

# Standard Test Method for Measurement of Corrosion Potentials of Aluminum Alloys<sup>1</sup>

This standard is issued under the fixed designation G69; 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  $(\varepsilon)$  indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers a procedure for measurement of the corrosion potential (see Note 1) of an aluminum alloy in an aqueous solution of sodium chloride with enough hydrogen peroxide added to provide an ample supply of cathodic reactant.

Note 1—The corrosion potential is sometimes referred to as the open-circuit solution or rest potential. See Practice G193.

- 1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.
- 1.3 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>

D1193 Specification for Reagent Water

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

G3 Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing

G193 Terminology and Acronyms Relating to Corrosion

# 3. Significance and Use

3.1 The corrosion potential of an aluminum alloy depends upon the amounts of certain alloying elements that the alloy contains in solid solution. Copper and zinc, which are two of the major alloying elements for aluminum, have the greatest effect with copper shifting the potential in the noble or positive direction, and zinc in the active or negative direction. For

diffusion of alloying elements from the core into the cladding of Alclad products (2).
4. Apparatus
4.1 The apparatus consists of an inert container for the test solution, a mechanical support for the test specimens that

example, commercially unalloyed aluminum (1100 alloy) has a potential of -750 mV when measured in accordance with this

method, 2024-T3 alloy with nearly all of its nominal 4.3 %

copper in solid solution, a potential of -600 to -620 mV,

depending upon the rate of quenching and 7072 alloy with

nearly all of its nominal 1.0 % zinc in solid solution, a potential

3.2 Because it reflects the amount of certain alloying ele-

ments in solid solution, the corrosion potential is a useful tool

for characterizing the metallurgical condition of aluminum

alloys, especially those of the 2XXX and 7XXX types, which

contain copper and zinc as major alloying elements. Its uses

include the determination of the effectiveness of solution heat

treatment and annealing (1), of the extent of precipitation

during artificial aging (4) and welding (5), and of the extent of

of —885 mV (SCE) (1-3).<sup>3</sup>

4.1 The apparatus consists of an inert container for the test solution, a mechanical support for the test specimens that insulates them electrically from each other and from ground, a saturated calomel electrode (SCE), wires and other accessories for electrical connections, and equipment for the measurement of potential. See Note 2.

Note 2—Saturated calomel electrodes are available from several manufacturers. It is a good practice to ensure the proper functioning of the reference electrode by measuring its potential against one or more reference electrodes. The potential difference should not exceed 2 or 3 mV.

4.2 High-impedance (> $10^{12}\Omega$ ) voltmeter is suitable for measurement of the potential. Measurement of this potential should be carried out to within  $\pm$  1 mV. Automatic data recording systems may be used to permit the simultaneous measurement of many specimens and the continuous recording of corrosion potentials.

## 5. Reagents

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

<sup>&</sup>lt;sup>1</sup> This test method is under the jurisdiction of ASTM Committee G01 on Corrosion of Metals and is the direct responsibility of Subcommittee G01.11 on Electrochemical Measurements in Corrosion Testing.

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<sup>&</sup>lt;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.

<sup>&</sup>lt;sup>3</sup> The boldface numbers in parentheses refer to the references at the end of this standard.

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>

- 5.2 *Purity of Water*—The water shall be distilled or deionized conforming to the purity requirements of Specification D1193, Type IV reagent water.
  - 5.3 Sodium Chloride (NaCl) Analytical Reagent (AR).
- 5.4 Hydrogen Peroxide ( $\rm H_2O_2$ ) (30 %)—In case of uncertainty (for example, whenever freshly opened reagent is not used), the concentration of hydrogen peroxide in the reagent shall be confirmed by chemical analysis as described in Annex A1. In no case shall reagent containing less than 20 % hydrogen peroxide be used.
  - 5.5 Nitric Acid—70 % (conc).
  - 5.6 Hydrochloric Acid—12 N (conc).
  - 5.7 Sulfuric Acid—36 N (conc).
  - 5.8 Sodium Hydroxide.

