

RECEIVED
DEC 16 1999
OSTI

Corrosion Resistance and Electrochemical Potentiokinetic Reactivation Testing
Of Some Iron-base Hardfacing Alloys

B.V. Cockeram

USDOE contract No. DE-AC11-98PN38206

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States, nor the United States Department of Energy, nor the United States Navy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

BETTIS ATOMIC POWER LABORATORY

WEST MIFFLIN, PENNSYLVANIA 15122-0079

Operated for the U.S. Department of Energy
by Bechtel Bettis, Inc.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

Corrosion Resistance and Electrochemical Potentiokinetic Reactivation Testing of Some Iron-base Hardfacing Alloys

B.V. Cockeram, Bettis Atomic Power Laboratory, Bechtel-Bettis, Inc., P.O. Box 79, West Mifflin, PA 15122-0079.

Abstract

Hardfacing alloys are weld deposited on a base material to provide a wear resistant surface. Commercially available iron-base hardfacing alloys are being evaluated for replacement of cobalt-base alloys to reduce nuclear plant activation levels. Corrosion testing was used to evaluate the corrosion resistance of several iron-base hardfacing alloys in highly oxygenated environments. The corrosion test results indicate that iron-base hardfacing alloys in the as-deposited condition have acceptable corrosion resistance when the chromium to carbon ratio is greater than 4. Tristelle 5183, with a high niobium (stabilizer) content, did not follow this trend due to precipitation of niobium-rich carbides instead of chromium-rich carbides. This result indicates that iron-base hardfacing alloys containing high stabilizer contents may possess good corrosion resistance with Cr:C < 4. NOREM 02, NOREM 01, and NoCo-M2 hardfacing alloys had acceptable corrosion resistance in the as-deposited and 885°C/4 hour heat treated condition, but rusting from sensitization was observed in the 621°C/6 hour heat treated condition.

The feasibility of using an Electrochemical Potentiokinetic Reactivation (EPR) test method, such as used for stainless steel, to detect sensitization in iron-base hardfacing alloys was evaluated. A single loop - EPR method was found to provide a more consistent measurement of sensitization than a double loop - EPR method. The high carbon content that is needed for a wear resistant hardfacing alloy produces a high volume fraction of chromium-rich carbides that are attacked during EPR testing. This results in inherently lower sensitivity for

detection of a sensitized iron-base hardfacing alloy than stainless steel using conventional EPR test methods.

INTRODUCTION

Hardfacing alloys are thick, multilayer weld deposits (0.2 to 0.5 cm thick) that provide wear resistance to a structural base metal¹. The common use of cobalt-base hardfacing alloys on nuclear plant components results in high plant radiation levels from activated cobalt wear and corrosion debris². The wear and corrosion of cobalt containing alloys produces cobalt debris that are circulated in the primary coolant through the reactor core where ⁵⁹Co is transmuted to ⁶⁰Co, which possesses a high and long lived nuclear activity. The deposition of ⁶⁰Co debris on nuclear plant components results in high radiation fields, which makes the maintenance and disposal of nuclear plant components both hazardous and costly². Replacement of cobalt-base hardfacings with a no-cobalt alloy would significantly reduce the costs associated with nuclear plant activation from ⁶⁰Co. Testing of commercial nickel-base and iron-base hardfacing alloys shows that iron-base alloys generally possess better galling wear resistance and more favorable fracture toughness values, but none of these hardfacing alloys exhibited properties comparable to the cobalt-base hardfacing alloy of choice, Stellite 6^{3,4}. Excellent corrosion resistance in a nuclear plant environment is required for any material considered for use in nuclear plant applications, and some iron-base hardfacing alloys have exhibited poor corrosion resistance in a humid environment⁵.

Corrosion screening of hardfacings is typically performed in highly oxygenated environments because these conditions are more severe⁵. Exposure a humid environment resulted in rusting of two commercial iron-base alloys (Delcrome 910, and Everit 50) with more severe attack observed for specimens that were given a 621°C/6h stress relief (SR) heat treatment⁵. The corrosion resistance of as-deposited NOREM 01 in a humid environment was acceptable, but rusting was observed for NOREM 01 coupons that had been given a 621°C/6h heat treatment⁵. NOREM 01 is an early variant of NOREM hardfacing alloys which were

developed through the Electric Power Research Institute (EPRI), and are based upon the galling resistant stainless steel Nitronic 60 (ARMCO Steel)⁶. The degradation in the corrosion resistance of iron-base hardfacing alloys such as NOREM 01 from the 621 °C/6h heat treatment is a form of sensitization.

Electrochemical potentiokinetic reactivation (EPR) is a rapid and quantitative method for detecting sensitization in austenitic stainless steels⁷⁻⁹, duplex stainless steels¹⁰, and Alloy 600¹¹. The ASTM G108-92 test method is a single loop-EPR (SL-EPR) test⁷; a large over-potential is initially applied to passivate the sample, and the reactivation scan is used to characterize the degree of sensitization. The reactivation cathodic scan produces preferential breakdown of regions that are deficient in chromium and these sensitized regions are detected by the area under the reactivation curve, which is proportional to the total measured charge (Q in coulombs/cm²). The total grain boundary area (GBA) is determined by measuring the grain size

$$GBA = A_s [5.09544 \times 10^{-3} \exp(0.34696 X)] \quad (1)$$

(ASTM grain size number (X)) for the specimen test area (A_s)⁷.

$$P_a = \frac{Q}{GBA} \quad (2)$$

A high value of P_a indicates sensitization for the SL-EPR test

Since the SL-EPR test method is very sensitive to experimental variables such as scan rate, surface finish, solution temperature, solution purity, and grain size measurement, a Double Loop - EPR (DL-EPR) method was initially used in this work^{8,9}. Both the anodic and reactivation scans are used in the DL-EPR test, and high values of the ratio of the maximum current density for the reactivation scan (I_r) to the anodic scan (I_a) or I_r/I_a indicates sensitization.

The purpose of this work is to evaluate the corrosion resistance of as-deposited and heat treated iron-base hardfacing alloys in highly oxygenated environments, and determine

temperature/time conditions that produce sensitization. Two more recent variants of NOREM alloys (NoCo-M2 and NOREM 02) and a vanadium-containing Fe-base hardfacing alloy (ELMAX) are evaluated. A feasibility study on the use of an EPR method to detect sensitization in NOREM hardfacing alloys is also reported.

EXPERIMENTAL

Materials

The hardfacing alloys (NOREM 01, NOREM 02, NoCo-M2, ELMAX, and Stellite 6) were weld deposited onto Alloy 600, AISI type 304, and/or AISI type 347 stainless steel bar (19.1 cm X 3.8 cm X 2.5 cm thick) using Plasma Transferred Arc Welding (PTAW) with a minimum preheat of 371°C. NOREM 01, ELMAX, and Stellite 6 were only PTAW deposited on AISI type 347 stainless steel. Stellite 6, the cobalt-base alloy of choice, was tested as a reference material. Two-layers of each hardfacing alloy were deposited to a total nominal thickness of 0.5 cm to minimize dilution from the base material. Comparison of the weld consumable chemistry and deposit chemistry in Table 1 shows that the difference in elemental concentration was generally less than 10%, which is consistent with the low base metal dilution characteristic of PTAW deposition¹. Slightly higher increases in nickel were observed for the NoCo-M2 and NOREM 02 deposits made on Alloy 600, which results from base metal dilution with the nickel-base alloy. The lower nitrogen content for deposits made on Alloy 600 is not clearly understood. Hardfacing deposits of NOREM 02, NoCo-M2, ELMAX, and Stellite 6 were tested in the as-deposited, 1150 SR, and 1625 SR stress relief (SR) heat treatment conditions given in Table 2. The hardfacing deposits were given a stress relief (SR) heat treatment prior to machining specimens.

Corrosion Testing

Corrosion coupons shown in Figure 1 were machined from the hardfacing deposits in accordance with Figure 2. Spare material from the NOREM 02 and NoCo-M2 deposits made on Alloy 600 and type 304 stainless steel were used for the chemistry measurements in Table 1. Any oxide scale was removed and only the top 0.10 cm of the hardfacing deposit was used for chemical analysis. The corrosion test consisted of a 4 week exposure to a humid environment with an interim examination followed by an 1 day exposure to highly oxygenated water, see Table 3. Weight change measurements, visual examinations, and metallographic sectioning were used to evaluate the condition of specimens after the corrosion test.

EPR Tests

EPR test coupons (1 cm X 1 cm X 0.2 cm thick) were machined from the hardfacing deposits, and contain no base metal. The NoCo-M2 and NOREM 02 EPR coupons were machined from the same deposit used in corrosion testing, see Figure 2. The NOREM 01 coupons were machined from the same lot of hardfacing deposits previously used for corrosion testing⁵. Three EPR tests were performed on each alloy for a total of 24 individual tests: (1) NOREM 01 in the as-deposited and 1150 SR conditions; (2) NoCo-M2 in the as-deposited, 1150 SR, and 1625 SR conditions; and (3) NOREM 02 in the as-deposited, 1150 SR, and 1625 SR conditions. The surfaces of the working electrodes (WE) were examined after EPR testing using optical microscopy, and compared with metallography from corrosion testing.

The EPR test procedure generally conforms with ASTM G108-92⁷. The characteristics of the potential and current measuring instrument were in accordance with ASTM G5-87¹² over the potential range used (-600 mV to +700 mV (Saturated Calomel Electrode (SCE) Reference)). A deaeration tube was not used in the test cell, but all other features of the test cell, SCE reference electrode, electrode holders, etc., were in accordance with ASTM G5-87¹². A platinum coated niobium mesh was connected to a platinum coated titanium rod and used as the counter electrode. Electrical contact with the back of the working electrode (WE) was achieved by using

silver paste and then epoxy to attach a stainless steel machine screw. A nickel ribbon intended to provide electrical connection was spot welded to the end of the screw prior to attachment of the screw to the specimen. The screw and nickel ribbon were isolated from the electrolyte test solution by a 1/4" glass tube that was attached to the back of the sample coupon. The WE was mounted in epoxy and then polished through 1 μm diamond within 1 hour of the experiment, and cleaned prior to testing by degreasing in Alconox detergent, rinsing in distilled water, rinsing with reagent grade methanol, and air drying. The test solution was prepared from reagent grade sulfuric acid (H_2SO_4), potassium thiocyanate (KSCN), and Type IV water as a 0.5 M H_2SO_4 + 0.02 M KSCN test solution. A quantity of 0.5 liters of test solution was used for each test cell, and the temperature was maintained at $30 \pm 1^\circ\text{C}$ with a controlled temperature water bath.

The open circuit potential (OCP or $E(\text{initial})$) was recorded within 1 to 2 minutes after immersion in the test solution. An increasing potential was then applied to the WE at a rate of $1.67 \pm 0.08 \text{ mV/s}$ (6 V/h) until a maximum potential of +500 mV was reached for the anodic scan. The reactivation scan was immediately started by decreasing the potential at a rate of $1.67 \pm 0.08 \text{ mV/s}$ to the initially measured OCP. The OCP was measured after the reactivation scan was completed ($E(\text{rest})$). The WE voltage and resulting current were continuously measured during the anodic and reactivation scans, and the maximum current density for the anodic scan (I_a) and reactivation scan (I_r) were each determined from the recorded data files. The area under the reactivation scan portion of the curve after passive breakdown was also obtained from the data files to determine the total charge (Q in Eq. (2)) for SL-EPR characterization.

