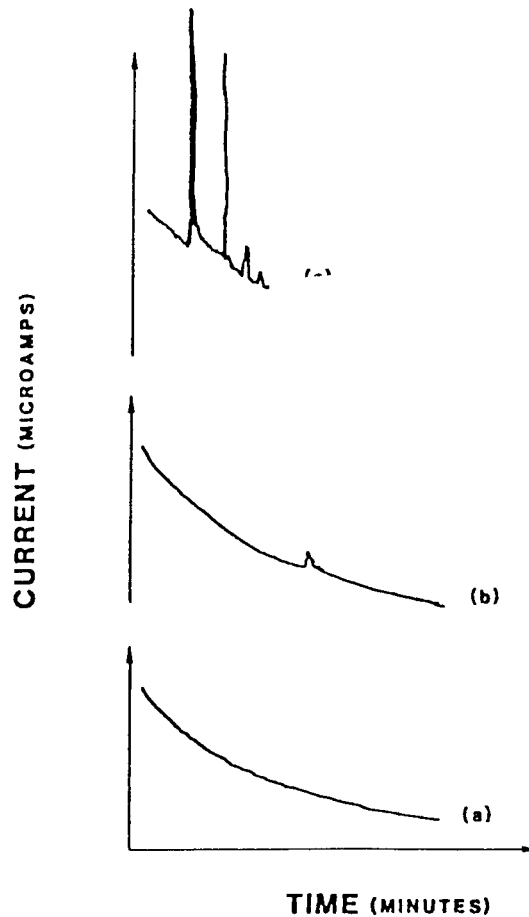


FIG. 5 Recorder Tracings Showing (A) Good Measurement, (B) Acceptable Measurement, and (C), Poor Measurement Which Must Be Repeated

presence of hydrogen; higher current densities indicate higher hydrogen concentrations. The higher the current density, the more chance there will be for hydrogen embrittlement (see 4.1 and 4.2).

11.2 Irregular recorder tracings, Fig. 5, indicate scratches or pits, crevices, or gas bubbles. If the cell is constructed and filled properly, gas bubbles should not form. A light tap on the cell should dislodge any bubbles. If, after doing this, the recorder trace is still poor, terminate the measurement, and start a new one in accordance with 9.2. To prevent problems as a result of deep scratches or pits, visually inspect the specimen before the measurement. 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 become deformed, thus changing the area. Corrosion in a pit or crevice, or an enlarged contact area, will all lead to excess measured current. If difficulties continue, they are most probably a result of the gasket. Test the cell tightening procedure in accordance with 8.2.

11.3 A high level of hydrogen is an indication of probable hydrogen embrittlement problems. The absence, or a low level, of hydrogen 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 diffusing out. Procedures, such as in Practices B 183 and B 242, must therefore be adhered to.

11.4 Care must also be exercised in inferring hydrogen levels over the whole part from limited measurements, especially when the part has quite variable geometries or possible local metallurgical variations. For example, an electroplated, massive part, having thin sections, may show a low hydrogen level when measured on the thick parts; however, the thin sections will have higher hydrogen concentrations because of higher surface-to-volume ratios (3). Thus, stresses at these areas would be more damaging than stresses on the bulk.

11.5 As this 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 which could contribute to delayed failure, would not be detected.

12. Report

12.1 The report shall include the following:

12.1.1 The 30-min current reading for each measurement and the calculated specimen mean.

12.1.2 The area and the calculated specimen mean current density.

12.1.3 The type of specimen: coupon or part, part number, lot, steel grade, temper/condition, plating applied, and baking time and temperature.

12.1.4 Any deviations from standard procedure, such as in surface preparation, delays in starting the measurement, or abnormal temperature.

13. Precision and Bias

13.1 *Precision*—Interlaboratory precision has not been determined; however, an interlaboratory testing program is being planned. Intralaboratory precision has been reported (2,3); typical data are shown in Table 1 (2).

13.2 *Bias*—There is no need to determine bias in this test method because the actual hydrogen concentration is not determined; however, the measured current densities can be related to relative hydrogen concentrations.

14. Keywords

14.1 barnacle cell; current transients; diffusion; electrochemical; electrodes; high strength steels; hydrogen contact; hydrogen embrittlement; mobile hydrogen

TABLE 1 Hydrogen Measurements on Cadmium-Plated 300-M Steel Coupons

NOTE 1—The measurements were made by the same operator over a period of two months. The 0.0005-in. (0.01-mm) thick bright cadmium plate was left on until the measurements were made.

Baking Time, h	Average Measurements, ^A μA/cm ²	Standard Deviation ^A
0	0.60	0.076
48	0.45	0.086
72	0.42	0.073
96	0.38	0.036

^AThe means and standard deviations were calculated from the specimen means (two measurements each) using four specimens for each baking time.

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