



# Tuning DOS measuring parameters based on double-loop EPR in H<sub>2</sub>SO<sub>4</sub> containing KSCN by Taguchi method

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## ARTICLE INFO

### Article history:

Received 13 October 2009

Accepted 18 April 2010

Available online 24 April 2010

### Keywords:

A. Stainless steel

B. Polarisation

C. Intergranular corrosion

C. Passivity

## ABSTRACT

In the present work, a higher resolution than that of standard DL-EPR technique was obtained by tuning the degree of sensitisation (DOS) measuring parameters. SS304 with different sensitisation conditions was chosen. Acid and depassivator concentration, temperature, scan rate and reverse potential were defined as key factors and Taguchi  $L'_{16}$  was applied. The optimal condition was found to be 1 M H<sub>2</sub>SO<sub>4</sub>, 0.02 M KSCN, 40 °C, 30 mV/min scan rate and 200 mV reverse potential. Main factors were acid concentration, scan rate, depassivator concentration. An increase in DOS from 18 to 42.2 in the 60 min sensitised sample was observed.

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## 1. Introduction

Intergranular corrosion (IGC) is one of the most important types of localized attack in stainless steel. Although various structural changes are conducive to a selective corrosion attack, the main reason of IGC is the phenomenon called sensitisation [1]. Austenitic stainless steel may be sensitised to IGC if it is reheated in a temperature range of 500–800 °C or is slowly cooled from high temperature during solution annealing or welding operations [2,3]. As a result, the corrosion resistance is deteriorated due to the chromium depleted zone adjacent to the chromium rich precipitates, such as Cr<sub>23</sub>C<sub>6</sub> carbide, along the grain boundaries. These chromium depleted regions are susceptible to attack and thus the corrosion in these regions proceeds intergranularly [3]. Due to the negligible weight loss involved and to the overshadowing of depleted zone by the unaffected bulk of the grain, sensitisation measurement is relatively difficult [1]. There are a number of standard methods, such as oxalic acid test, Strauss test, Huey test, Streicher test and Copper–Copper Sulfate-50% sulphuric acid test, which can be used to assess the susceptibility to IGC. None of these methods are a quantitative and non-destructive method. Moreover, performing the above mentioned tests is time consuming. During the past decades, much research has been conducted to innovate a test method by developing the electrochemical potentiodynamic reactivation test (EPR). EPR is a quantitative method which indicates degree of sensitisation (DOS) based on electrochemical

parameters obtained from the potentiodynamic polarisation curve [1–2,4–10]. EPR measurement tends to focus on single or double loop modes (SL-EPR and DL-EPR) as a technique used to establish the resistance of stainless steel to IGC and stress corrosion cracking (SCC) susceptibility [9,10]. The detailed description of SL-EPR and DL-EPR can be found in the literature [9,10]. Here in brief, it can be highlighted that the results of DL-EPR are reported as a ratio of current density (C-ratio) and/or the charge consumed during the reactivation scanning stage to the current and/or the charge created during the activation scanning stage:

$$\text{DOS \%} = \frac{i_r}{i_a} \times 100 \text{ or } \text{DOS \%} = \frac{Q_r}{Q_a} \times 100 \quad (1)$$

where,  $i_r$  is the maximum current density during reactivation scan,  $i_a$  is the overall current density during the activation scan,  $Q_r$  is the overall anodic charge measured during the reactivation scan and  $Q_a$  is the maximum charge measured during the activation scan [10].

Although a standard procedure has been already developed for SS304 [11], improving the EPR resolution to detect the lowest possible DOS is of great demand and several researchers have tried to improve the resolution by either modifying the technique [4,12–15], or the solution constituents [2,14,15] for SS304 and other alloy systems. Several factors can influence the resolution of DOS measurement, including acid and depassivator concentration, temperature, scan rate, reverse potential, etc. This indicates that DOS is a multi-variant parameter and investigating the effect of individual factors is essential. Since DOS includes a significant number of factors, a full factorial design of the experiments requires a large number of runs and measurements which are all time consuming and

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costly. One of the well-known statistical methods to reduce the number of tests with comparable accuracy is Taguchi method. Taguchi method is a combination of mathematical and statistical techniques used in an experimental study which determines the experimental condition having the least variability as the optimum condition [16–17]. A limited number of experiments from partial fraction which produces the most information are selected. It determines factors that have the most effects on the quality of the product with a minimum amount of experimentation [18]. Some of the main advantages of Taguchi method are simplicity in understanding and applying the method, reduction of variation without removing its causes, reduction of time and costs of the experiments and reduction of the required experimental trials [16–17]. In this study, Taguchi method was used to evaluate the effect of important factors on DOS measurement and to tune the DOS resolution by modifying them.

## 2. Materials and methods

A small sample of SS304 with 1 cm<sup>2</sup> cross sectional area was used. Chemical analysis of the steel in weight percent (%wt) is as follows: 18.13% Cr, 7.98% Ni, 0.059% C, 0.46% Si, 0.035% S, 0.045% P, 1.80% Mn, 0.12% Mo, other alloying elements <1%, and Fe bal. Specimens were held in an air atmosphere furnace at 650 °C for 10, 60 and 300 min, followed by quenching in water to produce different degrees of sensitisation. The microstructure of the samples were characterised by optical microscopy. All specimens were polished to 3 μm diamond slurry. Then, according to ASTM A-262 practice A standard, the specimens were etched in 10% oxalic acid solution by applying 1 A/cm<sup>2</sup> current density for 90 s [19]. In the next step, the specimens were rinsed with distilled water, washed with methanol and dried with hot air. The etched microstructures were classified into three categories: first, step structure, second, dual structure with some ditches at grain boundaries (but no single grain is completely surrounded by ditches) and the third is a ditch structure in which one or more grains are completely surrounded by ditches [19].