RESULTS AND DISCUSSION

Corrosion Testing

Small weight changes observed after exposure to the highly oxygenated conditions (-5 mg/dm² to 5 mg/dm²) indicate that the degree of tarnishing was small, and visual examinations were used to characterize the corrosion. After exposure to a humid environment, NoCo-M2 and NOREM 02 coupons in the as-deposited condition were shiny and similar in appearance to

stainless steel, see Figures 3a and 3b. Rust spots were observed on ELMAX in the as-deposited, 1150 SR, and 1625 SR conditions, which indicates that this alloy has unacceptable corrosion resistance. Rusting was previously observed for as-deposited Everit 50 and Delcrome 910 after exposure to a humid environment, but as-deposited NOREM 01 had acceptable corrosion resistance⁵. Examination of the nominal compositions in Table 1 indicates that hardfacing alloys with low Cr:C ratios generally have poor corrosion resistance. Since molybdenum generally improves corrosion resistance, while nitrogen can precipitate with carbon, an effective Cr:C ratio (CORR) is defined (in atomic%)

$$CORR = \frac{\%Cr + \%Mo}{\%C + \%N} \quad (3)$$

The plot of CORR values versus general corrosion resistance for as-deposited hardfacing alloys in Figure 4 shows that hardfacing alloys with CORR < 4 exhibit rusting in a humid environment, with the exception of Tristelle 5183. Iron-base hardfacing alloys have a high carbon content to produce the high volume fraction of interdendritic chromium-rich carbides that is needed for wear resistance. However, iron-base hardfacing alloys with low CORR values apparently do not have enough chromium remaining in solution to provide for corrosion resistance after precipitation of these interdendritic chromium-rich carbides. Tristelle 5183 contains a large amount of niobium, which is a stabilizer. The niobium in Tristelle 5183 forms the more stable Nb-carbide rather than Cr-carbide. The resulting precipitation of large, coarse Nb-rich carbides avoids excessive Cr-carbide precipitation to leave chromium in solution to provide corrosion resistance. This result indicates that hardfacing alloys with high stabilizer contents can have acceptable corrosion resistance with lower CORR values. However, exposure to highly oxygenated water produced significant selective phase attack (SPA) of the large Nb-rich carbides in Tristelle 5183⁵. As-deposited NOREM 02 and NoCo-M2 exhibited good corrosion resistance in highly oxygenated water, while severe attack was observed for ELMAX. The

relationship between CORR and corrosion resistance in Figure 4 is empirical, and more work would be needed to define a general relationship between corrosion resistance and alloy composition.

Figure 3 shows that the 1625 SR coupons for NOREM 02 and NoCo-M2 were similar in appearance to the respective as-deposited coupons. Rust spots are observed for the 1150 SR condition for NoCo-M2 and NOREM 02 in Figures 3a and 3b, respectively. The NoCo-M2 and NOREM 02 coupons shown in Figure 3 were deposited on type 347 stainless steel, but similar results were observed for NoCo-M2 and NOREM 02 deposited on type 304 stainless steel and Alloy 600. PTAW hardfacing deposition results in low base metal dilution¹, and the chemistries of NoCo-M2 and NOREM 02 deposits made on type 304 stainless steel or Alloy 600 in Table 1 are comparable, which results in no dependence of base metal on corrosion resistance. The results previously observed for NOREM 01 after exposure to a humid environment were similar to those observed for NoCo-M2 and NOREM 02: (1) good corrosion resistance for the as-deposited condition, and (2) rusting observed for the 1150 SR condition⁵.

The rusting of the 1150 SR condition of NOREM 01, NoCo-M2, and NOREM 02 is produced by a form of sensitization, or chromium-carbide precipitation that depletes the dendrites of the chromium needed for corrosion resistance. The temperature range for sensitization of NOREM hardfacings is estimated in Figure 5 to be the same as that observed in austenitic stainless steels, 510°C to 790°C (950°F to 1450°F)¹³. Extended exposure in the temperature range for sensitization explains the rusting observed for NOREM hardfacings in the 1150 SR condition. Faster cooling of as-deposited NOREM alloys through the 510°C to 790°C temperature range avoids sensitization, which explains their excellent corrosion resistance. Figures 6a and 6b show that the as-deposited NOREM 02 microstructure consists of an interdendrite matrix of carbide/austenite lamella which surrounds dendrites. The dendrites consist of austenite surrounding a δ-ferrite core with coarse carbide precipitates. The presence of δ-ferrite was confirmed by ferro-magnetism detected with a high strength Co-Sm magnet^{3,6}.

Little change in the scale of the dendrite and interdendrite regions is produced by the 1150 SR of NOREM 02, but Figure 6c shows coarse precipitates in the dendrites. These precipitates are likely chromium-carbide precipitates that have formed and coarsened in the dendrites during the 1150 SR to result in chromium depleted regions and rusting after exposure to a humid environment. The 1625 SR produces little coarsening of the microstructure, but dense precipitation is observed in the dendrites. Heat treatment of NoCo-M2 and NOREM 02 above the temperature range for sensitization during a 1625 SR results in re-solution of the chromium-carbide precipitates, and chromium-carbide precipitation occurs during slow cooling through the temperature range for sensitization to produce the dense precipitation shown in Figure 6d. Although dense precipitation is observed in the dendrites, the cooling rate is apparently too fast to result in sufficient chromium depletion that decreases the corrosion resistance.

The microstructures for NoCo-M2 and NOREM 01 were generally similar to NOREM 02 with the following exception: (1) higher dendrite volume fraction for NoCo-M2, and a much lower fraction of δ -ferrite in the dendrites, and (2) no δ -ferrite in the NOREM 01 dendrites but the dendrite volume fraction was similar to NOREM 02. Although the δ -ferrite content in the dendrites varied for NOREM 02, NoCo-M2, and NOREM 01, the precipitate density in the dendrites for the 1150 SR and 1625 SR conditions were similar. The 1150 SR produced rusting for NOREM 02, NoCo-M2, and NOREM 01, while good corrosion resistance was observed for the as-deposited and 1625 SR conditions, which indicates that the δ -ferrite content of the dendrites has little influence on corrosion resistance. These preliminary metallographic results indicate that precipitation and coarsening of the Cr-carbide precipitates during the 1150 SR apparently decreases the chromium content below the levels needed for corrosion resistance and results in sensitization in NOREM hardfacing alloys. However, the dense chromium-carbide precipitation in the dendrites for the 1625 SR in NOREM hardfacings does not produce sensitization.

EPR Feasibility Test Results

Since the DL-EPR test method is reported to be less sensitive to specimen preparation and produces less scatter, the DL-EPR test approach was initially pursued. Example polarization curves for one DL-EPR test of NOREM 02 (as-deposited, 1150 SR, and 1625 SR) are given in Figures 7a, b, and c, respectively. Data for all 24 DL-EPR tests are compiled in Table 4. Since partial breakdown of the passive film was produced during the reactivation scan, the corrosion potential after completion of the test ($E_{(rest)}$) was higher than the initial potential ($E_{(initial)}$). The summary plot in Figure 8 shows that the $I_r:I_a$ values for 1150 SR (sensitized) NOREM 02 and NoCo-M2 were generally higher than 0.5. The $I_r:I_a$ values for the 1150 SR condition of NOREM 01, NOREM 02, and NoCo-M2 are larger than the respective as-deposited and/or 1625 SR conditions, but the values for as-deposited and 1150 SR NOREM 01 overlap. The DL-EPR test can be used to differentiate between un-sensitized and sensitized conditions for NOREM 02 and NoCo-M2, but the sensitized condition was not resolved for NOREM 01. The $I_r:I_a$ values for the 1625 SR conditions given in Figure 8 are significantly less than the respective as-deposited and 1150 SR conditions for NOREM 02 and NoCo-M2, which indicates that the 1625 SR is the least sensitized, which is not consistent with previous test results and microstructure examinations, i.e. dense Cr-carbide precipitation in the dendrites of 1625 SR NOREM 02 in Figure 6d. For stainless steels, $I_r:I_a$ values greater than 0.1 are considered to be sensitized^{8,9,14,15}, which is much less than the values measured in Table 4 for as-deposited NOREM hardfacing alloys. The higher volume fraction of Cr-carbides in NOREM hardfacings, which are attacked during the DL-EPR test, produces inherently higher $I_r:I_a$ values and less sensitivity for detection of a sensitized iron-base hardfacing alloy.

The low sensitivity for the DL-EPR method results from higher I_a values for the 1150 SR and 1625 SR conditions compared to as-deposited, which result in less difference in $I_r:I_a$ values between the non-sensitized (as-deposited and 1625 SR) and sensitized (1150 SR) conditions. The higher I_a values for 1150 SR and 1625 SR in Table 4 likely result from attack of the

chromium-depleted regions in the dendrites. In order to remove the data bias resulting from the higher I_a values, the data curves were analyzed as a SL-EPR test by calculating the area under the reactivation curves after de-passivation to determine specimen charge (Q in Eq. (2)). The correction for grain size in Eq. (2) was not made, and the reported P_a values given in Table 4 are only charge (Q) divided by sample area. Since the as-deposited, 1150 SR, and 1625 SR conditions for each alloy were produced from the same heat of weld consumable using the same weld deposition parameters, large differences in the scale of microstructure are not expected. The hardfacing alloys consist of dendrites separated by interdendritic regions of carbide/austenite lamella and determination of grain size in terms comparable to stainless steels is difficult. Comparison of SL-EPR data in Figure 9 and Table 4 shows that the P_a difference between the as-deposited and 1150 SR conditions was more than a factor of 2 for NOREM 02 and NoCo-M2. Although the P_a differences between as-deposited and 1150 SR NOREM 01 were less than a factor of 2, the difference was more significant than the DL-EPR test. The SL-EPR results indicate that the 1625 SR condition was more sensitized than the as-deposited condition, but either significantly less sensitized than the 1150 SR condition (NoCo-M2) or only slightly less sensitized than the 1150 SR condition (NOREM 02). The trend of P_a values for as-deposited, 1150 SR, and 1625 SR condition for NOREM 02 and NoCo-M2 in Figure 9 were consistent with the corrosion test results: (1) 1150 SR (heavily sensitized), (2) 1625 SR (mildly sensitized), and (3) as-deposited (least sensitized). Based on the results of the SL-EPR scan data shown in Figure 9, a line at $P_a = 1.5 \text{ C/cm}^2$ was arbitrarily drawn to mark the boundary between the sensitized and unsensitized conditions. With the exception of one data point for 1150 SR NOREM 01, all data points in the "Non-Sensitized Zone" are not sensitized. Additionally, with the exception of one data point for 1625 SR NOREM 02, all data in the "Sensitized Zone" were sensitized and rusting was observed after exposure to a humid environment. Based on round-robin testing⁷, type 304 stainless steel is characterized as sensitized if $P_a > 0.4 \text{ C/cm}^2$. The higher carbon and chromium contents of NOREM hardfacing

alloys produce a large volume fraction of chromium-rich carbides that are subject to electrochemical attack and, consequently, inherently higher P_a values.

EPR testing resulted in preferential attack of chromium-rich carbides in the interdendritic carbide/austenite lamella and δ -ferrite regions in the center of the dendrites for as-deposited NOREM 02 in Figures 10a and 10b. Infrequent localized attack of coarse Cr-carbide precipitates in the austenite regions of the dendrites, which surround the δ -ferrite regions, is also observed for as-deposited NOREM 02. Micrographs of corrosion coupons machined from the same hardfaced deposit (Figures 6a and 6b) show that the microstructure was similar to the Working Electrode (WE). The chromium-rich carbides (mostly M_7C_3) in the interdendritic regions⁶ likely represent inclusions that are subjected to selective attack during the EPR test. The δ -ferrite regions in the dendrites probably contain a high density of carbide precipitates, due to the low solubility of carbon in δ -ferrite, that are subjected to selective attack in the EPR solution. Coarse Cr-carbide precipitates only infrequently occur in the austenite regions of the dendrites in as-deposited NOREM 02 due to the high cooling rate, and these coarse carbide precipitates or chromium-depleted regions adjacent to the carbides appear to be attacked by the EPR solution. This wide attack of the interdendritic carbides and dendritic regions for as-deposited NOREM 02 likely results in the inherently higher $I_r:I_a$ and P_a values for as-deposited NOREM 02, even though this material was not sensitized. Similar appearance was observed for the WE of as-deposited NoCo-M2 and NOREM 01.

