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THE EPR METHOD FOR THE DETECTION
OF SENSITIZATION IN STAINLESS STEELS

W. L. CLARKE

GENERAL ELECTRIC COMPANY

VALLECITOS NUCLEAR CENTER

PLEASANTON, CALIFORNIA

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The Reactor Primary Coolant System Pipe Rupture Study was conducted for the Metallurgy and Materials Research Branch of the Division of Reactor Safety Research, USNRC. The over-all objective of the program was to improve the reliability of reactor system piping by increasing knowledge of failure causing mechanisms and by enhancing the capability for design evaluation and analysis. Toward the attainment of that objective, a program was completed to develop a quantitative method (EPR) for nondestructively measuring the degree of sensitization in Types 304, 304L, 316, and 316L stainless steels. The technique was extended to characterize weld heat affected zones and to correlate the degree of sensitization with intergranular stress corrosion cracking (IGSCC) resistance. Studies were directed toward establishing procedures for, and qualifying, a technique to obtain EPR measurments in-situ on reactor components in the field.

Initially, a study was completed to assess the feasibility of measuring degree of sensitization in Type 304 stainless steel using the EPR (Electrochemical Potentiokinetic Reactivation) technique. On the basis of that study, the EPR was determined to be a viable method for quantitatively measuring sensitization in Type 304, and was considered superior to the presently accepted chemical methods. The EPR method clearly distinguished between annealed Type 304 stainless steel, and material subjected to sensitizing heat treatments. In addition, the method was found extremely useful in characterizing weld heat affected zones, where it appears that a correlation exists between the degree of sensitization, measured by EPR, and IGSCC resistance in a BWR coolant environment.

The susceptibility to sensitization was evaluated electrochemically by developing potentiokinetic curves of a polarized sample obtained by controlled potential sweep from the passive to the active region (reactivation) in a specific electrolyte. The criteria used to distinguish between sensitized and annealed steels is the value of the activation charge, Pa $(C/cm2)$, which is given by the intergrated area below the reactivation peak of the curve. Sensitized steels are easily activated and show higher Pa values than annealed steels which are not susceptible to IGSCC. The value of the Pa measured is dependent on polarization rate, composition and temperature of the electrolyte, composition of the steel tested, sample surface

condition, and other factors. These test parameters must therefore be kept constant to study the reactivation of passive steels.

In addition to the sensitization measurements obtained for numerous heats of Types 304 and 304L stainless steel, a number of parametric studies were completed to obtain the greatest sensitivity possible. This sensitivity is necessary, especially when evaluating marginally susceptible (IGSCC) materials, such as low and medium heat input welds. Also, one of these parameters, the reactivation scan rate, was modified to permit utilization of the EPR technique for Types 316 and 316L stainless steels. The technique is currently not adaptable for the stabalized stainless steels (Types 321 and 347), but can be modified for use on certain nickel alloys. The procedures for performing an EPR test are presented as an appendix at the end of this manuscript.

The primary emphasis of more recent EPR development studies was to establish a method for nondestructive measurement of sensitization in the field. To accomplish this objective, it was necessary to design and construct a miniaturized field cell, and a portable polarization system. A number of field cells were constructed, and one design qualified for in-situ field usage. The portable polarization system was designed in conjunction with an outside vendor*, and is currently being marketed commercially (together with the field cells). The field measurement procedures have been prepared and are being published in the final NRC program report (NUREG/CR-1095, Nov. 1979). The procedures require the evaluation of the outside of piping, consequently, judgements must be made relative to expected behavior on the inside (exposed to the coolant environment). The EPR field technique is very useful in assessing the metallurgical condition of the component base metal, and can easily identify sensitized material as-received from the supplier, or that produced during fabrication or installation. It is also possible to identify high heat input welds by measuring the weld heat affected zones on the outside of a pipe or component. However, until the EPR is used extensively so that a bulk of data is obtained for statistical analysis, no claims are currently being made relative to predictions of IGSCC resistance of weldments based solely on outside measurements.

The EPR technique is currently being used extensively as a quality control acceptance test by General Electric, Wilmington, manufacturing for all incoming Type 304, 304L, 316, and 316L materials. It is also specified for fabricated parts (forgings, flanges, etc.) where lack of sensitization in the finished product is specified. In

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*Instru Spec Associates
Walnut Creek, CA

addition, a number of steel suppliers have purchased EPR equipment and are using the technique in their Quality Control for material supplied to General Electric Company for nuclear applications. It is expected that the General Electric Company services group will provide EPR field measurement services on customer request in the near future. We are currently awaiting the supply of the portable polarization equipment, and the training of field service personnel.

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PREVIOUS REPORTS

Quarterly Reports

GEAP-10207-33	January-June	1975
GEAP-10207-34	July-December	1975
GEAP-10207-35	January-March	1976
GEAP-10207-36	April-June	1976
GEAP-10207-37	July-September	1976
GEAP-10207-38	October-December	1976
GEAP-10207-39	January-March	1977
GEAP-10207-40	April-June	1977
GEAP-10207-41	July-September	1977
GEAP-10207-42	October-December	1977
NUREG/CR-0306	January-March	1978
NUREG/CR-0567	April-June	1978
NUREG/CR-0541	July-September	1978

TOPICAL REPORTS

GEAP-21382 "Detection of Sensitization in Stainless Steel Using
Electrochemical Techniques", August 1976.