To determine the optimum condition with the highest resolution in DOS measurement, Taguchi method was used. Table 1 shows the controlling factors and their levels affecting the resolution in DOS measurement. Concentration ranges for sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and potassium thiocyanate (KSCN) were 0.05–1 M and 0.001–0.02 M, respectively [5]. Selected temperatures were 30 °C (used in standard procedure [11]), 25, 35 and 40 °C and the temperature was controlled through a water bath with an accuracy of ±1 °C. A range of scan rates from 30 to 120 mV/min was chosen. To study the extension of passive layer formation on DOS measurement, the reverse potential was also varied from 200 to 350 mV with an accuracy of ±5 mV.

Considering 5 factors each having 4 levels, 1024 (4<sup>5</sup>) experiments should have been conducted in order to analyze the effect of each factor on the resolution in DOS measurements. However, by applying Taguchi's method and using L<sub>16</sub> orthogonal array (OA), the number of experiments was reduced to 16. These 16

**Table 1**  
Defined factors and their levels.

Factor	Level			
	1	2	3	4
Acid conc. [H <sub>2</sub> SO <sub>4</sub> ] M	0.05	0.1	0.5	1.0
Depassivator conc. [KSCN] M	0.001	0.005	0.01	0.02
Temperature (°C)	25	30	35	40
Scan rate (mV/min)	30	60	90	120
Reverse potential (mV vs. SCE)	200	250	300	350

experiments are shown in Table 2. The results of the experiments conducted according to the orthogonal array in Taguchi's method can be reported as Signal to Noise (S/N) ratios. Different strategies for S/N calculation have been proposed [16–18,20]. In this study, the aim was to achieve the highest resolution of DOS measurement, therefore, type B was chosen with the following formula:

$$S/N_B = -10 \times \log_{10} \left( \frac{1}{r} \sum \frac{1}{y_i^2} \right) \quad (2)$$

where,  $y_i$  is the desired property which is DOS in this case, and  $r$  is the number of repetition of each experiment.

The DL-EPR experiments were carried out in different conditions as summarised in Table 2 and also in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M KSCN, 30 °C and with a 100 mV/min scan rate as a standard procedure [11]. All experiments were performed on SS304 samples sensitised for 60 min at 650 °C [11] and based on the obtained results, the optimum condition was achieved and applied to all the heat treatments including non-sensitised and sensitised specimens at 650 °C for 10 and 300 min. In DL-EPR, the specimens were polarised from 50 mV below OCP to the passive region and reversed from 200, 250, 300 and 350 mV toward the OCP. DOS was calculated as the ratio of the maximum reactivation to the maximum activation charge density. Saturated calomel electrode (SCE) and platinum wire were used as reference and counter electrodes, respectively. Electrochemical tests were conducted by means of Gill AC automated potentiostat (ACM Instruments). Before each polarisation test, the sample was kept at the corrosion potential for 15 min. Each experiment was repeated three times to ensure reproducibility.

## 3. Results and discussion

### 3.1. Microstructure analysis

Sensitisation can be observed by optical microscopy. Fig. 1 shows the microstructure of SS304 samples in non-sensitised and sensitised situations with different sensitisation times. IGC susceptibility can be evaluated by measuring the thickness of the dark region, continuity of the ditches at the vicinity of grain boundaries and also the number of grains which have been completely surrounded by ditches. The microstructure of the non-sensitised specimen is presented in Fig. 1(a). According to the ASTM A262-A standard [19], this is a typical step structure. Only steps can be seen in the grain boundaries and no ditches are observed. No

**Table 2**  
L<sub>16</sub> orthogonal array.

Experiment No.	Factor				
	[H <sub>2</sub> SO <sub>4</sub> ]	[KSCN]	Temperature	Scan rate	Reverse potential
1	1	1	1	1	1
2	1	2	2	2	2
3	1	3	3	3	3
4	1	4	4	4	4
5	2	1	2	3	4
6	2	2	1	4	3
7	2	3	4	1	2
8	2	4	3	2	1
9	3	1	3	4	2
10	3	2	4	3	1
11	3	3	1	2	4
12	3	4	2	1	3
13	4	1	4	2	3
14	4	2	3	1	4
15	4	3	2	4	1
16	4	4	1	3	2