## 6. Solution Conditions

- 6.1 The test solution shall consist of  $58.5 \pm 0.1$  g of NaCl and  $9 \pm 1$  mL of 30 % hydrogen peroxide reagent per 1 L of aqueous solution. (This solution is 1 M with respect to concentration of sodium chloride.)
- 6.2 The hydrogen peroxide reagent shall be added just before measurements are made, because it decomposes upon standing.
- 6.3 Freshly prepared solution shall be used for each set of measurements.
- $6.4\,$  Not less than  $500\,$  mL of solution shall be used for each set of measurements.
- 6.5 The total exposed area of all the specimens of the same composition in each set of measurements shall not exceed 100 mm<sup>2</sup> per 100 mL of solution.
- 6.6 The temperature of the test solution shall be maintained at 25  $\pm$  2°C.

# 7. Test Specimen

7.1 For measurement alone, specimen size is unimportant provided that the area for measurement is at least 25 mm<sup>2</sup>, but for convenience the specimen, wherever possible, should be large enough to permit ease of handling during preparation and an electrical connection outside the test solution. A specimen a few millimetres thick by about 15 mm wide and 100 mm long is a convenient size.

## 8. Specimen Preparation

8.1 Any convenient means, such as sawing or stamping, may be used to prepare a specimen to size provided that it does not heat the specimen enough to change its metallurgical structure.

- 8.2 Irregular-shaped specimens shall be machined or prepared with a coarse file to provide a reasonably flat surface and to remove nonrepresentative metal (for example, affected by sawing or stamping, or in case of clad product where core is to be measured). Further preparation consists of filing with a long lathe file. Original flat surface specimens are also filed with long lathe file to remove the original mill scale oxide layer.
- 8.3 No filing or machining is needed to prepare specimens that have original flat surface, representative of its metallurgical structure, or to prepare specimens that are too thin to permit more than minimal removal of metal; these include clad products with thin claddings which are to be measured.
- 8.4 Mechanical Preparation—The surfaces of all products selected for measurement, including those with no previous preparation, are abraded dry with No. 320 grade aluminum oxide or silicon carbide cloth and then with No. 00 steel wool.
- Note 3—Caution: Clad products with thin claddings should only be abraded lightly except to remove the cladding for measurement of the core.
- 8.4.1 Following mechanical preparation, the specimen is cleaned or degreased in an inert solvent (for example, acetone, MEK, EtOH).
- 8.5 Chemical Preparation—Anyone of the following five procedures may be used. The etch treatment is followed by a rinse in Specification D1193 Type IV water, desmut for one minute in conc. nitric acid, and final rinse in Specification D1193 water and air dry.
- 8.5.1 One minute immersion in HF/HNO<sub>3</sub> at  $93 \pm 2^{\circ}$ C containing 5 mL/L of 48% HF and 50 mL/L of concentrated nitric acid. Do not let the HF solution remain in the borosilicate glass vessels used in this method, because the HF solution will attack the glass.
  - 8.5.2 One minute in 10% NaOH solution at 71  $\pm$  2°C.
- 8.5.3 Thirty seconds immersion in 12 N HCL at room temperature (22  $\pm$  2°C).
- 8.5.4 Sixty seconds immersion in 5N HCl at room temperature (22  $\pm$  2°C).
  - 8.5.5 Five minute immersion in 1 N  $H_2SO_4$  at 60  $\pm$  2°C.
- 8.6 Measurement of the core alloy in Alclad alloys requires removal of the cladding surfaces. This can be accomplished by either mechanical or chemical means. It is important that the entire cladding alloy be removed from one or both sides of the product in order to obtain reliable and reproducible results. The thickness of the Alclad samples should be reduced to at least 1.5 times of the total thickness of the clad layer(s) on one or both sides of the Alclad product. Metallographic cross sectioning may be necessary to verify complete removal of the cladding.
  - 8.6.1 Mechanical Removal of Cladding—See 8.4.
- 8.6.2 Chemical Removal of Cladding—Immerse in 5% NaOH at  $60 \pm 2^{\circ}$ C for a few minutes. The time of immersion is dependent upon rate of etching and cladding thickness. Rinse in cold water, desmut in conc. nitric acid for 1 min, and final rinse in Specification D1193 Type IV water and air dry.

