

In-situ determination of the degree of sensitization in austenitic stainless steels by DL-EPR

Pablo M. Altamirano
INTI, Instituto Sabato (UNSAM/CNEA)
Av. Gral. Paz 5445
San Martín, Buenos Aires, B1650WAB
Argentina

Mariano A. Kappes
CNEA, CONICET, Instituto Sabato
(UNSAM/CNEA)
Av. Gral Paz 1449
Villa Maipú, Buenos Aires, B1650LWP
Argentina

Martín A. Rodríguez
CNEA, CONICET, Instituto Sabato (UNSAM/CNEA)
Av. Gral Paz 1449
Villa Maipú, Buenos Aires, B1650LWP
Argentina

ABSTRACT

The present study reports an ongoing research to use a standardized electrochemical test for determining the degree of sensitization (DOS) of austenitic stainless steel components and equipment non-destructively in the field. DOS is understood as the higher rate of dissolution at the grain boundary region vs. the bulk grain, which is related to a chromium-depleted zone near the grain boundary. The double loop electrochemical potentiokinetic reactivation method (DL-EPR) was taken as a reference. Tests were performed in austenitic stainless steel type AISI 304 (UNS S30400). The main parameter calculated from the electrochemical test is I_r/I_a , the ratio of peak current during reactivation (backwards) and activation (forward) scans. It is assumed that DOS increases with I_r/I_a . However, cold work and inclusion content could affect the test results, hence potentially acting as false positives. These variables were included in the experimental matrix. Thermal aging time at 677 °C, amount of cold work and inclusion content were varied to understand their effect on electrochemical response. The solution used for the tests contains sulfuric acid and thiocyanate ion, and common practice is to freshly prepare it just before the test. Measurements are usually performed under deaerated conditions. However, field deployment of the technique could be facilitated if naturally aerated solutions prepared in advance in a laboratory can be used. Hence, the influence of oxygen content in solution and the effect of solution aging on measured I_r/I_a was studied. A simple electrochemical cell was developed for field measurements, based on commercial falcon tubes and 3D-printed plastics parts.

Key words: Stainless steels, sensitization, corrosion tests, intergranular stress corrosion cracking

INTRODUCTION

Austenitic stainless steels are widely used in refineries and petrochemical industries due to their good combination of properties such as workability, mechanical strength and corrosion resistance [1]. However, one of the most important problems they show, and which can lead to failures in service, is the susceptibility to intergranular corrosion and intergranular stress corrosion cracking (IGSCC) [2]. When these materials are subjected to temperatures in the range from 500 °C to 800 °C, the precipitation of chromium-rich carbides occurs preferentially at grain boundaries (GB) [1]. In practice, the undesired exposure to this temperature range can happen due to excursions in process variables or during welding. The precipitation of carbides at GB causes chromium-depleted zones in areas adjacent to GB. When Cr concentration falls below 12%, the formation of an adequate passivating layer is impeded and corrosion resistance decreases [1]. This phenomenon is known as sensitization.

A sensitized microstructure has lower resistance to chloride stress corrosion cracking [1] and can experience IGSCC in high temperature water, polythionic acids [3] and fluoride solutions [4]. There are different tests to evaluate the sensitization of austenitic stainless steels, among them, the practices established in the ASTM A 262 standard and the electrochemical tests called electrochemical potentiokinetic reactivation (EPR), in the single-loop (SL-EPR) and double-loop (DL-EPR) variants. All these methods have been widely used for the characterization of austenitic stainless steel sensitization [5-8]. Despite the SL-EPR and DL-EPR methods were developed for non-destructive field measurements [5,9], in most cases they are performed in a laboratory on small samples. The aim of this work is to develop a method for determining the degree of sensitization (DOS) of austenitic stainless steels non-destructively in the field, based on the DL-EPR test. DOS is defined as the extent of chromium depletion along the grain boundaries due to $M_{23}C_6$ carbide precipitation [2]. DOS is controlled by the proportion of grain boundaries with chromium deficiency, the width of these areas and the minimum chromium level in these zones [2].

