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STATISTICAL MODELING OF ELECTROCHEMICAL REACTIVATION CONDITIONS FOR DETECTING SENSITIZATION TO IGC OF AUSTENITIC STAINLESS STEEL TYPE 316L

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1. Introduction

The austenitic stainless steels are susceptible to intergranular corrosion (IGC) and intergranular stress corrosion craking (IGSCC). The basic cause of both these forms of corrosion is sensitization. Exposure to a temperature range of 500-800°C, during welding or service, leads to precipitation of chromium rich carbides at the grain boundaries and formation of chromium depletion regions adjacent to these carbides. In 1978, the potentiodynamic reactivation technique was developed into a quantitative, nondestructive test method for measuring sensitization in welded and weldable AISI 304 and 304L stainless steel (SS) piping for use in boiling water nuclear reactor [1, 2]. It has been found that sensitization made the piping subject to intergranular stress corrosion cracking in high temperature (289 ^{0}C) water. This created the need for a non destructive method of determining sensitization at the grain boundaries.

Several investigations [2-21] have contributed to the development of the EPR (Electrokinetic Potentiodynamic Reactivation) method. Different versions of this technique exist today and the most frequently used, due to its lower sensitivity at the surface state [13, 18, 19] is the Double Loop Reactivation method (DL-EPR) [7, 10]. The high sensitivity of this technique has been proved on numerous grades of austenitic stainless steels and nickel alloys. The most published experimental data of EPR tests, relative to austenitic stainless steels, are summarized in Table 1. One can notice that the composition of the electrolyte is usually constituted by sulfuric acid (H_2SO_4) added with a depassivator as KSCN [13-15] or NH_4SCN [2, 17] or HCl [14] in the case of modified EPR method. The scan rate range is between 0,5 and 2,5 mV/s [13–15] and the temperature of the test is often ambient [2, 13, 17, 23] or 30°C [13, 15, 20]. However, the high precision to detect mild degrees of sensitization, i.e., in a range from where no carbide precipitation occurs to the level where one or more grains are completely surrounded by "ditches" in the etch structure, needs (i) a specific study of electrolyte composition, temperature, potential range and sweep rate [2, 13-17] and (ii) the selectivity required to detect sensitization Table 1.

The double loop EPR test consists of an anodic sweep from the corrosion potential to a peak potential in the passive region followed by a reactivation scan from the peak potential back to the corrosion potential. The degree of sensitization is then determined from the ratio of the maximum current in the reactivation scan divided by the maximum current in the anodic scan, or I_r/I_a. The greater the ratio, the greater the degree of sensitization. In order for the EPR test to be selective, there must be significant increases in the I_r/I_a value corresponding to increases in the level of sensitization in the material. Therefore, the electrolyte composition and parameters must be examined with outmost care, to determine changes that would make the test more selective and thus, to involve much better discriminating capacity of the test [22].

The electrochemical reactivation conditions for detecting sensitization to IGC of austentic stainless steels have not been widely studied in the literature. For this reason, we have conducted experiments to study the main parameters controlling the sensitivity of the EPR technique, in order to detect mild intergranular precipitation inducing sensitization of forged austenitic stainless steel to the IGC. 2^n factorial experimental design was used to determine the optimum conditions and a first-order model which relate the degree of sensitization (DOS) to process factors, was obtained.

Table 1. Main published experimental data of EPR tests

Specimen designation	Tempe-rature, °C	Electrolyte composition	Limits conditions of potential, mV/S.C.E	Scan rates, mV/s	Criteria of sensitization to IGC	References
304-304L	30	H_2SO_4 0,5M KSCN 0,01M	-400 to +300	1,67	_	[13]
316L	30	H_2SO_4 6N KSCN 0,005M	-600 to + 200	1,67	$I_r/I_a >> 0$	[15]
AISI 304	30	H_2SO_4 0,5M KSCN 0,01M	-400 to +300	1,67	I_r/I_a >0,005 Metallographic	[18]
AISI 304L	30	H_2SO_4 0,5M KSCN 0,01M	-500 to + 300	-	I_r/I_p >0,0182	[20]
Z2NCDU 25-20.04M Super austenitic	25	H_2SO_4 33% 0,3% HCl	-30 to + 560	0,5	I_r/I_a > 1%	[14]
304LN et 316LN	25	H_2SO_4 0,5M NH_4SCN 0,01M	-	1,67	-	[13] [2]
304LN-316LN	25	H_2SO_4 0,5M NH_4SCN 0,01M	+200 to E_{corr}	1,66	$I_r >> 0$ ou $Q_r >> 0$ Metallographic	[17]
316L	25-40	H_2SO_4 0,1- 4M NH_4SCN 0,01 – 0,1M	-400 to -300	0,5-5	I_r /I_a > to 1% metallographic	this study

With: I_a: activation peak current density; I_r: reactivation peak current density; Q_r: reactivation electric charge density; Q_a: activation electric charge density.

