

Spring 2019

Cataloging the Degree of Sensitization via Electrochemical Reactivation for Studying the Corrosion Behavior of Inconel 718, Austenitic, and Duplex Stainless Steels

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Abstract

Corrosion resistant materials can be expensive, but usually reduce the life cycle cost of metallic assets. However, negligent sensitization of these materials can lead to aggressive, intergranular corrosion. Using the methodology of the double loop electrochemical potentiokinetic reactivation (DL EPR), this project will investigate different steel reinforced bars and Inconel to determine the degree of sensitization after a heat treatment of 900°C for 2 hours. The purpose of this research is to validate and determine the appropriate test parameters for performing further DL-EPR test in the future. Additionally, the kinetics observed for each sample during the DL-EPR test will be analyzed and discussed. It was found that a DL-EPR solution of 0.5M H₂SO₄ and 0.01M KSCN was sufficient in facilitating the desired test behavior in Inconel 718, AISI 316, AISI 24100, SS 2205, and SS 2304 samples. SS 2205 displayed the lowest affinity for sensitization (0.18%) and Inconel 718 showed the highest (45.04%) according to the DL-EPR tests performed.

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Executive Summary

Problem Statement

Sensitization is a microstructural phenomenon that metals experience under specific heat regimes. Sensitization can drastically reduce the expected corrosion resistance of many alloys (primarily austenitic stainless steels), and therefore, it is important to discover methods to determine the degree of sensitization after an event or to select materials while considering affinity to sensitization as a factor. Double Loop electrochemical potentiokinetic reactivation (DL-EPR) is a method developed by Cihal to determine the degree of sensitization of stainless steels [16]. A desire to expand the application of DL-EPR to other alloys exists and limited success has been achieved by modifying the test parameters. It is the objective of this research to validate the DL-EPR test in the NCERCAMP laboratories at the University of Akron and to evaluate austenitic stainless steel samples as well as testing out parameters to evaluate duplex stainless steels and super alloys.

Summary of Results

After testing different solutions, 0.5M H₂SO₄ with 0.01M KSCN was determined to be the most applicable solution across all of the samples (Inconel 718, AISI 316, AISI 24100, SS 2205, and SS 2304). The laboratory set up was verified and produced results within what was expected. After a heat treatment was performed on all of the samples at 900°C for 2 hours; each of the samples was tested using DL-EPR. SS2205 was the least sensitized at 0.181%, followed by AISI 316 and AISI 24100 (1.527% and 2.602%) respectively. Both SS 2304 and Inconel 718 displayed large degrees of sensitization at 38.9% for SS 2304 and 45.035% for Inconel 718. The DL-EPR polarization plots yielded trends that agreed with the methodology presented in the DL-

EPR test; however, the Inconel sample displayed a more complex mechanism that is not fully understood.

Conclusions

Based on the results of this initial trial, both the molybdenum containing austenitic and duplex stainless steels showed the lowest affinity for sensitization. However the molybdenum containing Inconel 718 showed the highest degree of sensitization. None of these results were replicated and therefore the conclusions should be criticized.

Nevertheless, the trends observed from each of the DL-EPR polarization plots agreed with the selective reactivation mechanism proposed in the DL-EPR methodology. By adjusting the parameters (solution) of the DL-EPR, each of the alloys showed an active-passive transition on the upwards scan and gave evidence of a partial reactivation (presumably at the grain boundaries) when the scan was reversed. This affirms that the DL-EPR test is function in the University of Akron's laboratories.

Implications

The process of researching, developing, and evaluating the electrochemical mechanisms of the DL-EPR has produced many benefits. This test explores how kinetics can be explored by becoming critical of standard electrochemical techniques; furthermore, it proves how understanding the mechanisms and kinetics of a phenomena can be used with electrochemical techniques to provide meaningful and reproducible values that describe specific thresholds or relationships. More specifically, this research has increased the understanding of chromium depletion zones in regards to welding or other treatments and how this depletion affects the kinetics. It is a complex system where the kinetics of film formation is affected but also the quality of the film.

This research also led to many failures wherein a tested solution would not provide any sensible results according to the DL-EPR. Therefore, adjusting the test set up and determine the cause of failure was a routine process. This skill is common in research and is important to develop. Weekly meetings were also held to gain insight and new perspectives on issues affecting the process.

In terms of implications to society, optimize the DL-EPR technique could become a valuable corrosion management tool. DL-EPR is already among the fastest sensitization detection methods, and is non-destructive. Being an electrochemical technique also requires that the electrochemical process is understood and measured directly by the potentiostat. Therefore, by validating the procedure of the DL-EPR test in NCERCAMP and expanding its application to other alloys could provide additional information on remaining life time, updated life cycle costs, and better risk management when monitoring metallic structures that may be affected by sensitization.

Continual Progress

The conclusion of this research ended at a single trial of each sample at one heat treatment. From this point the samples should be treated at different temperatures and times to evaluate the response provided from the DL-EPR test. Furthermore, more work is planned to evaluate the effect of surface engineering of Inconel 718 on the affinity for sensitization [15]. Specifically, this DL-EPR test will be used to evaluate the effectiveness of the TMP and UNSM process suggested by Telang et al. [5,6].

1. Introduction

The most recent (March 2016) NACE Impact Report recited the 2013 estimated global cost of corrosion as 2.5 trillion US dollars [2, 3]. Nevertheless, those economic estimates do not incorporate the cost of safety incidents, environmental damage, reputational damage, nor the decreased financial efficiency of emergency re-construction. Furthermore, industry has found it not only ethical, but also economical, to address corrosion in the design process or as a continuous risk management system [4].

Beyond the potential financial benefits, corrosion resistant designing also works in conjunction with valuing life, health, and safety. Ignoring the decay of critical structural components (e.g. reinforcing bars) can endanger lives since the first external indication of an unsafe situation would be the critical failure of the design. This practice creates dangerous failures at the time of the incident, and it has the potential to impact the lives of people and industries (e.g. when a pipeline fails and forces families to relocate unexpectedly).

One potential mode of corrosion failure is an intergranular attack on metals thought to be corrosion resistant like Stainless Steels and high Nickel-Chromium-Iron Alloys (e.g. Inconel 718). These stainless steels and Inconel alloys are alloyed with protective elements, such as nickel and chromium, and are not expected to experience significant uniform corrosion. However, corrosion is not restricted to the mechanism of uniform corrosion. The mishandling of corrosion resistant materials may result in catastrophic failures via unexpected corrosion mechanisms, even in expensive material thought to be resistant to corrosion.

In particular, sensitization of these corrosion resistant alloys is the cause of unwanted intergranular corrosion. This is particularly problematic when the metal is susceptible to stress corrosion cracking (by means of the environment, metal, and tensile stress). A metal becomes

sensitized when the protective elements distributed in the grains form a product (typically in the more reactive grain boundaries). These products do not add corrosion resistance, but they do deplete the protective elements from grain boundary; this leaves the grain boundaries unprotected as well as forming a galvanic couple with the protected grain. The phenomenon of sensitization is not a quantizable characterization and therefore it is traditionally represented by a degree of sensitization (DOS). Nominal sensitization can be detected after heating an alloy (approximately 650°C) for a period of time and without further treatment; however, this depends on the alloy composition and microstructure [5]. Sources of sensitization could originate from improper heat treatment, welding, processing or unsuitable environmental conditions for the alloy, and therefore sensitization can drastically affect the integrity of metallic structures.