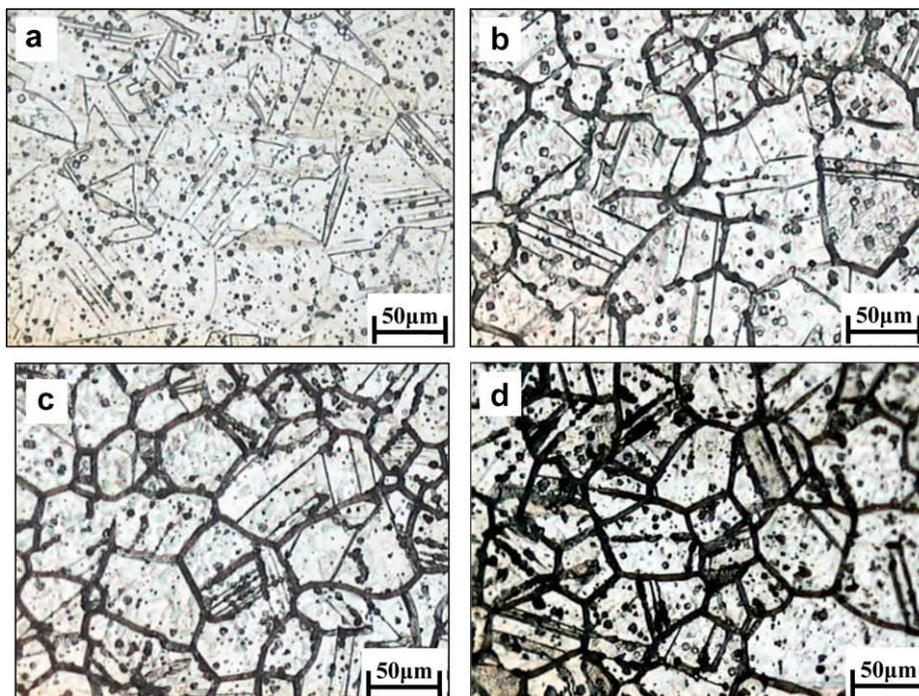


Fig. 1. Microstructure of SS304 in (a) non-sensitised, (b) 10 min, (c) 60 min and (d) 300 min sensitised condition (200 $\times$ ).

carbide precipitation can be detected in the grain boundaries and therefore, no sensitisation has occurred in this specimen, indicating no sensitisation in the as-received alloy. Fig. 1(b), represents the microstructure of the specimen with 10 min sensitisation time. Some ditches at grain boundaries characterised the dual microstructure. None of the grains are completely surrounded with ditches but some ditches on the grain boundaries are observed. This indicates that the specimen is slightly sensitised. In other words, carbides could not completely precipitate in grain boundaries. The microstructure of the sample which has been sensitised for 60 min is shown in Fig. 1(c). As can be seen from this figure, some grains are completely surrounded by ditches, i.e. carbides have precipitated at grain boundaries and almost all of the grains have chromium depleted regions at their grain boundaries. Most of the carbides were dissolved by oxalic acid electrochemical etching [19,21]. Therefore, the specimen is considered to be completely sensitised. This is even more noticeable in the 300 min sensitised sample. In summary, by increasing the sensitisation time, IGC susceptibility and therefore DOS increased. However, it should be noted that measuring sensitisation with the aid of microscopical examination is mostly a qualification method; it cannot provide any quantitative value for DOS. This is because the microscopic dimension of the depleted layer tends to be overshadowed by the unaffected bulk of the grain [1]. Therefore, an electrochemical method such as DL-EPR is more valuable for DOS measurement, which will be represented in the following section.

### 3.2. DL-EPR test

Fig. 2 shows the results of DL-EPR under standard conditions (0.5 M  $\text{H}_2\text{SO}_4$  + 0.01 M KSCN, 30  $^\circ\text{C}$  and with 100 mV/min scan rate) on SS304 sample sensitised for 60 min at 650  $^\circ\text{C}$  [11]. It has been proposed that during forward scanning, a passive layer could form on the surface of the sample by reaching the passivation potential [5]. The anodic current in forward (activation) scanning direction can be generated by the whole surface area including grains and grain boundaries [1]. The characteristics of the formed

passive layer depends on the chemical composition, surface constituents and distribution of alloying elements, particularly, chromium on the sample surface. On the other hand, during backward (reactivation) scanning, since the surface is already in the passive state, a lower current density will be recorded and consequently a slightly higher corrosion potential will be observed. This indicates that although during the activation stage higher current is generated by the entire sample surface, in the reactivation stage, current is exclusively generated from the defective regions of the passive layer (i.e. the sensitised grain boundaries) and the remainder area of the grains have less contribution [1,5,9]. Therefore, the difference in activation and reactivation behaviour can be considered as a criterion for DOS [1,4–5,9]. Taking into account the ratio of charge consumed during the reactivation scan (1006.6 mC/cm $^2$ )

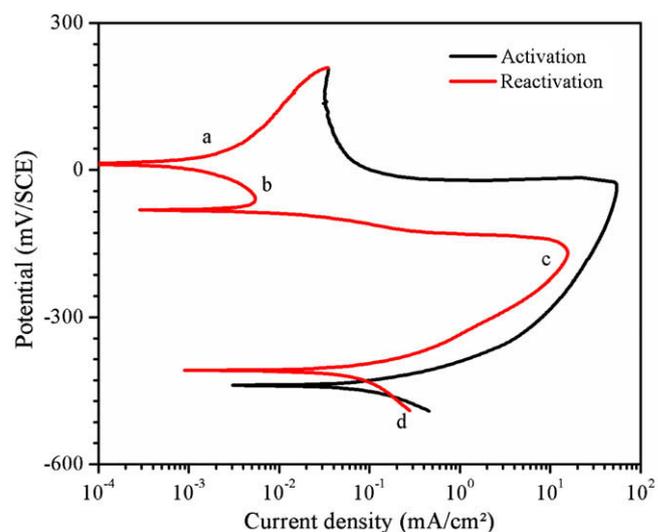


Fig. 2. DL-EPR result on SS304 in standard conditions; 0.5 M  $\text{H}_2\text{SO}_4$  + 0.01 M KSCN, 30  $^\circ\text{C}$ , 100 mV/min scan rate on candidate SS304 alloy sensitised for 60 min at 650  $^\circ\text{C}$ .