2. Experimental design

Experimental design is widely used for controlling the effects of parameters in many processes. Its usage decreases number of experiments, using time and material resources. Furthermore, the analysis performed on the results is easily realized and experimental errors are minimized. Statistical methods measure the effects of change in operating variables and their mutual interactions on process through experimental design way. Today, the mostly widely used experimental design to estimate main effects, in addition to interaction effects, is the 2^n factorial design, when each variable is investigated at two levels. According to 2^n factorial experimental design method, the principal steps of experiments are designed: determination of response variables, choice of factor levels, and statistical analysis of the data. Consequently, the final step of the work is to obtain a statistically regression model [24].

3. Experimental method

3.1. Materials and heat treatment

The austenitic stainless steel samples of type 316 L was used during the course of this investigation, and its chemical composition is given in Table 2. All specimens were solution heat-treated at 1100°C for 1h in argon protective atmosphere followed by water quenching. It was confirmed by microscopic examination that alloys were in fully solution annealed form.

Table 2. Chemical composition of austenitic stainless steel, type 316L used in this investigation weight percent (%)

Material	C	S	P	Si	Mn	Ni	Cr	Mo	Ti	Nb	Cu	N
316L	0,022	0,015	0,020	0,35	1,74	13,4	17,3	2,13	<0,005	<0,005	0,04	0,035

The sensitization treatment was carried out at 550°C for 80 000 h for 316 L stainless steels [25]. The sensitization heat treatment was selected so as to result in a full coverage of grain boundaries by the chromium-depleted regions and at the same time not to allow for a very high DOS.

3. 2. Microstructural analysis

The microstructures of the as received and aged states have been examined by metallographic microscope and Scanning Transmission Electron Microscope (STEM). The profiles of chromium, molybdenum and nickel concentration at grain boundaries of the aged state 550°C-80 000 h have been established by X-ray microanalysis on thin foils at 300 kV. The identification of intergranular carbides has been done by electronic diffraction and their contents in metallic elements have been determined also by X-ray microanalysis [25].

3.3. Factorial design and DL EPR test

3.3.1. Design of experiments

Factorial design is widely used in statistical planning of experiments to obtain empirical linear models relating process response to process factors [26-29]. 2^n factorial design, where each variable runs at two levels, is often used to obtain first-order models. If the variance analysis indicates that overall curvature is significant, auxiliary experiments are carried out to develop a second-order models [30]. A full factorial design was selected to study the influence of different factors in order to establish the optimum conditions of the degree of sensitization (I_r/I_a or Q_r/Q_a in %). These factors are the scan rates (*dE/dt*, mV/s), the concentration of sulphuric acid ([H_2SO_4], mol/l), and the concentration of depassivator [NH_4SCN], mol/l and the temperature of the electrolyte (°C).

3.3.2. DL -EPR test

The EPR test equipment consisted of a Tacussel-type PGT 24-1 potentiostat / galvanostat, a servovit generator and a millivoltmeter. The platinum sheet and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The curves were plotted on a SE-790 x-y recorder. The series of DL-EPR tests were conducted as mentioned by some authors [4, 17, 22, 18]. After establishing of E_{corr}, the specimen was polarized from the initial potential, E_{corr} = - 450 mV in the cathodic region to an anodic potential of +250 mV/SCE in the passivity region. As soon as this potential was reached, the scanning direction was reversed and the potential was decreased to the cathodic region (figure 1). The peak reactivation current (I_r) and the peak activation current (I_a) were measured during the backward and the forward scans, respectively. The degree of sensitization (DOS) is measured by determining the ratio of the maximum current generated by the reactivation scan to that of the anodic scan: (I_r/I_a %), or by the ratio of electric charges (Q_r/Q_a %) where Q_r is the reactivation surface charge density and Q_a the activation passivation surface charge density. The criteria of sensitization, indicated in Table 3, are in agreement with Y.Cètres et al [14].

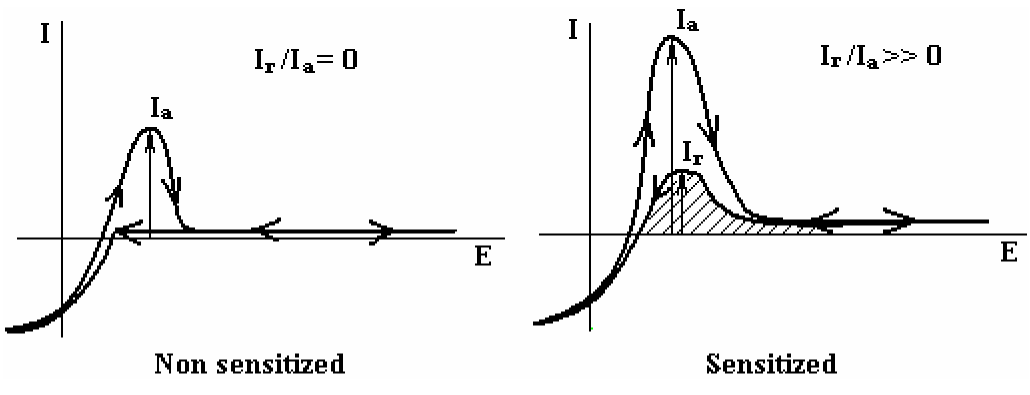


Fig.1. Methods of the data analysis

For the DL-EPR test, a 30 µm SiC paper was usually used for final polishing, the finer finish of 1 µm was used to enhance the quality of photographs. The specimens of section equal 1 cm^2, aged at the same mentioned above conditions have been polished mechanically and mounted in an epoxy resin. The freshly polished specimen was immersed in the electrolyte for 120 s to determine the corrosion potential.

