

AN EVALUATION OF ELECTROCHEMICAL POTENTIOKINETIC
REACTIVATION TECHNIQUES FOR IN-SERVICE MEASUREMENTS ON
TYPE 304 STAINLESS STEEL*

By

Karen J. Stoner

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

A paper proposed for presentation
*22nd Annual Technical Meeting of the International
Metallographic Society*
Charlotte, NC
July 25-26, 1989

*This paper was prepared in connection with work done under Contract No. DE-AC09-76SR00001 (now Contract No. DE-AC09-88SR18035) with the U.S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

AN EVALUATION OF ELECTROCHEMICAL POTENTIOKINETIC REACTIVATION
TECHNIQUES FOR IN SERVICE MEASUREMENTS ON TYPE 304 STAINLESS STEEL

Karen J. Stoner

ABSTRACT

Electrochemical potentiokinetic reactivation (EPR) tests can be used to measure quantitatively the sensitization of Type 304 stainless steel. The single loop (SL) and double loop (DL) EPR techniques were compared as non-destructive methods for determining sensitization under both laboratory and simulated field environments. Measurements were performed on specimens heat-treated to produce levels of sensitization from no sensitization to heavy sensitization. At temperatures of 22°C and 30°C testing with standard laboratory and portable field apparatus, both EPR techniques were capable of distinguishing sensitization levels at the range spanning those characterized as being non-susceptible and susceptible to intergranular stress corrosion cracking (IGSCC). Through correlations developed for the test data, it is possible to translate field results to the standard laboratory test conditions. This was demonstrated for the SL test through measurements performed on a pipe specimen containing IGSCC.

INTRODUCTION

The incidence of IGSCC in piping in the nuclear industry has prompted the development of a non-destructive quantitative test for determining sensitization in Type 304 stainless steel. Sensitization in Type 304 stainless steel is characterized by the precipitation of chromium-rich carbides ($M_{23}C_6$) which form along grain boundaries when the metal is heated in the range of 430 to 870°C (1). The formation of these carbides leaves the adjacent matrix region depleted in chromium. This region, having less than 12 weight percent

Westinghouse Savannah River Company, Savannah River Site, Materials Technology Section,
Aiken, S.C. 29802 USA

chromium, has an unstable passive film and is susceptible to preferential attack in a corrosive environment. Combined with a tensile stress and a corrosive environment, the depleted zone is susceptible to IGSCC (1).

The quantitative determination of the degree of sensitization (DOS) would be beneficial in examining Type 304 stainless steel in service to distinguish levels susceptible and non-susceptible to IGSCC. The standard practice for detecting sensitization is outlined in ASTM A 262-85 (2). The standard describes five practices that are either destructive to the sample or qualitative only. The recently developed EPR tests overcome many of the limitations of the ASTM standards (3). EPR techniques, SL and DL, detect the extent of the chromium depleted region by passivating the metal and then reactivating it through a decreasing potential sweep. These tests provide quantitative non-destructive indication of the DOS.

EXPERIMENTAL PROCEDURE

The SL and DL are routine procedures described by W. L. Clarke, V. M. Romero and J. C. Danko (4) and by M. Akashi, et al. (5) respectively and evaluated by A. P. Majidi and M. A. Streicher (3). Both tests are performed in a solution of 0.5 M H_2SO_4 and 0.01 M KSCN, that must be changed periodically to avoid decomposition (3).

For the SL test, the specimen is passivated by making it anodic, and then reactivated by reversing the potential at a constant rate. During this reversal, the current is measured. Since the potential is decreased at a controlled rate, it is possible to calculate the total electrical charge, Q , that passes through the exposed sample surface (1). During the reactivation phase, the passive film dissolves more readily over the chromium depleted regions; thus, the more depleted regions, the larger the surface current.

Since the attack is basically along the grain boundaries, it is necessary to normalize the charge with respect to the grain boundary area. This is done through the following equation:

$$Pa = Q/GBA$$

where Pa is the DOS in coulombs per cm^2 , Q is the integrated charge measured from the

reactivation sweep, and GBA is the grain boundary area (1). The GBA is calculated as:

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

where A_s is the exposed specimen area, and X is the ASTM grain size at a magnification of 100x (1).

The DL test involves polarizing the sample anodically at a constant rate to a potential in the passive region of Type 304 stainless steel and then reversing the scan direction until the open circuit potential, E_{corr} , is reached (6). The surface current is measured throughout the test. I_a represents the maximum current for the anodic loop, and I_r represents the maximum current for the reactivation loop. The value for the DOS is calculated by:

$$DOS = I_r / I_a$$

Tests have demonstrated that the maximum anodic current, I_a , is fairly independent of the degree of sample sensitization while the I_r is extremely sensitive to the degree of sensitization (6). The more sensitized the sample, the greater the breakdown in the passive film, the higher the surface current, the larger the value of I_r , and the greater the DOS.