EXPERIMENTAL PROCEDURE

SL-EPR and DL-EPR, for type 304 stainless steel (UNS S30400), are usually conducted in an acidic solution of 0.5 mol/L H_2SO_4 with KSCN as a depassivator agent, at a concentration of 0.01 mol/L [7,8].

Figure 1 (left) presents a schematic of the SL-EPR method applied to sensitized and unsensitized 304 stainless steel [7]. The potential is first set into the passive zone region. Then a scan in the active direction is carried out from this potential, this process is called reactivation. The area under the reactivation peak is proportional to the electric charge that circulated during the reactivation process, and it is assumed that it comes from the dissolution of the chromium-depleted areas near the grain boundary, which are adjacent to the $Cr_{23}C_6$ precipitates [2,5]. This method allows estimating the DOS of a stainless steel by normalizing the electric charge by the ASTM grain size and the specimen area exposed to the solution [7]. However, the SL-EPR method has certain disadvantages: the ASTM grain size of the material must be known, it requires mirror polishing with 1 μm diamond paste and it is very sensitive to surface contamination of the specimen.

Another option developed to circumvent those difficulties is the DL-EPR [2,9]. Figure 1(right) presents a schematic of this technique [8]. In this method, a potential sweep is carried out in the noble direction from the corrosion potential (E_{CORR}) to a predetermined potential in the passive region. Then the direction of the potential sweep is reversed, and the sweep ends upon reaching the initial value of E_{CORR} . During the forward scan, surface irregularities present on the sample dissolve and a passive film is formed above the Flade potential [2]. During the backward scan, the polarization in the active direction decreases the stability of the passive layer and the attack takes place preferentially at Cr

depleted GB. The main parameter calculated in this case is I_r/I_a , the ratio of the reactivation peak current (reverse scan) and the activation peak current (forward scan) [8]. This ratio is independent of the area of the specimen used, which simplifies the analysis of results. It is assumed that I_r/I_a increases as DOS increases. Unlike the SL-EPR method, the DL-EPR method does not require knowing the grain size of the material and it is less sensitive to variations in the surface roughness of the specimens, in practice a surface ground to 100 grit is sufficient [9].

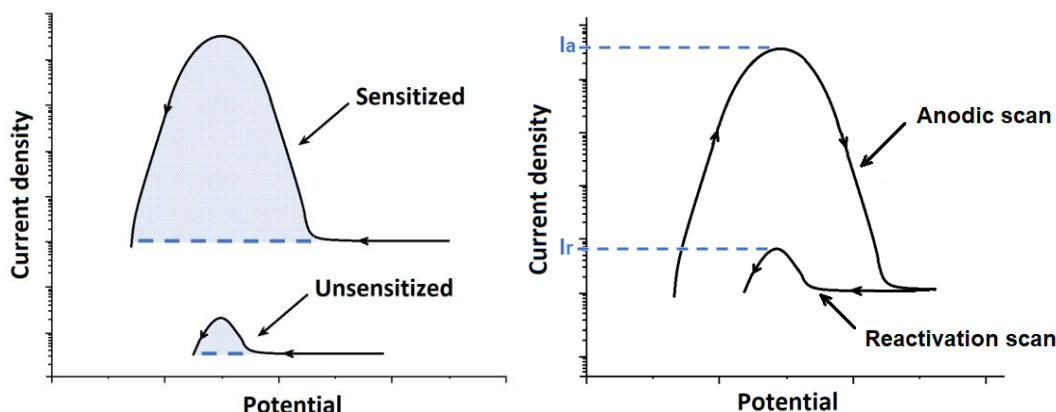


Figure 1: Schematic curves for SL-EPR (left) and DL-EPR (right) test methods [7,8]

Due to the mentioned advantages, the DL-EPR variant is the best suited for in situ measurements. The ISO 12732 [8] standard has a general guide for the interpretation of results, for information purposes, which indicates:

- $I_r/I_a < 0.01$ unsensitized materials
- $0.01 < I_r/I_a < 0.05$ slightly sensitized materials
- $I_r/I_a > 0.05$ sensitized materials

But, ISO 12732, unlike the procedure developed by Majidi and Streicher [9], requires grain size measurements of sensitized specimens to normalize the results. In order to use a simple and rapid test in the field, the determination of grain size would be impractical, therefore, I_r/I_a was calculated without taking into account the grain size. Generally, $I_r/I_a < 0.05$ is considered as acceptable (unsensitized or slightly sensitized materials) and $I_r/I_a > 0.05$ is unacceptable (sensitized materials) [8-10].