to the activation scan (5421 mC/cm<sup>2</sup>) as the DOS value, Fig. 2 gives a value of about 18% [1,5,9]. This value can be considered as a criterion for the DOS value. It should be noted that while the forward scan gives a single corrosion potential as is usual, interestingly, the backward scanning provides three corrosion potentials. This complicated behaviour can be correlated to the fact that while in forward scanning, the anodic and cathodic branches cross at one point, during backward scanning; cathodic reaction crosses the anodic branch at three points [22]. Therefore, it gives three cross points, first in passive state, second in transition and third in active state. As a result, four regions are created in the reactivation stage as shown with labels *a*, *b*, *c* and *d* in Fig. 2, where *a* and *c* have absolute anodic current, but *b* and *d* have absolute cathodic current. Therefore, to calculate DOS, the summation of anodic charges in *a* and *c* regions was considered. As was reported previously, DL-EPR is also a fast technique in comparison with other techniques [1,5,9–11]. It is expected that by decreasing the sensitisation time, the DL-EPR technique might reveal a lower DOS value which is similar to the results obtained by optical observation. However, measuring the lowest possible and reliable DOS value requires improvement in the values of the parameters that affected DL-EPR under standard conditions. This has been a great motivation for researchers for decades [1–2,4–8,10,12–15]. Particularly, DOS measurement at low sensitisation times and also in alloys with higher resistance to the sensitisation such as 316L and DSS 2205 is still a scientific and an industrial challenge. The following section describes Taguchi method as a statistical tool to tune DOS value measurement by regulating the affected parameters.

### 3.3. Taguchi results

Table 3 shows the DOS values and *S/N* ratios calculated for each experiment using Eq. (2). To compare the influence of the factors on the DOS the average *S/N* ratio of each level of each factor is summarised and shown in Fig. 3. A higher average *S/N* ratio for a level means that level has greater effect on the DOS measurement. Moreover, a large difference between the average *S/N* ratios of all levels of a certain factor means that the factor has a larger effect on the DOS measurement. The average *S/N* ratio of each level for each factor is the mean value of *S/N* ratios for all the experiments with the same level of that factor. For example, if factor “scan rate” is considered the average *S/N* ratio for level 2 of this factor is the average of *S/N* ratios of experiment numbers 2, 8, 11 and 13 in the OA. According to the above description, it is seen that H<sub>2</sub>SO<sub>4</sub> concentration has the most significant influence on the DOS value. A negligible difference between 0.05 and 0.1 M concentration of

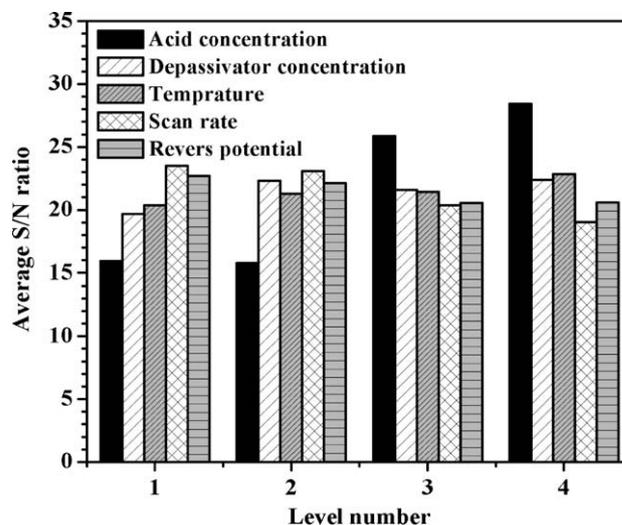


Fig. 3. Average *S/N* ratio for each factor in all levels, obtained from 60 min sensitised specimen at 650 °C.

H<sub>2</sub>SO<sub>4</sub> could be observed, but by increasing H<sub>2</sub>SO<sub>4</sub> concentration from 0.1 to 1.0, the average *S/N* ratio increases from 15.76 to 28.43 and, resolution of the DOS measurement increases consequently. This indicates that the most important factor in the DOS measurement is the acid concentration, since it yields a higher average *S/N* ratio in comparison to the other factors.

In addition, scan rate and KSCN concentration have significant effects on the DOS measurement, however less than the acid concentration. By increasing the scan rate, resolution of the DOS measurement decreases; i.e. increasing scan rate from 30 to 120 mV/min decreases *S/N* ratios from 23.48 to 19.03. Generally, lower scan rates in potentiodynamic polarisation measurements leads to more stable condition, and therefore in the reactivation stage, passivity breakdown occurs easily at the vicinity of grain boundaries which in turn leads to higher DOS values. This has been illustrated by the other authors, too [4].

The influence of KSCN concentration as a depassivator agent is less than the two factors “scan rate” and “acid concentration”. This can be explained by the fact that the effect of KSCN is compensated during the calculation of the reactivation-activation charge ratio. The main role of depassivator in DOS measurement is to accelerate passivity breakdown particularly in chromium depleted regions in the reactivation state [5,9]. KSCN acts as a strong depassivator and by increasing the concentration of KSCN, both critical current density and passivation potential increase. This is shown in Fig. 4, where polarisation curves are presented for a SS304 specimen in a similar condition with two different concentrations of KSCN (0.02 and 0.1 M). Clearly, by increasing the concentration of KSCN, both the critical current density and the passivation potential increase. For instance, the specimen polarised in 0.02 M KSCN shows a passivity potential of 100 mV where as the sample polarised in 0.1 M KSCN was not passive even up to the 350 mV. However, it has been reported that at very high concentrations, KSCN acts as an inhibitor [15]. From Fig. 3, it can be seen that lower concentrations of depassivator corresponds to lower *S/N* ratios. This allocates that there is a low sensitivity of DL-EPR method at low concentrations of depassivator. By increasing the KSCN concentration from 0.001 to 0.005, the *S/N* ratio increases from 19.66 to 22.33 and remains almost unchanged up to 0.02 M KSCN concentration. A slight decrease in the average *S/N* ratio is observed at 0.01 M which is the concentration of KSCN in the standard solution [11].

By increasing the temperature from 25 to 40 °C, the average *S/N* ratio increases but the difference between the average *S/N* ratios of

Table 3

The DOS value and *S/N* ratio calculated for each experiment applied to 60 min sensitised specimen at 650 °C.