The microstructure of the WE for 1150 SR NOREM 02 shown in Figure 10c exhibits features that were generally similar to those observed for as-deposited NOREM 02, but more extensive attack of coarse Cr-carbide precipitates or Cr-depleted regions in the dendrites was observed for 1150 SR NOREM 02. Large Cr-carbide precipitates in austenite dendrite regions and dense Cr-carbide precipitates in the δ -ferrite regions of the dendrites is observed in the 1150 SR NOREM 02 microstructure shown in Figure 6c. Cr-carbide precipitation and coarsening in the dendrites during the 621°C/6h SR heat-treatment in the temperature range for

sensitization (Figure 5) produces numerous Cr-depleted regions in the dendrites. The attack of these regions during the reactivation scan gives higher $I_r:I_a$ and P_a values for 1150 SR. Since the only significant differences between 1150 SR and as-deposited is the greater frequency of Cr-depleted regions in the dendrites of the 1150 SR material, the differences in $I_r:I_a$ (Figure 8) and P_a (Figure 9) values are not large. The microstructure of the WE for 1150 SR NoCo-M2 and NOREM 01 exhibited similar features.

The three WEs for 1625 SR NOREM 02 appeared similar to as-deposited NOREM 02, but the etching of the 1625 SR dendrites appeared more significant and uniform than observed for as-deposited and 1150 SR NOREM 02. The microstructure for 1625 SR NOREM 02 shown in Figure 6d consists of Cr-carbide/austenite lamella regions that separate dendrites which contain a dense distribution of fine Cr-carbide precipitates from slow cooling through the temperature range for sensitization (Figure 5). Although a high precipitate density was observed in the dendrites of 1625 SR NOREM 02, the local chromium-depletion produced by the dense precipitation did not produce a significant degradation in corrosion resistance. The slight sensitization that results from the 1625 SR can be detected using the SL-EPR test, but the wide data scatter shows the results can vary from sample to sample. The appearance of the WE for 1625 SR NoCo-M2 was similar in appearance.

Summary

Iron-base hardfacing alloys are an unique class of materials with a fundamentally different microstructure than common stainless steels. Corrosion testing has been used to show that iron-base hardfacing alloys in the as-deposited condition with effective Cr:C ratios < 4 exhibit rusting in a humid environment. An exception to this result was Tristelle 5183 which had an effective Cr:C ratio < 4 and good corrosion resistance in a humid environment, but the high niobium content resulted in the precipitation of coarse Nb-carbide precipitates and limited chromium-carbide precipitation. Iron-base hardfacing alloys containing high stabilizer contents may possess good corrosion resistance with Cr:C < 4 . This work indicates that the Cr:C

composition ratio can be used as a general guideline for the corrosion resistance of iron-base hardfacing alloys.

NOREM hardfacing alloys exhibited excellent corrosion resistance in the as-deposited condition. Rusting was observed for the 1150 SR condition due to a form of sensitization, while fairly slow cooling through the estimated temperature range for sensitization did not degrade the corrosion resistance of the 1625 SR condition for NOREM hardfacing alloys. The dendrites of the 1625 SR conditions contained a high precipitate density while 1150 SR dendrites contained fewer and coarser precipitates, which indicates that precipitate coarsening of chromium-rich carbides produces chromium-depleted regions (sensitized) and poor corrosion resistance for the 1150 SR condition of NOREM hardfacing alloys.

Based upon the DL-EPR and SL-EPR data, and examination of WE microstructures, the SL-EPR method is a better method for detection of sensitized NOREM hardfacings. The heavily sensitized 1150 SR condition was detected using DL-EPR, but the 1625 SR condition was characterized as less sensitized than as-deposited, which contradicts the corrosion testing results, metallographic and WE examinations. Additionally, the 1150 SR condition of NOREM 01 was not characterized as more sensitized than as-deposited NOREM 01 using the DL-EPR method. The differences in maximum current density of the anodic scan (I_a) for the as-deposited, 1150 SR, and 1625 SR condition of each NOREM alloy reduced the sensitivity of the DL-EPR measurement of sensitization ($I_r:I_a$). The SL-EPR measurement of sensitization involves only the characterization of the reactivation curve, but provided a more accurate detection of sensitization. The P_a values for 1150 SR NOREM 01 were larger than as-deposited, and the difference between the as-deposited and 1150 SR conditions for both NOREM 02 and NoCo-M2 was almost a factor of three (Figure 9). The P_a values were consistent with the results from previous corrosion testing and microstructure examinations: (1) 1150 SR (heavily sensitized), (2) 1625 SR (mildly sensitized), and (3) as-deposited (least sensitized). The higher carbon and chromium content for NOREM hardfacings results in a 0.12

to 0.20 volume fraction of Cr-carbides that are attacked during the EPR test, resulting in higher P_a values and less difference in P_a between the non-sensitized and sensitized conditions than observed for stainless steels.

ACKNOWLEDGMENT

This work was performed under USDOE Contract No. DE-AC11-98PN38206. Thanks to J.L. Hollenbeck, W.L. Ohlinger, S.A. Shiels, W. L. Wilson, A.J. Bradfield, J.P. Moran, and J.M. Bradshaw for technical direction and comments. Thanks to S.R. Taylor (University of Virginia) for completing the EPR studies.

REFERENCES

1. "Friction, Lubrication and Wear Technology", Materials Handbook, Vol. 18, (ASM-I. Materials Park, OH, 1992).
2. E.W. Ohriner and E.P. Whelan, "Development of Cobalt-Free Hard-facing Alloys for Nuclear Applications: 1984 Progress", EPRI NP-4237, (Palo Alto, California: 1985).
3. B.V. Cockeram, R.F. Buck, and W.L. Wilson, Surface and Coatings Technology 94/95 (1997): p. 495.
4. B.V. Cockeram, Surface and Coatings Technology 108/109 (1998): p. 377.
5. S.A. Shiels, W.L. Wilson, K.W. Rosengarth, and G.L. Wire, "Laboratory Evaluation of Low Cobalt Wear Materials for Nuclear Applications", Proceedings of the Third International Symposium on the Contribution of Materials Investigation to the Reduction of Problems Encountered in Pressurized Water Reactors, (Fontevraud, France, September 12-16, 1994). Available as WAPD-T-3032, DOE/OSTI (Oak Ridge TN, 1994).
6. E.K. Ohriner, T. Wada, E.P. Whelan, and H. Ocken, Met. Trans. 22A (1991): p. 983.
7. ASTM Book of Standards, Vol. 03.02, G 108, (ASTM, Philadelphia, PA, 1992).
8. A.P. Majidi and M.A. Streicher, Corrosion 40 (1984) p. 393.
9. A.P. Majidi and M.A. Streicher, Corrosion 40 (1984) p. 584.
10. J.B. Lee, Corrosion 42 (1986) p. 106.
11. A. Roelandt and J. Vereecken, Corrosion 42 (1986) p. 289.
12. ASTM Book of Standards, Vol. 03.02, ASTM G5-87, (ASTM, Philadelphia, PA, 1987).
13. "Corrosion Engineering", M.G. Fontana, (McGraw-Hill, New York, 1986).
14. J.F. Grubb and J.D. Fritz, NACE International Corrosion'97 Conference, Paper No. 185, (NACE, Houston, TX, 1997).

TABLE 1.
Reported Chemistry Certifications for the Weld Consumables and Combustion and
Inductively Coupled Plasma Chemistry Measurements of NoCo-M2 and NOREM 02 Weld Deposits.

Alloy	Fe	Ni	Cr	C	Si	Mn	Mo	N	O	Co	W	Nb	Other
WELD CONSUMABLE CHEMICAL CERTIFICATION [in Weight%]													
Stellite 6 ⁽¹⁾ HT# 5191-2	3.0	2.0	29.5	1.19	1.1	0.4	0.1	--	--	BAL	4.80	--	--
Delcrome 910 ⁽²⁾	BAL	--	25.0	2.5	0.4	0.9	3.0	--	--	--	--	--	--
Everit 50 ⁽²⁾	BAL	--	25.0	2.5	<0.5	<1.0	3.2	--	--	--	--	0.5 V, 1.1 Cu	--
Tristelle 5183 ⁽²⁾	BAL	10.0	20.0	2.0	5.0	--	--	--	--	--	8.0	--	--
ELMAX ⁽³⁾	BAL	0.13	18.2	1.71	0.88	0.32	1.10	0.091	--	--	0.34	--	3.05 V, .021 S
NOREM 01 ⁽¹⁾ HT# 3515-1	BAL	4.49	24.50	1.26	3.24	7.85	2.25	0.273	.016	0.10	<.10	<.15	<.05 Cu .021 P .003 S <.05 V
NoCo-M2 ^(1,4) HT# 5262-1	BAL	8.08	24.76	0.97	2.76	5.01	1.80	0.15	--	0.07	0.10	--	.017 P .013 S
NoCo-M2 ^(1,5) HT# 5393-1	BAL	7.62	24.42	0.95	2.76	5.15	1.95	0.09	--	<.05	--	--	.017 P .013 S
NOREM 02 ^(1,6) HT# 5927-1	BAL	4.15	25.43	1.24	3.28	4.41	2.08	0.16	--	<.05	--	--	.012 P .011 S
MEASURED WELD DEPOSIT CHEMISTRY [in Weight%]													
NoCo-M2 on 304SS	53.97	9.02	25.6	0.913	3.63	4.99	1.84	--	--	--	--	.01	.017 P, .0132 S
NoCo-M2 on A600	53.47	9.18	25.9	0.924	3.57	4.98	1.89	.0056	.0007	--	--	.01	.017 P, .0132 S
NOREM 02 on 304SS	59.06	5.25	24.6	1.205	3.73	4.25	1.81	.0608	.0045	--	--	<.01	.010 P, .0108 S
NOREM 02 on A600	57.66	6.15	25.2	1.196	3.95	4.00	1.79	.0055	.0008	--	--	.01	.011 P, .0108 S

Notes:

1. Tradename of Stoody Deloro Stellite Div. Of Thermodyne Industries, Goshen, IN.
2. Nominal weld consumable compositions reported in Reference (2).
3. Tradename of Uddeholm Corp., Rolling Meadows, IL.
4. This NoCo-M2 weld consumable was deposited only on type 347 stainless steel.
5. This NoCo-M2 weld consumable was deposited on Alloy 600 and type 304 stainless steel.
6. Trademark of Electric Power Research Institute, Palo Alto, CA.
7. The symbol “--” means the chemistry for this element was not measured.