3.3.3. Microstructural examination

After each DL-EPR test, the microstructure was observed and the mode of attack was determined using an optical microscope**.** The extent of the attack is compared with the ratio I_r/I_a % value.

The Test selectivity is a qualitative evaluation of the sample attack with the optical microscope. It refers to grain boundary attack without causing others forms of corrosion during the DL-EPR test.

The test sensitivity is the absolute value of the test criterion, as indicated in Table 3.

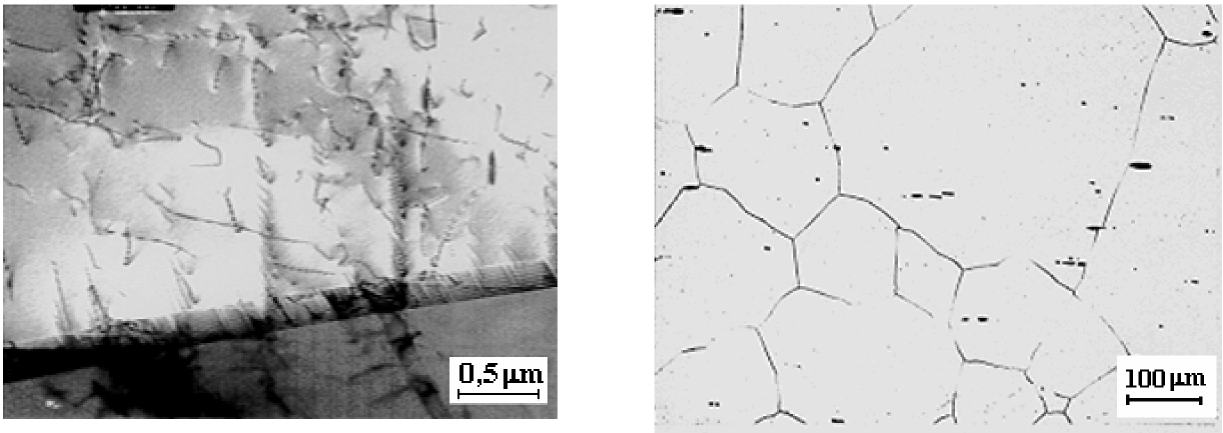
Table 3. Evaluation of the test criteria

Criteria of sensitization	Annealed state	Sensitized state
I_r / I_a (%)	< 0,03	> 1
Q_r/Q_a (%)	< 0,05	> 1

4. Results and discussion

4.1. Microstructural analysis

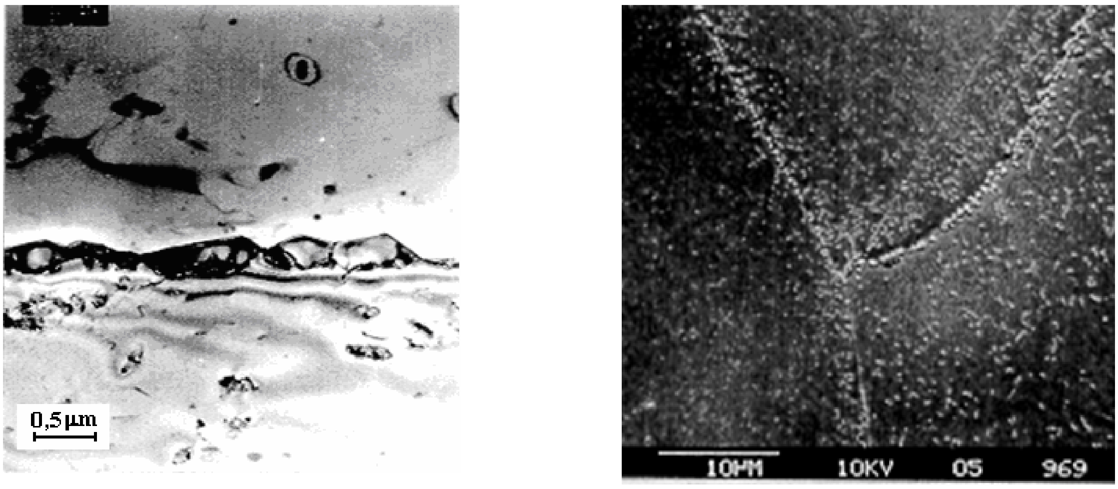
The microstructural examination of annealed samples was performed by optical microscope and Scanning Transmission Electron Microscope (STEM). The results reveal an austenitic structure, perfectly homogenized and without intergranular precipitation (fig. 2).



a *b*

Fig. 2. perfectly homogenized austenitic structures obtained after annealing. Structure of sample on optical microscope (a), structure on thin foil by STEM (b)

On the other hand, the aged state at 550°C for 80 000 h shows a discontinuous precipitation of $M_{23}C_6$ carbides at grains boundaries and abundant intragranular precipitation (fig.3). At this point, the chromium depletion consecutive to intergranular precipitation shows denuded zones of intragranular carbides at grains boundaries (fig.3,*a*).



a *b*

Fig. 3. Precipitations of M23C6 carbides after heat -treatment at 550°C for 80 000h. M23C6 carbides precipitations using MES (a), intergranular precipitation M23C6 carbides using MET (b)

The X-ray microanalysis on thin foils in STEM, performed on $M_{23}C_6$ carbides, permits to determine the average concentration of metallic elements of these carbides without taking into account the carbon. Table 4 shows that these carbides, rich in chromium (68,7%), contain other significant metallic elements as iron, nickel and molybdenum.