MATERIAL

Five specimens of Type 304 stainless steel from the Savannah River reactor primary coolant piping were examined. The specific material was sectioned into specimen blocks (1 1/2" x 3/8" x 1/2"). Four of the blocks were solution quenched in water following an anneal at 1000°C for one hour, and specimens 1 through 4 were subsequently held at 600°C for 0, 1, 3, and 6 hours, respectively. Specimen 5 was heated at 600°C for 16 hours to produce a heavily sensitized microstructure with no prior solution anneal (7).

To prepare the specimens for testing, a flat-head No. 8 screw was silver-soldered to the back face of the specimen for the purpose of electrical contact. The specimens were then individually mounted in cold set plastic resin. Grain size measurements were made using ASTM procedure E112 (8). The Three-Circle (Abrams) Method, circular intercept procedure, was applied to each sample.

In addition, a specimen of Type 304 stainless steel pipe, that had been in service, was

examined. The section studied came from a 16 inch diameter elbow, and was a curved section with a welded carbon steel attachment brace. The specimen grain size was also determined through the Abrams method (8).

EQUIPMENT AND TECHNIQUE

For both the SL and DL EPR measurements, a Princeton Applied Research (PAR) Potentiostat/Galvanostat model 273 was used. The system was controlled by a PAR model 351. For equipment comparison, measurements were also performed on an Instru-Spec WC-5 Sensi-Test, a unit designed to perform SL tests in the field. SL and DL measurements were made in a standard 1 L glass corrosion cell (9). Simulated field measurements were made in an Instru-Spec Model 750 Nondestructive Probe, a 7.6 cm tall and 2.5 cm diameter cylindrical cell.

For the PAR SL and DL tests in the laboratory cell, the tests were performed at 22°C, a simulated field temperature, and at 30°C, the standard laboratory temperature. The field cell tests were performed at 22°C. Due to the strong dependence of the SL test on surface finish, a fresh 1 μm diamond paste finish was used for all of the tests (1). DL tests have been reported to be less sensitive to surface, due to the initial anodic sweep (6). In this study, DL tests were performed on 180 grit, 600 grit, and 1 μm diamond paste fresh surface finishes. To control the area tested each sample was masked with a piece of electroplating tape.

The SL test began with a surface cleaning of -600 mV versus a standard calomel electrode (SCE) for 12 seconds. E_{corr} was measured. The potential was then held at +200 mV for two minutes and subsequently was scanned in a negative direction at 6 V/hr until the E_{corr} was reached. The value of Q was calculated. After all test (SL and DL), a photomicrograph of the test area was taken. Figure 1 shows a plot of a SL test with the PAR unit in the lab cell, SL-PAR-LAB.

The DL test began with the measurement of E_{corr} . An anodic potential scan was then initiated at 6 V/hr with a vertex potential of +300 mV versus SCE. Values for I_r and I_a were recorded. Figure 2 shows a plot of a DL test with the PAR unit in a lab cell, DL-PAR-LAB.

SL tests were performed on the actual specimen of pipe with the WC-5 unit in a field cell at 22°C. A square inch of the pipe was polished to 1 µm diamond polish with a portable polisher. The field cell was mounted to the pipe by velcro straps. Replicas of the test area were taken after some tests using replicating tape and acetone. The replicas were sputtered with platinum and examined on the metallograph.

RESULTS AND DISCUSSION

Table 1 and 2 show the SL and DL data collected for the five specimens reduced through statistical analysis methods. The data was grouped by a specific EPR condition with a specific sample, typically two or three individual trials. A sample mean and confidence interval for the sample mean (assumed t-distribution) was determined to provide the level of sensitization with a confidence interval of 90% for the specimen mean sensitization level (10).

The EPR measurements contain an inherent variability in the individual test results due to non-identical specimen conditions with each successive trial. These conditions include a new grain orientation, and the specific masked region following the specimen repolish and preparation for testing. At low sensitization levels, both the SL and DL methods have large uncertainties as measured by the sample standard deviation divided by the sample mean. The large uncertainties occur at values that are very close to zero, where small absolute changes in sensitization level yield large percent changes of the average sensitization.

Both the SL and DL tests are based on passive film reactions, and thus it is apparent that temperature, sample geometry and surface finish impact the test results. While correlations can be made through Table 1 and 2 for the results at two specific temperatures, changes in temperature affect a sample differently based on its DOS (1). Sample geometry is critical in DL tests due to the anodic scan which leaves corrosion product as it cleans off the surface affecting the reactivation area (11). This is apparent by comparing lab and field cell DL tests. Three surface finishes were investigated for the DL test. Tests run at 30°C with 1 µm and 600 grit finishes indicate similar values. However, initial tests (not reported in Table 2) run at 22°C with 1 µm and 180 grit finishes with the field cell, show dissimilar values

that indicate that the DL test may not be totally insensitive to surface finish over a range of temperatures.

The SL and DL tests are compared in Figure 3 with each test being performed at 30°C in a laboratory cell with a surface finish of 1 µm diamond. The tests correlate with a straight line over a majority of the data. The non-sensitized specimen 1 does not fit into the correlation. At such low values of sensitization, it is apparent that the DL test does not account for the difference in reacting area during the test. The difference in area affects the ratio at low levels of sensitization.

