ACTIVITY PLAN

Parametric Studies: Use of Linear-Sweep Polarization to Determine Pitting Potentials

Sub-activity E-20-18a of Activity E-20-18 of the Scientific Investigation "Metal Barrier Selection and Testing"

Joseph C. Farmer

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Revision 0
June 22, 1989

L.J.Jardine, YMP Project Leader	9/3/89 Date
D.W.Short, YMP QA Manager	7/31/89 Date
W.L.Clarke, Technical Area Leader	7/11/89 Date
Wm. G. Walady, Deputy T.L., For R.D.McCright, Task Leader	7/26/89 Date

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Use of Linear-Sweep Polarization to Determine Pitting Potentials

Sub-Activity E-20-18a of Activity E-20-18 of the
Scientific Investigation "Metal Barrier Selection and Testing"
WBS # 1.2.2.3.2

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1.0 INTRODUCTION

1.1 Identification of activity

This activity plan is for sub-activity E-20-18a and is written pursuant to quality procedure 033-YMP-QP-3.0 [1]. Sub-activity E-20-18a is part of activity E-20-18, which is known as "Parametric Studies." Activity E-20-18 is part of the scientific investigation known as "Metal Barrier Selection and Testing," which is identified with WBS # 1.2.2.3.2. and published in UCID-21262.

1.2 Quality Assurance Level Assignment

A quality assurance level of QA-II has been assigned to this activity (E-20-18).

1.3 Responsibilities

Joseph C. Farmer is the Principal Investigator for this activity (E-20-18) and is responsible for completion of this work. R. Daniel McCright is the Task Leader for the Metal Barrier Selection and Testing investigation. Willis L. Clarke is the Technical Area Leader for Container Materials Modeling and Testing.

2.0 PURPOSE AND OBJECTIVES

One of the objectives of activity E-20-18 is to obtain experimental data necessary for the selection of the metal barrier (container) material. Specifically, the objective of sub-activity E-20-18a is to determine the corrosion and pitting potentials. This data is required by activity E-20-15, the selection criteria, and by activity E-20-16, modeling.

3.0 ACTIVITY DESCRIPTION

Pitting potentials for the austenitic candidate alloys in sea water have been found in the literature [2-4]. Comparable data for the copper-based candidate alloys does not exist [5-7]. Pitting potential data for candidate alloys in electrolytes having the the same relative concentrations of ions as water from well J-13 (reference condition) have not been published. This data is crucial for the materials selection process, activity E-20-15.

Linear sweep polarization will be used to determine pitting potentials. To the extent possible, measurements will be performed as specified in ASTM Standard G5-87 [8]. Any necessary deviations from the ASTM standard will be noted in a laboratory notebook used for recording data. The test solution will have concentrations of ions similar to that found in concentrated water from well J-13 (concentration factor of 1X-20X). Experimental procedures and data will be documented in a laboratory notebook and a formal UCID report.

3.1 Technical Reviews

A formal <u>Readiness Review</u> will be held before any experimental

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A formal Readiness Review will be held before any experimental work begins. This review will insure that:

1. Measurement and test equipment (M&TE) are properly calibrated as specified in quality procedure 033-YMP-QP-12.0.

2. Test samples were procured as specified in quality procedure 033-YMP-QP-4.0 and controlled as specified in quality procedure 033-YMP-QP-8.0.

3. Collected data will be controlled as specified in quality procedure 033-YMP-QP-8.0.

4. Laboratory notebooks are being maintained as specified in quality procedure 033-YMP-QP-3.4.

After completion of an experiment or a series of experiments, a UCID report will be written. The UCID report will undergo Technical Review as specified in quality procedure 033-YMP-QP-3.3.

3.2 Hold Points

Results will be evaluated on a continuous basis by the Principal Investigator to insure that work is proceeding according to plan. If significant unanticipated problems arise, the Principal Investigator will inform the Task Leader. A joint decision will be made about corrective actions.

Progress will be reported to the Task Leader in a monthly report. If changes in project scope require that experimental work change direction, it is the responsibility of the Task Leader to communicate this to the Principal Investigator in writing.

3.3 Equipment

Required M&TE includes a potentiostat, data recorder, and electrochemical cell. See ASTM Standard G5-87 [8]. Specifically, the potentiostat will be a Princeton Applied Research (PAR) Model 273 [9]. We have two such instruments: Identification Nos. 4053581 and 4066826. Both of these instruments are found on the list of calibrated equipment (See Section 11.2). The data recorder consists of a PAR Model 351 Microprocessor-Based Controller (Identification No. 4066819) and a Bausch and Lomb Model DMP40 Digital Plotter (Identification No. 4066833) [10]. Both the controller and plotter are digital and require no calibration. The electrochemical cell is a PAR Model K47 Corrosion Cell System [11].

3.4 Materials

All samples tested in the electrochemical cell will be procured as specified in quality procedure 033-YMP-QP-4.0 and controlled as specified in quality procedure 033-YMP-QP-4.0. The PAR Model K47

Corrosion Cell System discussed in Section 3.3 accepts cylindrical or flat samples [11]. Cylindrical samples are 1/2 inch long and 3/8 inch diameter. One end of the cylinder is drilled with a hole 1/4 inch deep. The hole is tapped to accept a 3-48 thread. Flat samples are 0.625 inches in diameter and 1/8 inch thick. The flat geometry is preferred.

3.5 Special Environmental Conditions

Electrolytes used for testing will be prepared so as to maintain the same relative concentrations of ions as found in water from well J-13, if possible. Absolute concentrations may be greater or less than those found in water from well J-13 (reference condition). Measurements in other aqueous environments (NaCl solutions, etc.) will also be made.

3.6 Special Training/Qualification Requirements

Qualifications of the Principal Investigator and Technicians are specified by the Task Leader in accordance with 033-YMP-QP-2.10 "Qualification of Personnel". The Principal Investigator must have a Ph.D. in electrochemistry, electrochemical engineering, or metallurgical engineering with expertise in electrochemical corrosion testing. Technicians must have experience in electrochemical instrumentation and techniques. Only personnel qualified in the quality assurance procedures of the Yucca Mountain Project will be allowed to participate in the experiment.

3.7 Activity Closeout

The final product of this sub-activity will be a UCID report documenting all results. Supporting documentation such as laboratory notebooks and technical review comments will be retained by the responsible individual until the document package is transferred to the local records center at the conclusion of the sub-activity.

4.0 RANGE, ACCURACY AND PRECISION

The minimum range of potential to be explored will extend from the corrosion potential to the thermodynamic limit of the electrolyte (oxygen evolution). The potential range specified in ASTM Standard G5-87, Section 4.2.1 is -0.6 to 1.6 V relative to the reference electrode [8]. This is within the +/- 2 V range of potential of the PAR Model 273 Potentiostat.

The accuracy of the controlled potential specified in ASTM Standard G5-87, Section 4.2.1 is +/- 1 mV. This requirement will not be met for two reasons. First, the PAR Model 273 Potentiostat can control the potential of the working electrode relative to the reference electrode with an accuracy of only +/- 0.2 % of the range. In the case of ASTM Standard G5-87 the accuracy will be approximately +/- 2 mV. Second, Accuracy will be limited by the reproduceability of reference electrodes. Typical variability observed in commercial reference electrodes is approximately +/- 5 mV (see Section 4.3).

According to ASTM Standard G5-87, Section 4.2.1, the range of output current from the potentiostat must extend from 1 uA to 0.1 A (10^5 uA). The PAR Model 273 Potentiostat can deliver up to 1 A, thereby exceeding the requirement. For the 100 nA and 1 uA ranges, the accuracy of the current monitor is +/- 0.5 % of the range. For the 10 uA to 1 A ranges, the accuracy of the current monitor is +/- 0.2 % of the range.