Experiment no.	% DOS	<i>S/N</i> ratio
1	6.417	16.14664
2	8.684	18.7744
3	4.959	13.90788
4	5.519	14.83721
5	3.853	11.71598
6	4.013	12.06938
7	9.831	19.85195
8	9.346	19.41252
9	12.807	22.14895
10	25.53	28.14102
11	18.853	25.50761
12	24.031	27.61544
13	27.062	28.6472
14	32.845	30.32939
15	22.548	27.06216
16	24.277	27.7039

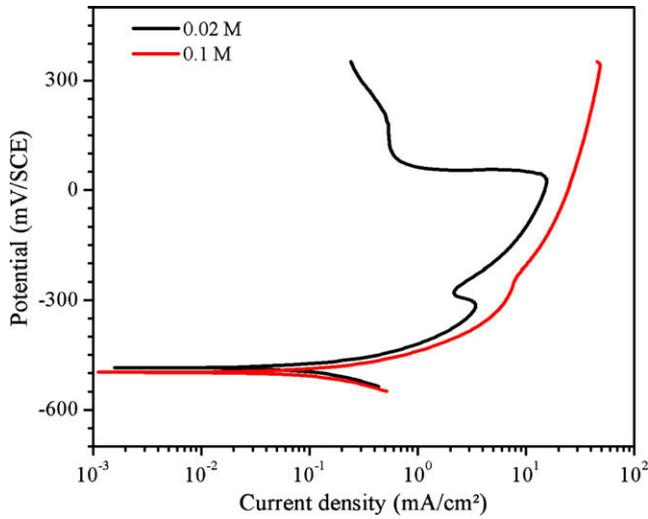


Fig. 4. Polarisation curves for SS304 in a similar condition to 0.02 M and 0.1 M KSCN concentration.

the levels is low and therefore the effect of temperature is negligible in comparison with the other factors. As was expected, by increasing the reverse potential from 200 to 300 mV, the resolution of the DOS measurement decreased. However, a slight increase in the average *S/N* ratio can be observed in the reverse potential of 350 mV. Similar to temperature, the effect of reverse potential is also negligible but its effect is greater than that of temperature. It can be seen from Fig. 3 that the optimum condition for DOS measurement would be 1.0 M H<sub>2</sub>SO<sub>4</sub>, 0.02 M KSCN, 30 mV/min scan rate, temperature of 40 °C and reverse potential of 200 mV. All the specimens with sensitisation heat treatments were examined under this optimum condition and results were compared with the standard procedure.

### 3.4. Analysis of variance (ANOVA)

The purpose of the ANOVA is to investigate which parameters of the process significantly affect the DOS value. Details of ANOVA can be found in the literature [16]. But in brief, the analysis can be accomplished by separating the total variability of the *S/N* ratios, which is measured by the sum of the squared deviations (*SS*) from the total mean of the *S/N* ratio, (*S<sub>m</sub>*), into contributions by each process parameter and the error. Equations for calculating the variance of DOS measurement are presented in this section [16,20]:

$$S_m = \frac{\left(\sum_{i=1}^N S/N_i\right)^2}{n} \quad (3)$$

where *S<sub>m</sub>* is the correction factor and *n* is the number of experiments in the orthogonal array which is 16 in this research.

$$SS_i = \frac{\sum_{j=1}^L \left(\frac{n}{L} m_{ij}\right)^2}{L} - S_m \quad (4)$$

*SS<sub>i</sub>* is the sum of squares of factor *i*; *m<sub>ij</sub>* is the average of *S/N* ratios of factor *i* in level *j* and *L* is the number of levels for each factor which is 4 in this research.

$$S_T = \sum_{i=1}^N (S/N_i)^2 - S_m \quad (5)$$

*S<sub>T</sub>* is the total sum of squares.

$$MS_i = \frac{SS_i}{DF_i} \quad (6)$$

*MS<sub>i</sub>* is the mean sum of squares for factor *i* and *DF<sub>i</sub>* is the degree of freedom of factor *i* and that is number of levels of factor *i* minus 1.

$$SS_e = S_T - \sum SS_i \quad (7)$$

*SS<sub>e</sub>* is the sum of squares of the error.

$$MS_e = \frac{SS_e}{DF_e} \quad (8)$$

*MS<sub>e</sub>* is the mean sum of squares of the error where *DF<sub>e</sub>* is the degree of freedom of the error and is calculated as:

$$DF_e = n - 1 - \sum DF_i \quad (9)$$

$$F_i = \frac{MS_i}{MS_e} \quad (10)$$

*F<sub>i</sub>* is the variance ratio for factor *i*

$$\rho (\%) = \frac{SS_i - DF_i(MS_e)}{S_T} \times 100 \quad (11)$$

where, *ρ* (%) is the percent of contribution of factor *i*. Calculated values of *SS<sub>i</sub>* for temperature and reverse potential are 12.9 and 13.99, respectively. According to Table 4, this indicates a very minor effect of these two parameters in comparison with the values of the other factors. Since 16 experiments were conducted and also 5 factors each having 4 levels were considered, the *DF<sub>e</sub>* in this experiment is zero and ANOVA analysis cannot be performed because in Eq. (8), *MS<sub>e</sub>* cannot be obtained and therefore it is not possible to calculate other parameters. In other words, in Taguchi data analysis, *DF<sub>e</sub>* must be higher than zero [16,20]. To resolve this problem, the factors that have the lowest *SS* can be ignored. Here, the *SS* of temperature and reverse potential in comparison with other factors are very low and hence, these two factors can be ignored. Therefore, temperature and reverse potential are ignored and the sum of their degrees of freedom has been added to *DF<sub>e</sub>*. By ignoring these two factors and based on Eq. (9), *DF<sub>e</sub>* will equal 6 (see Table 4). Table 4 shows the percent of contribution of each factor. As discussed above, the main factor in the DOS measurement is the acid concentration which has a contribution percent of 81.61%. Its effect is about 12.2 times higher than that of scan rate. After acid concentration, scan rate and KSCN concentration have 6.69% and 1% contribution on the DOS measurement, respectively. Noticeably, the contribution of error has been raised up to 10.74%, since the influence of temperature and reverse potential have been added to it as described above.