Table 4. Concentration in metallic elements of the determined carbides M23C6 by X-ray microanalysis on thin foils in STEM

Weight %	Si	Cr	Mn	Fe	Ni	Mo
$M_{23}C_6$	0,3	68,7	1,8	14,1	3,3	11,8

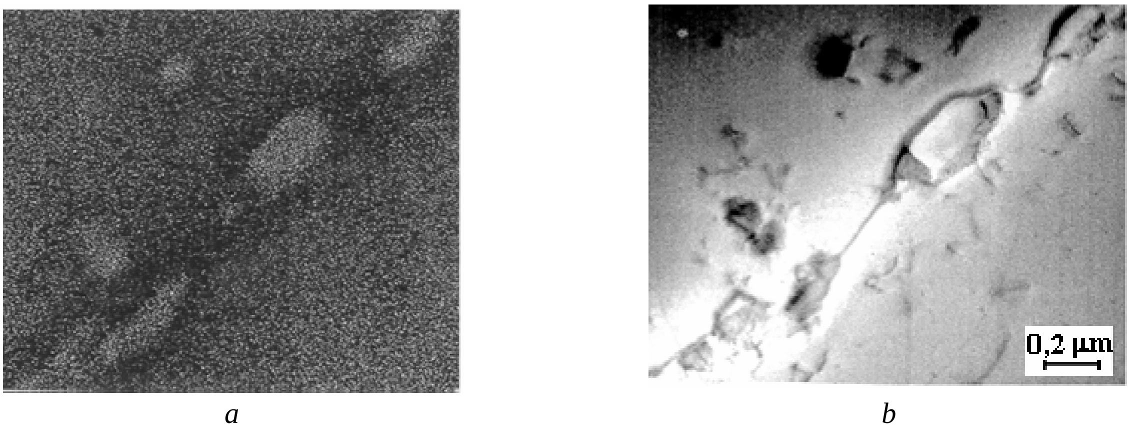


Fig. 4. Cr-depleted zones obtained after intergranular precipitation of M23C6 carbides (Aged state 550°C for 80 000h). Cr-depleted zones obtained after electrolytic polishing (a), qualitative distribution of the chromium in depleted zones (b)

The involvement of elements as chromium and molybdenum to intergranular carbides composition, decreases appreciably their content in the vicinity of grain boundaries and contribute to the formation of Cr-depleted zones responsible for sensitization to IGC (fig. 4).The profiles of concentration associated to these zones, confirm the depletion in elements of $M_{23}C_6$ carbides composition, compensated by an increase of Fe and Ni content (fig. 5).

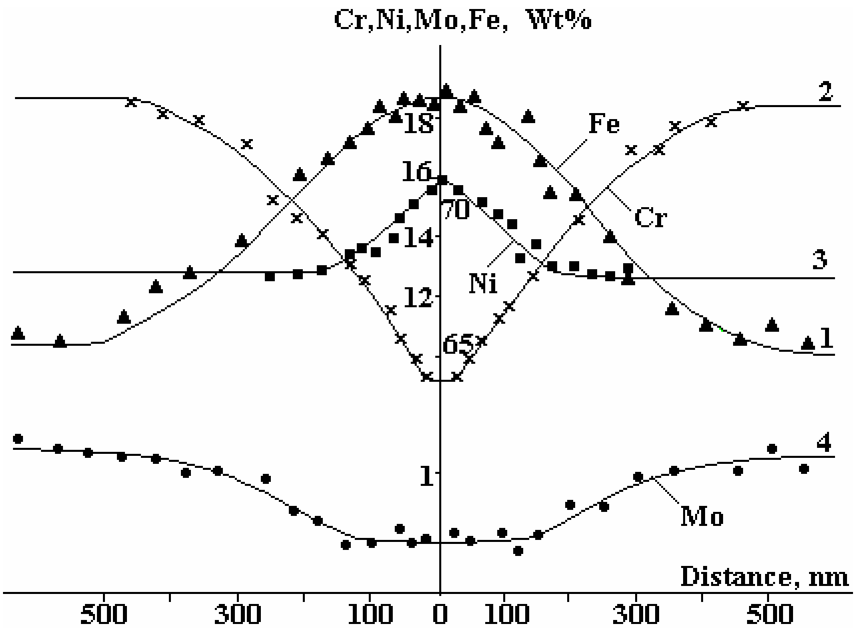


Fig. 5. Profiles of iron, chromium, and nickel and molybdenum concentration associated to Cr- depleted zone shown in figure 4 (Aged state 550°C for 80 000h). Nominal content : 1 – [Fe] 65,2; 2 – [Cr] 18,6; 3 – [Ni] 12,7; 4 – [Mo] 1,2 Wt.%