TABLE 2

Condition of Hardfaced Bars with Time/Temperature Schedules for Stress Relief Heat Treatments

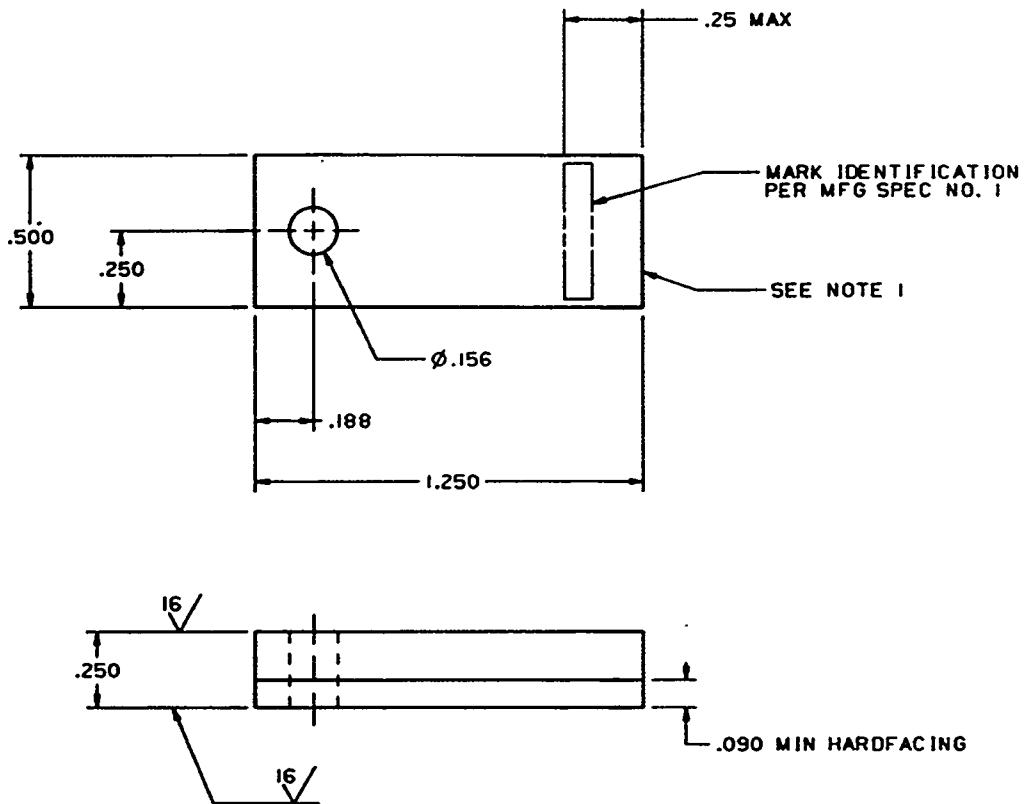
Alloy Condition	Procedure
As-deposited	Cooled in Vermiculite After Weld Deposition.
621°C/6 hour Stress Relief (1150 SR)	<ol style="list-style-type: none"> 1. Heat to 621°C \pm 13°C in 5 hours. 2. Hold at 621°C \pm 13°C for 6 hours. 3. Cool at 55.6°C/hour to 204°C. 4. Furnace cool from 204°C to room temperature.
885°C/4 hour Stress Relief (1625 SR)	<ol style="list-style-type: none"> 1. Heat to 885°C \pm 13°C in 8 hours. 2. Hold at 885°F \pm 13°C for 4 hours. 3. Cool at 55.6°C/hour to 204°C. 4. Furnace cool from 204°C to room temperature.

TABLE 3.
Environment for the Corrosion Tests.

TEST	TEST ENVIRONMENT	EXPOSURE TIME
(1) Humid Environment	Suspend in 90-100% relative humidity Vapor @ 65.5°C. Air Present.	4 weeks
(2) Highly Oxygenated Water	Demineralized water saturated with air at room temperature. Starting Solution 4.5-5.0 pH using Chromic Acid (CrO ₃). pH adjusted during test with Nitric Acid if required. Chloride <0.1 ppm. Test Temperature = 279.5°C	1 day

TABLE 4.
Summary of EPR data for NOREM 01 (as-deposited and 1150 SR),
NOREM 02 (as-deposited, 1150 SR, and 1625 SR),
and NoCo-M2 (as-deposited, 1150 SR, and 1625 SR).

Sample	Sample Area [cm ²]	E(initial) [mV _{SCE}]	E(rest) [mV _{SCE}]	I _a [A/cm ²]	I _r [A/cm ²]	I _r :I _a	P _s [A/cm ²] SL-EPR
NOREM 01							
As-deposited							
1-1	0.955	-435	-423	0.0290	0.0114	0.393	0.882
1-2	0.963	-427	-415	0.0270	0.0109	0.404	0.857
1-3	0.891	-424	-416	0.0305	0.0146	0.479	1.078
1150 SR							
1A-1	0.973	-423	-413	0.0428	0.0245	0.572	2.029
1A-2	0.981	-423	-413	0.0448	0.0256	0.571	2.042
1A-3	0.965	-422	-414	0.0376	0.0163	0.434	1.440
NOREM 02							
As-deposited							
2-1	0.992	-426	-414	0.0226	0.00768	0.340	0.594
2-4	1.012	-410	-411	0.0222	0.00540	0.243	0.461
2-3	0.963	-431	-417	0.0183	0.00784	0.428	0.649
1150 SR							
2A-1	0.951	-427	-415	0.0419	0.0253	0.604	2.032
2A-2	0.973	-427	-423	0.0196	0.0224	1.143	1.851
2A-3	0.971	-423	-415	0.0403	0.0223	0.553	1.713
1625 SR							
2B-1	1.017	-420	-420	0.0706	0.0127	0.180	1.388
2B-2	0.970	-431	-427	0.1240	0.0203	0.164	1.475
2B-3	0.952	-427	-423	0.1240	0.0296	0.239	1.925
NoCo-M2							
As-deposited							
M-1	0.965	-425	-399	0.0143	0.00652	0.456	0.485
M-2	0.939	-399	-399	0.0211	0.00512	0.243	0.422
M-3	1.002	-401	-399	0.0146	0.00662	0.453	0.512
1150 SR							
MA-1	0.969	-420	-398	0.0286	0.0226	0.624	1.655
MA-2	0.971	-398	-398	0.0296	0.0237	0.641	1.769
MA-3	0.987	-415	-398	0.0277	0.0218	0.619	1.658
1625 SR							
MB-1	0.136	-317	-317	0.0744	0.00108	0.015	0.00852
MB-2	0.989	-374	-374	0.0968	0.00990	0.102	0.543
MB-3	0.151	-310	-310	0.0962	0.01200	0.125	0.106



NOTE:

1. ^{63/} ALL OVER UNLESS OTHERWISE NOTED

FIGURE 1. Hardfaced corrosion coupon.

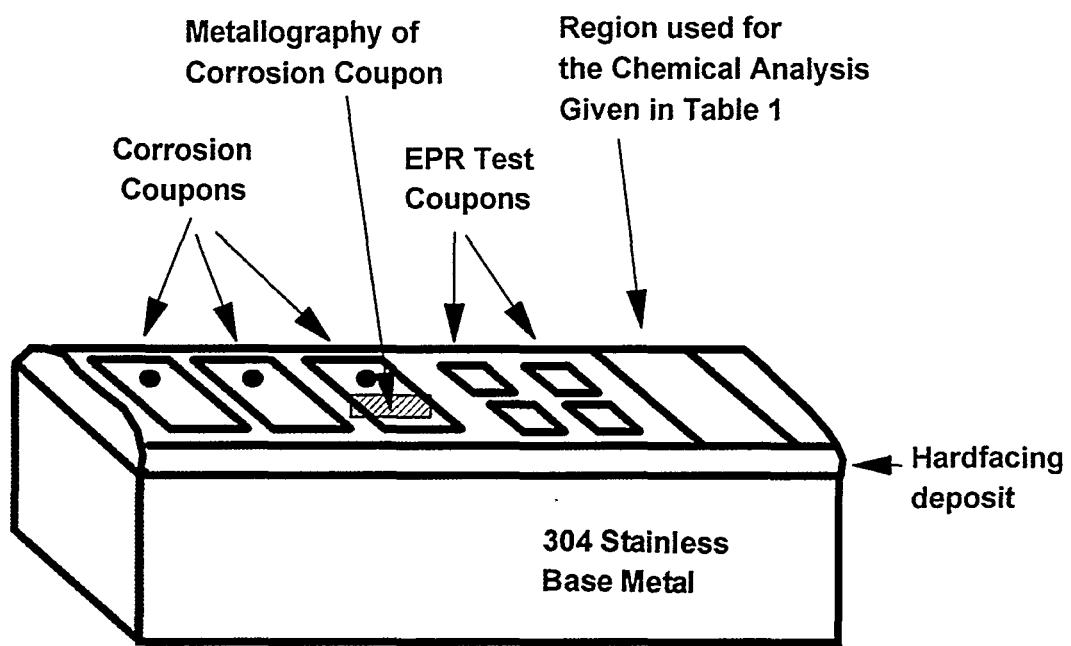


FIGURE 2. Schematic of machining orientation for the corrosion coupons, EPR test specimens taken from the top 0.20 cm of the 0.50 cm thick hardfacing deposits, and region used for chemical analysis for NOREM 02 and NoCo-M2 deposited on type 304 stainless steel.

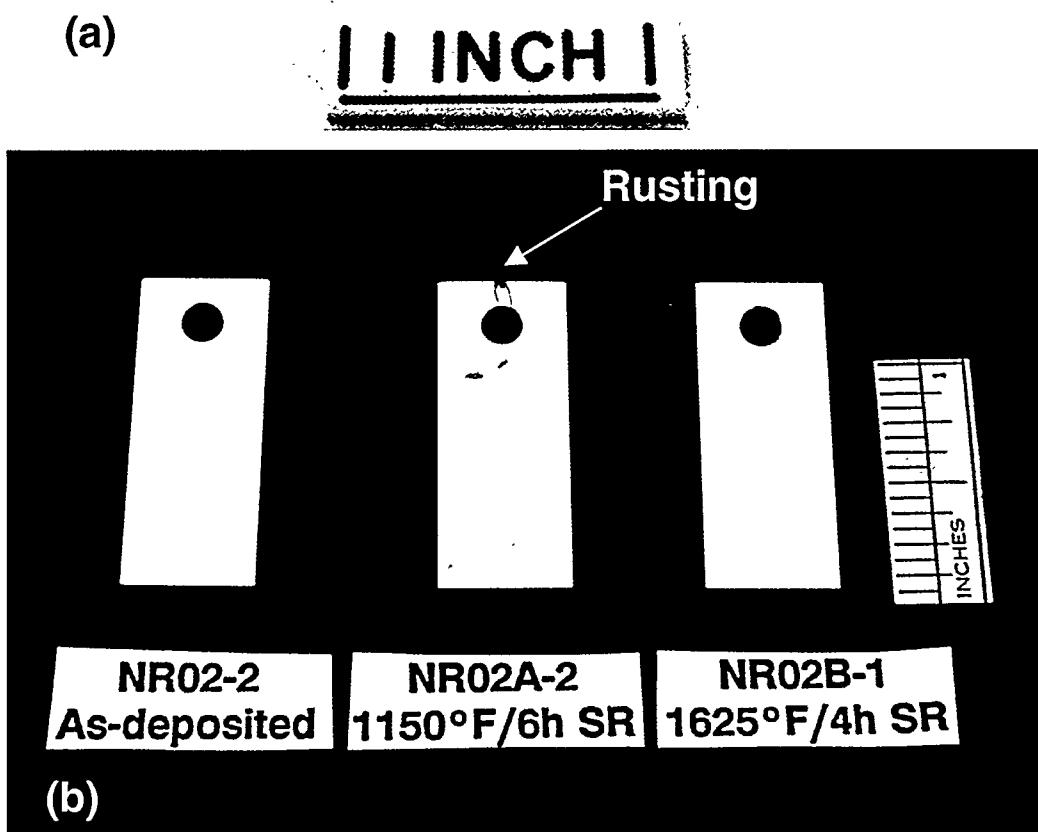
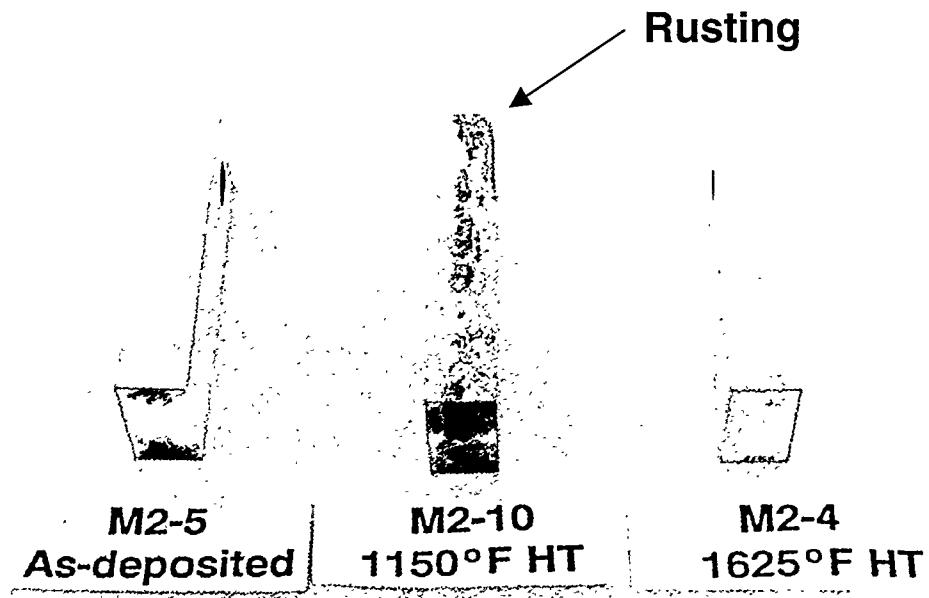