1.1 Cataloguing of Reinforcing Bars

When managing corrosion, it is desirable to assess the current condition and lifetime of metallic assets. In environments where sensitization can occur, it is valuable to determine how a heat anomaly has affected the substrate's microstructure and how the expected lifetime is affected. In these events, the critical factors affecting damage are the temperature, time at the elevated temperature, and the materials affinity towards sensitization. Therefore an alloy's affinity to sensitize could become a factor in the material selection phase of construction. Furthermore, finding methods to enhance the sensitization resistance of alloys would become preferable in applicable environments.

However, in order to characterize the current sensitization of alloys and their relative affinity for sensitization, standard tests are required to determine the degree of sensitization. Non-electrochemical tests have been performed to determine how sensitized a sample is; ASTM A262 details 3 standardized laboratory tests that can be used: (a) the Oxalic acid test, (b) the

Ferric Sulfate-Sulfuric acid test, (c) Nitric acid test (Huey), (d) Nitric-Hydrofluoric acid test, and (d) the Copper-Copper Sulfate-Sulfuric acid test (Strauss) [9, 10]. These tests have been helpful in relating data to Time-Temperature-Sensitization diagrams, from which threshold time-temperature data sets can be classified as whether or not intergranular corrosion is significant [10].

More recently, electrochemical techniques have been developed, proposed, and improved in an attempt to provide better, alternative testing methods for sensitization. Standard electrochemical techniques, such as potentiodynamic polarization, proved inadequate because while the sensitization had an effect on the current response, there is no baseline to compare the curve to for determining the degree of sensitization; furthermore, the mechanism of how sensitization affects the transition from cathodic, to active anodic, to passive, to transpassive during a potential sweep does not directly measure the sensitization. Therefore, the single loop and double loop electrochemical potentiokinetic reactivation tests (SL-EPR and DL-EPR respectively) were introduced. ASTM G108 defines a general EPR procedure that follows the SL-EPR methodology [1]. ISO 12732:2006 details a test based on Cihal's method that follows the DL-EPR methodology [11, 16]. These electrochemical tests explicitly target AISI type 304 and 304L steel and therefore the parameters are specified as such. ASTM G108 notes that other stainless steels and nickel based alloys have been used in the SL-EPR, but the test parameters had been modified [1]. It is within the scope of this project to explore the DL-EPR test and to modify the parameters accordingly to evaluate different stainless steel rebars. The University of Akron has been attempting to prepare and validate the DL-EPR test so that the labs in NCERCAMP will be equipped to perform DL-EPR in the future.

1.2 Baseline Evaluation of Inconel

Teleng et al. from the University of Cincinnati proposed two processing techniques that have shown preliminary success in reducing the propensity of sensitization. In particular an iterative thermal process of cold working and strain annealing can affect the microstructure to increase the frequency of low coincident site lattice boundaries, CSL, between the grains and thus disrupt the network to resist sensitization [5, 6, 15].

The primary objective of this research is to prepare and validate DL-EPR parameters for Inconel 718, AISI 316, AISI 24100, SS 2205 (duplex), and SS 2304 (duplex) – see Appendix A for more details. This task will provide NCERCAMP experience in electrochemical testing for sensitization

2. Background

DL-EPR is an electrochemical technique that uses a potentiodynamic scan to determine the degree of sensitization. To understand the mechanism that DL-EPR attempts to measure, it is beneficial to understand how potentiodynamic scans reveal information regarding electrochemical processes. Thus the interpretation of a Tafel polarization (potentio-dynamic polarization) will be described first.

In a Tafel polarization a metallic sample is polarized (the potential is held) at a negative potential in reference to the reference electrode. When performed properly for the sample (in relation to the open circuit potential) the test sample acts as a cathode. When held at this negative potential, the current required to pass is measured. The magnitude of this current is proportional to the rate of the corrosion reaction because the movement of electrons is a part of the half-cell reactions occurring. At this point the potential is slowly increased at a prescribed scan rate (this rate can build a capacitance so it must be slow). As the potential approaches the open circuit

potential (the potential at which the sample would freely corrode) the current required begins to drop. At the OCP, the sample becomes anodic and the current required begins to describe the anodic half reaction, and the current begins to increase with an increase in potential. Depending on the solution, as the potential continues to increase, the anode can exhibit many behaviors. The anode may remain active and show large increases in the current as the potential increases. The anode may also passivate by forming a species that inhibits the half-reaction, and therefore the current remains static as the potential is increased until a point (e.g. the passive layer is no longer stable due to breakdown and pitting). Lastly, the anode may display active-passive behavior where the anode actively corrodes (large increase in current as potential increases) until a potential where a passive species is stable such that the current will drop and become static as the potential rises.

The Tafel polarization is the first step in the DL-EPR. The goal for a successful DL-EPR trial is to observe the active-passive anodic behavior on increasing potentiodynamic scan. It is important that the sample in the DL-EPR test starts from its OCP in the solution (or below so that the cathodic half-reaction is observed) and then experiences active dissolution followed by passivation. When a sample is sensitized, the passivation during the upwards potentiodynamic scan is affected; namely in that the passivation current (the static current response when the material is passivated) may be higher in a sensitized sample because the grain boundaries cannot passivate due to the local depletion of chromium (from the Cr_{23}C_6 formation at the grain boundaries during sensitization).

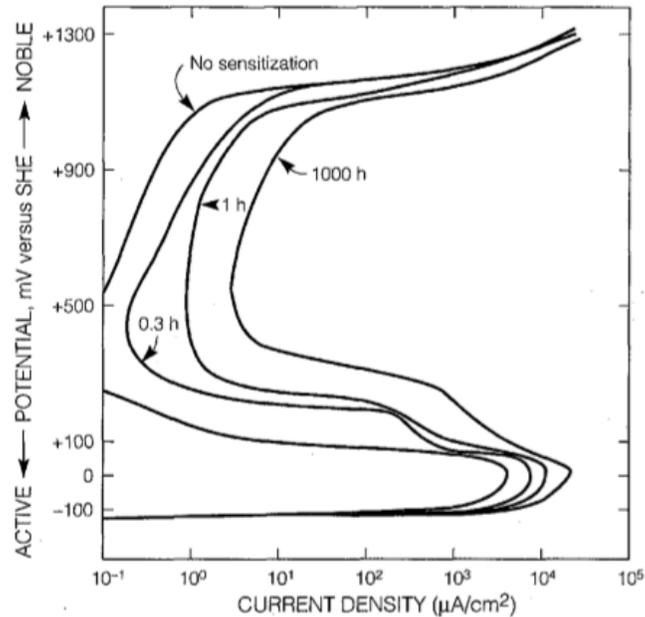


Figure 1. Denny Jones' schematic of the effect sensitization can have on the potentiodynamic polarization [12].

Figure 1 displays how the passivation current can be much lower for a non-sensitized sample when compared to a sample that was sensitized for 1000 hours at 900°C.

However, the EPR test does not quantify the degree of sensitization based on the rightward shift of the initial passivation region. Rather it evaluates the critical current density (i_{crit}), which is the maximum current between the active and passive regions of Figure 1. When the upwards potentiodynamic scan reaches the i_{crit} it is assumed that the entire sample is active and contributing to the current response, therefore this is viewed as the maximum current on the entire surface area when the sample is anodic between the active and passive behaviors. This is the important value that is recorded from the upwards scan of the DL-EPR.

The second part of the DL-EPR is a reverse scan where the potentiodynamic polarization is dropped from the passive region back down to the OCP. In the case of a sensitized sample, the passive film on the sample may not be continuous or as protective as a non-sensitized sample

(see Figure 1). Furthermore, the passive film that does film over grain boundaries will be considerably less protective due to the lack of available chromium and increased defects. Therefore, as the potential is dropped from the passive regions the grain boundaries are thought to re-activate (depassivate) before the bulk. This phenomena leads to a large current increase as the potential drops. Note that in this event only the sensitized grain boundaries are thought to be actively corroding, and therefore the active area is significantly smaller than the entire surface area of the sample. This causes the current peak on the reverse scan to be less than critical current of the forward scan; however, the peak on the reverse scan can correlate to the degree of sensitization. It is also worth mentioning that the passive layer on the grains (not grain boundaries) will eventually re-activate as the potential drops but the solution should be designed such that this complete reactivation occurs after the peak and near the OCP (slow kinetics for this process).