### 3.5. Prediction

It is also possible to predict the optimum condition by the results obtained through Taguchi's method. The predicted *S/N* ratio (*S/N<sub>p</sub>*) can be calculated by the following equation [16,17]:

$$S/N_p = S/N_m + \sum (S/N_i - S/N_m) \quad (12)$$

where, *S/N<sub>m</sub>* is the overall average of all the *S/N* ratios in the OA and *S/N<sub>i</sub>* is the signal to noise ratio at the optimum level for each factor.

Table 4  
ANOVA results for factors.

	DF	SS	MS	F	ρ (%)
[H <sub>2</sub> SO <sub>4</sub> ]	3	524.59379	174.8646	38.99274	81.61178
[KSCN]	3	19.430053	6.476684	1.444224	0.954233
Scan rate	3	55.375743	18.45858	4.116046	6.693543
Error	6	26.9072	4.484542	—	10.74044

In this experiment,  $S/N_m$  is 21.49, therefore, the predicted  $S/N$  ratio is 31.33 ( $S/N_p = 21.49 + (33.09 - 21.49) + (26.72 - 21.49) + (26.35 - 21.49)$ ). By reversing Eq. (2), the DOS value of 36.87% ( $y_i$ ) can be predicted. Comparing the predicted DOS value (36.87%) with the standard value (18%) reveals a 100% improvement in resolution. The predicted value can be verified by running an experiment with the new optimum condition, i.e. 1.0 M  $H_2SO_4$ , 0.02 M KSCN, 30 mV/min scan rate, temperature of 40 °C and reverse potential of 200 mV vs. SCE, as shown in Fig. 5. In comparison with the standard condition, both the activation and reactivation charge densities increased and the alloy did not experience an integrated passivity (Fig. 2 and Fig. 5). Moreover, the complicated behaviour with three corrosion potentials in the reactivation stage was replaced by a simple appearance. This makes the calculation of Q-ratio more straightforward. Considering the consumed charge density, an experimental DOS value of 48.04% can be measured from the optimum new condition for the 60 min sensitised specimen. This is appreciably higher than the estimated DOS value by the Taguchi method, 36.87%. However, comparing the  $S/N$  ratio is more essential and by using Eq. (2), a  $S/N$  ratio of 33.63 can be calculated for this experimental condition. This is analogous with the predicted value, 31.33, with an error of 6.83% which is less than the maximum acceptable error predicted by Taguchi method, i.e. 10.74%. This means that Taguchi method was performed appropriately and the obtained results are reliable.

Obtaining a higher DOS resolution under the new optimum condition can be explained by the intrinsic characteristics of this new condition. The new condition is more aggressive due to its higher acid and depassivator concentrations at higher temperature. Running the DL-EPR test at a lower sweep rate increases the stability which in turn, leads to more facile passivity breakdown at defective regions during the reactivation stage.

DL-EPR test was performed under the new optimum condition and extended to all the other heat treatment conditions. The results were compared with the standard procedure.

### 3.6. Comparing new optimum and standard conditions

Fig. 6 shows the results of DOS under standard and new optimum conditions applied on non-sensitised and sensitised SS304 specimens for 10, 60 and 300 min at 650 °C. It is clear that in all heat treatment procedures, the new optimum condition provides higher resolution than the standard one. Although the results of Fig. 6 are presented based on Q-ratio, calculated results from cur-

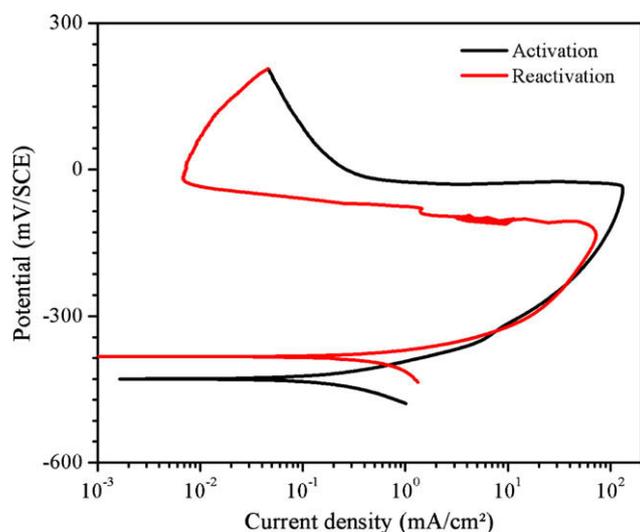


Fig. 5. DL-EPR result on SS304 in standard conditions; 1 M  $H_2SO_4$  + 0.02 M KSCN, 40 °C, 30 mV/min scan rate on candidate SS304 alloy sensitised for 60 min at 650 °C.