Figure 4 shows a correlation for the SL test on the PAR unit at 30°C in a laboratory cell with a surface finish of 1 µm diamond to a SL test on the WC-5 unit at 22°C in a field cell with a similar surface finish. While the two machines can be compared, they have different resolutions. The WC-5 unit measures to 10 µA while the PAR unit can measure to 0.01 µA (1). The difference in resolution is apparent when very low levels of sensitization are measured, since the current measured is very small. This correlation allows for field measurements to be adjusted to values that would have been achieved with laboratory standards.

When the measurements are adjusted to laboratory standards, proposed limits that determine sensitization and susceptibility can be applied. To interpret SL results in terms of IGSCC susceptibility, Clarke has proposed that 5 C/cm² (as measured with the SL test at 30°C on a pipe inner diameter, 3 C/cm² for the outer diameter) is the maximum DOS acceptable before a sample is sufficiently sensitized to be susceptible to IGSCC (12).

The actual pipe section (Figure 5) was tested with the portable WC-5. Figure 6 shows the averages of the SL tests performed. The data clearly shows that the pipe has a localized region of sensitization in the vicinity of the brace, and that the bulk of the material is not sensitized. This region suggests that the pipe received some form of localized heating after it was formed and annealed. This speculation is reinforced by the results along the elbow seam weld that indicate almost 0 C/cm² in all the regions tested except for the localized zone. It is possible that the heating was performed as a flame washing technique in order to fit up the pipe or the

attachment brace. The measurements presented from the WC-5 can be correlated to laboratory standards through the application of data presented in Figure 4.

After all tests, including those on the pipe specimen, photomicrographs were taken. No additional preparation (etching) was performed. Grain boundary attack due to the carbide precipitation in the sample is evident in the photomicrographs. Figure 7 to 9 illustrate the post-EPR SL conditions for samples 1, 4, and 5. Sample 1, with no sensitization, shows no precipitation, while, sample 5, with high sensitization, shows a large degree of precipitation. The pipe replica, Figure 10, was taken of the sensitized pipe edge, post-SL test, and clearly shows sensitization. The replica technique can be used on sensitized pipes after an EPR test to get an indication of grain size. Figures 11 and 12 show post-DL conditions illustrating ditching on the severely sensitized sample 5. The difference in post-EPR test appearance between the SL and DL is attributed to the initial anodic "cleaning" scan of the DL test.

CONCLUSIONS

The SL and DL EPR tests are capable of detecting and quantifying sensitization in Type 304 stainless steel. Both EPR techniques are capable of distinguishing sensitization levels at the range spanning those characterized as being non-susceptible and susceptible to IGSCC. Both tests involve passive film reactions, and are therefore impacted by temperature, electrolyte, sweep rate, and specimen or grain size. The SL and DL methods were compared at different test conditions including simulated field conditions. Correlations can be made from a variety of test conditions to a laboratory standard for both the SL and DL tests thereby allowing for the application of proposed limits that determine sensitization and susceptibility to IGSCC (12). The DL technique for the field requires more development as the effect of surface finish at various temperatures needs to be examined, along with the effect of sample size. Finally, photomicrographs of the post-test condition give a clear indication of the sample sensitization level and an indication of grain size. For the SL and the DL techniques, post-test metallography has proven to be valuable for confirmation of EPR results.

ACKNOWLEDGEMENTS

The author would like to recognize Dr. R. L. Sindelar for his technical assistance and Mr. S. O. Brunson for his assistance in performing the EPR technique.

REFERENCES

1. A.P. Majidi and M.A. Streicher, "Potentiodynamic Reactivation Method for Detecting Sensitization in AISI 304 Stainless Steels," *Corrosion*, Vol. 40, No. 1, pp. 21-32 (January 1984).
2. "Standard Practices for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels," ASTM Designation: A262-85, American Society for Testing and Materials, Philadelphia, pp. (1984).
3. A.P. Majidi and M.A. Streicher, "Four Non-Destructive Electrochemical Tests for Detecting Sensitization in Type 304 and 304L Stainless Steel," *Corrosion '85*, Paper 62, National Association of Corrosion Engineers, Texas, pp. 1-17 (1985).
4. W.L. Clarke et al., "Detection of Sensitization in Stainless Steels Using Electrochemical Techniques," NACE/77, Paper 180, National Association of Corrosion Engineers, Houston, Texas, (1977).
5. M. Akashi et al., "Evaluation of IGSCC Susceptibility of Austenitic Stainless Steels Using Electrochemical Reactivation Method," *Corrosion Engineering*, 29, p. 163 (1980).
6. A.P. Majidi and M.A. Streicher, "The Double Loop Reactivation Method for Detecting Sensitization in AISI 304 Stainless Steels," *Corrosion*, Vol. 40, No. 11, pp. 584-593 (November 1984).
7. G.R. Caskey, jr., E.I. du Pont De Nemours & Company Laboratory Notebook, DPSTN-4321, Copy Series E37276, pp. 1-156 (1989).
8. "Standard Methods for Determining the Average Grain Size," ASTM Designation: E112-85, American Society for Testing and Materials, Philadelphia, pp. 403-436 (1985).
9. "Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements," ASTM Designation: G5-87, American Society for Testing and Materials, Philadelphia, pp. 124-131 (1985).
10. P.L. Meyer, Introductory Probability and Statistical Applications, 2nd ed., Addison-Wesley Publishing Company (1972).
11. F. Umemura et al., "Development of Automatic Sensitization Detector and Its Application," *IHI Engineering Review*, Vol. 6, No. 2, pp. 1-7 (April, 1983).
12. W.L. Clarke, The EPR Method for the Detection of Sensitization in Stainless Steels, NUREG/CR-1095, GEAP-24888, (April, 1981).