FIGURE 3. Photographs of NOREM 02 and NoCo-M2 coupons after exposure to a humid environment showing rusting for the 1150 SR condition: (a) side of NoCo-M2 coupons in the as-deposited, 1150 SR (621°C/6h) and 1625 SR (885°C/4h) with hardfacing on the right side, and (b) face of NOREM 02 coupons in the as-deposited, 1150 SR (621°C/6h) and 1625 SR (885°C/4h).

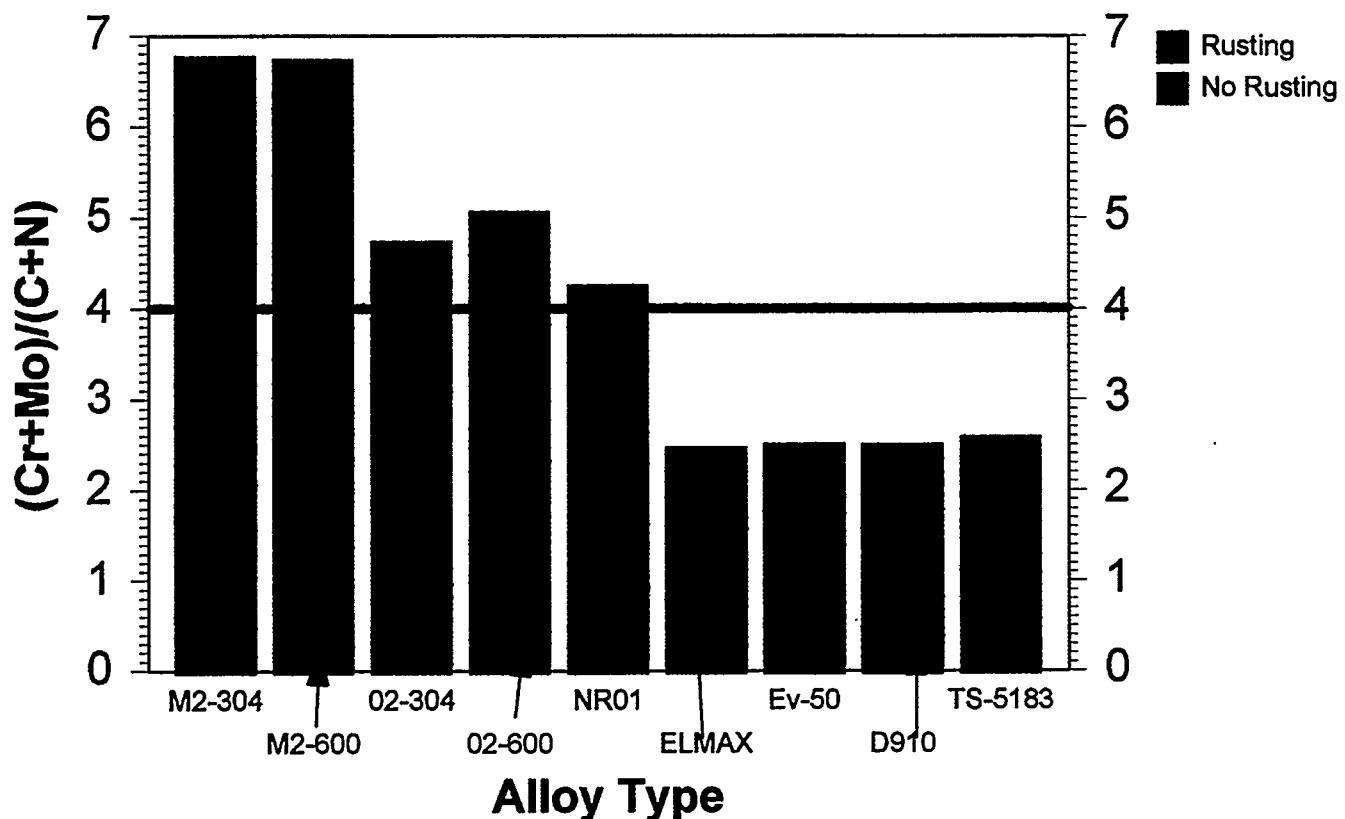


FIGURE 4. Summary plot of CORR ratio (Eq. (3)) versus corrosion results after exposure to a humid environment for various commercial iron-base hardfacing alloys in the as-deposited condition (NoCo-M2 on 304SS (M2-304) and A600 (M2-600), NOREM 02 on 304SS (02-304) and A600 (02-600), NOREM 01 (NR01), ELMAX, Everit 50 (Ev-50), Delchrome 910 (D910), and Tristelle 5183 (TS-5183)). Green means no rusting was observed for the as-deposited alloy. Red means that rusting was observed following exposure to a humid environment for the as-deposited alloys.

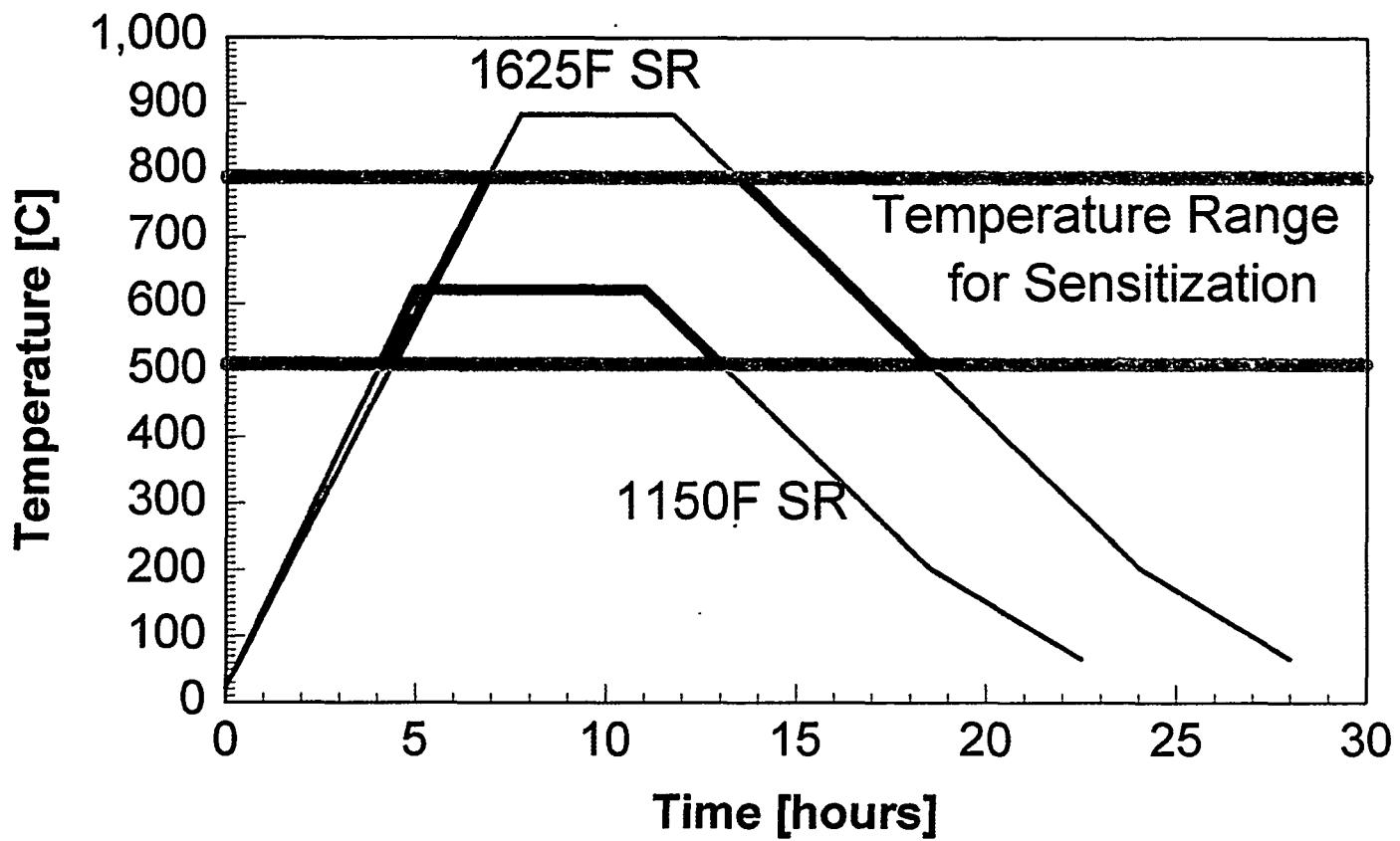


FIGURE 5. Plot of temperature versus time for the 1150 SR (621°C/6h) and 1625 SR (885°C/4h) heat treatments, see Table 2. The temperature range for sensitization of stainless steels (510°C to 790°C)¹³, which also is assumed to be the sensitization temperature range for NOREM hardfacings, is marked.