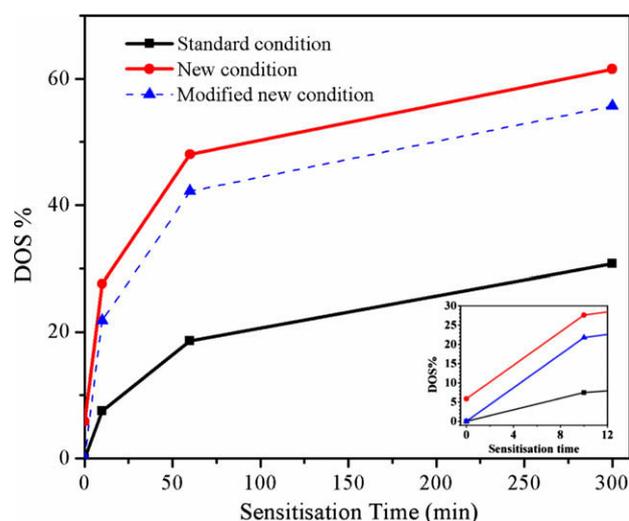
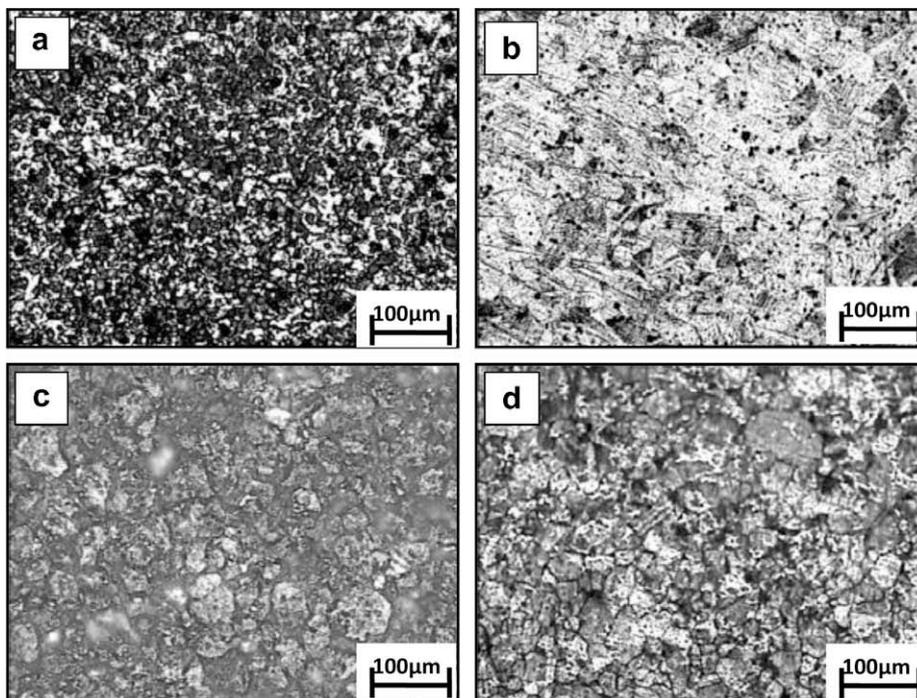


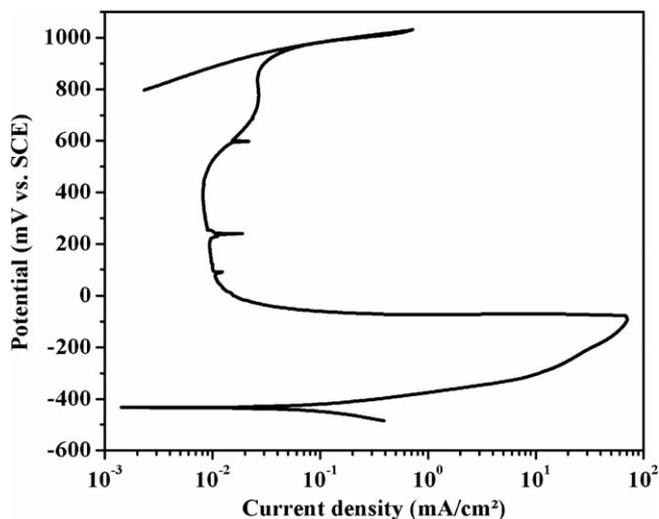
Fig. 6. Compare the results of DOS in standard, new conditions and modified new condition by using charge ratio criterion. The inserted graph highlights the results in the first few minutes.

rent ratio criterion shows similar trend; Eq.(1), which is not presented here. For example, a specimen which is sensitised for 60 min has DOS of 48% and 18% (charge ratio criterion) under the new optimum condition and standard one, respectively. This represents about 167% improvement in DOS resolution by tuning the standard condition. As can be seen from Fig. 6, what is more interesting is that the new optimum condition is more responsive to the lower sensitisation times. While under the standard condition, a DOS value of about 0.02% in the non-sensitised specimen was calculated, under the new optimum condition, a DOS value of 5.86% could be determined. This is due to the fact that, under the new optimum condition, an integrated passivity does not take place. Therefore, even in the non-sensitised specimen, the significant passivity breakdown in the Cr-rich surface layer could be detected (see Fig. 7). Since this situation exists in all the specimens, all data points under the new optimum condition can be modified by subtracting the value of 5.84 from the obtained data which is shown as the modified line in Fig. 6. Even though, these modified DOS values under the new optimum condition are higher than the standard condition as shown in Fig. 6. For example, a DOS value of 42.2% can be reported for the 60 min sensitised specimen which is remarkably higher than the standard condition which has 18% DOS.