ASTM G108 and the Cihal's method suggest a solution of H_2SO_4 and KSCN. Similarly, Telang performed the initial DL-EPR tests in a solution of 0.01M H_2SO_4 and 20ppm KSCN solution [5, 6, 11]. Therefore, those were the base conditions that were considered. The H_2SO_4 is used to make the solution corrosive, and encourage the active-passive behavior desired. The sample needs to be active, passivate, and then reactivate; therefore, it is important that the sample experiences an active-passive shift with a definitive critical current. The KSCN acts as a depassivator in the solution by acting as a catalyst for metal dissolution [7]. This further promotes the kinetics of the reactivation of the chromium depleted zones so that the reactivation current peak is more identifiable [8]. The solution used should also always be deoxygenated. The presence of O_2 in the solutions would permit the oxygen evolution reaction to occur as opposed to the hydrogen evolution reaction. This stronger cathodic half reaction could disrupt the stability

of the polarization (keep the OCP from stabilizing) and support a more aggressive reaction. However, the deoxygenation should not prevent the formation of a passive oxide film when the polarization scans up from the active to passive region. The objective is to minimize or eliminate the supply of oxygen for the ORR cathodic reaction (on either the sample or counter electrode).

From the DL-EPR test, two current values are used in analysis: the critical current of the upward scan (called I_a) and the peak current of the reverse scan (I_r). I_a represent the current density of the activation loop (i.e. total possible anodic current) and I_r represents the current density of the reactivation loop (i.e. response from only the chromium depleted zones). Therefore the ratio of I_r to I_a is thought to represent the degree of sensitization (see Equation 1).

$$R = \frac{I_r}{I_a} \times 100 \quad (1)$$

This simple equation provides a percentage describing the relative sensitization of a material. DL-EPR does not require any modification regarding the grain size; however, some have attempted to modify the degree of sensitization to normalize the values. However, it was assumed that the chromium depleted zones were the grain boundaries and so it is necessary to perform optical microscopy on the samples after DL-EPR to note if chromium carbide is found inside of the grains. This is an important factor because it is a deviation from the underlying assumption in this test.

DL-EPR has proven to be a reproducible test that works best at low to moderate levels of sensitization (above 0.1%), in which it can detect the preferential reactivation of depleted zones due to the KSCN activator [18]. Therefore, this is an ideal test to non-destructively test a material that may have become sensitized to a small degree.

The selection of test samples was chosen to reflect attention to materials commonly used and to explore the possible range of samples that the test applies to if the parameters are adjusted

accordingly. AISI 316 stainless steel is an austenitic stainless steel that is similar to 304, which the tests were designed for. AISI 316 also has molybdenum alloyed into it for pitting resistance. AISI 24100 is also an austenitic stainless steel; however, it is alloyed with 11-14% manganese and low carbon. Both of these are austenitic stainless steels and therefore are known to be susceptible to IGC; therefore, they are excellent samples to test with DL-EPR. Stainless Steels 2205 and 2304 are both duplex stainless steels and therefore have nearly equal amounts of austenite and ferrite. Both duplex steels have about 4-6 % nickel (SS 2205 has 5-6% and SS has 4%) as an austenite stabilizer and SS 2205 also has about 3% molybdenum (See Appendix B). The presence of both ferrite and austenite increases the yield strength of the material, but also introduces the possibility of galvanic corrosion and IGC. Inconel 718 is a super alloy of 50-55% nickel, 17-21% chromium, about 5% niobium, about 3% molybdenum, and the balance is mostly iron. Inconel 718 is considered a very corrosion resistant alloy based on the amount of chromium and other protective alloys present. Therefore, it is important to identify if and how Inconel could become sensitized and to what degree.

3. Experimental Methods

The DL-EPR test solution used by Telang was used as the starting point since one of the research objectives was to validate the test described. Therefore, 1 liter of solution was measured out consisting of 0.01M H₂SO₄ and 20ppm of KSCN. The solution was stirred well and then set aside. Each of the samples was polished up to 800 grit at 100 rpm and then polished at 1200 grit at a lower rotation. The polishing paper was not shared between the austenitic samples, the duplex samples, not the super alloys. The samples were then rinsed with deionized water and ethanol, dried, and then stored in a desiccator.

The glassware setup was designed to deaerate the solution and transfer it to the test cell without reintroducing air. Therefore, an inlet of nitrogen was sealed to a gas trap. The gas trap was sealed to pipe that lead to the bottom of a sealed, conical flask full of solution (bubbling nitrogen). A second rigid tube was sealed from the top of the conical flask that transferred the bubbling nitrogen into a 3 cell green-flask. The green flask was sealed and was already set up with an SCE reference electrode, graphite counter electrode, sample electrode, and an outlet tube that led to a gas trap. See Figure 2 below to see a picture of this set up.



Figure 2. The DL-EPR glassware set-up.

The nitrogen was aggressively bubbled in the left (see Figure 2) conical flask for at least one hour to deaerate the $\text{H}_2\text{SO}_4/\text{KSCN}$ solution. The vertical tube was then pushed down into the bottom of the solution. This caused the bubbling nitrogen to build pressure in the top of the conical flask and cause the solution to flow to the green-flask. Once all of the solution transferred to the green-flask and the electrodes were connected to the Gamry potentiostat, then

an OCP test was run. If the OCP was too high or unstable, the sample was held potentiostatically at -1.0 volt vs SCE. Then the OCP was run again for 2 minutes to verify stability. The Gamry was then programmed with a sequence to scan from -0.6 V vs SCE to 0.3 V vs SCE at a scan rate of 1.67 mV/s. Then held at 0.3 V vs SCE for 2 minutes to ensure that the passive film was stable. The potential was then dropped from 0.3 V vs SCE to -0.6 V vs SCE at 1.67 mV/s. After the scan was completed the sample was removed and looked at under the microscope up to $100\times$. The solution was disposed of and the glassware was cleaned between each trial.

In total each test took about 2 hour to complete. The samples were prepared as sample electrodes by using black electrical tape with a 1cm^2 cutout and attaching sealing the sample with the tape and a connecting wire attached to the back of the sample. Hot glue was then used to cover edges or any other part that could have permitted solution to reach the coupon.

The samples were sensitized by means of furnaces located at the University of Akron. The first batch of samples was heated to 650 °C for 1 hour. The second batch was heated to 900 °C for 2 hours. The samples were polished on the side that was open to the atmosphere in the furnace (i.e. not face down).

Further along, the solution was modified to a more aggressive 0.05M H_2SO_4 and 0.01M KSCN solution. This was in response to previous results showing no reactivation or purely passive behavior. A more concentrated solution of both species was tested later but the results did not represent the expected mechanisms of DL-EPR.

To compute the resulting degree of sensitization, plots of each DL-EPR were computed in Origin software and then the I_a and I_r were determined. For the trials that were in agreement with the expected mechanism and trials that promote discussion, the degree of sensitization was determined.

4. Data and Results

The DL-EPR test that showed the most consistent results was the 0.5M H₂SO₄ and 0.01M KSCN solution [17]. This solution is significantly more concentrated than the original 0.01M H₂SO₄ and 20ppm of KSCN suggested by Telang and ASTM G108. Nevertheless, across austenitic steels, duplex steels, and super alloys this solution provided the expected mechanism for most of the trials. DL-EPR was originally designed to evaluate an austenitic stainless steel and therefore AISI 316 and AISI 24100 will be presented first.

