



Designation: F1113 – 87 (Reapproved 2005)<sup>1</sup>

## Standard Test Method for Electrochemical Measurement of Diffusible Hydrogen in Steels (Barnacle Electrode)<sup>1</sup>

This standard is issued under the fixed designation F1113; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>e1</sup> NOTE—Editorial changes were made throughout in June 2005.

### 1. Scope

1.1 This test method covers 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:*<sup>2</sup>

**B183** Practice for Preparation of Low-Carbon Steel for Electroplating

**B242** Guide for Preparation of High-Carbon Steel for Electroplating

**B766** Specification for Electrodeposited Coatings of Cadmium

**D1193** Specification for Reagent Water

**F519** Test Method for Mechanical Hydrogen Embrittlement Evaluation of Plating/Coating Processes and Service Environments

**G3** Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee F07 on Aerospace and Aircraft and is the direct responsibility of Subcommittee F07.04 on Hydrogen Embrittlement.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

### 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 **B766** and Practices **B183** and **B242**. 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 **F519**.

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**),<sup>3</sup> 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

<sup>3</sup> Boldface numbers in parentheses refer to the list of references at the end of this standard.

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 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 cm<sup>2</sup>.

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

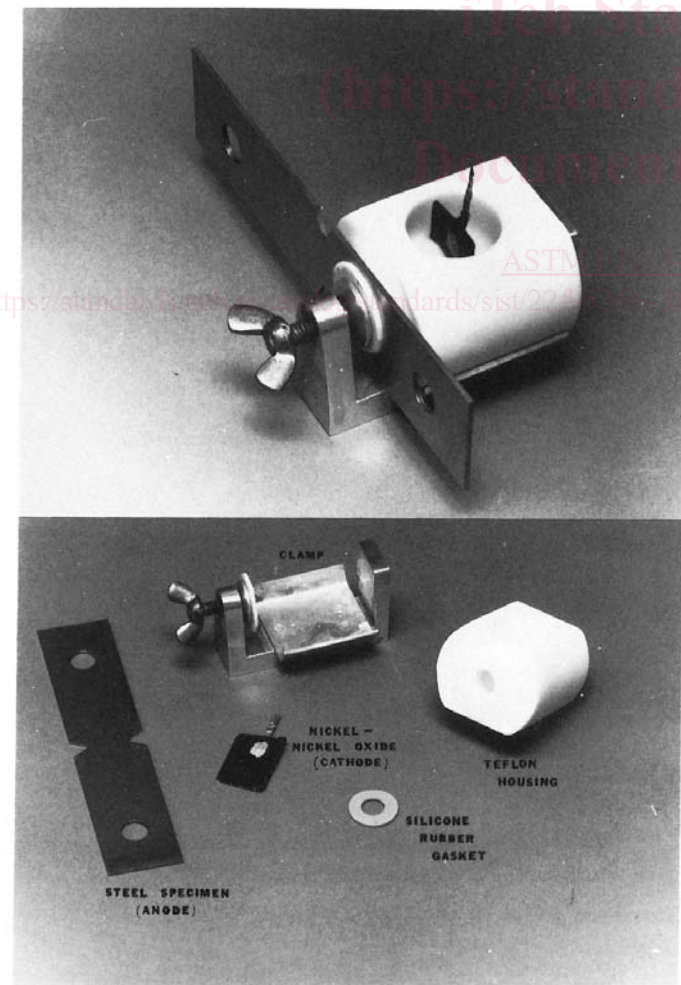


FIG. 1 Photograph of Cell

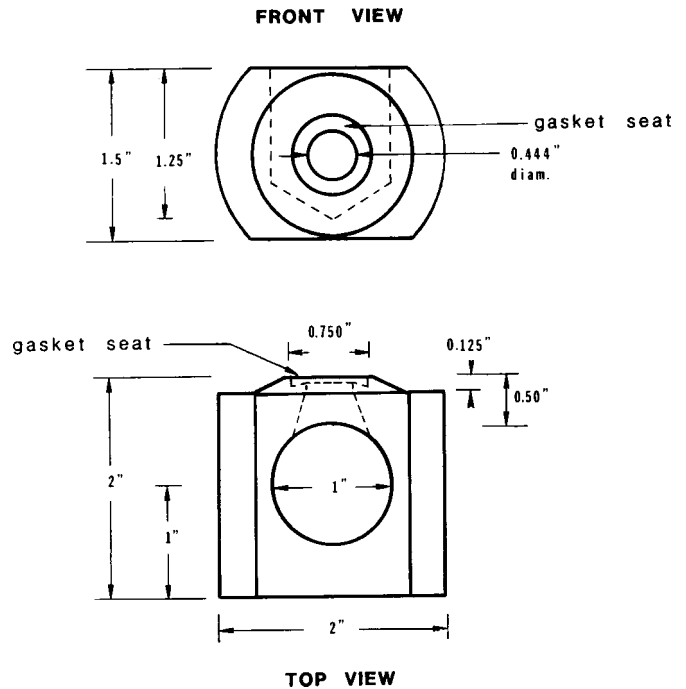


FIG. 2 Engineering Drawing of Cell (3)

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.

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-k $\Omega$  resistor with an electrometer having an input impedance of 10<sup>12</sup>  $\Omega$  and a 1-mA output has been found to be satisfactory.

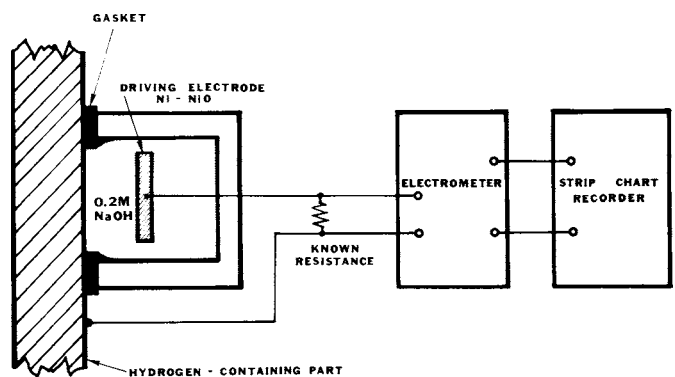


FIG. 3 Schematic of Measuring Apparatus (1)

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 all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>4</sup> 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 D1193, 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 (NH<sub>4</sub>NO<sub>3</sub>) in water and dilute to 1 L.

6.5 *Methyl Alcohol (CH<sub>3</sub>OH)*.

6.6 *Ethyl Alcohol (C<sub>2</sub>H<sub>5</sub>OH)*.

## 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 G3. 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/cm<sup>2</sup>.

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).

8.2.4 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 removably 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.



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

<sup>4</sup> *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.