TABLE 1:

SINGLE LOOP DATA

CALCULATED AVERAGES AND UNCERTAINTY

SAMPLE #	SL-PAR-LAB 30°C	SL-PAR-LAB 22°C	SL-PAR-FC 22°C	SL-INST-FC 22°C
<i>Pa (C/cm sq)</i>				
1	0.03 ± 0.06	0.015 ± 0.032	0.025 ± 0.032	0.0 ± 0.0
2	1.2 ± 0.8	0.79 ± 0.91	0.86 ± 0.47	0.17 ± 0.32
3	4.2 ± 0.2	1.93 ± 0.32	1.85 ± 1.14	1.33 ± 0.96
4	9.1 ± 2.9	5.8 ± 2.1	5.8 ± 4.2	4.7 ± 1.3
5	12.9 ± 3.9	7.8 ± 0.0	8.3 ± 1.5	5.0 ± 2.1

NOTE:

PAR = PAR Potentiostat
 INST = WC-5 Unit

LAB = Lab Cell
 FC = Field Cell

TABLE 2:

DOUBLE LOOP DATA

CALCULATED AVERAGES AND UNCERTAINTY

SAMPLE #	DL-PAR-LAB 30°C	DL-PAR-LAB 22°C	DL-PAR-FC 22°C	DL-PAR-LAB 30°C 600 GRIT
<i>I_r / I_a</i>				
1	2.18 ± 3.8 E-4	7.90 ± 8.83 E-5	2.03 ± 8.86 E-4	2.11 ± 2.78 E-4
2	1.50 ± 0.10 E-3	7.95 ± 4.10 E-4	2.19 ± 0.09 E-3	10.2 ± 3.1 E-4
3	1.22 ± 0.13 E-2	7.29 ± 5.55 E-3	1.52 ± 0.91 E-2	9.04 ± 0.57 E-3
4	5.32 ± 0.03 E-2	4.08 ± 1.96 E-2	7.14 ± 1.80 E-2	4.20 ± 0.76 E-2
5	1.68 ± 0.04 E-1	0.119 ± 0.035	0.168 ± 0.009	0.126 ± 0.019

NOTE:

PAR = PAR Potentiostat

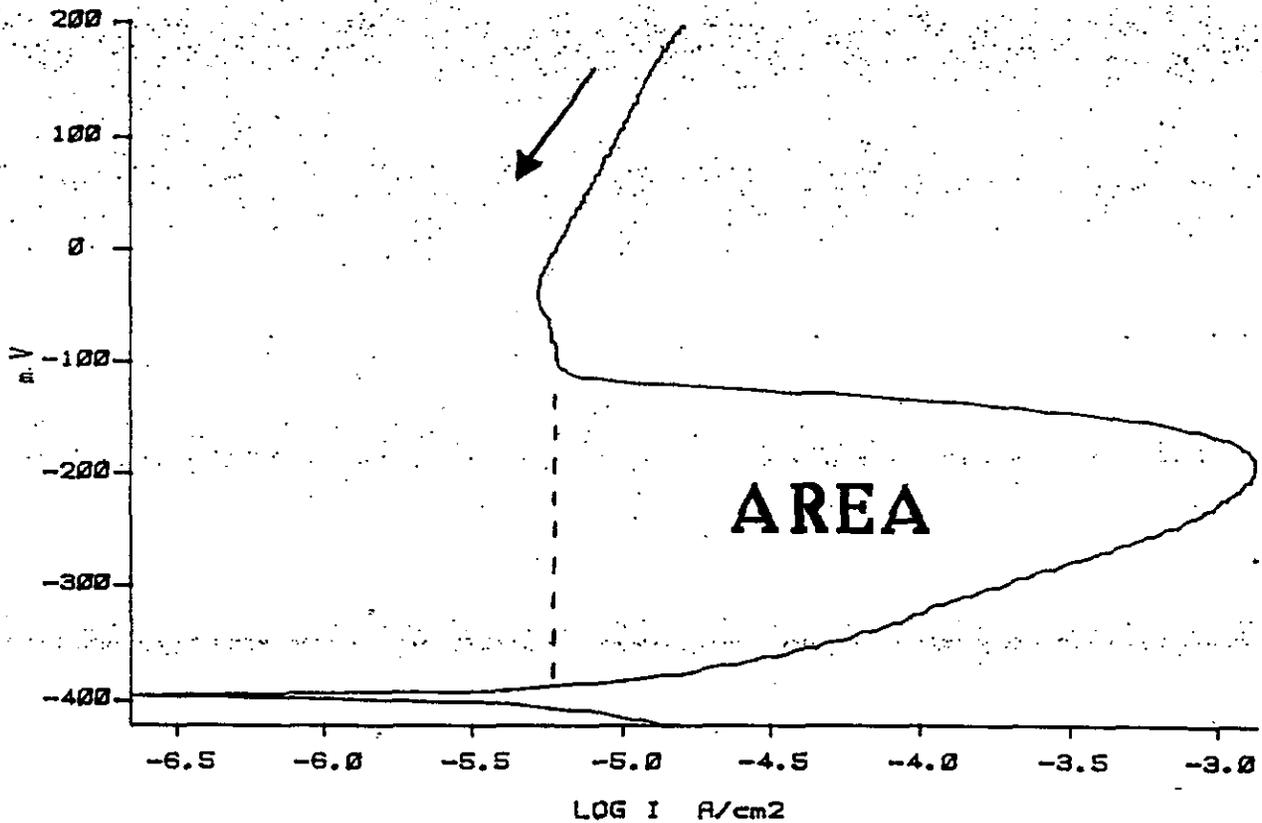
LAB = Lab Cell
FC = Field Cell

MODEL 351
CORROSION MEASUREMENT SYSTEM

SL3LH3

9 JAN 1989

COMMENT:
30C



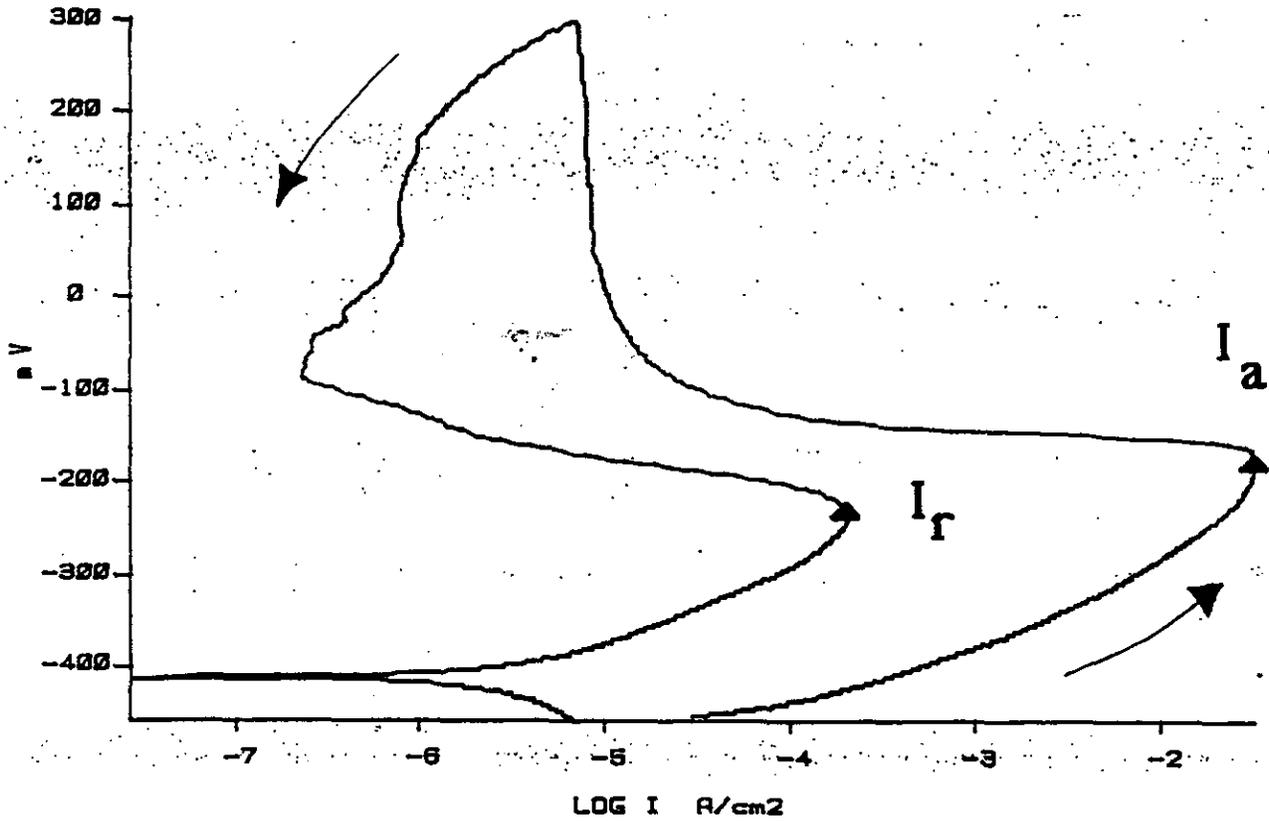
POTENTIOKINETIC REACTIVATION

Figure 1: SL-PAR-LAB, a Single Loop EPR Test on the PAR Potentiostat in the PAR Corrosion Cell at 30°C

MODEL 351
CORROSION MEASUREMENT SYSTEM

DL3LL1
12 JAN 1989

COMMENT:
22E



CYCLIC POLARIZATION

Figure 2: DL-PAR-LAB, A Double Loop Test on a PAR Potentiostat
in a PAR Corrosion Cell at 22°C