AISI 316 is a standard stainless steel with molybdenum alloyed in. The sample was treated at 900°C for 2 hours. For this heat treatment, a significant degree of sensitization can be expected. Figure 3 displays the result from the DL-EPR scan from -0.6 V vs SCE to 0.3 V vs SCE and then back down at a scan rate of 1.67 mV/s.

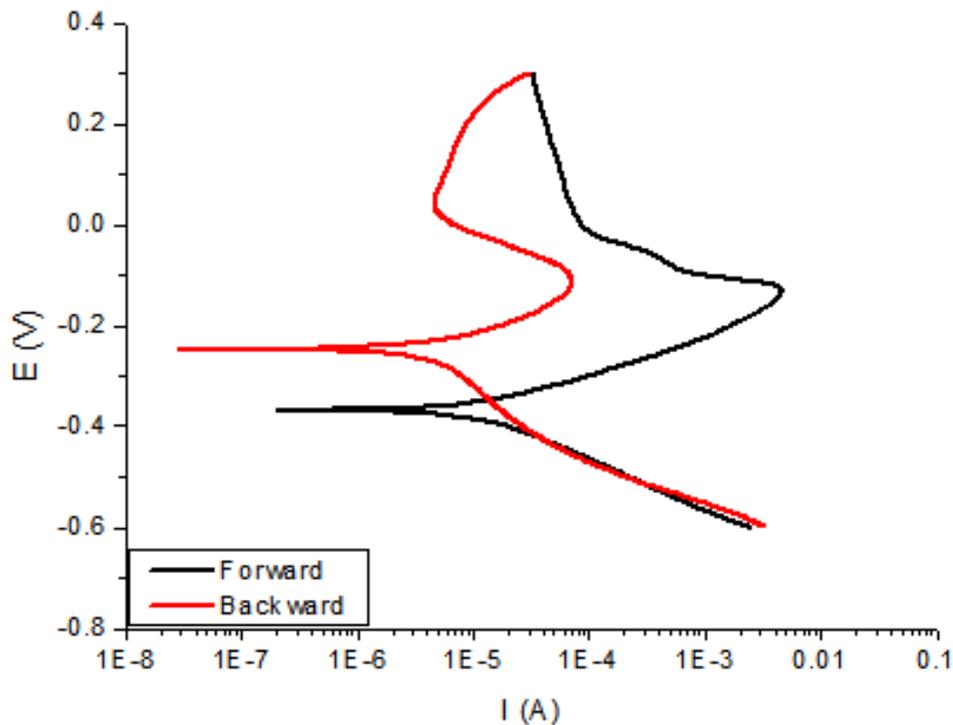


Figure 3. DL-EPR of AISI 316 treated at 900°C for 2 hours. Note: the surface area of the sample was 1cm² and so the current can be converted to current density in the units of A/cm².

Figure 3 is the expected shape for DL-EPR since the Ir is smaller than Ia and the potential at Ir seems to be above the potential associated with Ia; however they are close. After the AISI 316 sample finished the DL-EPR, the sample was taken to the microscope and was imaged to determine if there was any visible chromium carbide. Unfortunately the sample was not polished well enough to provide a clear indication as to the location of the carbides in figure 4 below.

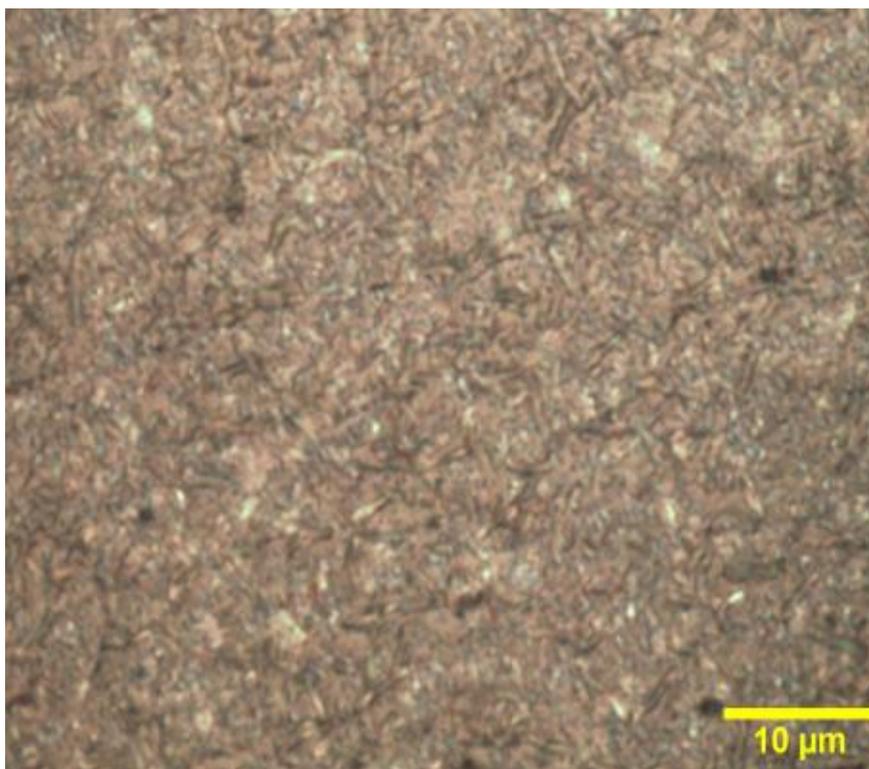


Figure 4. The microstructure of AISI 316 at 100X after the DL-EPR etching.

The other austenitic sample tested was AISI 24100 which contains a significant amount of Manganese. The sample was treated at 900°C for 2 hours. For this heat treatment, a significant degree of sensitization can be expected due to its relation to other austenitic steels. Figure 5 displays the result from the DL-EPR scan from -0.6 V vs SCE to 0.3 V vs SCE and then back down at a scan rate of 1.67 mV/s.