In situ application of the method requires some clarification on a number of issues, which will be analyzed in this work:

- **Environmental factors:**
 - Deaeration: Majidi and Streicher originally required to deaerate the solution with N_2 [9], however this is not required by ISO 12732 standard. In a recent interlaboratory test program conducted to assess the repeatability and reproducibility of the DL-EPR method, naturally aerated solutions were used [10]. Deaeration is impractical when making a field measurement, so its usefulness must be clarified.
 - Solution aging: test solution is usually prepared just before the time of use in the laboratory, because the KSCN decomposes in the acidic medium used [11]. In situ application of the technique could be simplified if the solution can be prepared in advance in the lab, therefore the effect of solution aging on I_r/I_a must be understood.
- **Metallurgical factors:** the inclusion content and cold work can affect the values of activation and reactivation currents [12,13], the effect of these metallurgical parameters on I_r/I_a was studied in this work.
- **Electrochemical cell:** it is necessary to design a versatile electrochemical cell that can be attached to components to be evaluated non-destructively in the field.

DL-EPR method was used taking as initial conditions those indicated in ISO 12732, 6 V/h for the potential scan rate, 0.50 mol/L H₂SO₄ + 0.01 mol/L KSCN solution at room temperature, polarization from E_{CORR} to 300 mV (SCE), and reversing the sweep until reaching E_{CORR} again. The same procedure and parameters were suggested by Majidi and Streicher and in a recent interlaboratory test program [10]. Potential was measured with a saturated Ag/AgCl electrode (E= -0.047 V vs. SCE).

Specimens were cut from a 0.8 mm diameter wire of AISI 304 austenitic stainless steel. These specimens were encapsulated in an inert atmosphere of argon inside a sealed quartz tube, and subjected to two different heat treatments. All specimens were first solution annealed (SA) by heating at 1050 °C for 1 h followed by water quenching. This treatment allows dissolving the carbides originally present in the microstructure, if any, and the fast water-cooling prevents precipitation in the 500 °C to 800 °C temperature range during cooling. After this treatment, a group of specimens was sensitized (S) by heat-treatment at 677 °C for 2 h. According to the time-temperature-transformation diagram for this material [1], chromium carbides should precipitate at grain boundaries during this second heat-treatment.

To determine the deaeration effect on the I_r/I_a obtained, some DL-EPR measurements were made after displacing the dissolved oxygen in the solution with nitrogen for an hour prior to starting the test and maintaining the bubbling during the measurement. The rest of the tests were conducted under naturally aerated conditions.

To evaluate the effect of solution aging, the results obtained with the solution prepared immediately before starting the measurement were compared with those obtained on the same specimens with a solution prepared and stored for two weeks.

To analyze the effect of the stainless steel inclusion content on I_r/I_a, 12 mm x 19 mm x 5 mm specimens were prepared from a square bar with a high inclusion content and chemical composition as indicated in table 1. This bar was originally supplied as UNS S30400 stainless steel but after material reception tests it was qualified as out of specification, returned to the supplier and a sample of it was saved for this work. According to the chemical composition, it is likely that the alloy is an UNS S30300 alloy, which contains a minimum S content of 0.15% for improved machinability. The specimens were polished with diamond paste, electrochemical attacked by immersion in oxalic acid solution and observed in an optical microscope. In addition, the inclusions were analyzed by energy dispersive microanalysis in an environmental scanning electron microscope. These specimens were encapsulated in an argon filled quartz tube, SA by heating at 1050 °C for 1 h and then heat treated for different times at 677°C as detailed in table 2. The specimens were identified according to the sensitization time to which they were exposed. DL-EPR measurements were made with nitrogen deaeration and compared with the results obtained under normal aeration conditions. DL-EPR tests were conducted in the cross-transverse section in all cases.