FIGURE 3:

STANDARD DL to STANDARD SL Correlation

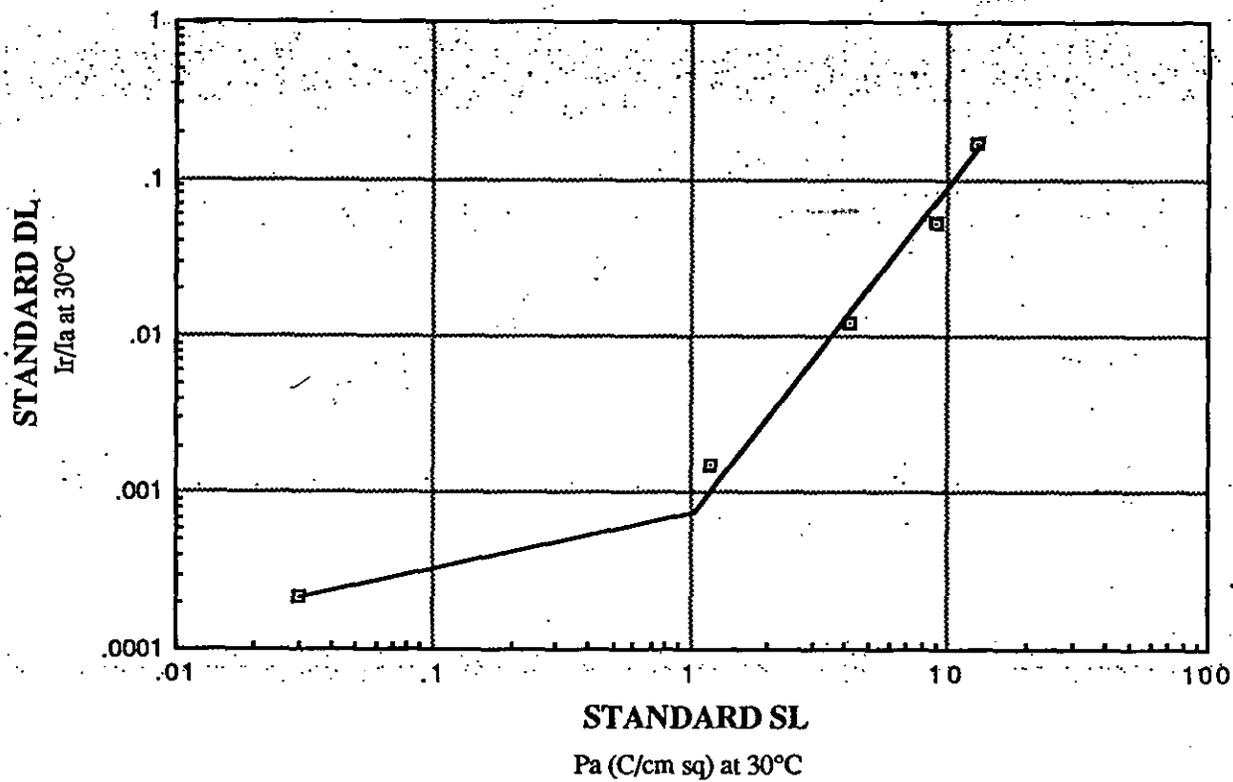
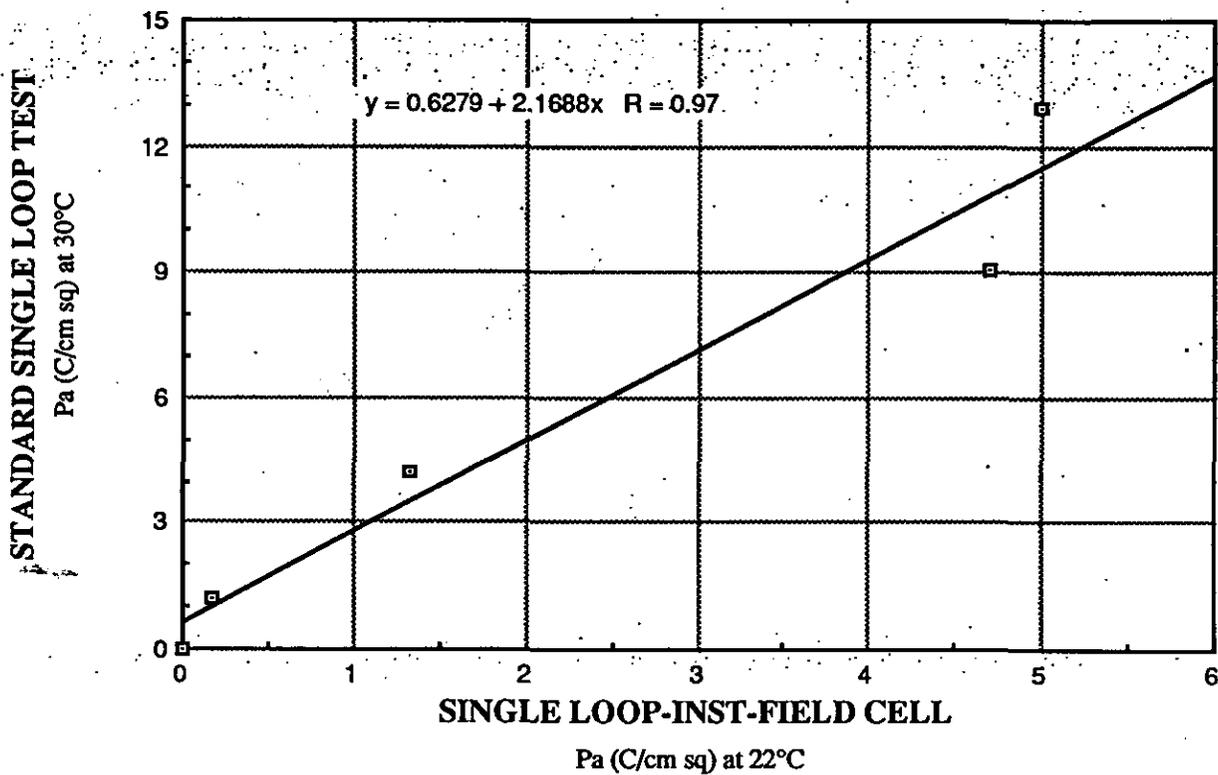