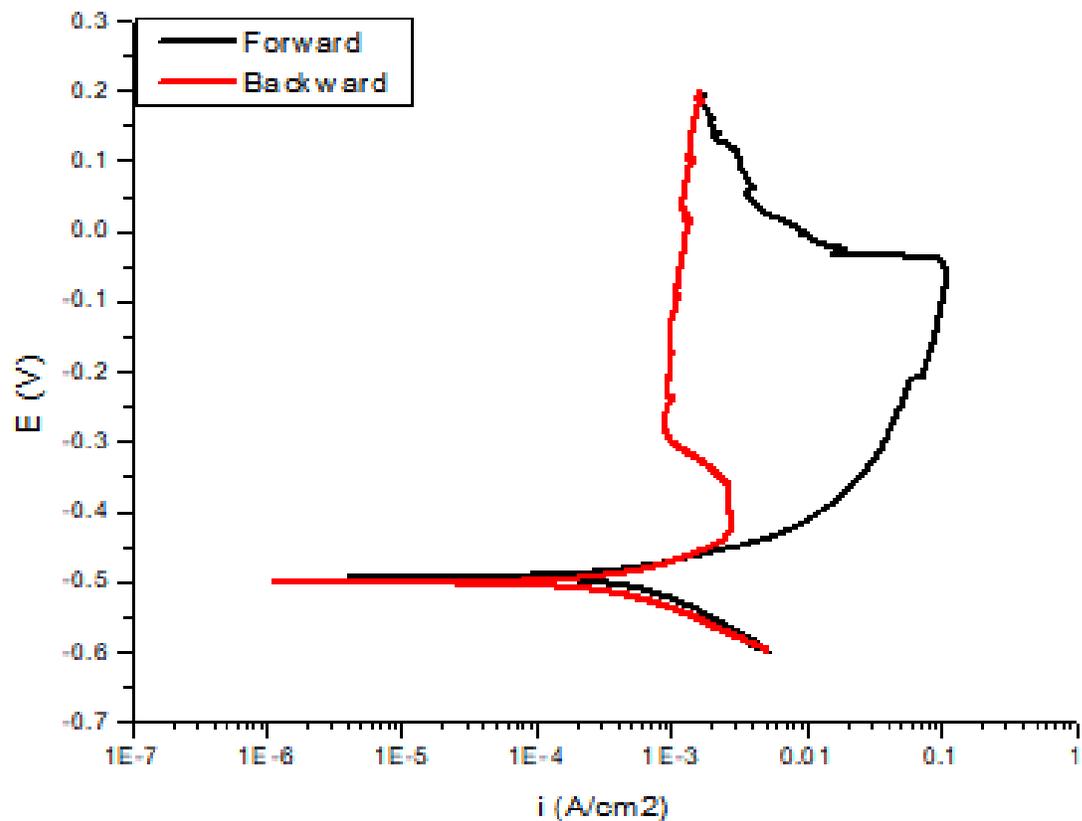


Figure 5. DL-EPR of AISI 24100 treated at 900°C for 2 hours.

The DL-EPR polarization for austenitic AISI 24100 shows identifiable values for I_a and I_r by means of current density peaks on each loop. It does appear that the kinetics of the reactivation were slower than in the AISI 316 sample because the reactivation occurred at a very low potential that was nearly at the OCP. The AISI 24100 sample was also evaluated under optical microscopy and the results are shown in Figure 6.

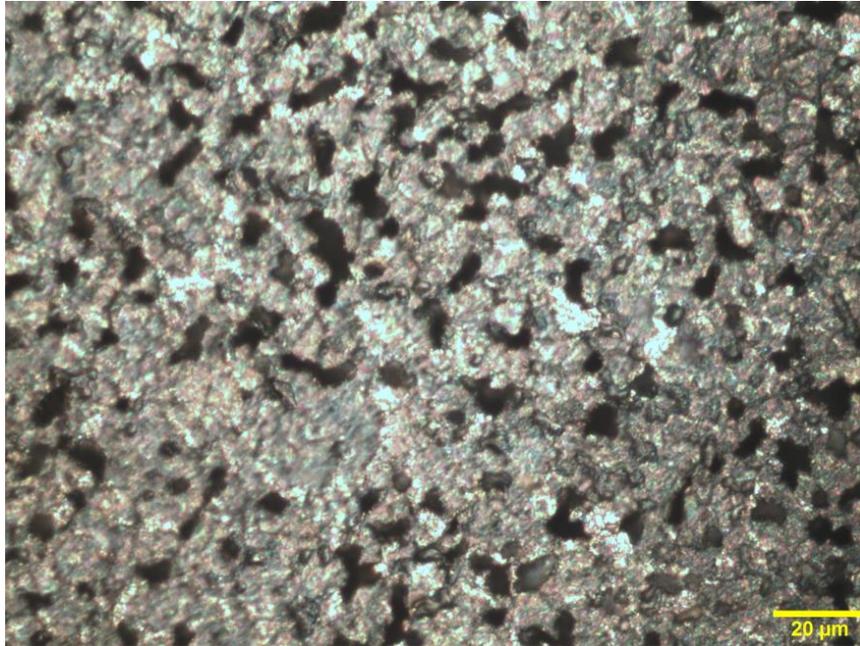


Figure 6. The microstructure of AISI 24100 at 50X after the DL-EPR etching.

The dark spots in Figure 6 are not darkly colored grains, rather they are continuous channels that formed along the surface. This was found to be very aggressive etching from the DL-EPR test which is intended to be non-destructive. It is not known if the channels are chromium depleted areas that were preferentially attacked or if there is another mechanism causing this phenomena. Nevertheless, optical microscopy was unable to identify carbides due to the rough surface and the deep etching that occurred.

The duplex stainless steel samples tested were SS 2205 and SS 2304. SS 2205 is the most widely used duplex stainless steel with molybdenum. The sample was treated at 900°C for 2 hours. For this heat treatment, sensitization would be expected despite the presence of Molybdenum. Figure 7 displays the result from the DL-EPR scan from -0.6 V vs SCE to 0.3 V vs SCE and then back down at a scan rate of 1.67 mV/s.

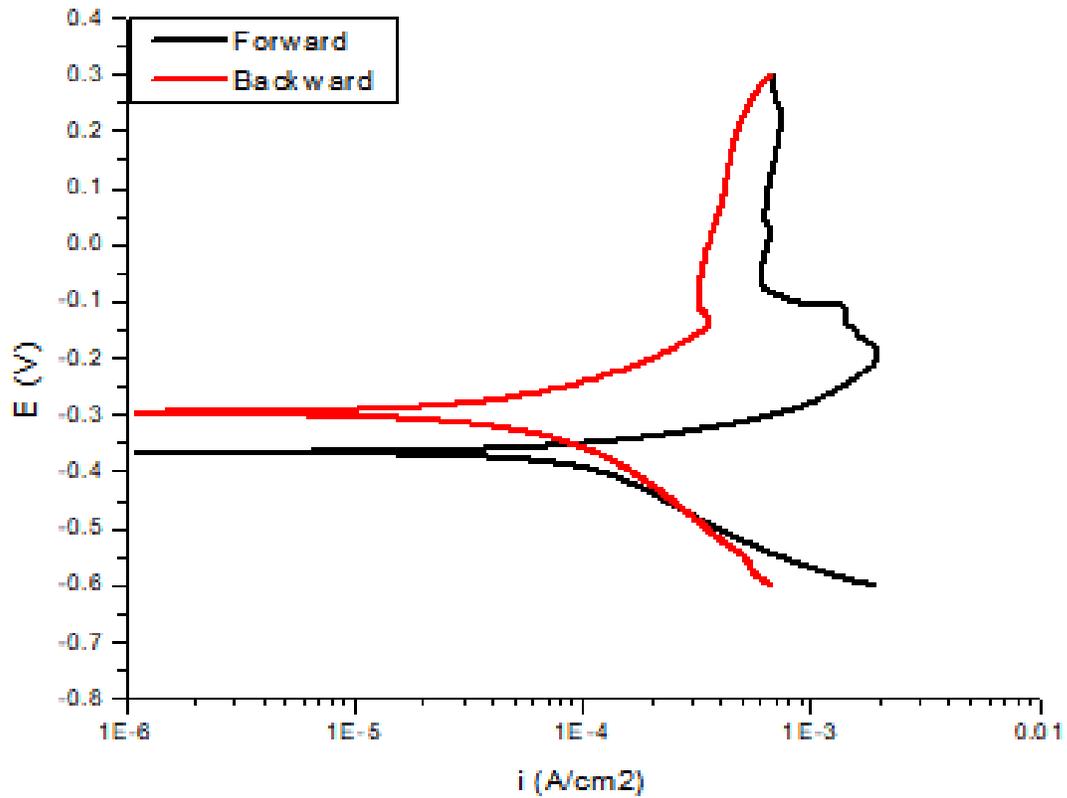


Figure 7. DL-EPR of SS 2205 (duplex) treated at 900°C for 2 hours.

The DL-EPR for the duplex SS 2205 shows a small reactivation loop. Out of all of the samples tested, SS 2205 seems to have the smallest relative reactivation current density compared to the activation loop. The SS 2205 sample was viewed at 100x. The result is shown below in Figure 8.