Note 4—Measure the reduction in thickness of the sheet or plate sample to insure complete removal of the cladding.

<sup>&</sup>lt;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 Annual 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.

**TABLE 1 Repeatability** 

Alloy	Surface	Average	S <sub>r</sub>	±r (95 %)
1100-H18	Any	−759.2 mV	3.0 mV	8.4 mV
3003-H18	Any	–750.7 mV	3.0 mV	8.4 mV
5052-H32	Mech.	–756.5 mV	3.0 mV	8.4 mV
5052-H32	Chem.	–738.4 mV	5.6 mV	15.7 mV
2024-T3	Any	–605.6 mV	3.0 mV	8.4 mV
7075-T6	Any	−725.2 mV	3.0 mV	8.4 mV

8.7 All parts of a specimen and its electrical connection to be exposed in the test solution, except for the area of the specimen prepared for measurement, are masked off. Any material that masks a surface physically and electrically and that is inert in the test solution may be used (see Annex A2).

### 9. Procedure

- 9.1 For corrosion potential measurements, the test specimens and the reference electrode are immersed in the appropriate quantity of test solution; the test specimens are connected to the positive terminal of the equipment for measuring potential, and the reference electrode to the negative terminal.
- 9.2 Care should be taken to ensure that all the unmasked area of each test specimen prepared for measurement is exposed to the test solution and that any other unmasked area is not exposed. Care should also be taken to ensure that any unmasked portion of the electrical connection is outside the test solution.
- 9.3 The potential of each specimen shall be measured and recorded with a high impedance voltmeter after 20, 25 and 30 min in a 30-min run or after 50, 55 and 60 min in a 60-min run.
- 9.4 The 30-min potential of each specimen shall be reported together with the average of the last three measurements, that is, at 20, 25 and 30 min. If the test is continued for 60 min, the potential at 60 min shall be reported together with the average of potentials at 50, 55 and 60 min.
  - 9.5 Duplicate specimens shall be measured.
- 9.6 The average of the values for duplicate specimens shall be used if the values agree within 5 mV. If they do not agree within 5 mV, at least one additional specimen shall be measured. The values for the three or more specimens shall be averaged if they agree within 10 mV, but they shall be reported individually if they do not.

# 10. Standardization of Test Procedure

10.1 The test procedure shall be standardized by measurement of the free corrosion potential of a sample of commercially produced 3003 alloy sheet. Sheet of any temper is

suitable because the potential of this product is not affected significantly by temper.

10.2 The procedure shall be considered acceptable if the value obtained is  $-751 \pm 20$  mV (SCE).

# 11. Report

- 11.1 The following information shall be recorded:
- 11.1.1 Identification of product, alloy, and temper, including reference to applicable specifications.
- 11.1.2 Whether mechanical or chemical pretreatment was used; specify which chemical pretreatment.
- 11.1.3 The results of all measurements with an indication of whether they represent individual values or averages; and if averages, also the number of values averaged and the range.

# 12. Precision and Bias<sup>5</sup>

- 12.1 *Precision*—The precision of this test method was determined by analysis of the results of an interlaboratory test program with eight laboratories participation. Practice E691was used in the analysis of the data.
- 12.1.1 *Repeatability*—The repeatability, r, (within laboratory variation) and the repeatability standard deviation ( $S_r$  were determined as in Table 1.
- 12.1.2 *Reproducibility*—The reproducibility, R, (between laboratory variation) and the reproducibility standard deviation  $(S_R)$  were determined as in Table 2.It should be noted that the apparent cause of the interlaboratory variation was variation of the reference electrodes used. The chemical etch treatments of 5000 series alloys apparently causes an unstable surface for this method and that is responsible for the larger variation in results both in repeatability and reproducibility.
- 12.2 *Bias*—This test method has no bias because this corrosion potential is defined only in terms of this test method.