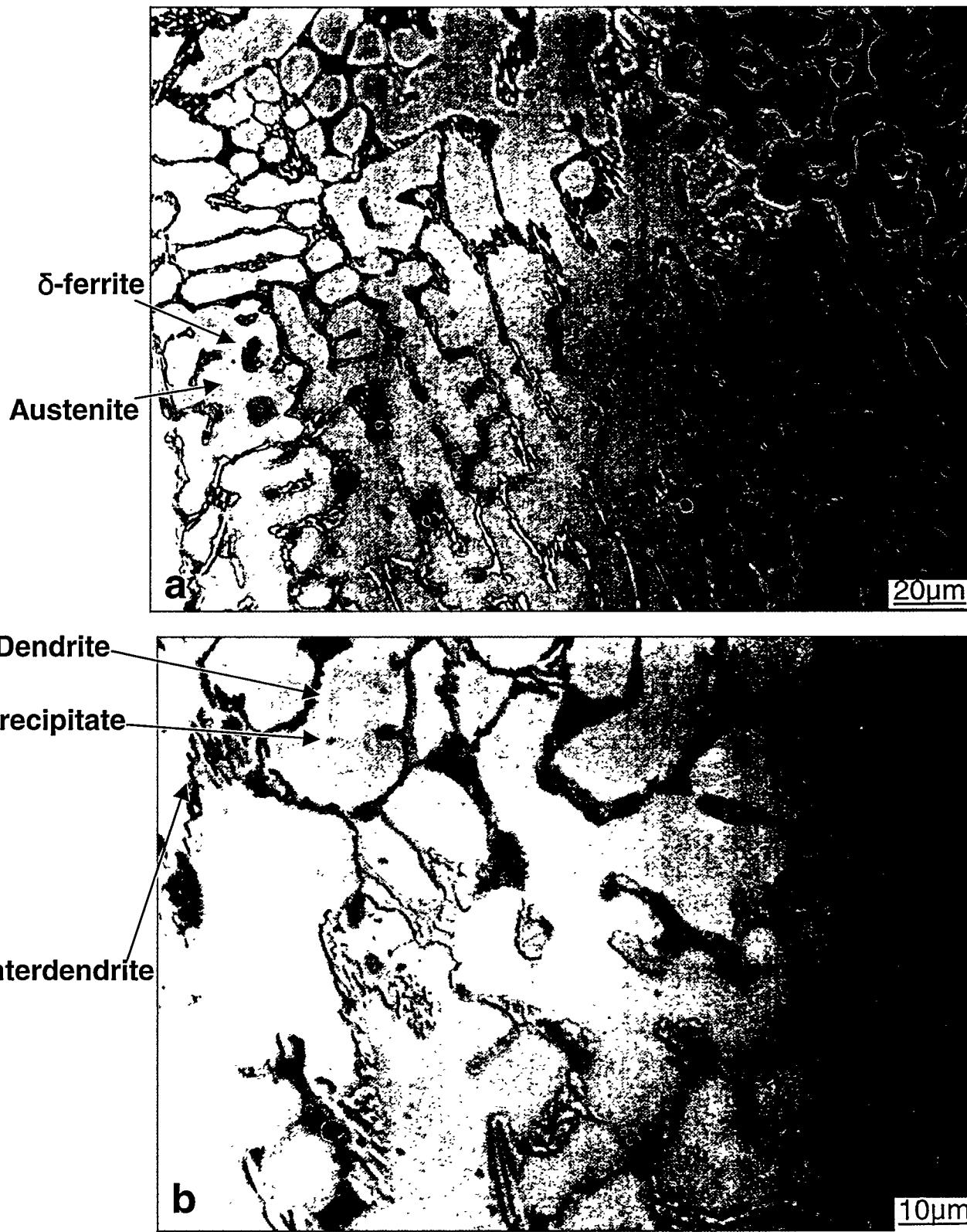


FIGURE 6. Optical micrographs of NOREM 02 coupons after corrosion testing that were metallographically prepared by electrolytic etching in 40% nitric acid: (a) as-deposited microstructure (Mag=500X), (b) as-deposited NOREM 02 (Mag=1000X), (c) 1150 SR NOREM 02 (Mag=1000X), and (d) 1625 SR NOREM 02 (Mag=1000X). The NOREM 02 coupons were machined from deposits made on Type 304 stainless steel.

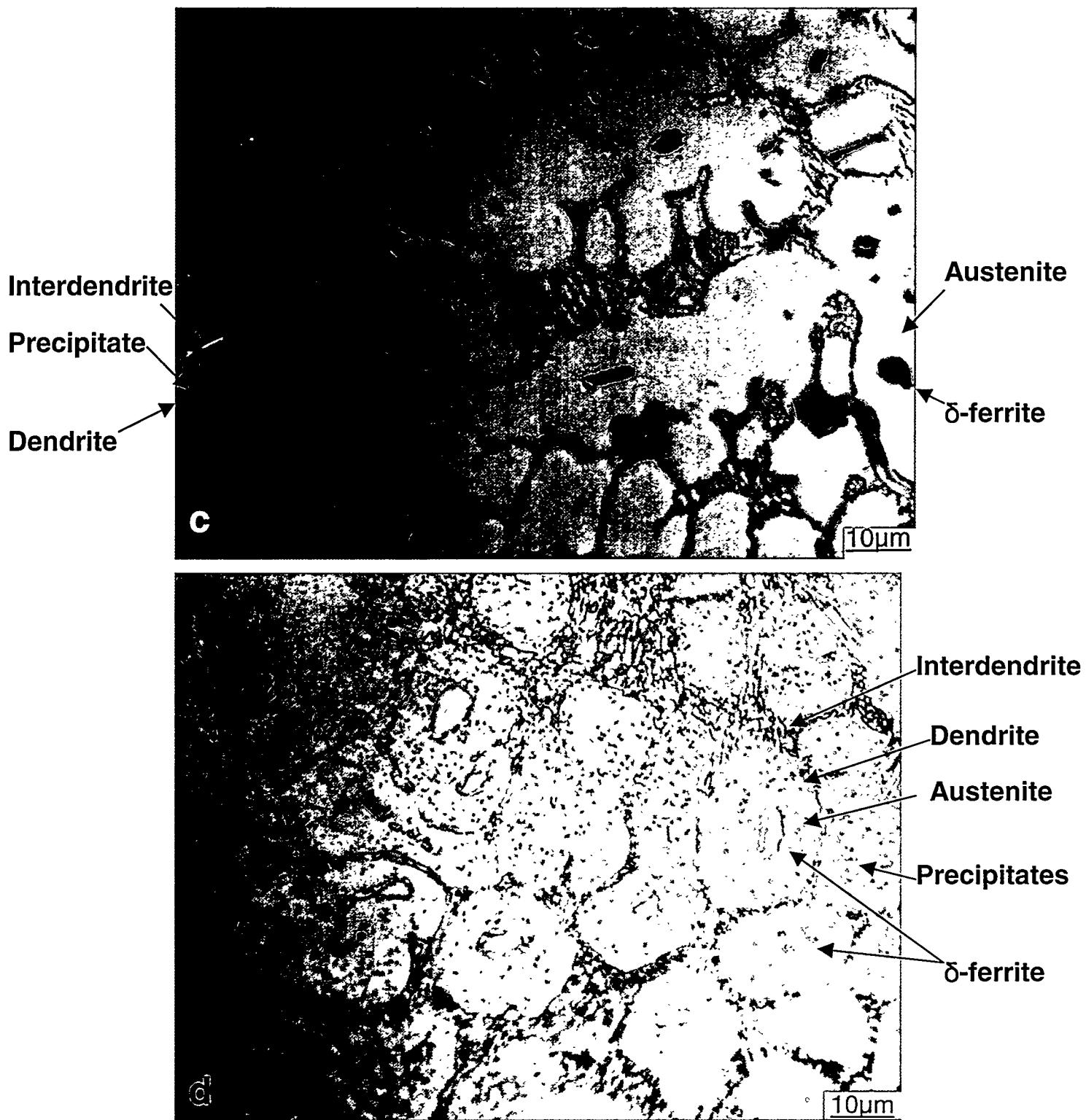


FIGURE 6. (Continued) Optical micrographs of NOREM 02 coupons after corrosion testing that were metallographically prepared by electrolytic etching in 40% nitric acid: (a) as-deposited microstructure (Mag=500X), (b) as-deposited NOREM 02 (Mag=1000X), (c) 1150 SR NOREM 02 (Mag=1000X), and (d) 1625 SR NOREM 02 (Mag=1000X). The NOREM 02 coupons were machined from deposits made on Type 304 stainless steel.

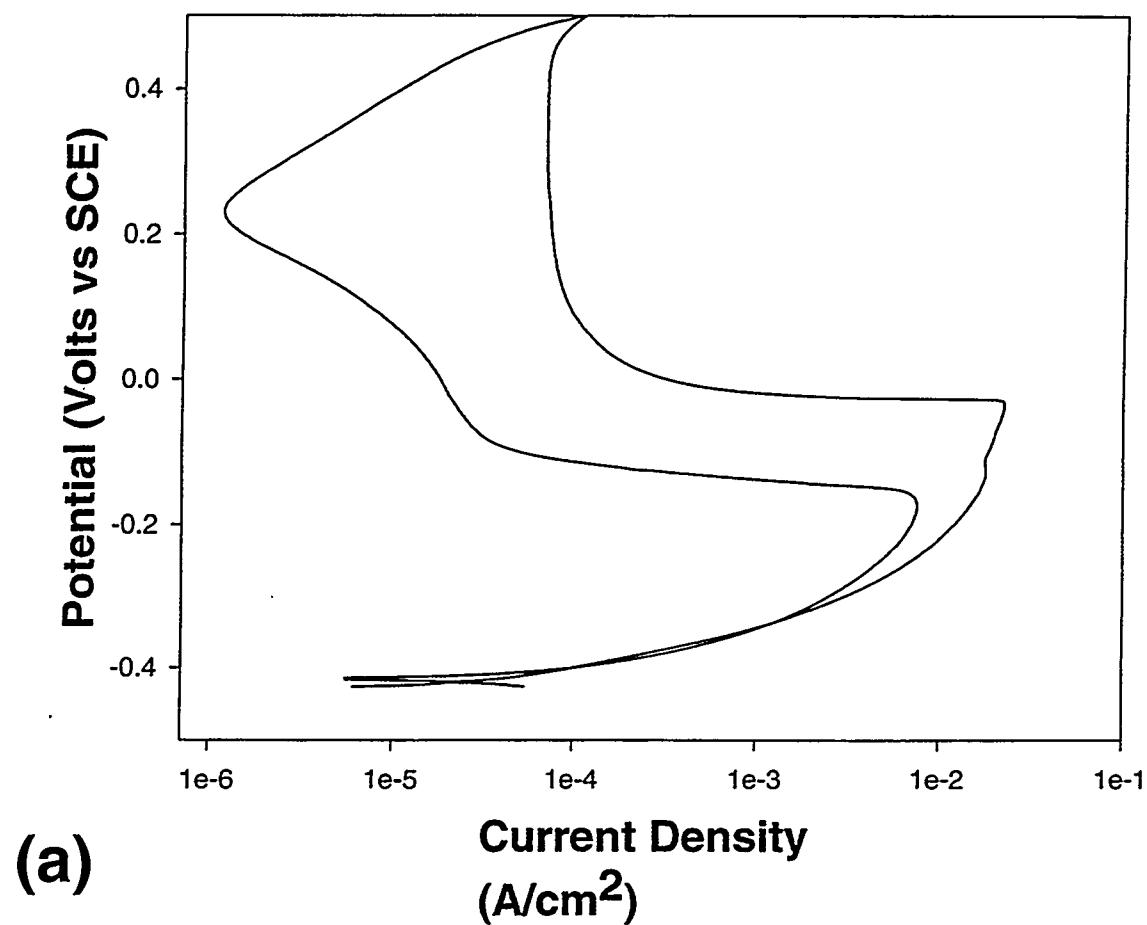


FIGURE 7. Example polarization curves measured for NOREM 02 (Plot of Potential (Volts vs SCE reference) versus log Current Density (Amps/cm²)): (a) as-deposited condition (sample 2-1), (b) 1150 SR condition (sample 2A-1), and (c) 1625 SR condition (sample 2B-1) .