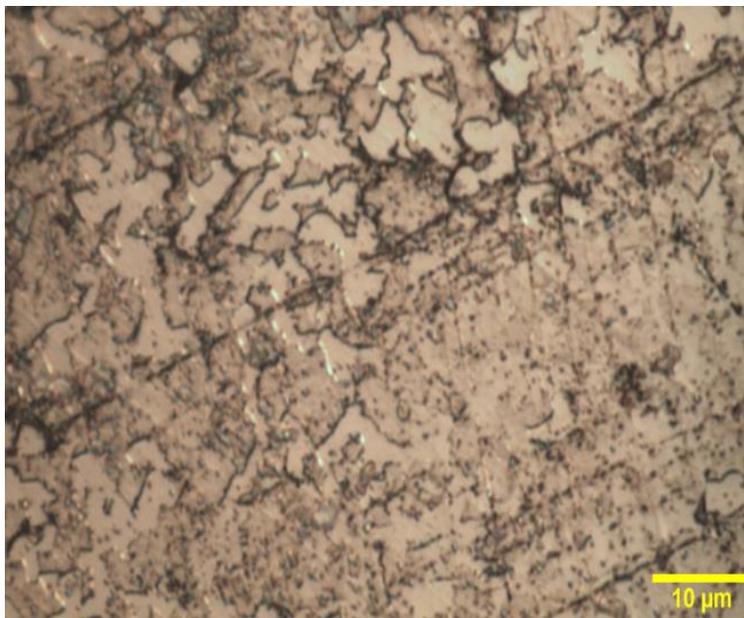


Figure 8. The microstructure of SS 2205 (duplex) at 100X after the DL-EPR etching.

The microstructure of SS 2205 in Figure 8 shows clear dark grains (ferrite) or boundaries. The grains themselves cannot be identified in the image due to the poor etching (from the DL-EPR). However, does seem as though the grain boundaries and some particles in between have been attacked, which is consistent with intergranular corrosion.

The other duplex sample, SS 2304, displayed a similar morphology of corrosion; however, the DL-EPR results were not. The sample was treated at 900°C for 2 hours. For this heat treatment, a significant degree of sensitization can be expected due to its relation to other austenitic steels. Figure 9 displays the result from the DL-EPR scan from -0.6 V vs SCE to 0.3 V vs SCE and then back down at a scan rate of 1.67 mV/s.

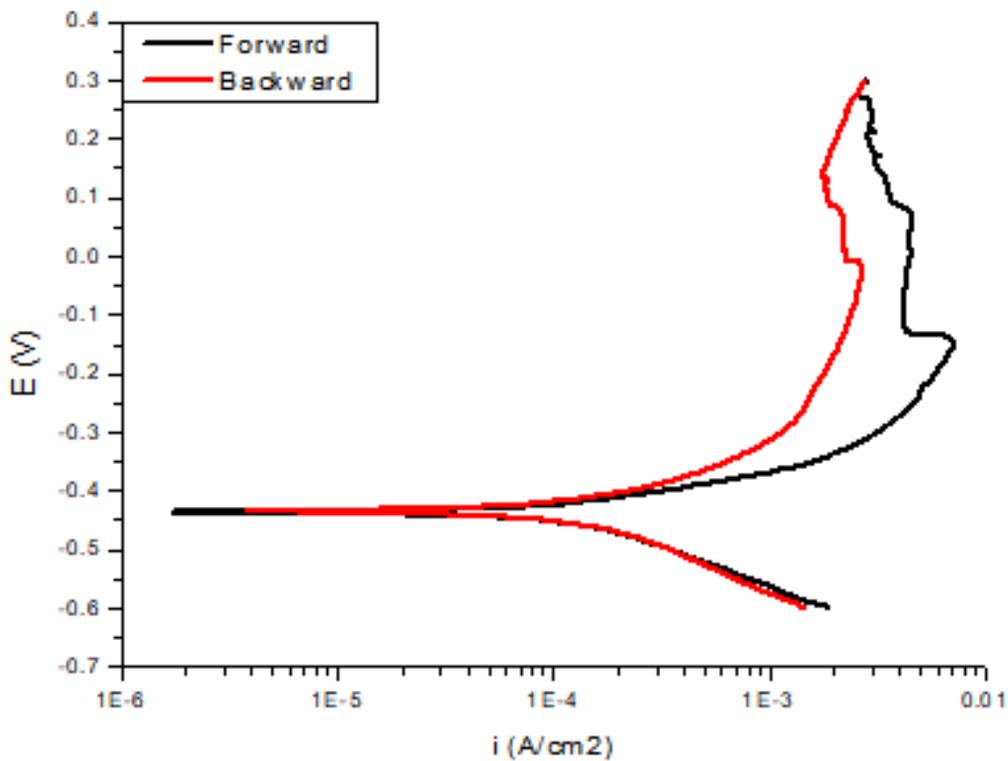


Figure 9. DL-EPR of SS 2304 (duplex) treated at 900°C for 2 hours.

Duplex SS 2304 is similar to SS2205 except that it does not have molybdenum. The shape of the DL-EPR plot looks similar to Figure 7; however, the actual calculation of the degree of sensitization is much higher. The reactivation loop does not resemble a single consistent mechanism because it seems irregular; almost as though some sort of meta-stable formation/dissolution was occurring. However, as stated earlier the microstructure of SS2205 in figure 8 does resemble the microstructure of SS2304 provided in Figure 10.

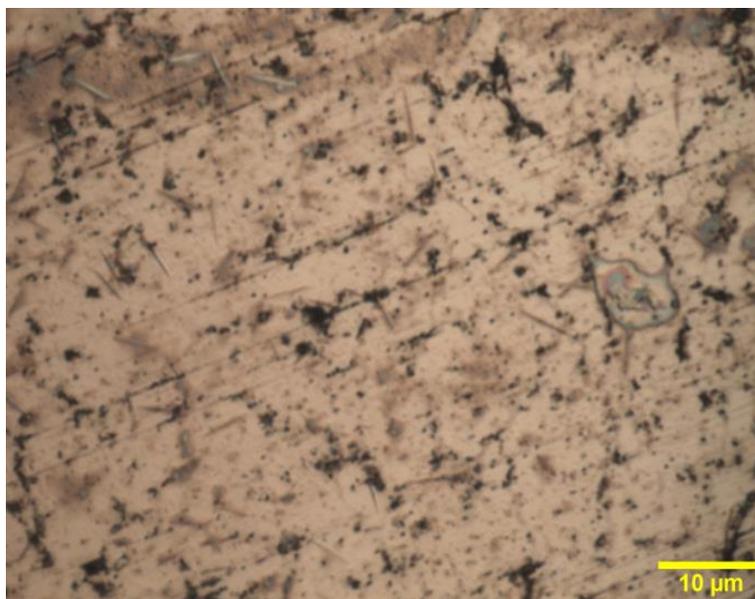


Figure 10. The microstructure of SS 2304 (duplex) at 100X after the DL-EPR etching.

The microstructure of SS 2304 in Figure 10 shows clear dark grains (ferrite) or boundaries like the other duplex sample [20]. The grains themselves cannot be identified in the image due to the poor etching (from the DL-EPR). However, does seem as though the grain boundaries and some particles in between have been attacked, which is consistent with intergranular corrosion.

The super alloy, Inconel 718, deviated from the previous sample in the DL-EPR and displayed a different behavior and possibly a more complicated mechanism. The sample was treated at 900°C for 2 hours. For this heat treatment, a significant degree of sensitization can be expected due to its relation to other austenitic steels. Figure 11 displays the result from the DL-EPR scan from -0.6 V vs SCE to 0.3 V vs SCE and then back down at a scan rate of 1.67 mV/s.