4.1 Calibration Requirements

All M&TE must be calibrated as specified in quality procedure 033-YMP-QP-12.0. Identification numbers of potentiostats must be found on the list of calibrated equipment.

4.2 Conditions Which May Adversely Affect Results

Electrical connections must be isolated from corrosive media to avoid a loss of continuity due to the build-up of corrosion products at points of contact. Since pitting potential is very sensitive to chloride ion concentration, special care must be taken to avoid introduction of saturated KCl into the test cell from the saturated calomel reference electrode. See Section 4.3.

4.3 Sources of Uncertainty and Error to be Controlled and Measured

As discussed in Section 4.0, variability is observed in lots of commercial reference electrodes. The variability will be determined by measuring potential differences existing between several identical reference electrodes.

Care must be taken to avoid inadvertent contamination of the electrolyte in the test cell with saturated KCl from the saturated calomel reference electrode (SCE). A double-junction reference electrode configuration will be used to minimize cross contamination. Ion concentrations will be verified before and after linear polarization experiments by analytical techniques such as ion chromatography. Alternatively, reference electrodes without KCl or NaCl can be used to avoid this problem. For example, the $Hg/Hg_2SO_4/K_2SO_4$(sat'd) reference electrode can be used. This particular reference electrode has a standard potential of 0.4 V verses a SCE reference.

Actual pitting potentials will also vary from sample to sample, due to random variations in alloy composition, as well as random variations in the number of sulfide inclusions near the sample surface. For a given alloy, several measurements of the pitting potential will be made in order to establish good statistics.

Once the pitting potential is determined from polarization curves, the value will be verified by potentiostatic polarization tests at potentials above and below the pitting potential. Post-exposure examination of the samples should show that no pitting occurs below the pitting potential, whereas significant pitting occurs above the pitting potential.

5.0 IN-PROCESS DOCUMENTATION

In-process documentation will include polarization curves, optical and electron micrographs of sample surfaces before and after polarization, and analytical data for metal and electrolyte samples. Data will be kept in a controlled laboratory notebook identified as Metal Barrier Selection and Testing Task Notebook No. 5 with LLNL Serial No. 00086. Results will be periodically transmitted to the Task Leader in the monthly report.

5.1 Data Recording and Data Reduction

Polarization curves will be recorded with the PAR Model 351 Microprocessor-Based Controller and PAR Model R93 Digital Plotter. Electrochemical potential of the sample will be recorded on the x-axis and electrochemical current (or logarithm of the current) will be recorded on the y-axis.

5.2 Analysis

The resistance of a given alloy will be calculated by subtracting the corrosion potential from the critical pitting potential. Large differences are indicative of good resistance to pitting. Determination of the pitting potential from polarization curves is somewhat subjective, therefore, the pitting potential must be marked on each polarization curve.

6.0 INTERFACES

This activity can proceed independent of any other activity, however, activity E-20-19 ("Metal Barrier Selection") cannot proceed without this activity. The Technical Area Leader and Task Leader for activity E-20-19 are the same as for activity E-20-18.

7.0 SCHEDULE

The readiness review for this sub-activity is tentatively scheduled for the last week in July of 1989. The final UCID report will summarize all of the data and will be completed prior to the first week in April of 1990.

8.0 TECHNICAL IMPLEMENTING PROCEDURES

Since we will follow an established ASTM procedure, no Technical Implementing Procedure (TIP) will be required. As previously discussed, the applicable ASTM procedure is designated G5-87 [8]. As stated in Section 11, see Appendix 1 for a copy of ASTM Standard G5-87.

9.0 SPECIAL CASES (PROCUREMENT)

Not applicable.

9.1 QA Requirements Specification

Not applicable.

9.2 Statement of Work

Not applicable.

9.3 Subcontractor Interface Control

Not applicable.

9.4 Materials/Equipment Provided

Not applicable.

9.5 Deliverables

Not applicable

10.0 REFERENCES

1. "Scientific Investigation," 033-YMP-QP-3.0, in LLNL Yucca Mountain Project Quality Procedures Manual, 1989.

2. J. C. Farmer, R. A. Van Konynenburg, R. D. McCright, D. B. Bullen, "Localized Corrosion and Stress Corrosion Cracking of Austenitic Steels," in Survey of Degradation Modes of Candidate Materials for High-Level Radioactive-Waste Disposal Containers, UCID-21362, Vol. 3, April 1988.

3. T. Hodgkiess, S. Rigas, "A Comparison of the Corrosion Resistance of Some Higher-Alloy Stainless Steels in Seawater at 20-100°C," Desalination, Vol. 44, 1983, pp. 283-294.

4. R. C. Scarberry, E. L. Hibner, J. R. Crum, "Assessment of Pitting-Potential Measurements in Severely Corrosive Environments," Paper Number 245, Corrosion 79, Atlanta, Georgia, March 12-16, 1979, National Association of Corrosion Engineers, Katy, Texas.

5. J. C. Farmer, R. A. Van Konynenburg, R. D. McCright, G. E. Gdowski, "Localized Corrosion of Copper-Based Alloys," in Survey of Degradation Modes of Candidate Materials for High-Level Radioactive Waste Disposal Containers, UCID-21362, Vol. 5, June 1988.

6. H. S. Campbell, "A Review: Pitting Corrosion of Copper and Its Alloys, " Proceedings of the U. R. Evans Conference on Localized Corrosion, Williamsburg, Virginia, December 6-10, 1971, R. W. Staehle, B. F. Brown, J. Kruger, A. Agrawal, Editors, National Association of Corrosion Engineers, Houston, Texas, 1974, pp. 625-635.

7. Z. Szklarska-Smialowska, "Pitting of Copper, Zinc, and Other Metals and Alloys," Chapter 10, in Pitting Corrosion of Metals, National Association of Corrosion Engineers, Houston, Texas, 1986.

8. "Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements," Designation G5-87, in 1987 Annual Book of ASTM Standards, Section 3.0, Metals Test Methods and Analytical Procedures, Vol. 3.02, Wear and Erosion; Metal Corrosion, ASTM 1916 Race Street, Philadelphia, Pennsylvania, 1987, pp. 124-133.

9. Operating Manual for the Model 273 Potentiostat/Galvanostat, EG&G Princeton Applied Research, Princeton, New Jersey, 1985.

10. Operating Manual for the Model 351 Corrosion Measurement System, EG&G Princeton Applied Research, Princeton, New Jersey, 1985.

11. Instruction Manual for the Model K47 Corrosion Cell System, EG&G Princeton Applied Research, Princeton, New Jersey, 1985.

11.0 APPENDICES

1. Copy of ASTM Standard G5-87.

2. Current List of Calibrated Equipment, p. 2.

Appendix 1.