FIGURE 4: SL-INST-FC at 22°C to SL STANDARD Correlation



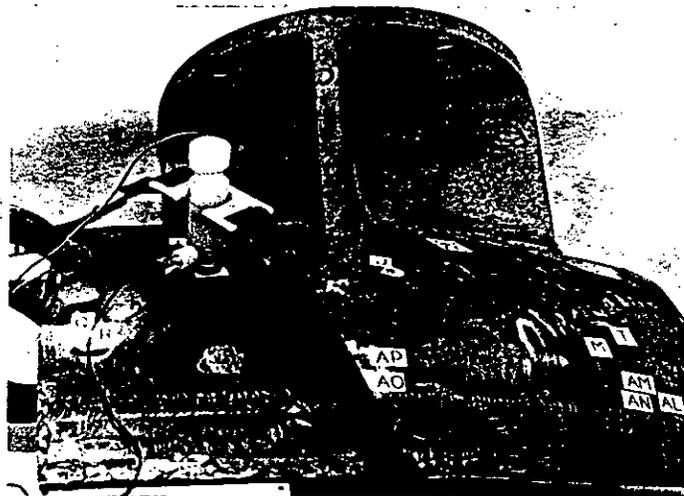
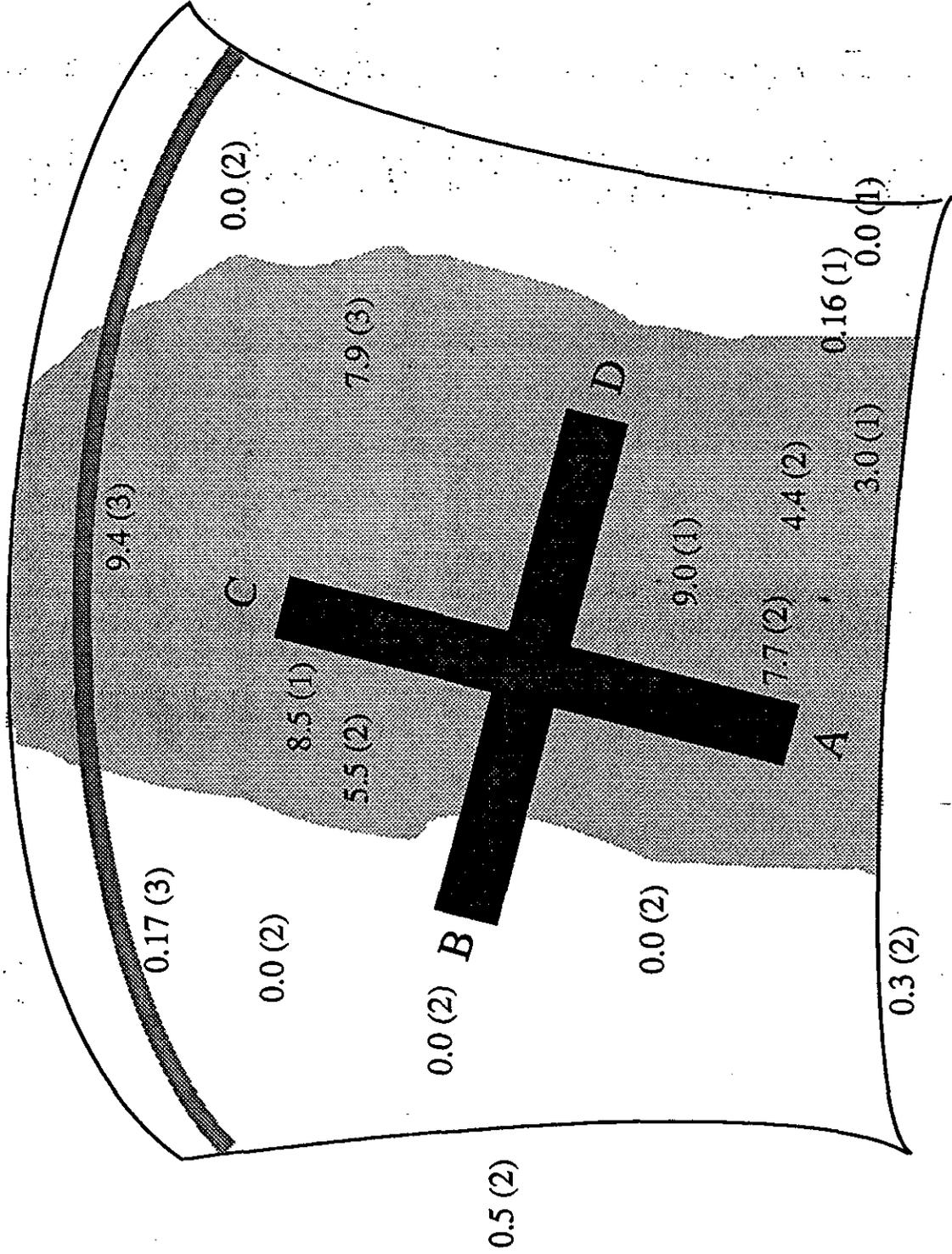