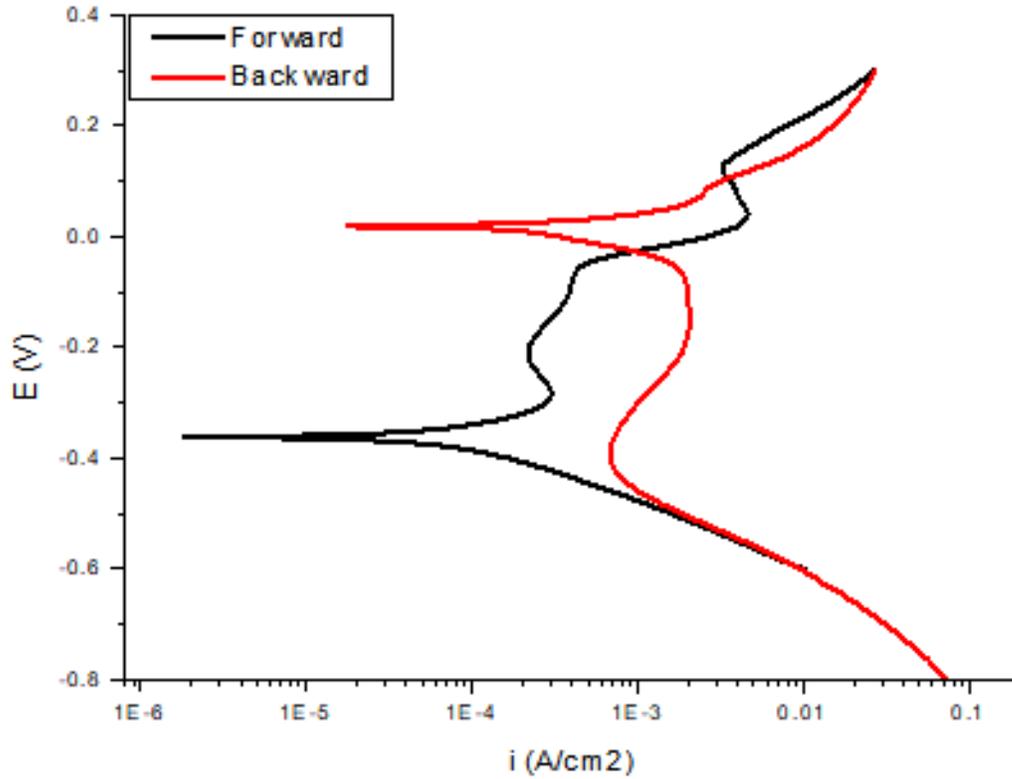


Figure 11. DL-EPR of SS 2304 (duplex) treated at 900°C for 2 hours.

The forward scan of the DL-EPR shows a concerning trend of active-passive-active-passive transitions. This should not be expected if chromium is the only film forming oxide and only the hydrogen evolution reaction is occurring cathodically. This trend makes it difficult to determine an I_a value because there is no clear activation loop. The reactivation scan also doesn't look like any of the other reactivation loops; however, Momeni suggests a possible mechanism that matches this trend. This be further explored later in the discussion section [13].

Compiling all of the I_a and I_r values from Figures 3,5,7,9, and 11; the DOS value can be determined by using Equation 1. All of the results are reported in Table 1.

Table 1. Compiled results of the DL-EPR from Figures 3, 5, 7, 9, and 11.

Catalogue of Results from DL-EPR tests		
Category	Material	DOS (R%)
Austenitic Stainless Steel	AISI 316	1.53%
	AISI 24100	2.60%
Duplex Stainless Steel	SS 2205	0.18%
	SS 2304	38.90%
Super Alloy	Inconel 718	45.04%

Briefly looking at Table 1, the duplex stainless steel SS 2205 seemed to have the lowest affinity for sensitization, although anything above 0.1% indicate the start of sensitization. However, the duplex stainless steel SS 2304 was nearly the worst. Both austenitic stainless steels displayed damaging sensitization. Inconel displayed the worst sensitization.

5. Discussion and Analysis

Referring back to figures 3,5,7,9, and 11; the DL-EPR process can be visualized for a solution of 0.5M H₂SO₄ and 0.01M KSCN. The original solution recommended (0.01M H₂SO₄ and 20ppm of KSCN) did not guarantee active-passive polarization behavior and some metals did not reactivate in this solution [17]. Therefore, the concentration of both species was increased to adapt the DL-EPR to work for austenitic steels, duplex steels, and a super alloy [20]. The OCP of each of these species in the solution was different and that consideration must be taken when determining the solution concentration because it will always be necessary to polarize high enough to reach passivity; if the test ends too soon the active-passive shift will be missed.

The AISI 316 sample showed the expected DL-EPR trend in figure 3. The only unexpected deviation was the decreasing current at the beginning of the reverse scan. At the start of the reverse scan the passive layer should be continuous and protective. Figure 3 suggests that the passive layer may have continued to grow as the reactivation loop began. This is not ideal

and could potentially be avoided by holding the potential at 0.3 V vs SCE for a longer amount of time between the scans. The degree of sensitization determined for AISI 316 was 1.5%. This value is reasonable for an austenitic stainless steel sensitized at 900°C for 2 hours. The microstructure of the AISI 316 is not clearly identifiable due to the severe etching and imperfect polishing.

The AISI 24100 sample is another austenitic stainless steel that has manganese alloyed into it. With the same heat treatment as the AISI 316 sample, AISI 24100 seemed to sensitize to a further degree by reaching 2.6%. The major difference between the two is the presence of Manganese and so it may be beneficial to investigate the role that Manganese has on the chromium depleted zones and diffusion through the microstructure. The optical images of the AISI 24100 sample showed extensive etching by means of tunneling. It is possible that these regions of accelerated corrosion are due to chromium depletion or galvanic corrosion between the grains. However, the image was not polished enough to identify any chromium carbides to confirm this process. Concerning the DL-EPR scan for the AISI 24100 sample, the behavior seemed reasonable as the critical current and the peak reactivation current can be identified from the plot; however, the micrographic image suggests that the process reflected in the DL-EPR may not be solely due to the preferential reactivation of the chromium depleted zones.

The duplex stainless steels were the first expanded application for the DL-EPR testing method. The DL-EPR polarization curves produced are not as ideal as the austenitic stainless steel samples because the presence of another grain (ferrite) drastically affects the microstructure of the material and therefore, impacts the corrosion and corrosion mechanism.

Duplex SS 2205 displayed a kinetic behavior of identifiable passivation on the active loop and an ambiguous reactivation loop. It is clear that there is a reactivation loop; however, it

is not well defined. The current during passivity was similar between the forward and backwards scan which indicates that the passive layer was completed and did not require more time to develop. The DOS was determined to be 0.18% for SS 2205. This value is very low and implies that SS 2205 has a low affinity to sensitization. Any value above 0.1% is thought to show the initiation of sensitization so SS 2205 is not immune to the heat treatment but it showed significant resistance in this trial. From the microstructural images of SS 2205 the ferrite can be identified dispersed along with the austenite. Unfortunately neither the magnification nor the polishing were conducive to identifying and chromium carbide. Duplex SS 2205 has molybdenum added into the structure of the ferrite and austenite. Duplex SS 2304 does not have molybdenum and displayed significantly worse resistance to sensitization.