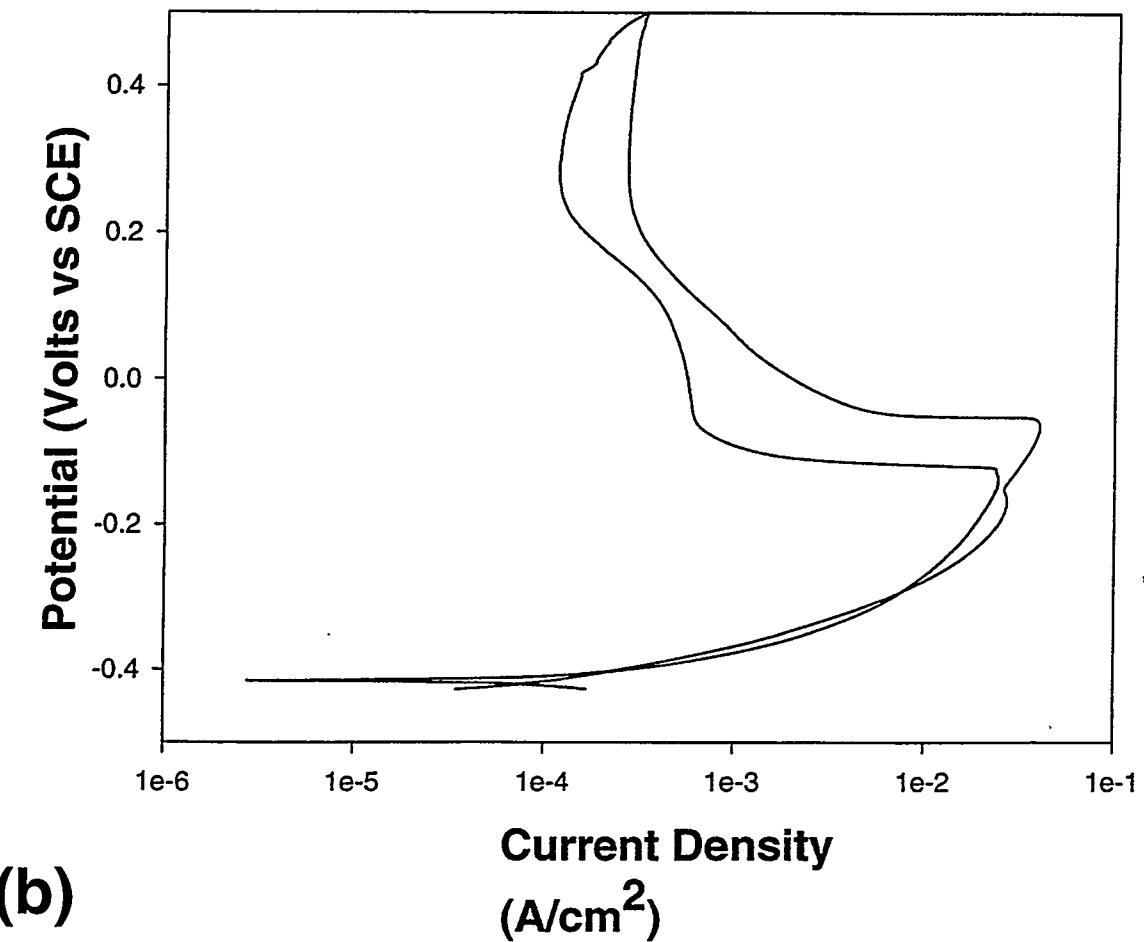


FIGURE 7. (Continued) Example polarization curves measured for NOREM 02 (Plot of Potential (Volts vs SCE reference) versus log Current Density (Amps/cm²): (a) as-deposited condition (sample 2-1), (b) 1150 SR condition (sample 2A-1), and (c) 1625 SR condition (sample 2B-1).

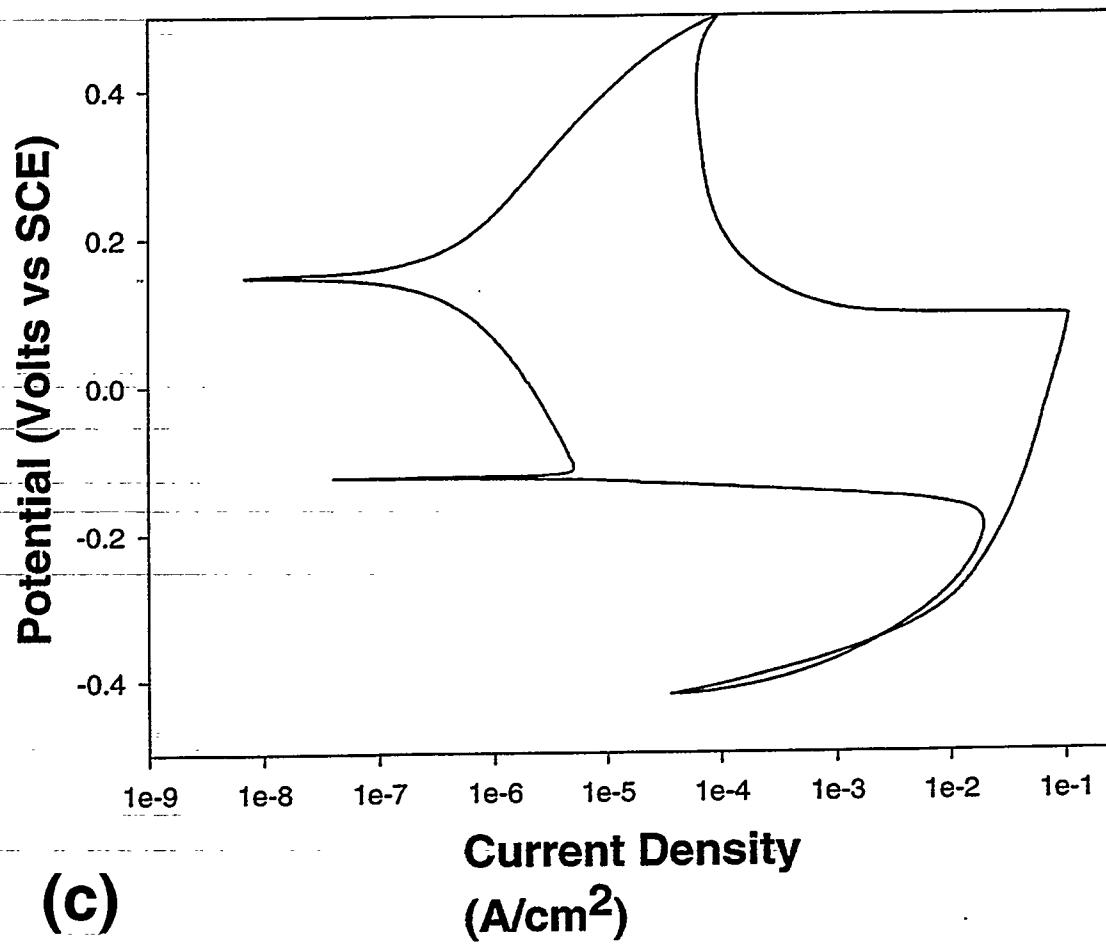


FIGURE 7. (Continued) Example polarization curves measured for NOREM 02 (Plot of Potential (Volts vs SCE reference) versus log Current Density (Amps/cm²)): (a) as-deposited condition (sample 2-1), (b) 1150 SR condition (sample 2A-1); and (c) 1625 SR condition (sample 2B-1).

$I_r : I_a$

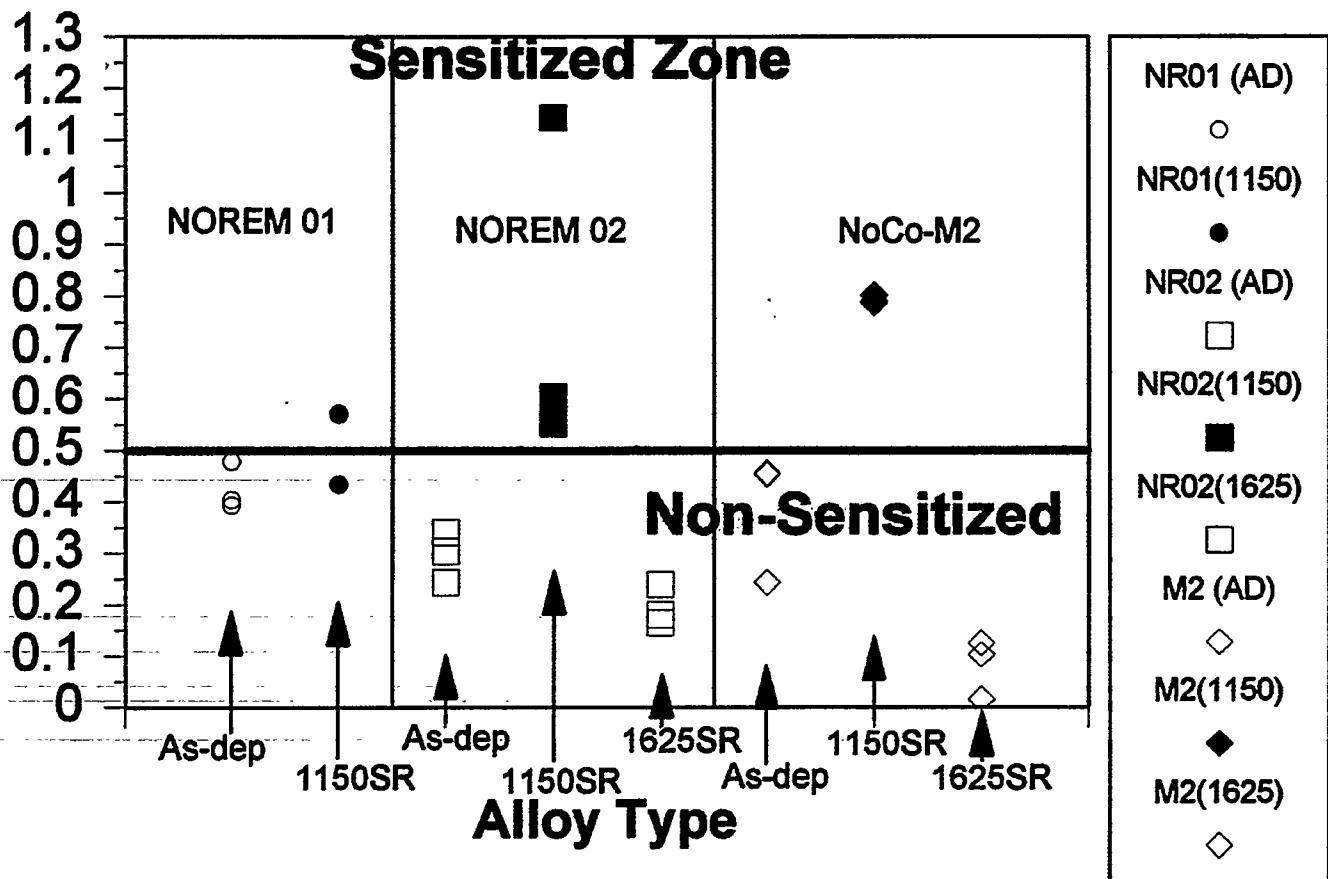


FIGURE 8. Results of DL-EPR measurement of sensitization ($I_r : I_a$) for NOREM 01, NOREM 02, and NoCo-M2. The heavily sensitized data points (1150 SR condition) are given in red while the non-sensitized conditions are given in green (as-deposited, least sensitized) and blue (1625 SR, lightly sensitized).