Copy of ASTM Standard G5-87

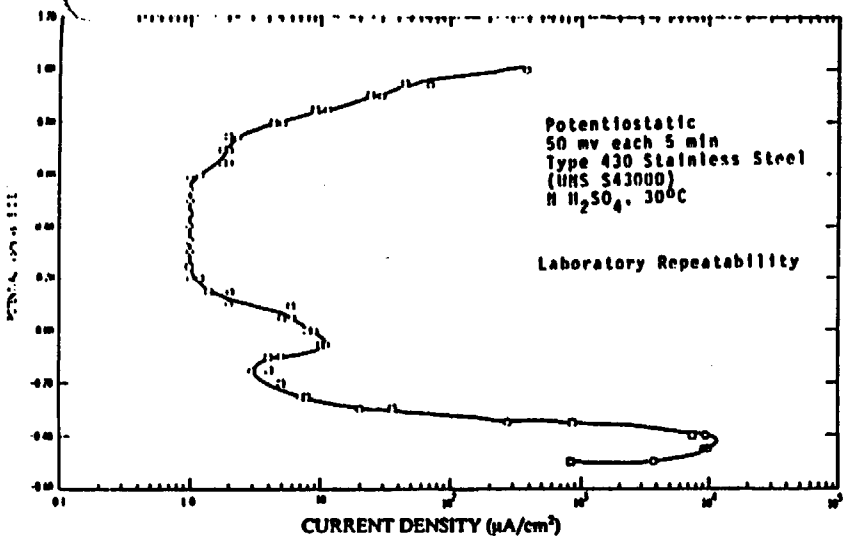


FIG. 6 Laboratory Repeatability of Potentiostatic Anodic Polarization Curve

APPENDIX

(Nonmandatory Information)

X1. DEVIATIONS FROM STANDARD POLARIZATION PLOTS

X1.1 High Passive Current Densities (Crevice Effect)

X1.1.1 Examples of passive current densities which are greater than those for a standard potentiostatic plot are shown in Fig. X1.1. This effect is attributable to a crevice between the specimen and mounting material (6). The crevice may be the result of the mounting technique or the material used for mounting.

X1.1.2 The potential drop along the narrow path of the electrolyte within the crevice between the specimen and the mounting material prevents this area from passivating. Although the face of the specimen passivates, the high current density associated with the active crevice contributes to an increase in the measured current density. Specimen electrodes for polarization measurements must be mounted without crevice sites to avoid such erroneous passive current densities.

X1.2 Low Passive Current Densities (Instrumental Effect)

X1.2.1 The low passive current densities shown in Fig. X1.2 are undoubtedly the result of instrumental problems. This effect can be eliminated by calibrating the current over the entire range of interest before conducting an experiment.

X1.3 Cathodic Currents During Anodic Polarization (Oxygen Effect)

X1.3.1 The "negative loop" at potentials between −0.350 V and −0.050 V, shown by dashed lines in Fig. X1.3, occurs when the total cathodic current exceeds the total anodic current. Such results are characteristic of oxygen being present in the solution (7). This effect can be anticipated if the recorded platinum potential is considerably more noble than −0.26 V. The gas purge should remove oxygen from the system, but there may be an air leak or the purge gas may be contaminated with oxygen. It is necessary to take extreme care in the design of glassware equipment and to ensure a high order of purity in the gas that is used to avoid oxygen contamination.

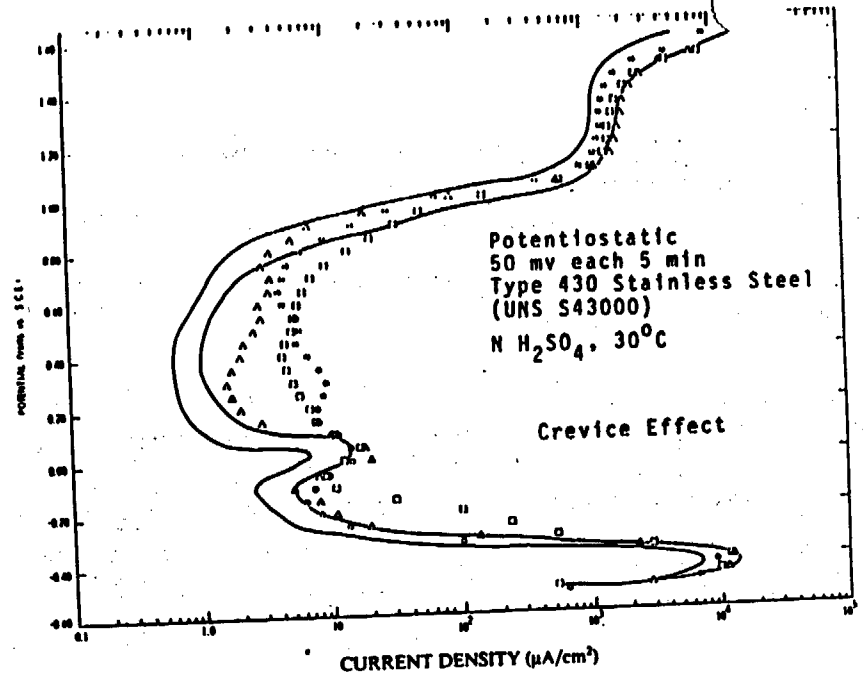
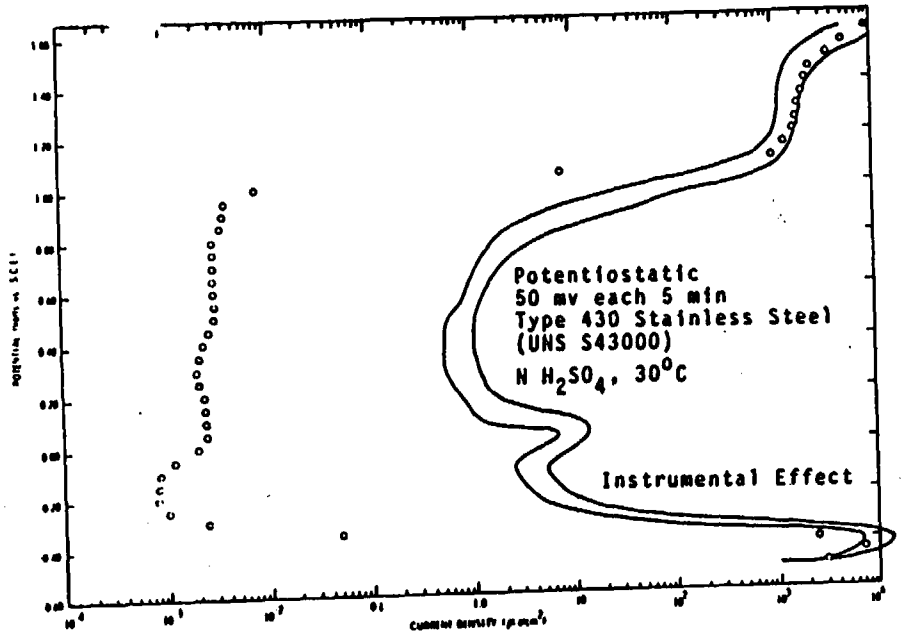
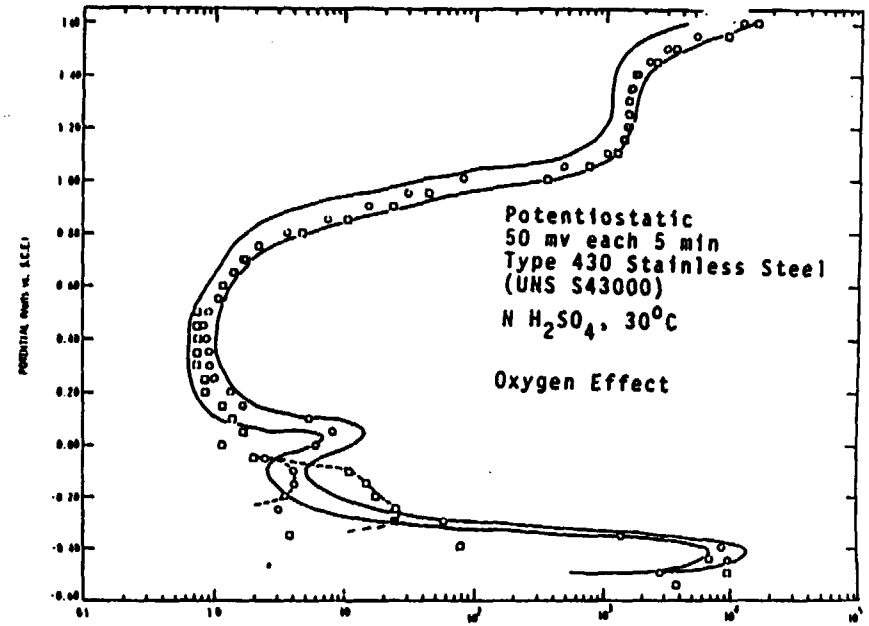


FIG. X1.1 Crevice Effect During Potentiostatic Anodic Polarization



CURRENT DENSITY (μA/cm²)

FIG. X1.2 Instrumental Effect During Potentiostatic Anodic Polarization



CURRENT DENSITY (μA/cm²)

FIG. X1.3 Oxygen Effect During Potentiostatic Anodic Polarization

REFERENCES

(1) Greene, N. D., *Experimental Electrode Kinetics*, Rensselaer Polytechnic Institute, Troy, NY, 1965.