The DL-EPR test for the duplex SS 2304 sample was not as ideal as that of SS 2205. The activation loop showed a brief region of activity followed by passivity; however the active region is small and unstable (i.e. the curve has a large roughness). Furthermore, the reactivation loop was just as unstable and could resemble simply passive behavior. There is a small reactivation loop around 0 V vs SCE on the reactivation scan. This reactivation loop is also identified in the correct spot compared to the activation peak because it occurs at a slightly higher potential, suggesting that the peak is occurring when part of the passive layer is still intact (assumed the grain's passive layer is still intact). The SS 2304 was cathodically polarized at the end of the test (per DL-EPR) and so no optical confirmation could be given to verify the presence of the passive layer on the grains during the reactivation peak. Since these peaks are reasonably located, the analysis was performed using equation one and the DOS was determined to be 38.9%. This value is large because the activation and reactivation are similar, and assuming that the reactivation loop is only due to the chromium deplete regions, it can be implied that the chromium depleted

region is large. Unfortunately DL-EPR is not as effective in determining the DOS for large sensitization degrees. Therefore, speculation should be placed on the 38.9% value. Further tests could be performed to explore the reproducibility of the DOS; nevertheless, it can be seen that the DOS is high for SS 2304.

Inconel 718 is a super alloy that is known to be corrosion resistant [19]. The DL-EPR scan for Inconel was mechanically the most deviant from the rest of the samples. The upwards scan was characterized by two distinct active-passive transitions; one near -0.3 V vs SCE and a second above 0 V vs SCE. The downward scan showed an anodic/cathodic switch near 0 V vs SCE and then displayed a loop before switching to a cathodic region again. The forward scan suggests the formation of two distinct protective mechanisms; therefore it is difficult to identify the current associated with the maximum, entire surface area dissolving.

The reactivation scan was unlike the other samples. In literature, Momeni has shown the presence of several corrosion potentials. Momeni has shown that these regions appear in SS304 treated at 650 °C for 1 hour in a solution of 0.5 M H_2SO_4 and 0.01 M KSCN [13]. This is the same solution used in these tests. Momeni suggested that during the reverse scan the “cathodic reaction crosses the anodic branch at three points”. These three points are identified for a passive state, a transition state, and an active state [13]. In figure 11, two corrosion potentials are seen. One appears to be between the two passive regions of the upward scan and the other occurs near the OCP. Therefore the two branches might be considered a transition and active branches according to Momeni. It is worth noting that each of the loops present in the re-activation scan contribute to the charge passed; therefore, the I_r should be summed to encompass the total effect of the chromium depletion. This would be better accounted for if the degree of sensitization was determined via the charge passed (area of each loop) as in SL-EPR. However, this method was

not used. Roelandst also tested Inconel in the DL-EPR and noted that pitting can occur and skew the results of the DL-EPR [19]. Therefore, it may be that each peak corresponds to pitting phenomena; hence Roelandst recommends that DL-EPR works best for Inconel when the pitting is well prevented.

According to the DL-EPR, the Inconel sample had a DOS of 45.0%. This is the highest result out of all the samples even though Inconel is regarded to be a corrosion resistant alloy. Sato performed a study on the sensitization of Inconel due to welding [14]. From the DL-EPR of a brief welding event, the DOS was determined for the base material, gray zone, black zone, and the thermos-mechanically affected zone. The DOS ranged from 14.2% in the grey zone to 21.1% in the heat affected zone [14]. These values are smaller than the 45.0% value in this study because the heat treatment in this study was more severe and the solution was adjusted. Nevertheless, both tests agree that Inconel is sensitive to sensitization. DL-EPR is not precise at higher DOS and therefore both tests simply imply that sensitization has affected the structure of the material.

A potential issue with Inconel is that the OCP is difficult to achieve a stable value. The Inconel had to be cathodically polarized to achieve a stable OCP before running the electrochemical tests. It is possible that a disruption occurred during the DL-EPR that effected the response in Figure 11. Oxygen contamination would have a significant impact on the test that could shift the OCP.

6. Conclusions

The main objective of this research was to initiate the understanding and capability for NCERCAMP to perform DL-EPR tests. The laboratory set-up has been established and verified to function properly. The solution of 0.5M H₂SO₄ and 0.01M KSCN was found to be adequate in

allowing a range of samples to display active-passive behavior on potential scans as well as sufficiently attacking the passive layer at the grain boundaries during the reverse scan from passivity.

A range of metals were evaluated from austenitic stainless steels to duplex stainless steel to a super alloy. The austenitic stainless steels performed the most resistant overall to sensitization in this trial. However, the duplex SS 2205 alloy containing molybdenum performed the best overall. Both the duplex SS 2304 and the super alloy 718 performed poorly with high values of sensitization. However, high DOS determinations become less accurate and therefore less confidence is placed in the magnitude of the DOS.

The high DOS value of Inconel in these parameters can be a good baseline for further testing if grain boundary engineering is found to drastically reduce Inconels affinity for sensitization because there sufficient room to see a reduction in the DOS with these parameters.

7. Recommendations

Continued work is planned at NCERCAMP to continue running and optimizing the DL-EPR test. The procedure concerning the glass-ware proved effective. The solution can be further optimized to active better precision in the I_a and I_r loop values by enhancing the active-passive transitions via solution composition. Ideally, the same materials should be tested with different heating treatments to validate the increase of DOS based on increased temperature or time of the treatments. This would further expand the catalogue of expected DOS values given different heating regimes and even surface engineered processes (e.g TMP and UNSM).

Potential sources of error have been identified from the experimental process. Figure 11 shows erratic current responses. This could be partially explained by the mechanism that Momeni proposed, but it is possible that O_2 was able to enter the cell. Furthermore, the stability

of the Inconels OCP could be improved to provide better results. The restriction of the surface area on the test samples was also done with tape. Some sample experience poor adhesion of the tape and therefore the test had to be rerun or modified to account for the increased area. Other methods of cell construction should be explored to prevent this issue. Lastly, to obtain a stable OCP, some samples were polarized cathodically at first; this led to hydrogen evolution to occur on the sample, thus producing bubbles. In some tests, the hydrogen bubbles remained on the sample for the entire polarization. This is a clear error that should be avoided because this reduces the surface area, changes the solution concentration near the surface, and possible other effects.

Optimizing the DL-EPR test is an effective way to quickly test a structure to determine the damage to sensitization in a non-destructive way (like ASTM A262). The capability to perform this test quickly opens opportunities to improve corrosion monitoring programs as well as assess the expected lifetime of structures after a heating event. Additionally DL-EPR can be used to classify materials to aid in the material selection phase if a material is likely to experience a heating event.

Utilizing the DL-EPR test improved the capacity and scope of what a corrosion engineer can monitor by providing a tool to quickly and accurately detect sensitization. This promotes the accountability and accuracy of the corrosion engineering process and allows for the safety, reputation, and capital to be preserved and protected.

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10. Appendix

10.1 Appendix – A

Composition of the Alloys analyzed

Identification		Composition (by wt%)													
Type	Material	Fe	Cr	Ni	Mo	Mn	Si	N	C	P	Cu	Co	Al	Ti	Cb/Ta
Austenitic	AISI 316	bal	16.5-18.5	8-13	2-2.25	2	1	0.11	0.1	0.04					
	AISI 24100	bal	16.5-19.5	0.5-2.5		11-14		0.2-0.45							
Duplex	SS 2205	bal	22	5-6	3	2	1	0.1-0.2	0.03	0.03					
	SS 2304	bal	23	4	0.20			0.1	0.02		0.3				
Super Alloy	Inconel 718	bal	17-21	50-55	2.8-3.3	0.35	0.35		0.08	0.015	0.15	1	0.35-0.8	0.65-1.15	4.75-5.5

10.2 Appendix – B

Solutions tested

Solutions	Test Volumes	H ₂ SO ₄	KSCN	Note
1	1 L	0.01 M	20 ppm	Suggested by previous trials [5,6]
2	1 L	0.5 M	0.01 M	Used in this Report