4.2. DL-EPR test results

It is well known that during The EPR test, an oxide layer is electrochemically built up at the passivation potential. This layer protects the underlying matrix from corrosion during subsequent reactivation. Assuming a chromium depletion mechanism, the zones adjacent to the grain boundaries are deficient in free chromium once they have become sensitized. At these sites, the passivation layer preferentially breaks down during reactivation, allowing active dissolution to occur. The inside of the grain, where no chromium depletion has occurred, remains unattacked [22, see references therein]. The quality of the oxide layer depends primarily on the passivation circumstances, on the one hand, and the local composition of the underlying matrix, on the other hand. The extent of the grain boundary attack depends on the reactivation circumstances and the local quality of the built up oxide layer [22].

Table 5. Factor levels used in the full factorial design

Symbols Of factors	Factors	High level (+)	Medium level (0)	Low level (-)	Increment
X1	Sweep rate(mV/s)	5	2,25	0,5	2,75
X2	H_2SO_4concentration (mol/l)	4	2,05	0,1	1,95
X3	NH_4SCNconcentration (mol/l)	0,1	0,055	0,01	0,045
X4	Temperature °C	40	32,5	25	17,5

The assessment of sensitization to the IGC of austenitic stainless steel, type 316L by DL EPR test was investigated. The ratios I_r/I_a % and charge density Q_r/Q_a % determined for annealed and aged samples at 550°C for 80 000 h, are reported in Table 5. Experimentally, for the reproducibility, all the tests were at least repeated in twice in order to reduce the scatter of the test results. As is seen in Table 6, annealed samples show low DOS in DL-EPR test (I_r/I_a % = 0). A laboratory solutionizing heat treatment [1100°C WQ (water quenching)] shows no IGC with DL EPR test (fig. 6). On the other hand, aged samples show different levels of sensitization depending of the parametric values of the DL-EPR test (fig. 7).

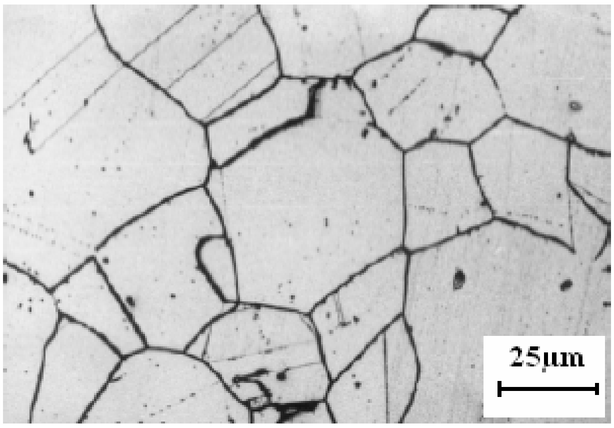


Fig. 6. Microstructure produced on non sensitized sample after DL-EPR test in an electrolyte at 25°C. (No intergranular attack is observed)

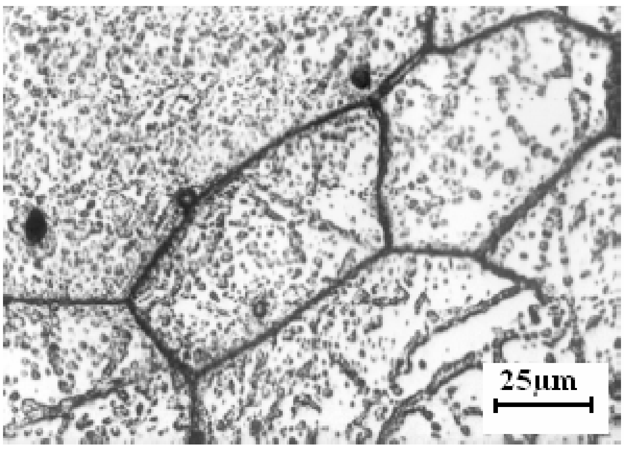


Fig. 7. Microstructure produced on a sensitized sample (550°C-80000 h) after DL-EPR test at 25°C. The electrolyte was 4M H_2SO_4+0,01M NH4SCN, the scan rate was 0,5 mV/s (severe grain boundary attack and general corrosion produced on this sample)

The collected data were analyzed by a PC using NEMRODW computer software package for the evaluation of the effect of each parameter on the optimization criteria. In order to determine optimum conditions and derive a model for the criteria I_r/I_a, a full factorial of the type 2^4 has been used. Sweep rate (X_1), sulphuric acid concentration (X_2), ammonium thiocyanate concentration (X_3) and temperature (X_4) were chosen as independent variables to model. Factors level is shown in table 6. The matrix for four variables is varied at two levels (+1 and –1). The higher level of variable was designed as "+" and the lower level was designed as "-".