(2) France, Jr., W. D., "Controlled Potential Corrosion Tests, Their Applications and Limitations," *Materials Research and Standards*, Vol 9, No. 8, 1969, p. 21.

(3) Mellon, M. G., *Quantitative Analysis*, Thomas Y. Crowell Co., New York, 1955.

(4) Ives, D. J., and Janz, G. J., *Reference Electrodes, Theory and Practice*, Academic Press, New York, NY, 1961.

(5) "The Reproducibility of Potentiostatic and Potentiodynamic Anodic Polarization Measurements ASTM Subcommittee G-1/X1, Section 1, Interlaboratory Testing Program, June, 1967. Availabl from ASTM Headquarters as RR: G01-1000.

(6) Greene, N. D., France, Jr., W. D., and Wilde, B E., "Electrode Mounting for Potentiostatic Anodic Polarization Studies," *Corrosion*, CORRA Vol 21, 1965, p. 275.

(7) Greene, N. D., "Effect of Oxygen on the Active Passive Behavior of Stainless Steel," *Journal the Electrochemical Society*, JESOA, Vol 107 1960, p. 457.

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1987 ANNUAL BOOK OF ASTM STANDARDS

SECTION 3

Metals Test Methods and Analytical Procedures

VOLUME

03.02 Wear and Erosion; Metal Corrosion

Includes standards of the following committees:

G-1 on Corrosion of Metals
G-2 on Wear and Erosion

Publication Code Number (PCN): 01-030287-27

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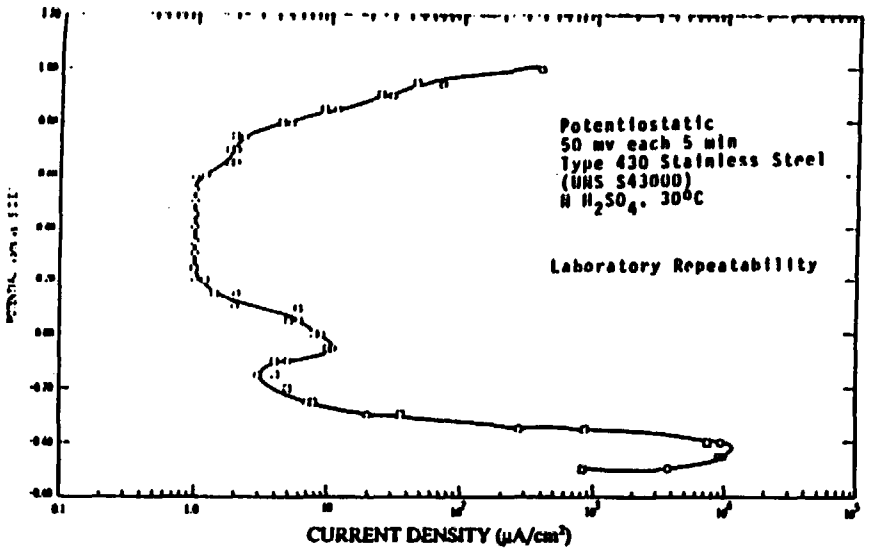

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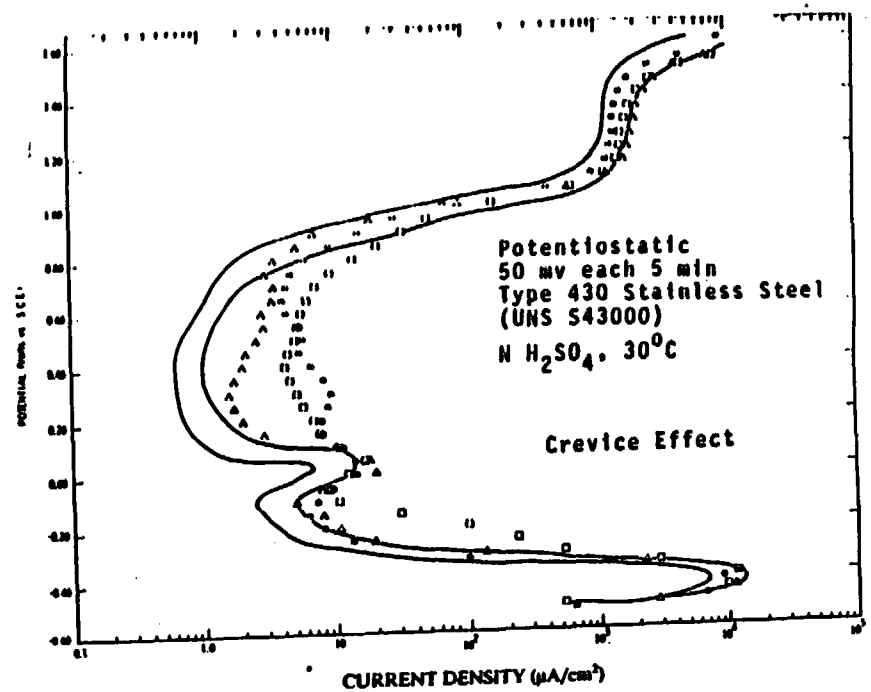
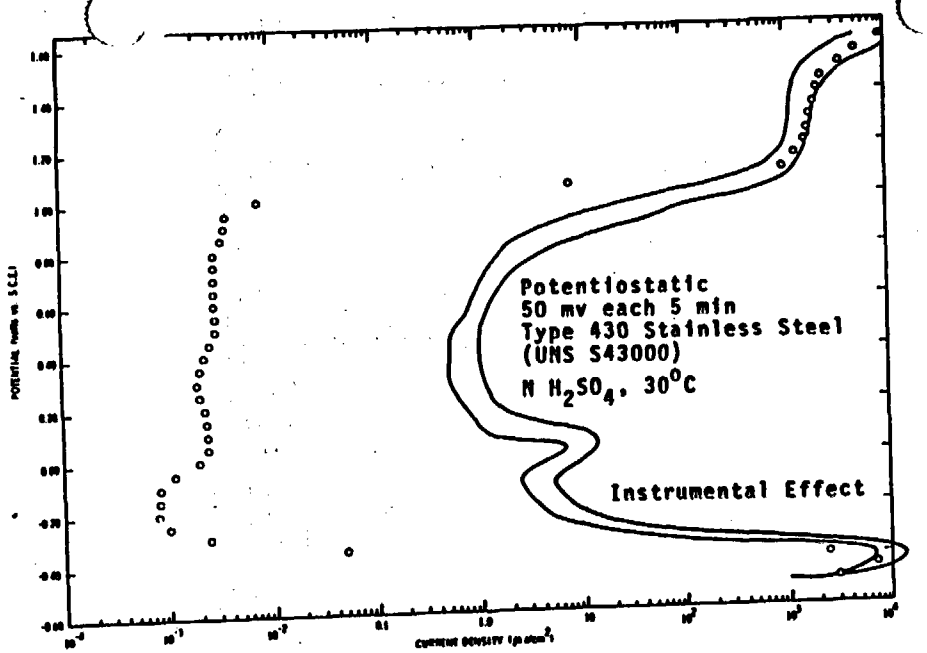
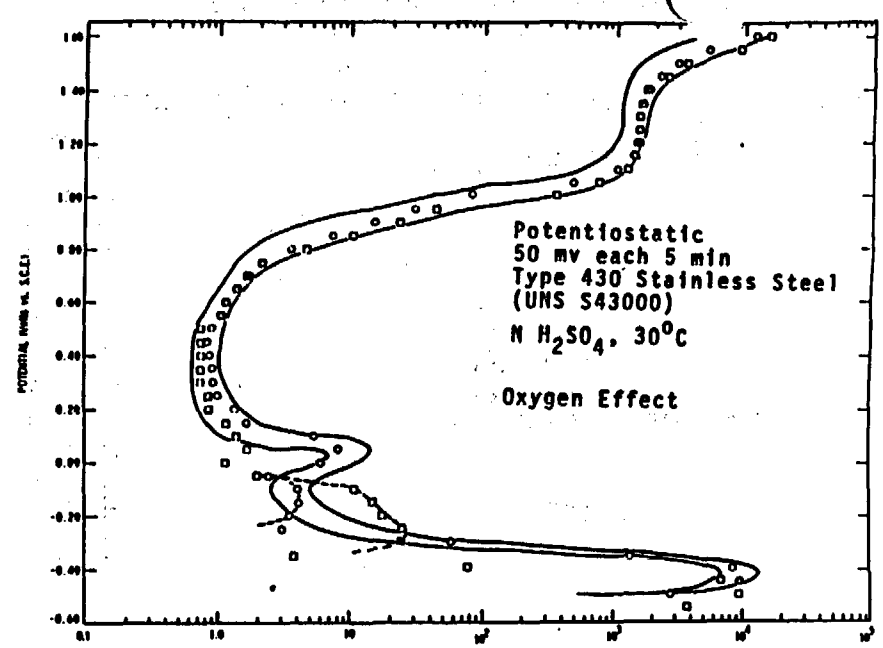