P_a [C/cm²]

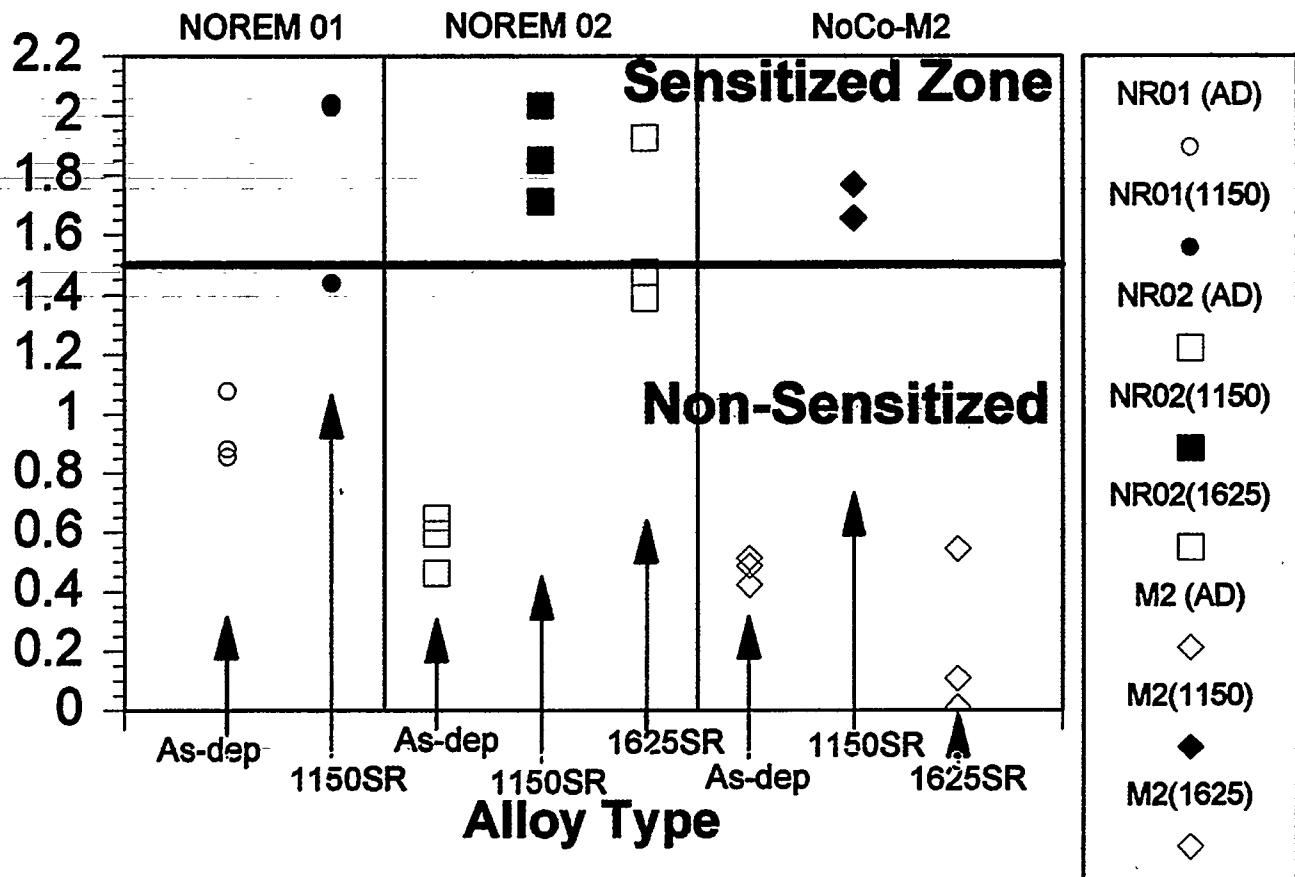


FIGURE 9. Results of SL-EPR measurement of sensitization (P_a) for NOREM 01, NOREM 02, and NoCo-M2. The heavily sensitized data points (1150 SR condition) are given in red while the non-sensitized conditions are given in green (as-deposited, least sensitized) and blue (1625 SR, lightly sensitized).

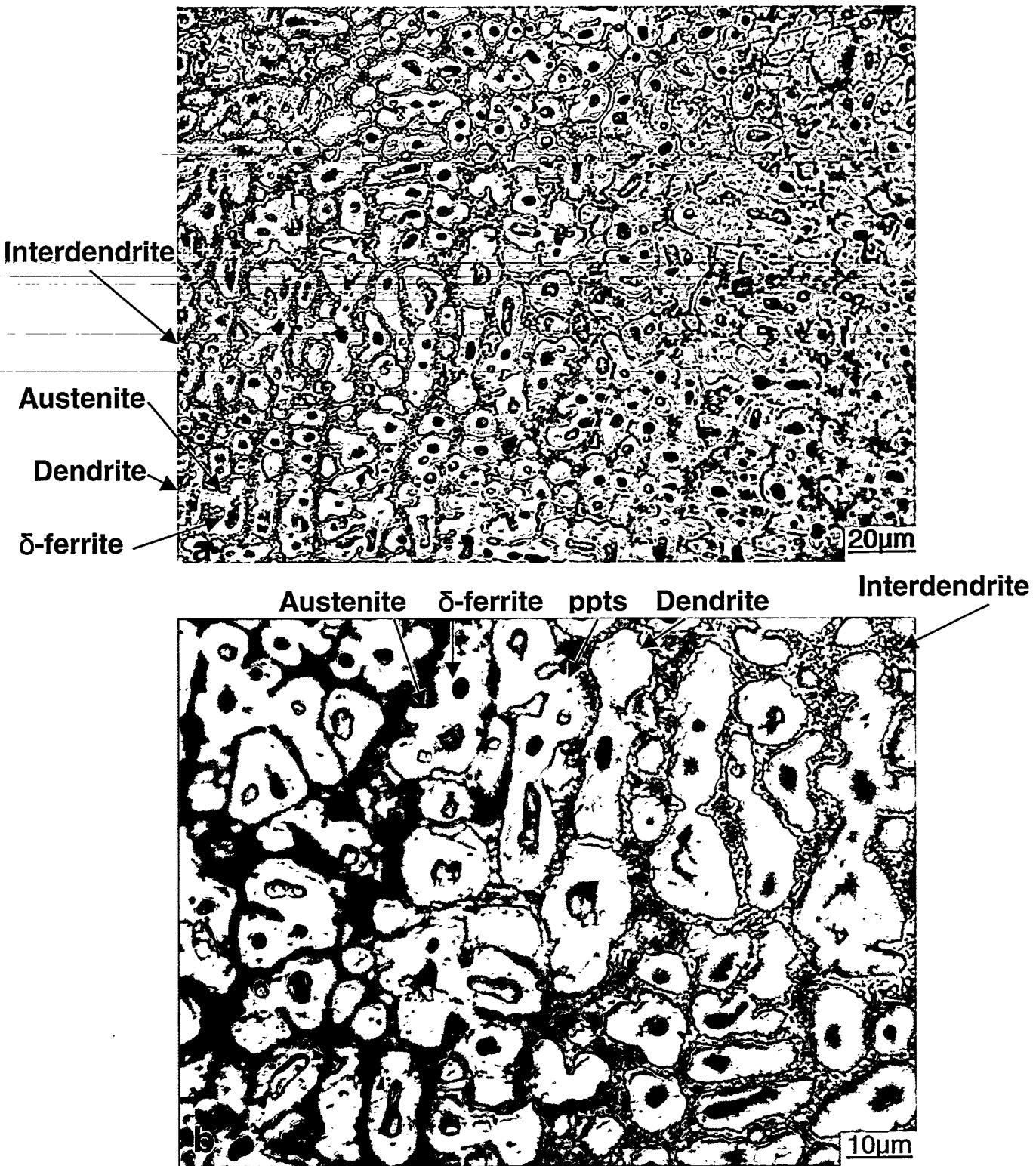


FIGURE 10. Optical micrographs of the surface of NOREM 02 WE after EPR testing: (a) as-deposited microstructure for coupon 2-1 (Mag=500X), (b) as-deposited NOREM 02, coupon 2-1 (Mag=1000X), (c) 1150 SR NOREM 02, coupon 2A-1 (Mag=1000X), and (d) 1625 SR NOREM 02, coupon 2B-1 (Mag=1000X). The NOREM 02 EPR coupons were machined from deposits made on Type 304 stainless steel.

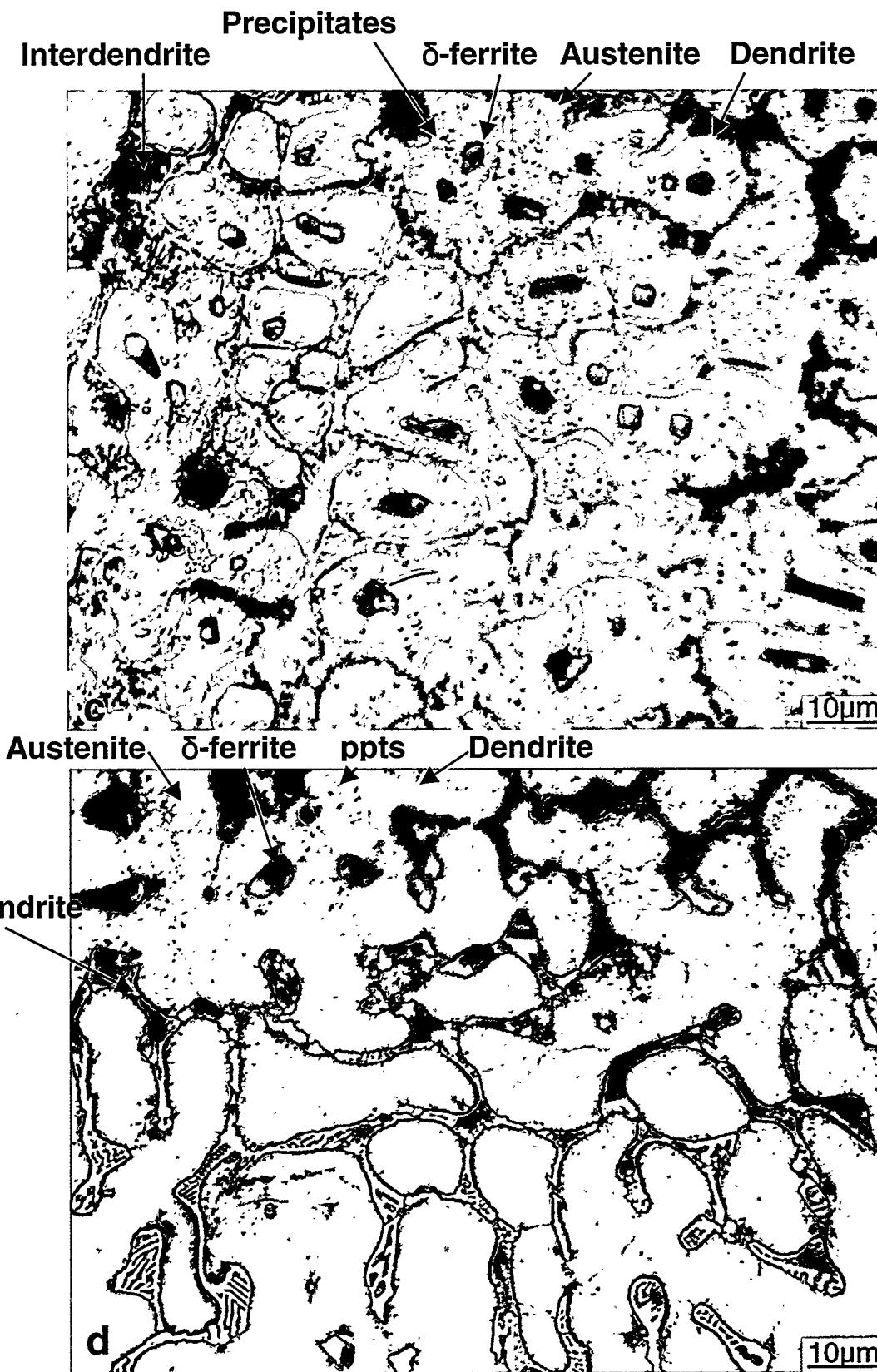


FIGURE 10. (Continued) Optical micrographs of the surface of NOREM 02 WE after EPR testing: (a) as-deposited microstructure for coupon 2-1 (Mag=500X), (b) as-deposited NOREM 02, coupon 2-1 (Mag=1000X), (c) 1150 SR NOREM 02, coupon 2A-1 (Mag=1000X), and (d) 1625 SR NOREM 02, coupon 2B-1 (Mag=1000X). The NOREM 02 EPR coupons were machined from deposits made on Type 304 stainless steel.