Table 6. Experimental design matrix and response value

Exp. no.	X_1 *dE/dt*	X_2 H_2S0_4]	X_3 [NH_4SCN]	X_4 Temperature	***Annealed state***		***Aged state***			
					I_r/I_a, %	Q_r/Q_a, %	I_a, mA/cm^2	I_r, mA/cm^2	I_r/I_a, %	Q_r/Q_a, %
6	-1	-1	-1	-1	0	0	32,0	2,54	7,93	7,19
7	+1	-1	-1	-1	0	0	11,49	1,05	9,1	15
12	-1	+1	-1	-1	0	0	5,237	3,435	65,6	53,65
9	+1	+1	-1	-1	0	0	8,033	1,267	15,8	28,57
1	-1	-1	+1	-1	0	0	42,28	10,17	24,07	21,68
8	+1	-1	+1	-1	0	0	32,14	4,432	13,78	31,98
13	-1	+1	+1	-1	0	0	162,4	56,89	35,03	34,65
4	+1	+1	+1	-1	0	0	250,2	45,82	18,31	18,70
5	-1	-1	-1	+1	0	0	2,02	0,340	16,83	23,33
10	+1	-1	-1	+1	0	0	0,558	0,186	33,33	33,33
16	-1	+1	-1	+1	0.04	0	2,892	1,071	37,03	45,45
2	+1	+1	-1	+1	0	0	6,145	1,584	25,77	30
11	-1	-1	+1	+1	0	0	69,88	8,68	12,42	9,89
14	+1	-1	+1	+1	0	0	73,63	6,832	9,27	8,81
3	-1	+1	+1	+1	0.02	0	143,6	21,66	15,08	20,04
15	+1	+1	+1	+1	0	0	157,0	14,44	9,19	14,04
1*	0	0	0	0	0	0	16,73	3,67	21,93	17,85
2*	0	0	0	0	0	0	31,14	6,52	20,94	15,65
3*	0	0	0	0	0	0	21,61	4,82	22,30	18,75

* Central point replicates

The 2^4 full factorial design was used to obtain first-order model with interaction terms. As usual, the experiments were performed in random order to avoid systematic error. In addition, three central replicates were also added to the experimental design to calculate pure experimental error. The results are given in Table 6. In order to confirm the predictability of the obtained model, two tests have been performed on both sides of experimental central domain (Table 7). A first order model with interaction terms was chosen to fit the experimental data:

$$\tilde{Y} = и_0 + и_1Ч_1 + и_2Ч_2 + и_3Ч_3 + и_4Ч_4 + и_{12}Ч_1Ч_2 + и_{23}Ч_2Ч_3 + и_{14}Ч_1Ч_4 + и_{24}Ч_2Ч_4 + и_{34}Ч_3Ч_4 + и_{123}Ч_1Ч_2Ч_3 + и_{124}Ч_1Ч_2Ч_4 + и_{134}Ч_1Ч_3Ч_4 + и_{234}Ч_2Ч_3Ч_4 + и_{1234}Ч_1Ч_2Ч_3Ч_4,$$

Table 7. Tests carried out on both sides of the experimental central domain

Exp.no	*dE/dt*	[H_2SO_4]	[NH_4SCN]	Temperature	Y_{exp}	Y_{cal}
1	1 mV/s	1 M	0,03 M	30 °C	21,75	20,67
2	2,5 mV/s	3 M	0,06 M	40 °C	19,84	20,06

where $\tilde{Y}$ is the degree of sensitization expressed by the ratio I_r/I_a %, b_0-b_{1234} are the interaction coefficients and X1-X4 are dimensionless coded factors for the variables; the first order model obtained by variance analysis conducted at 95 % confidence interval is as follows:

$\tilde{Y}_{Ir/Ia}$ = 21,784 – 4,965X_1 + 5,942 X_2 -4,640 X_3 – 1,919 X_4 – 5,494 X_1X_2 – 3,684X_2X_3 + 4,490 X_1X_4 – – 4,04 X_2X_4 – 3,735 X_3X_4 + 4,348 $X_1X_2X_3$ + 1,681 $X_1X_2X_4$ – 2,224 $X_1X_3X_4$ + 2,426 $X_2X_3X_4$ – 1,220 $X_1X_2X_3X_4$.

Table 8 gives the optimal conditions of the sensitization to IGC of austenitic stainless steel, type 316L (annealed and aged states) by DL EPR test. The results are shown in Table 9. The highest I_r /I_a value for AISI 316L steel, (aged state 550°C-80000 h) was obtained at 0,5 mV/s sweep rate, 4M H_2SO_4 concentration, 0,01 M NH_4SCN concentration and temperature 25°C. Contrarily The lowest I_r/I_a value was obtained for AISI 316L steel, (aged state 550°C-80000 h) at 0,5 mV/s sweep rate, 0,1M H_2SO_4, 0,01M NH_4SCN concentration and temperature 25°C.