FIG. X1.1 Crevice Effect During Potentiostatic Anodic Polarization



CURRENT DENSITY (μA/cm²)

FIG. X1.2 Instrumental Effect During Potentiostatic Anodic Polarization



CURRENT DENSITY (μA/cm²)

FIG. X1.3 Oxygen Effect During Potentiostatic Anodic Polarization

REFERENCES

(1) Greene, N. D., *Experimental Electrode Kinetics*, Rensselaer Polytechnic Institute, Troy, NY, 1965.

(2) France, Jr., W. D., "Controlled Potential Corrosion Tests, Their Applications and Limitations," *Materials Research and Standards*, Vol 9, No. 8, 1969, p. 21.

(3) Mellon, M. G., *Quantitative Analysis*, Thomas Y. Crowell Co., New York, 1955.

(4) Ives, D. J., and Janz, G. J., *Reference Electrodes, Theory and Practice*, Academic Press, New York, NY, 1961.

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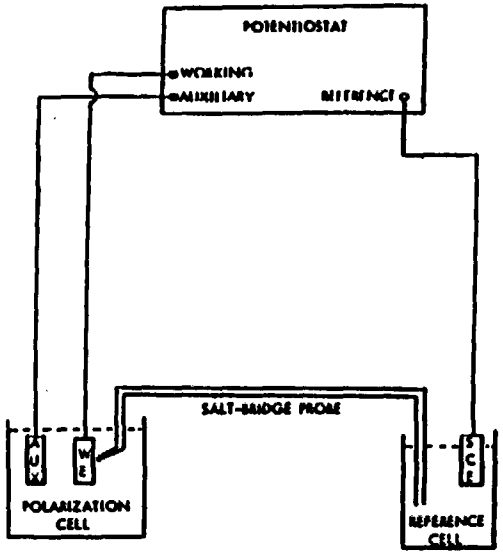

FIG. 2 Schematic Potentiostatic Anodic Polarization Wiring Diagram (2)