## 13. Keywords

13.1 aluminum alloy; aqueous; copper; corrosion potential; sodium chloride; solid solution; zinc

 $<sup>^5</sup>$  Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:G01-1024.

**TABLE 2 Reproducibility** 

Alloy	Surface	Average	S <sub>R</sub>	±R (95 %)
1100-H18	Any	−759.2 mV	7.0 mV	19.6 mV
3003-H18	Any	–750.7 mV	7.0 mV	19.6 mV
5052-H32	Mech.	–756.5 mV	7.0 mV	19.6 mV
5052-H32	Chem.	–738.4 mV	9.2 mV	25.8 mV
2024-T3	Any	–605.6 mV	7.0 mV	19.6 mV
7075-T6	Any	–725.2 mV	7.0 mV	19.6 mV

#### **ANNEXES**

# (Mandatory Information)

## A1. ANALYSIS OF HYDROGEN PEROXIDE REAGENT

- A1.1 Dilute a sample of the hydrogen peroxide reagent to contain approximately 6 g H<sub>2</sub>O<sub>2</sub>/L. Then pipet a 10-mL aliquot of this solution into a beaker to which has already been added 400 mL of water and 15 mL of 50 % sulfuric acid. Titrate this solution with standard 0.1 N potassium permanganate solution.
- A1.2 To obtain the grams of hydrogen peroxide per litre of reagent, multiply the millilitres of potassium permanganate solution used by 0.1 times 0.017 times the aliquot factor. Tables in chemical handbooks provide the data required to convert grams per litre of hydrogen peroxide to percent.
- A1.3 Some stabilizers used with hydrogen peroxide react with permanganate, but this interference can be ignored whenever the analysis given by the manufacturer was also determined by permanganate analysis.

# A2. MASKING MATERIALS

- A2.1 Materials suitable for masking are made by several manufacturers. For the interlaboratory study, see Research Report RR:G01-1024,<sup>5</sup> 3M's #470 electroplate tape was used by most of the participating laboratories.
- A2.2 One laboratory used the time-honored, but tedious, beeswax-rosin masking material, made by adding powdered rosin gradually to melted beeswax until saturation is obtained. Several hours may be required because of the slow rate of dissolution of the rosin.



#### APPENDIX

(Nonmandatory Information)

#### X1. CONVERSION FACTORS FOR POTENTIALS

X1.1 Many corrosion potentials of aluminum alloys in the literature were measured in an aqueous solution at 25°C containing 53 g of NaCl and 9 mL of 30 % H<sub>2</sub>O<sub>2</sub>/L. The potentials were measured with a 0.1 N calomel electrode with its tip immersed directly into the solution without bridging.

X1.2 To a good approximation, values measured under X1.1 may be converted to those measured by this test method by the addition of 92 mV (for example, -830 mV converts to -738 mV).

X1.3 Alternatively, values measured by this test method may be converted to those measured under X1.1 by the subtraction of 92 mV (for example, -738 mV converts to -830 mV). See Practice G3 for a more complete description of converting electrode potential for various standard reference electrodes.

# REFERENCES

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- (3) Anderson, W. A., and Stupf, H. C., *Corrosion Magazine*, Vol 6, 1980, p. 212.
- (4) Lifka, B. W., and Sprowls, D. O., "Significance of Intergranular Corrosion in High Strength Aluminum Alloys," Symposium on Localized Corrosion—Cause of Metal Failure, ASTM STP 516, Am. Soc. Testing Mats., 1972, pp. 120–44.
- (5) Shumaker, M. B., Kelsey, R. A., Sprowls, D. O., and Williamson, J. G., "Evaluation of Various Techniques for Stress Corrosion Testing Welded Aluminum Alloys," *Symposium on Stress Corrosion Testing*, ASTM STP 425, Am. Soc. Testing Mats., 1967, pp. 317–41.

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