To assess the types of corrosion under both new optimum and standard conditions, after DL-EPR test, the surface of the specimens were analysed by optical microscopy. As an example, the microstructures of as-received and 300 min sensitised specimens are shown in Fig. 7. Under the new optimum condition, corrosion of some grains as well as grain boundary corrosion in the sensitised specimen (Fig. 7(c)) was observed. On the other hand, Fig. 7(a) shows that under the new optimum condition, uniform corrosion also appeared in the as-received specimen. This means that corrosion of the grains appears in both sensitised and non-sensitised samples. Consequently, any difference in DOS of sensitised and non-sensitised samples under the new optimum condition can be attributed to grain boundary chromium depletion. In addition to this, after the tests, some pits in the microstructure can be observed. Usually, the presence of aggressive ions such as  $Cl^-$  is necessary for pitting corrosion to occur [22] and under both standard and new optimum conditions this aggressive ion is not present. Therefore, pitting corrosion most likely does not occur which can be proved by anodic polarisation of the specimens in the new solution (Fig. 8). The observed cavities under both standard and new



**Fig. 7.** Microstructure of SS304 after DL-EPR test (a) non-sensitised specimen in new condition, (b) non-sensitised specimen in standard condition, (c) 300 min sensitised specimen in new condition, and (d) 300 min sensitised specimen in standard condition (100 $\times$ ).



**Fig. 8.** Potentiodynamic polarisation of SS304 in new proposed solution.

optimum conditions were pit shaped. These pits probably formed due to the dissolution of imperfections (inclusions). Fig. 9 confirms that the observed pits in the microstructure of the specimens after DL-EPR test formed during activation process (the image has been taken right after activation current peak shown in Fig. 9(a) prior to reactivation stage). The inclusions can be categorised into two groups: (1) inclusions formed during the production process. Dissolution of these inclusions is almost equal in the sensitised and non-sensitised specimens and (2) the inclusions formed due to the sensitisation process. As a result, if the higher value of DOS under the new optimum condition is due to the dissolution of those inclusions, it is due to the sensitisation process, too. On the other hand, the microstructural analysis after the corrosion test (Fig. 7) and the microstructure of the activation state (Fig. 9) prove this idea that the new optimum condition has higher resolution of

detection of DOS in the SS304 specimen. As can be seen from Fig. 7(a–d), the non-sensitised specimen did not show any IGC after DL-EPR test under both the standard and new optimum conditions. On the other hand, the 300 min sensitised specimen showed IGC attack, but under the new optimum condition this attack is greatly higher than the standard condition. In other words, the reason for higher obtained DOS values was due to higher amount of IGC attack. Therefore, the higher value of DOS under the new optimum condition was not due to the pitting and/or uniform corrosion.

The higher resolution of this new optimum condition is assuring to be employed for stainless steels such as 316L, 2205DSS, etc. which have higher IGC resistance. These topics are under investigation.

#### 4. Conclusion

The optimal condition for DOS measurement based on Double-loop EPR technique in H<sub>2</sub>SO<sub>4</sub> containing KSCN solution was obtained using the Taguchi method. The results can be summarised as follows:

(1) The new optimum condition for DOS measurement is 1 M H<sub>2</sub>SO<sub>4</sub>, 0.02 M KSCN, 40 °C, 30 mV/min scan rate and reverse potential from 200 mV. The new optimum condition provided significantly higher IGC detection, improving DOS resolution.

(2) ANOVA results showed that the main factor affecting DOS measurement is the acid concentration with about 82% of contribution. However, the influences of scan rate and depassivator concentration are also significant. The effects of temperature and reverse potential are negligible.

(3) A DOS value of 42.2% could be reported for the specimen sensitised for 60 min which was remarkably higher than the standard condition with DOS value of 18%.

(4) By tuning, the new optimum condition gives significantly higher resolution than the standard solution in particular at low sensitisation times less than 10 min.

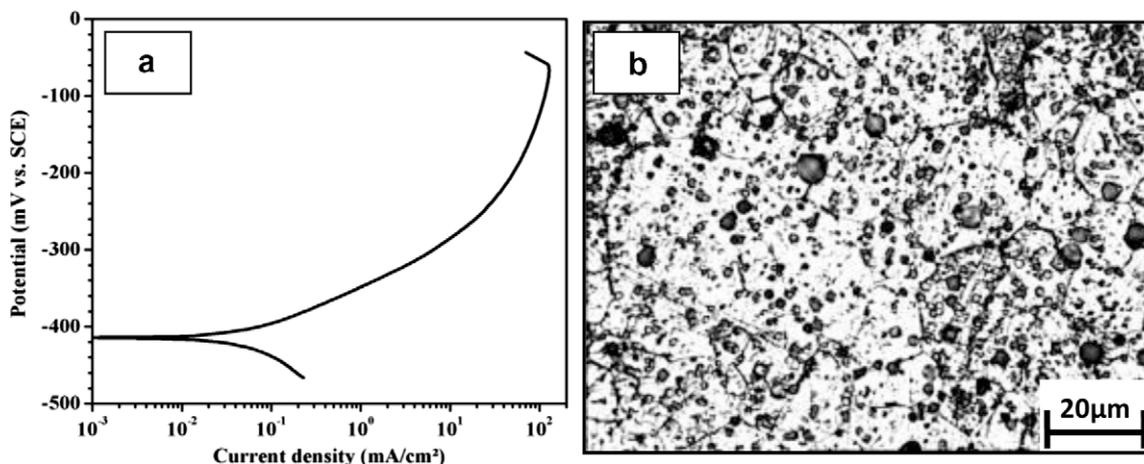


Fig. 9. (a) Potentiodynamic polarisation of 300 min sensitised SS304 and (b) microstructure of specimen right after activation current peak prior to reactivation stage (500 $\times$ ).

(5) Microstructural analysis of the surface after DL-EPR test in both optimum and standard conditions revealed that higher DOS value in the new optimum condition is due to an increase in IGC detection, although in the new optimum condition uniform corrosion is considerably higher than the standard condition.

#### Acknowledgments

Authors appreciate the financial support from Ferdowsi University of Mashhad provision of laboratory facilities during the period that this research was conducted and A. Kamyabi Gol for his valuable assistance on ANOVA.

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