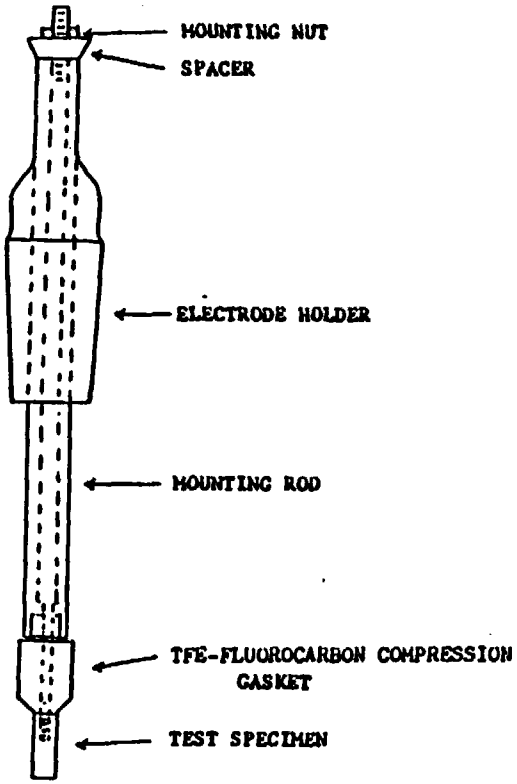

FIG. 3 Specimen Mounted on Electrode Holder

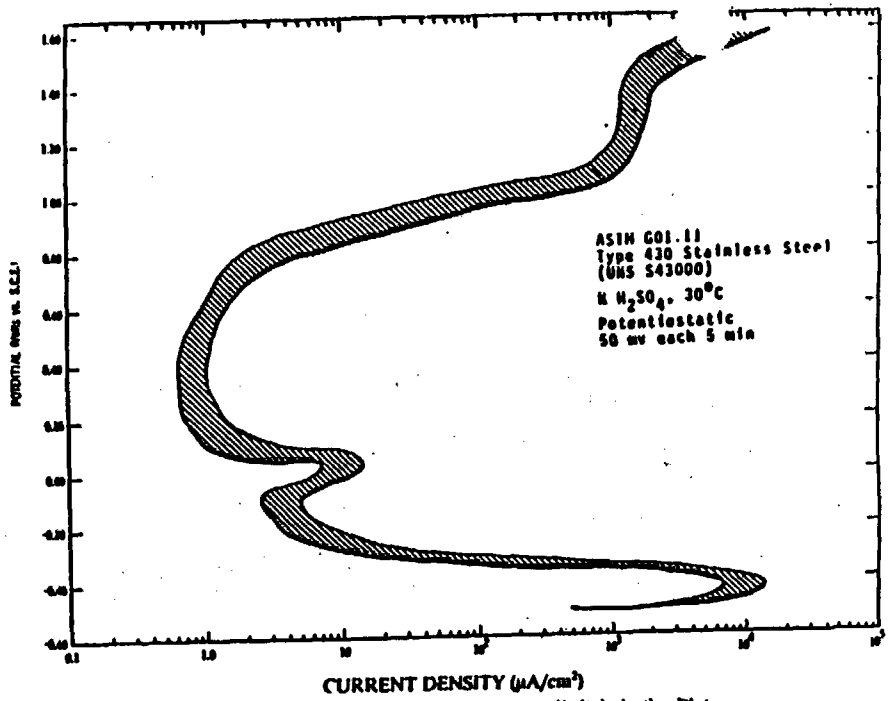

FIG. 4 Typical Standard Potentiostatic Anodic Polarization Plot

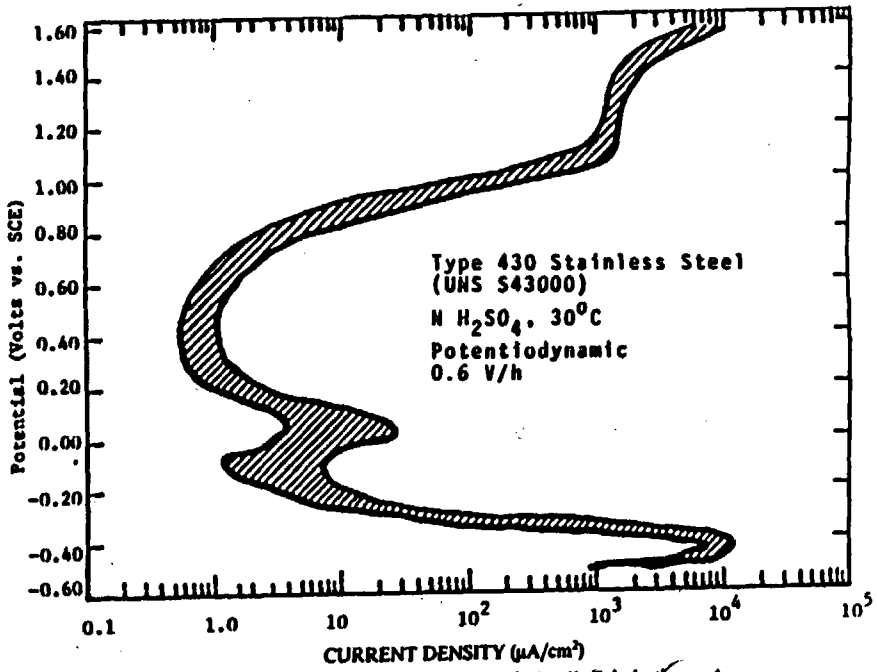

FIG. 5 Typical Standard Potentiodynamic Anodic Polarizat

Standard Reference Test Method for MAKING POTENTIOSTATIC AND POTENTIODYNAMIC ANODIC POLARIZATION MEASUREMENTS[1]

This standard is issued under the fixed designation G 5; 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 an experimental procedure which can be used to check one's experimental technique and instrumentation. If followed, this test method will provide repeatable potentiostatic and potentiodynamic anodic polarization measurements that will reproduce data determined by others at other times and in other laboratories.

1.2 Values stated in SI units are to be regarded as the standard. Inch-pound units given in parentheses are for information only.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems 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 Document

2.1 *ASTM Standard:*

G 3 Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing[2]

3. Significance and Use

3.1 The availability of a standard procedure, standard material, and a standard plot should make it easy for an investigator to check his techniques. This should lead to polarization curves in the literature which can be compared with confidence.

3.2 Samples of a standard ferritic Type 430 stainless steel (UNS SA 300) used in obtaining standard reference plot are available for those who wish to check their own test procedure and equipment.[3]

3.3 Standard potentiostatic and potentiodynamic polarization plots are supplied with the purchase of the reference material. These reference data are based on the results from different laboratories that followed the standard procedure, using that material in 1.0 *N* H_2SO_4. Maximum and minimum current values are shown at each potential to indicate the acceptable range of values.

3.4 This test method may not be appropriate for polarization test of all materials or in all environments.

4. Apparatus

4.1 The test cell should be constructed to allow the following items to be inserted into the solution chamber: the test electrode, two auxiliary electrodes, a Luggin capillary with salt-bridge connection to the reference electrode, inlet and outlet for an inert gas, and a thermometer. The test cell shall be constructed of materials that will not corrode, deteriorate, or otherwise contaminate the test solution.

NOTE 1—Borosilicate glass and TFE-fluorocarbon have been found suitable.

4.1.1 A suitable cell is shown in Fig. 1 (**1**).[4] A 1-L, round-bottom flask has been modified by the addition of various necks to permit the introduction of electrodes, gas inlet and outlet tubes, and a thermometer. The Luggin probe-salt bridge separates the bulk solution from the saturated calomel reference electrode, and the probe tip can be easily adjusted to bring it in close proximity with the working electrode.

4.2 *Potentiostat* (Note 2):

4.2.1 A potentiostat that will maintain an electrode potential within 1 mV of a preset value over a wide range of applied currents should be used. For the type and size of standard specimen supplied, the potentiostat should have a potential range from −0.6 to 1.6 V and an anodic current output range from 1.0 to 10^5 μA.

4.3 *Potential-Measuring Instruments* (Note 2):

4.3.1 The potential-measuring circuit should have a high input impedance on the order of 10^{11} to 10^{14} Ω to minimize current drawn from the system during measurements. Such circuits are provided with most potentiostats. Instruments should have sufficient sensitivity and accuracy to detect a change of 1.0 mV over a potential range between −0.6 and 1.6 V.

4.4 *Current-Measuring Instruments* (Note 2):

4.4.1 An instrument that is capable of measuring a current accurately to within 1 % of the absolute value over a current range between 1.0 and 10^5 μA for Type 430 stainless steel (UNS S43000) specimen with a surface area of approximately 5 cm^2.

4.5 *Anodic Polarization Circuit:*

4.5.1 A schematic potentiostatic anodic polarization wiring diagram (**2**) is illustrated in Fig. 2.

4.5.2 A scanning potentiostat is used for potentiodynamic measurements. For such measurements the potentiostat shall be capable of automatically varying the potential at a constant rate between two preset potentials. A record of the potential and current is plotted continuously using such instruments as an *X-Y* recorder and a logarithmic converter incorporated into the circuit shown in Fig. 2. Some potentiostats have an output of the logarithm of the current as a voltage, which allows direct plotting of the potential log current curve using an *X-Y* recorder.

NOTE 2—The instrumental requirements are based upon values typical of the instruments in 15 laboratories.

4.6 *Electrode Holder* (**1**):

4.6.1 The auxiliary and working electrodes are mounted in the type of holder shown in Fig. 3. A longer holder is required for the working electrode than for the auxiliary electrode. A leakproof assembly is obtained by the proper compression fit between the electrode and a TFE-fluorocarbon gasket. (Too much pressure may cause shielding of the electrode or breakage of the glass holder, and too little pressure may cause leakage and subsequently crevice corrosion which may affect the test results.)

4.7 *Electrodes:*

4.7.1 *Working Electrode*, prepared from a 12.7-mm (½-in.) length of 9.5-mm (⅜-in.) diameter rod stock. Each electrode is drilled, tapped, and mounted in the manner discussed in 4.6.1.

NOTE 3—If specimen forms are used other than those called for by this test method, for example, flat sheet specimen, care should be taken since it was shown that crevices may be introduced which can lead to erroneous results (see Fig. X1.1).

4.7.1.1 The standard AISI Type 430 stainless steel (UNS S43000) should be used if one wishes to reproduce a standard reference plot. This material is prepared from a single heat of metal that is mill-annealed for ½ h at 815°C (1500°F) and air cooled. The chemical composition of the standard stainless steel is supplied with the purchase of reference material.