Table 8. Optimal conditions of the sensitization to IGC by DL EPR test

dE/dt, mV/s	[H_2SO_4], mol/l	[NH_4SCN], mol/l	Temperature, °C	EPR DL response			
				Aged state		Annealed state	
				I_r/I_a	Q_r/Q_a	I_r/I_a	Q_r/Q_a
0,5	4	0,01	25	65,6	53,65	0	0

Table 9. Effect of factors and their interactions

Factors and interactions	Coefficient	degree of freedom (d.o.f)	standard error	t_{exp}^*	Significance or Decision (α = 0,05)
X_1	-4,97	2	0,175	28,4	effective
X_2	5,94	-	-	33,94	effective
X_3	-4,64	-	-	26,51	effective
X_4	-1,92	-	-	10,97	effective
X_1X_2	-5,49	-	-	31,37	effective
X_1X_3	0,46	-	-	2,63	ineffective
X_2X_3	-3,68	-	-	21,03	effective
X_1X_4	4,49	-	-	25,67	effective
X_2X_4	-4,04	-	-	23,08	effective
X_3X_4	-3,74	-	-	21,37	effective
$X_1X_2X_3$	4,35	-	-	24,86	effective
$X_1X_2X_4$	1,68	-	-	9,6	effective
$X_1X_3X_4$	-2,24	-	-	12,8	effective
X_2X3X_4	2,43	-	-	13,89	effective
$X_1X_2X_3X_4$	-1,22	-	-	6,97	effective

t_{exp} is t - Student [28,29], $t_2^{0.05}$ = 4,303 (from statistic table, where α = 0,05 and d.o.f =2. If $t_{exp} < t_2^{0,05}$, the factor is ineffective).

To test the significance of the factor effects, an analysis of variance has been conducted at 95% confidence interval. The significant main and interaction terms are schown in Fig. 8. From the statistical analysis, described in Table 9, sweep rate, sulfuric acid concentration, ammonium thiocyanate concentration and temperature have positive effects on DOS of austentic stainless steel, of type 316L, evaluated by the ratio I_r/I_a %. Also, the second order interaction effects, given in fig. 9, were an important factor on DL-EPR tests. In fact, the interactions study reveals five significant second-order interactions (X1X2, X_1X_4, X_2X_3, X_2X_4 and X_3X_4). In the other side, in order to validate this model, our approach to operate is as follows (i) the analysis of residuals ($\tilde{Y}_{exp}$ –$\tilde{Y}_{cal}$) shown in Table 10, are consistent with experimental and calculated values of I_r/I_a in % and (ii) the analysis of variance, shown in Table 11, and established also at 95% confidence interval, substantiates that the overall effective factors retained for the first-order model, has significant effect on the response I_r/I_a %. Moreover, the analysis of variance indicate that the first–order model can be satisfactorily used in such multiple linear regression analysis ($F_{0,05\,(12,4)} > F_{0,05\,(14,4)} > F_{0,05\,(24,4)}$). The correlation coefficient, r^2, was found to be 99,427 %, indicating the pertinency of the model. Based on these results, it was not obviously necessary to conduct auxiliary experiments, using an orthogonal central composite design to obtain second-order model. The NEMRODW of the obtained results shows that all of variables studied and their combinations, affect the degree of sensitization of austenitic stainless steel, evaluated by the ratio I_r/I_a in %.

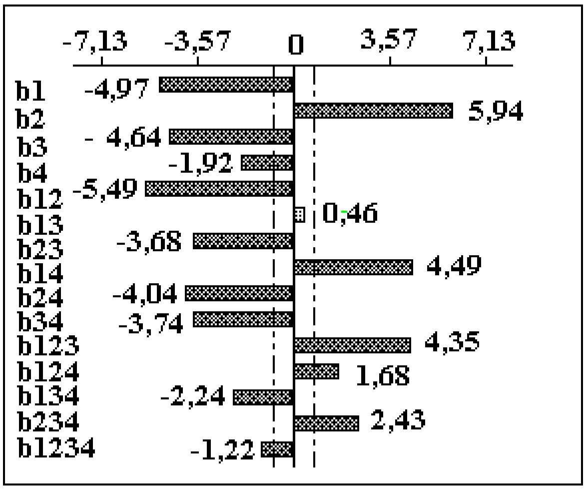


Fig.8. Significant main, second order and interaction terms on the DOS of AISI 316L steel using DL-EPR tests (aged state 550°C-80000 h)