Figure 5: Instr-Spec, Model 750, Portable Field Cell in Use on the Pipe Specimen

SENSI-TEST - FIELD CELL - 22°C



Outer Diameter

5L-PW-17-16

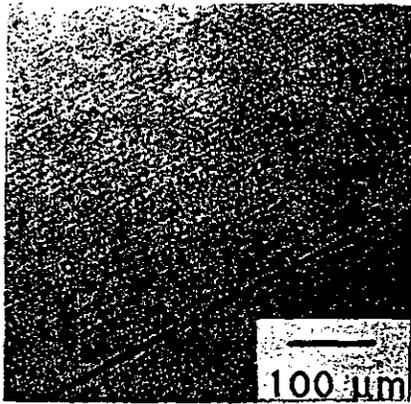


Figure 7: (Left) Specimen 1 After a SL Test on the PAR Potentiostat with the Field Cell at 22°C



Figure 8: (Right) Specimen 4 After a SL Test on the PAR Potentiostat with the Field Cell at 22°C

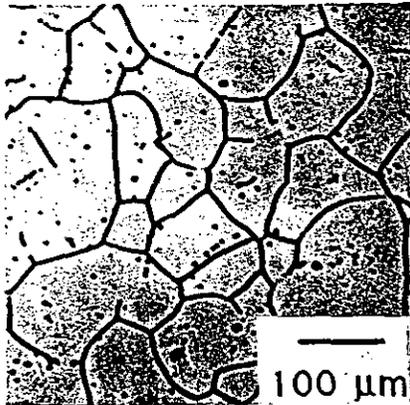


Figure 9: (Left) Specimen 5 After a SL Test on the PAR Potentiostat with the Field Cell at 22°C

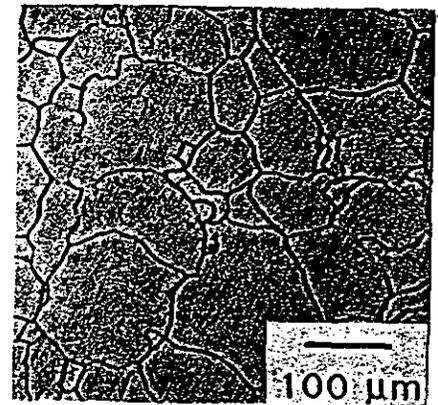


Figure 10: (Right) The Pipe Specimen After a SL Test on the WC-5 with the Field Cell at 22°C

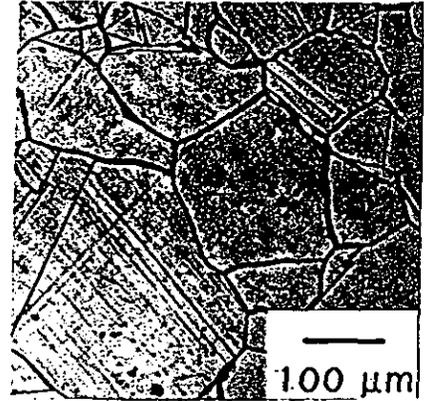
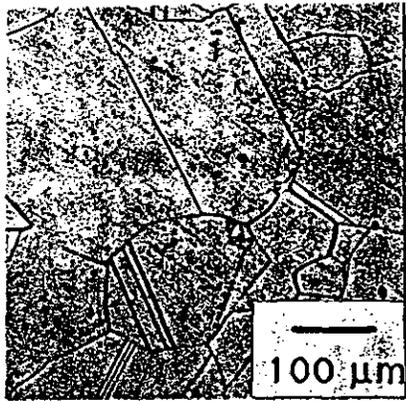


Figure 11: (Left) Specimen 1 After a DL Test on the PAR Potentiostat
in the Lab Cell at 30°C

Figure 12: (Right) Specimen 5 After a DL Test on the PAR Potentiostat
in the Lab Cell at 30°C