GEAP-12697 "Detection of Sensitization in Stainless Steel: II.
EPR Method for Nondestructive Field Tests", February 1978.

NUREG/CR-1095 "The EPR Method for the Detection of Sensitization
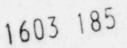in Stainless Steels", November 1979.

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PAPERS

"Detection of Sensitization in Stainless Steel Using Electrochemical Techniques", NACE Corrosion Conference, Paper No. 180, San Francisco, CA, March 1977.

"Comparative Methods for Measuring Degree of Sensitization in Stainless Steel", ASTM STP 656, 1978.

"Nondestructive Measurement of Sensitization of Stainless Steel: Relation to High Temperature Stress Corrosion Behavior", NACE Corrosion Conference, Paper No. 91, Atlanta, GA, March 1979.

"The Effects of Sensitization on the SCC Behavior of Types 316 and 316L Stainless Steel", accepted for publication, NACE Corrosion Conference, Chicago, Ill., March 1980

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APPENDIX A
ELECTROCHEMICAL POTENTIOKINETIC REACTIVATION (EPR)
METHOD FOR DETERMINING DEGREE OF SENSITIZATION IN STAINLESS STEELS

1. SCOPE

1.1 This Appendix describes a method for quantitatively determining the degree of sensitization in thermally treated AISI Type-304, -304L, -316 and -316L stainless steel.

1.2 This document will be the referee method for the conduct of tests where a requirement for running an electrochemical potentiokinetic reactivation (EPR) test is specified.

2. APPLICABLE DOCUMENTS, CODES AND STANDARDS

2.1 **Codes and Standards.** The following codes and standards form a part of this specification to the extent specified herein.

    a. ASTM E112-63, Standard Methods for Estimating the Average Grain Size of Metals.

    b. ASTM G5-71, Recommended Practice for Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements.

    c. ASTM G3-68, Recommended Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing.

    d. ASTM E3-62, Preparation of Metallographic Specimens.

3. EQUIPMENT

3.1 **Standard Polarization Cell.** Requirements shall be in accordance with Section 2.1 of ASTM G5-71.

3.2 **Electrode Holder.** Requirements shall be in accordance with Section 2.2 of ASTM G5-71.

3.3 **Potentiostat.** Requirements shall be in accordance with Section 2.3 of ASTM G5-71.

3.4 **Potential Measuring Instruments.** Requirements shall be in accordance with Section 2.4 of ASTM G5-71.

3.5 **Current Measuring Instruments.** Requirements shall be in accordance with Section 2.5 of ASTM G5–71.

3.6 **Current Integration Measurement Instruments.** An instrument that is capable of integrating the current under the curve developed during reactivation should be used. The instrument should be capable of measuring a current integral (in coulombs) to within an accuracy of 1% of the absolute value of a current range between 0.001 and 1000 mA.

3.7 **Anodic Polarization Circuit.** Requirements shall be in accordance with Section 2.6 of ASTM G5–71, except the current integration instrument should be inserted in series with the lead between the working electrode and potentiostat.

3.8 **Electrodes**

3.8.1 Working electrodes can be any shaped piece of metal at least 0.32 cm (1/8 in.) in diameter or on a side, by any suitable thickness, which has a stainless steel electrode holder mounting screw spot-welded on the side opposite to where the measurement will be taken, and is potted in a suitable innocuous compound such that only one planar surface is exposed to the electrolyte.

3.8.2 **Counter Electrodes.** Requirements are in accordance with Section 2.7.2 of ASTM G5–71.

3.8.3 **Calomel Reference Electrode.** Requirements are in accordance with Section 2.8 of ASTM G5–71.

4. STANDARD EXPERIMENTAL PROCEDURES

4.1 **Test Specimen Preparation**

4.1.1 Prepare the surface within 1 hour of the experiment, or store the prepared specimen in a suitable desicatting cabinet. Wet grind with 240-grit and 400-grit SiC paper, followed by wet polish with 600-grit SiC paper until previous coarse scratches are removed, rinse with water and dry. The specimens should be final polished in two additional stages with 6 and 1 μm diamond paste on a microcloth prepared polishing wheel per ASTM E3–62.

4.1.2 Mount the specimen on the electrode holder as described in Section 2.2.1 of ASTM G5–71. 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.

4.1.3 Clean the specimen just before immersion into the electrolyte by degreasing with a suitable detergent, rinsing in distilled water then alcohol, and air drying.

4.2 Prepare 1 liter of 0.5 M H_2SO_4 + 0.01 M KSCN from reagent grade chemicals and distilled water (solution can be made up in bulk and stored for 1 month). Transfer approximately 500 to 600 ml of solution to clean polarization cell.