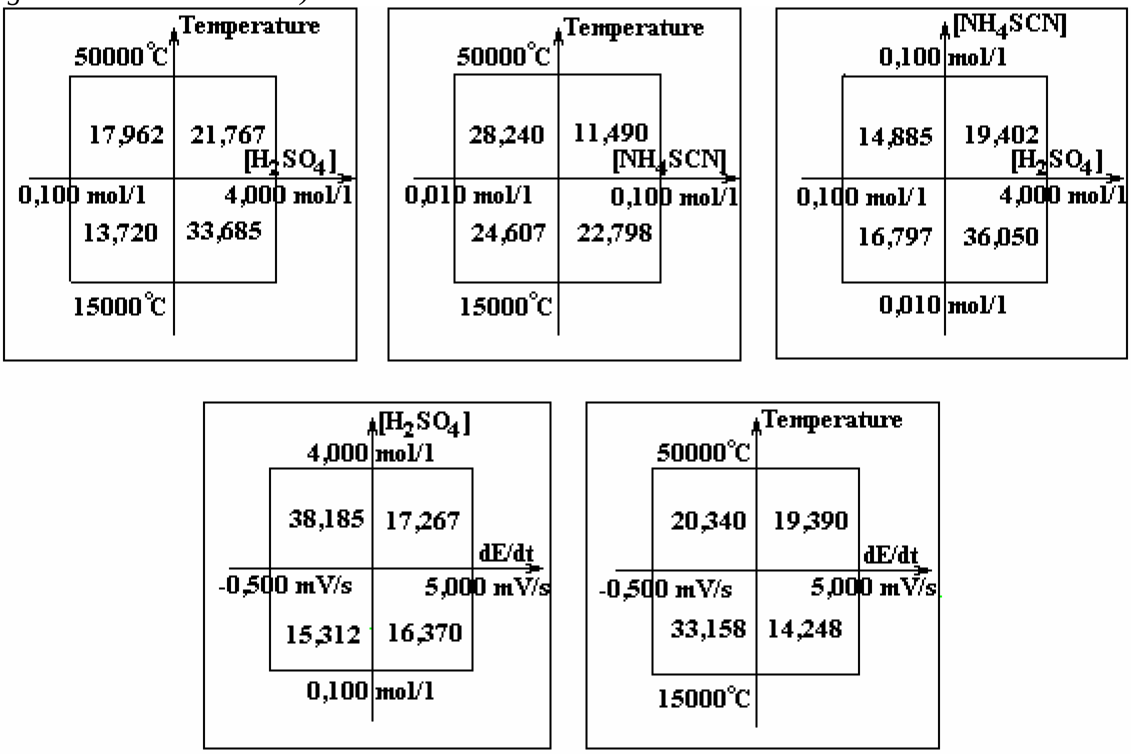


Fig. 9. Significant second order interactions on the DOS of AISI 316L steel using DL-EPR tests (aged state 550°C-80000 h)

Table10. Residuals

I_r/I_a exp (%)	7.93	9.1	65.6	15.8	24.07	13.78	35.03	18.31	16.83	33.33	37.03	25.77	12.42	9.27	15.08	9.19
I_r/I_a cal (%)	7.47	9.56	65.14	16.26	24.53	13.32	35.49	17.85	16.37	33.79	36.57	26.23	12.88	8.81	15.54	8.73
residuals	-0.46	0.46	-0.46	0.46	0.46	-0.46	0.46	-0.46	-0.46	0.46	-0.46	0.46	0.46	-0.46	0.46	-0.46

Table 11. Analysis of variance

Source of variation	Sum of squares	d.o.f	Mean squares	F ratio	Signifiance
regression	3415.9815	14	243.998679	223.989424	<0,01***
residual	4.357325	4	1.08933125		
total	3420.29046	18	190.016137		

$F_{0,05\,(12,4)}$ = 5,91 and $F_{0,05\,(24,4)}$ = 5,77 (statistical table).

The significant factors, deducted from experimental design that have a direct influence on the quality of the DL-EPR test results, will be discussed in next paper. This parametric study is needed in order to further improve the selectivity of the test.

5. Conclusion

The optimum conditions of the criteria to the sensitization to IGC of austenitic stainless steels, type 316L were investigated. The ratio I_r/I_a % was determined with respect to temperature, sweep rate, concentration of H_2SO_4 and NH_4SCN by means of factorial design. The 2^4 full factorioal design was used to obtain first-order model with interaction terms. From the experimental results, the optimal conditions were obtained as the sweep rate 0,5 mV/s, the [H_2SO_4] 4M, the [NH4SCN] 0,01M and temperature 25°C. In this tudy, the highest degree of sensitization for AISI 316L obtained was 65,6%. The correlation coefficient calculated for the first-order model at 95% confidence level has a high value of 99,427 %. The model has nearly fitted the full first-order model. Thus, the model supports the experimental data very well. It is very efficient, pertinence and has no systematic errors. All the parameters studied, affect the response I_r/I_a %. It is believed that the model obtained for the DOS to IGC of AISI 316L may provide a background for pilot and industrial scale applications.

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Summary

The aim of this study was to determine optimum conditions of the DL EPR test in order to evaluate the highest values of the degree of sensitization (DOS) of a forged austenitic stainless steel type 316L, evaluated by the ratio I_r/I_a or Q_r/Q_a in %. The criteria of sensitization to the IGC corresponds to I_r/I_a >1% and Q_r/Q_a >1%. A model using a full factorial design has been established and the selected factors were the sweep rate (dE/dt), sulphuric acid concentration (H_2SO_4), ammonium thiocyanate concentration (NH_4SCN) and temperature in °C. A first order model is obtained by using 2^4 full factorial design. An experimental test carried out using a factorial design 2^4 indicated that all the factors and their interactions have a positive effect on the response I_r/I_a. Furthermore, the highest value detected of I_r/I_a was found to be 65,6 %. On the other hand, a microstructural study based on optical microscope and Scanning Transmission Electron Microscope (STEM), have been carried out for annealed and aged samples (550°C-80 000 h). The profiles of chromium, nickel and molybdenum concentration established by X-ray microanalysis in STEM, confirm a decrease of content of these elements leading to the formation of Cr-depleted zones responsible of the sensitization to the IGC.