4.7.2 *Auxiliary Electrodes:*

4.7.2.1 Two platinum auxiliary electrodes are prepared from high-purity rod stock. Each electrode is drilled, tapped, and mounted with a TFE-fluorocarbon gasket in the same manner as the working electrode. A large platinum sheet sealed into a glass holder is also acceptable.

4.7.2.2 A platinized surface may be utilized because of the increased surface area. This may be accomplished by cleaning the surface in hot aqua regia (3 parts concentrated HCl and 1 part concentrated HNO_3), washing, and then drying. Both electrodes are platinized by immersing them in a solution of 3 % platinic chloride and 0.02 % lead acetate and electrolyzing at a current density of 40 to 50 mA/cm^2 for 4 or 5 min (**1,3**). The polarity is reversed every minute. Occluded chloride is removed by electrolyzing in a dilute (10 %) sulfuric acid solution for several minutes with a reversal in polarity every minute. Electrodes are rinsed thoroughly and stored in distilled water until ready for use. Since certain ions

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[1] This test method is under the jurisdiction of ASTM Committee G-1 on Corrosion of Metals.

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[2] *Annual Book of ASTM Standards*, Vol 03.02.

[3] These standard samples are available from ASTM Headquarters. Generally, one sample can be repolished and reused for many runs. This procedure is suggested to conserve the available material. Order PCN 12-700050-00.

[4] The boldface numbers in parentheses refer to the list of references at the end of this test method.

can poison these electrodes, periodic checks of platinized platinum potentials against a known reference electrode should be made.

4.7.2.3 Alternatively, graphite auxiliary electrodes can be used, but material retained by the graphite may contaminate subsequent experiments. This contamination can be minimized by using high-density graphite or avoided by routinely replacing the graphite electrode.

4.7.3 *Reference Electrode* (4):

4.7.3.1 A saturated calomel electrode with a controlled rate of leakage (about 3 μL/h) is recommended. This type of electrode is durable, reliable, and commercially available. Precautions shall be taken to ensure that it is maintained in the proper condition. The potential of the calomel electrode should be checked at periodic intervals to ensure the accuracy of the electrode. For other alloy-electrolyte combinations a different reference electrode may be preferred in order to avoid contamination of the reference electrode or the electrolyte.

4.7.3.2 Alternatively, a saturated calomel electrode utilizing a semi-permeable membrane or porous plug tip may be used. These may require special care.

5. Experimental Procedure

5.1 Prepare 1 L of 1.0 *N* H_2SO_4 from A.C.S. reagent grade acid and distilled water, for example, by using 27.8 mL of 98 % H_2SO_4/L of solution. Transfer 900 mL of solution to the clean polarization cell.

5.2 Place the platinized auxiliary electrodes, salt-bridge probe, and other components in the test cell and temporarily close the center opening with a glass stopper. Fill the salt bridge with test solution.

NOTE 4—When using a controlled leakage salt bridge, the levels of the solution in the reference and polarization cells should be the same to avoid siphoning. If this is impossible, a closed solution-wet (not greased) stopcock can be used in the salt bridge to eliminate siphoning, or a semi-permeable membrane or porous plug tip may be used on the salt bridge.

5.3 Bring the temperature of the solution to 30 ± 1°C by immersing the test cell in a controlled-temperature water bath or by other convenient means.

5.4 Reduce oxygen levels in solution prior to immersion of the test specimen. This may be accomplished by bubbling an oxygen-free gas such as hydrogen, argon, or nitrogen at a rate of 150 cm³/min for a minimum of ½ h.

5.5 Prepare the working electrode surface within 1 h of the experiment. Wet grind with 240-grit SiC paper, wet polish with 600-grit SiC paper until previous coarse scratches are removed, rinse, and dry. (Drilled and tapped specimens can be threaded onto an electrode holder rod and secured in a lathe or electric drill for this operation.)

5.6 Determine the surface area by measuring all dimensions to the nearest 0.01 mm, subtracting the area under the gasket (usually 0.20 to 0.25 cm²).

5.7 Mount the specimen on the electrode holder as described in 4.6.1. Tighten the assembly by holding the upper end of the mounting rod in a vise or clamp while tightening the mounting nut until the gasket is properly compressed.

5.8 Degrease the specimen just prior to immersion and then rinse in distilled water.

5.9 Transfer the specimen to the test cell and adjust the salt-bridge probe tip so it is about 2 mm or 2 times the tip diameter, whichever is larger from the specimen electrode.

5.10 Record the open-circuit specimen potential, that is, the corrosion potential, after 55 min immersion. If platinum counter electrodes and hydrogen gas are used, record the platinum potential 50 min after immersion of the specimen.

5.11 *Potential Scan:*

5.11.1 Start the potential scan or step 1 h after specimen immersion, beginning at the corrosion potential (E_{corr}) for potentiodynamic measurements and the nearest 50-mV increment above E_{corr} for the potentiostatic measurements. Proceed through +1.60 V versus saturated calomel electrode (SCE) (active to noble).

5.11.2 In the potentiostatic method, use a potentiostatic potential step rate of 50 mV every 5 min, recording the current at the end of each 5-min period at potential. These steps are repeated until a potential of +1.6 V SCE is reached.

5.11.3 In the potentiodynamic method, use a potentiodynamic potential sweep rate of 0.6 V/h (±5 %) recording the current continuously with change in potential from the corrosion potential to +1.6 V SCE.

5.12 Plot anodic polarization data on semilogarithmic paper in accordance with Practice G3, (potential-ordinate, current density-abscissa). If a potentiostat with a logarithmic converter is used, this plot can be produced directly during measurement.

6. Standard Reference Plots

6.1 Standard polarization plots prepared from data obtained by following the standard procedure discussed in this test method are supplied with the purchase of reference material. Typical data are shown in Figs. 4 and 5 (5). The plots show a range of acceptable current density values at each potential. The average corrosion potential is −0.52 V, and the average platinized platinum potential is −0.26 V.

6.2 Typical deviations from the standard potentiostatic plot are shown and discussed in Appendix X1. Reference to this discussion may be helpful in determining the reasons for differences between an experimental curve and the standard plots.

6.3 The potentiodynamic standard curve shows good agreement with the potentiostatic standard curve determined at an equivalent overall polarization rate.

7. Precision and Bias

7.1 The repeatability of this test method is illustrated by Fig. 6. Current variability in regions where the effect of potential on current is small will generally be 10 % or less.

7.2 The ability of different laboratories to reproduce the results in this test method is shown in Fig. 4. The band shows a better than plus or minus two standard deviations for all laboratories providing results.

7.3 Factors that contribute bias to this test method are discussed in Appendix X1. In general, the major effects which can bias results are: reference electrode problems, crevice problems in the specimen mounting assembly, oxygen contamination, and current measurement instrument inaccuracies.

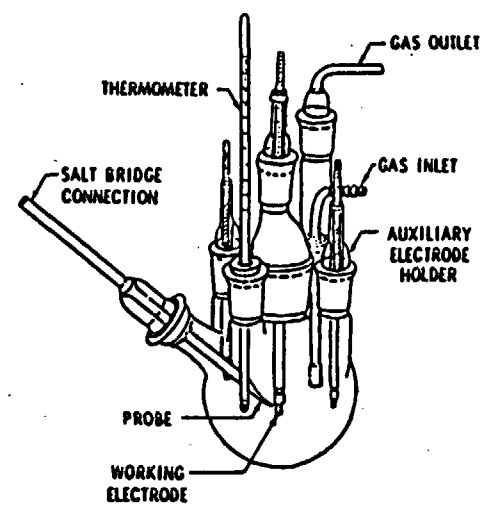

FIG. 1 Schematic Diagram of Polarization Cell (1)

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Appendix 2.