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

4.4 Place the specimen, platinum auxiliary electrodes, salt bridge probe, and other components in the test cell. Ensure the salt bridge is filled with the test solution and contains no air bubbles, particularly in the restricted space within the tip region. The levels of the solution in the reference and polarization cells should be the same to avoid siphoning.

4.5 Purge the solution before test initiation for about 2 minutes, and continuously during the test with high purity nitrogen gas (99.90% minimum) at 150 cm^3/min.

4.6 Adjust the salt bridge probe tip so it is as close to the specimen surface as possible, but not touching the sample or mount.

4.7 Record the open-circuit (rest) specimen potential, that is, the corrosion potential, after about a 2-minute immersion. If the rest potential does not register normal for the class of alloys being evaluated (−350 to −450 mV for Type−304 stainless steel), then cathodically charge the specimen at −600 mV for 2 to 5 minutes and recheck the rest potential. If the rest potential is still abnormal (usually around −200 mV), the specimen must be removed from the flask and repolished to eliminate the tarnish film.

4.8 Passivation is accomplished by setting the potential to + 200 mV versus standard calomel electrode and holding for 2 minutes. Complete passivation can be checked by observing the lack of change on the current integrator instrument output.

4.9 **Reactivation Scan**

4.9.1 Start the potential backscan (cathodic direction) using a potentiodynamic sweep rate of 6 V/h (± 5%).

4.9.2 Re-zero and start the current integrator instrument, recording the current continuously with change in potential.

4.9.3 The recorder automatically plots the anodic polarization data on semilogarithmic paper in accordance with ASTM G3–68. It is acceptable for the EPR evaluation to plot with the potential as the abscissa and the current as the ordinate, in opposition to the recommended standard reference plot in ASTM G3–68.

4.9.4 Lock reading on current integrator when current is close to the initial corrosion potential and has just reversed polarity. Record this reading as the integrated current value (in coulombs) in data record sheet.

4.9.5 Put all electrochemical polarization equipment on standby and remove E versus log i plot from recorder for inclusion in data file.

4.9.6 Remove specimen from cell and holder, rinse in distilled water followed by alcohol rinse, then air dry.

5. DATA ACQUISITION AND ANALYSIS

5.1 Test parameters should be recorded as follows: EPR Run No., Specimen No., Material, Heat; Surface Condition; Specimen Location; Test Temperature, Sweep Rate; Passivating Potential/Time; Rest Potential. Use the attached data record sheet form or equivalent for recording these data.

5.2 Test data to be recorded include the charge, Q, in coulombs (integrated current under anodic portion of curve during reactivation); maximum anodic curve peak height in milliamperes; Flade potential in millivolts (potential at which anodic curve breaks upward during reactivation). Record in data record sheet.

5.3 Each potted specimen should be photographed after test (without additional preparation or etching) at suitable magnification to document the microstructures and extent of grain boundary grooving after the EPR test. An additional photomicrograph must be taken at 100X to measure grain size. If the specimen is not sufficiently etched after the EPR test to delineate the microstructure for grain size determination, then the specimens should be etched with 10% oxalic acid, electrolytically per ASTM A262-Practice A, and a photomicrograph obtained. Attach photos to data record sheet.

5.4 Determine the surface area by measuring all dimensions to the nearest 0.1 mm.

5.5 The integral charge value, Q, should be normalized to the grain boundary area (GBA) of each specimen using the relationship below:

$$P_a(C/cm^2) = \frac{Q}{GBA}$$

and

Q = Charge measured on current integrating instrument (coulombs),

GBA = $A_s [5.09544 \times 10^{-3} \exp(0.34696 X)]$,

where

A_s = Specimen Area (cm^2) and

X = ASTM Grain Size at 100X

Note: Show calculation in data record sheet.

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Electrochemical Potentiokinetic Reactivation – Data Record Sheet

1. EPR Run Number _____

2. Specimen Number_____

3. Material and Product Form_____

4. Material Heat Number_____Heat Treat Lot No._____

5. Specimen Location_____ _____

6. Specimen Surface Area, A_s_____ cm^2

7. Initial Rest (Corrosion) Potential_____ mV vs SCE

8. Test Temperature_____ ^oC

9. Passivating Potential/Time_____ mV vs SCE/Time

10. Sweep Rate_____ V/h

11. Integrated Current, Q,_____ Coulombs

12. Maximum anodic current_____ mA

13. Flade potential_____ mV vs SCE

14. Grain Size, X_____ ASTM Grain Size

15. Normalized Charge per Grain Boundary Area (P_a) calculation

    GBA = Grain Boundary Area

    GBA = $A_s[5.09544 \times 10^{-3} \exp(0.34696X)]$

    GBA = _____

where

    A_s = Specimen area in cm^2

    X = ASTM Grain Size at 100X

    P_a = Q/GBA where: Q = integrated current in coulombs

    P_a - _____

        _____

16. Attach:

    1. Micrograph characterizing microstructure and extent of grain boundary grooving.

    2. Separate micrograph, if needed, used to determine grain size.

Date: _____

Determined by: _____