Table 1.
Chemical composition of UNS S30300 stainless steel.

Element	Weight %	Element	Weight %
C	0.09	Cr	17.6
Mn	1.96	Ni	9.76
P	0.163	Mo	0.51
S	0.209	Cu	0.23
Si	0.53	V	<0.20

Table 2.
Summary of heat treatments performed in stainless steels.

Designation	Material	Heat treatment
SA 304 SS	UNS S30400	1 h at 1050 °C
SA + S 2h 304 SS	UNS S30400	1 h at 1050 °C + 2 h at 677 °C
SA 303 SS	UNS S30300	1 h at 1050 °C
SA + S 1h 303 SS	UNS S30300	1 h at 1050 °C + 1 h at 677 °C
SA + S 2h 303 SS	UNS S30300	1 h at 1050 °C + 2 h at 677 °C
SA + S 3h 303 SS	UNS S30300	1 h at 1050 °C + 3 h at 677 °C
SA + S 10h 303 SS	UNS S30300	1 h at 1050 °C + 10 h at 677 °C

To analyze the effect of cold work on I_i/I_a , the wire samples were deformed at a constant extension rate until fracture in a universal tensile machine. Elongation to failure was close to 50% in solubilized specimens and 46% in sensitized specimens. DL-EPR measurements were then conducted in the zone of uniform deformation, away from the neck that forms in ductile metals after the maximum in load. The uniform axial deformation can be estimated from the tensile test curve since deformation is uniform up to the point of maximum load. For the wire used in this work uniform axial deformation was approximately 47% in solubilized specimens (SA 304 SS) and 44% in sensitized specimens (SA + S 2h 304 SS).

Experiments under a given set of conditions were made, at least, in triplicate. To compare the I_i/I_a obtained after changing a given parameter (inclusion content, cold work, deaeration, solution aging), Student's *t* test was used to determine if the results obtained under different conditions can be considered statistically equivalent at a confidence level of 95% [14].

Previously to applying the Student's *t* test, an *F* test was performed to compare the standard deviations of tests under a given set of conditions. A value of *F* was calculated according to equation 1, where s_1 and s_2 are the standard deviations of each group of results. *F* must be greater or equal to 1, so the larger standard deviation goes to the numerator of equation 1. The $F_{calculated}$ is compared with an F_{table} depending on the degrees of freedom of the system, according to equation 2, where *n* is the number of measurements in each group. The criterion of a 95% confidence level was adopted, which is common practice [14]. If $F_{calculated} > F_{table}$ [14], standard deviations are considered different.

$$F_{calculated} = \frac{s_1^2}{s_2^2} \quad (1)$$

$$Degrees\ of\ freedom = n - 1 \quad (2)$$

When standard deviations are considered equivalent, *t* is calculated according to equation 3; otherwise, *t* is calculated according to equation 4. $\bar{x}_1$ and $\bar{x}_2$ are the average values of the evaluated parameter (I_i/I_a) for each set of conditions, and n_1 and n_2 are the number of measurements for each group performed under a given set of conditions. Then, $t_{calculated}$ is compared with a t_{table} , depending on the pooled degrees of freedom, according to equation 5, when standard deviations are considered equivalent, or to equation 6, when standard deviations are considered different. Again, the criterion of a 95% confidence level was adopted [14]. If $t_{calculated} > t_{table}$, the results obtained under different conditions can be considered statistically different, under the confidence level adopted. F_{table} and t_{table} were obtained from the literature [14].

$$t_{calculated} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{\frac{s_1^2(n_1-1) + s_2^2(n_2-1)}{n_1+n_2-2}}} \sqrt{\frac{n_1 n_2}{n_1+n_2}} \quad (3)$$