Current List of Calibrated Equipment

Page 2 Only

INSTRUMENT	MODEL	MFG	IDENT NO	LAST CAL	CAL EXP	RECALL	ACTIVITY	BLDG	ROOM	TAL	TL
THERMOCOUP	TYPE K	OMEGA	34	8/09/88	8/09/89	6/28/89	B-20-4	281	1160	WILDER	GLASSLEY
T[illegible] OUP	TYPE K	OMEGA	17	8/09/88	8/09/89	6/28/89	B-20-4	281	1160	WILDER	GLASSLEY
[illegible] GAU	5550	PRECISE SE	23479	8/09/88	8/09/89	6/28/89	B-20-4	281	1160	WILDER	GLASSLEY
STRAIN GAU	5550	PRECISE SE	24380	8/09/88	8/09/89	6/28/89	B-20-4	281	1160	WILDER	GLASSLEY
STRAIN GAU	5550 V5	PRECISE SE	23342	8/09/88	8/09/89	6/28/89	B-20-4	281	1160	WILDER	GLASSLEY
STRAIN GAU	5550 V6	PRECISE SE	23341	8/09/88	8/09/89	6/28/89	B-20-4	281	1160	WILDER	GLASSLEY
STRAIN GAU	2105	TABER	721223	8/09/88	8/09/89	6/28/89	B-20-4	281	1160	WILDER	GLASSLEY
WEIGHT SET	NONE	TROEMNER	4935825	9/14/88	9/15/89		D-20-31	243	2026	SHAW	RYERSON
WEIGHT SET	6137/1540	TROEMNER	4935832	9/15/88	9/15/89		D-20-31	243	2026	SHAW	RYERSON
CONTROLLER	SC12	CORTEST	4403461	CAL LAB		INITIAL	E-20-23	241	1878	CLARKE	McCRIGHT
STRIP CHAR	585/11/13	OMEGA	4347352	CAL LAB		INITIAL	E-20-23	241	1877	CLARKE	McCRIGHT
STRIP CHAR	585/11/13	OMEGA	4414849	CAL LAB		INITIAL	E-20-23	241	1877	CLARKE	McCRIGHT
STRIP CHAR	585/11/13	OMEGA	4076603	CAL LAB		INITIAL	E-20-23	241	1877	CLARKE	McCRIGHT
STRIP CHAR	585/11/13	OMEGA	4350130	CAL LAB		INITIAL	E-20-23	241	1877	CLARKE	McCRIGHT
POTENTIOST	173	PAR	4015329	4/28/89	10/28/89		E-20-23	241	1878	CLARKE	McCRIGHT
POTENTIOST	173	PAR	4369149	CAL LAB		INITIAL	E-20-23	241	1877	CLARKE	McCRIGHT
CONTROLLER	175	PAR	3676767	4/28/89	10/28/89		E-20-23	241	1878	CLARKE	McCRIGHT
POTENTIOST	273	PAR	4053581	4/21/89	10/20/89		E-20-23	241	1877	CLARKE	McCRIGHT
POTENTIOST	273	PAR	4066826	CAL LAB		INITIAL	E-20-23	241	1878	CLARKE	McCRIGHT
POTENTIOST	362	PAR	4272227	3/13/89	9/13/89		E-20-23	241	1878	CLARKE	McCRIGHT
POTENTIOST	363	PAR	4345822	1/09/89	7/09/89	6/5/89	E-20-23	241	1878	CLARKE	McCRIGHT
POTENTIOST	363	PAR	4277185	3/07/89	9/07/89		E-20-23	241	1878	CLARKE	McCRIGHT
POTENTIOST	363	PAR	3328949	3/07/89	9/07/89		E-20-23	241	1878	CLARKE	McCRIGHT
POTENTIOST	363	PAR	3711963	3/06/89	9/06/89		E-20-23	241	1878	CLARKE	McCRIGHT
POTENTIOST	363	PAR	3329106	CAL LAB			E-20-23	241	1878	CLARKE	McCRIGHT
C[illegible] TER	376	PAR	4764128	4/29/89	10/29/89		E-20-23	241	1878	CLARKE	McCRIGHT
[illegible] CELL	D/3971-01	SENSOTEC	5015939	4/28/89	10/28/89		E-20-23	241	1878	CLARKE	McCRIGHT
LVDT	351-000	TRANS-TEK	4764111	CAL LAB		INITIAL	E-20-23	241	1878	CLARKE	McCRIGHT
WEIGHT SET	NONE	TROEMNER	4935818	9/15/88	9/15/89		E-20-23	241	1883	CLARKE	McCRIGHT
PROFILEOME	DEKTAK IIA	SLOAN	88503	1/12/89	1/12/90		G-20-3.1	151	1034A	SHAW	RYERSON
OSCILLOSCO	2465	TEKTRONIX	4160616	9/01/88	9/10/89		H-20-6	327		CLARKE	RUSSELL
WATT TRANS	S73-25-230	AME	4763411	10/07/88	10/07/90		S-20-1	G	TNL	WILDER	RAMIREZ
WATT TRANS	S73-25-230	AME	4763428	10/07/88	10/07/90		S-20-1	G	TNL	WILDER	RAMIREZ
DEPTH PROB	5010R	CPN	4737900	7/28/88	7/28/89	6/5/89	S-20-1	G	TNL	WILDER	RAMIREZ
DA CONTROL	3497A	HP	3854172	9/26/88	9/26/89		S-20-1	G	TNL	WILDER	RAMIREZ
PRES TRAN	2279-1	ASHCROFT	5038761	4/12/89	4/12/90		S-20-1	G	TNL	WILDER	RAMIREZ
PRES TRAN	2279-2	ASHCROFT	5038785	4/12/89	4/12/90		S-20-1	G	TNL	WILDER	RAMIREZ
PRES TRAN	2279-3	ASHCROFT	5038792	4/12/89	4/12/90		S-20-1	G	TNL	WILDER	RAMIREZ
PRES TRAN	2279-4	ASHCROFT	5038761	4/12/89	4/12/90		S-20-1	G	TNL	WILDER	RAMIREZ
BALANCE	2404	SARTORIUS	3792559	CAL LAB		INITIAL	J-20-8	281		AINES	SILVA
BALANCE	MG5D	METTLER	3559879	CAL LAB		INITIAL	J-20-8	281		AINES	SILVA
OSCILLOSCO	11402	TEKTRONIX	4928490	CAL LAB		INITIAL	J-20-8	281		AINES	SILVA
OSCILLOSCO	2335	TEKTRONIX	4728496	CAL LAB		INITIAL	J-20-8	281		AINES	SILVA
PULSE GEN	DG535	SRS	4778699	CAL LAB		INITIAL	J-20-8	281		AINES	SILVA
[illegible]RX THERM	2804A	HP	5038655	CAL LAB		INITIAL	J-20-8	281		AINES	SILVA
VERT AMP	11A34	TEKTRONIX	4921767	CAL LAB		INITIAL	J-20-8	281		AINES	SILVA
THERMOCOUP	TYPE K	OMEGA	3977512	3/15/89	3/15/90		B-20-4	281		WILDER	GLASSLEY
THERMOCOUP	TYPE K	OMEGA	3977529	3/15/89	3/15/90		B-20-4	281		WILDER	GLASSLEY
THERMOCOUP	TYPE K	OMEGA	3977536	3/15/89	3/15/90		B-20-4	281		WILDER	GLASSLEY
T[illegible] OCOUP	TYPE K	OMEGA	3977543	3/15/89	3/15/90		B-20-4	281		WILDER	GLASSLEY