Experimental Procedures and Diagnostics of Sensitization by DL-EPR

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Introduction

There is great industrial interest in developing non-destructive tests for the detection of deleterious phases in stainless steels. In this context, the Electrochemical Potentiodynamic Reactivation [EPR] technique, described by the standard ISO 12732, can be used as a tool for quantitative analysis of the degree of sensitization [DOS] of austenitic stainless steels[1]. The influence of the experimental parameters on the results is an important limitation for practical use of the technique[2, 3, 4]. This study performs a critical analysis of the standard usefulness, mainly evaluating the influence of potential scan rate and concentration of potassium thiocyanate [KSCN] in the test solution. Actually, the EPR method can be sensitive to the DOS of the studied material. However, the classification given by ISO 12732 can lead to errors whether standard curves previously established for the steel are not considered.

Experimental

1) **Material -** Austenitic stainless steel, AISI 304, with a composition of (mass %): 0.073 C, 1.120 Mn, 17.710 Cr, 0.041 Mo, 8.170 Ni, 0.025 Nb, 0.001 Ti, and bal. Fe, was tested in solution-annealed and heat-treated conditions. The material was solution-annealed at 1100 ºC/1h and the heat treatments were performed at 650 ºC by 1, 6, 18 and 24 hours in order to obtain different DOS.
2) **EPR Test**
   The EPR measurements were carried out according to ISO 12732[5] and ASTM G108[6] standards. The testing conditions were:

- Minimum and maximum scan rate specified by ISO 12732: 0.56 and 4.2 mV/s;
- Minimum and maximum concentrations of KSCN specified by ISO 12732: (0.5 mol/L H_2SO_4 + 0.001 mol/L KSCN) and (0.5 mol/L H_2SO_4 + 0.05 mol/L KSCN).
- Scan rate of 1.67 mV/s and solution 0.5 mol/L H_2SO_4 + 0.01 mol/L KSCN as specified by ASTMG108.

The tests were conducted in conventional three electrodes cell, using the AISI 304 steel as working electrode. The apparatus consisted of an AUTOLAB PGSTAT 302N station, platinum gauze as counter electrode and a saturated calomel electrode [SCE] used as reference. The working electrodes were embedded in epoxy resin and ground until 600 mesh paper. The open circuit potentials were obtained during 15 minutes before the test start. After graphics plotting, the ratio between reactivation (I_r) and activation (I_a) currents were calculated as well as the ratio between reactivation (Q_r) and activation (Q_a) charges.

3) **Material Characterization**
   Metallographic characterization of DOS was done according to ASTM E407[7] standard, method 31c and ASTM A262-02a[8] standard.

Results and Discussion

1) **Material Characterization**
   The DOS of the samples for each heat treatment are presented in Table 1.

Table 1: DOS of the samples according to ASTM E407, method 31c.

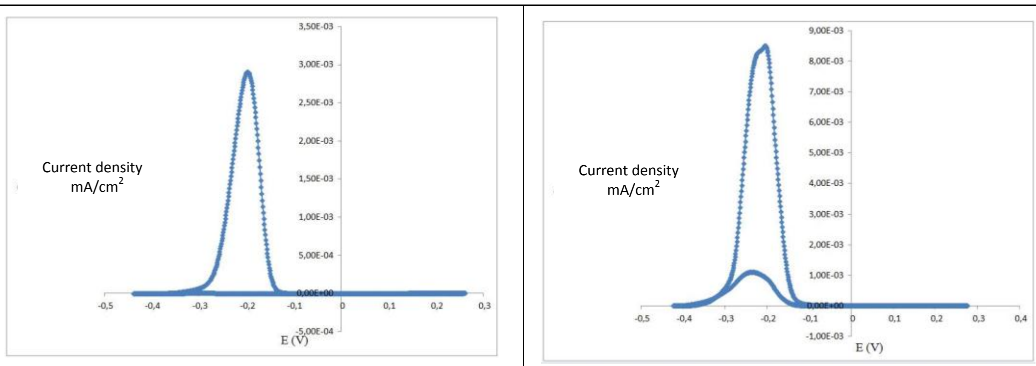
Heat Treatment	1.100°C/1h	650°C/1h	651°C/6h	652°C/18h	653°C/24h
DOS (%)	0	1	3	7	8

Solution-annealed and 650ºC/1h heat treated samples presented grain boundaries without chromium carbides. The grain boundaries of 650ºC/6h heat treated samples were partially covered by carbides and for 650ºC/18h and 650ºC/24h samples, the grain boundaries were totally covered by chromium carbides.

2) EPR

Figure 2 presents the EPR plots obtained to solution-annealed and heat treated at 650ºC/24h conditions. It was used the minimum scan rate (0.56mV/s) and minimum concentration of KSCN (0.001mol/L) in this test. It was observed the appearance of a reactivation peak and highest current densities to the heat treated condition compared to solution annealed one.

0.56 mV/s and 0.001 mol/L KSCN



(a) (b)

Figure 2: DL-EPR graphics for solution annealed (a)
and heat treated at 650°C/24h (b) conditions

It was verified that an increase of scan rate from 0.56 mV/s to 4.2 mV/s decreases both I_r/I_a and Q_r/Q_a ratios. Table 2 presents the results obtained to all conditions proposed herein, including an intermediate condition suggested by ASTM G108, specifically to AISI 304 steel.

Table 2: Classification of the samples evaluated.

Condition / Heat Treatment	0.001 mol/L KSCN	0.05 mol/L KSCN	0.01 mol/L KSCN	0.001 mol/L KSCN	0.05 mol/L KSCN
	0.56 mV/s	**0.56 mV/s**	**1.67 mV/s**	**4.2 mV/s**	**4.2 mV/s**
1100 °C/1 h	non sensitized	non sensitized	non sensitized	non sensitized	non sensitized
650 °C/1h	non sensitized	partially sensitized	non sensitized	non sensitized	non sensitized
650 °C/6h	partially sensitized	sensitized	partially sensitized	non sensitized	partially sensitized
650 °C/18h	sensitized	sensitized	sensitized	partially sensitized	sensitized
650 °C/24h	sensitized	sensitized	sensitized	sensitized	sensitized

According to this table, changing the KSCN concentration or the scan rate, different kinds of classification can be verified to some heat treated conditions. For example, samples treated with 650°C/6h were classified as "partially sensitized", "sensitized" or "non sensitized". The most sensitive testing parameters suggested by data on Table 2 were afforded by the higher [KSCN] and lower scan rate.

A more realistic proposal to use the I_r/I_a or Q_r/Q_a ratios to quantify DOS in a steel should include standard curves previously obtained for a established reliability and reproducibility. These curves should be obtained in lab for controlled conditions and serve as reference for interpolation of in-plant data for the same kind of steel. Another important aspect to be considered is the frontier of DOS which defines approval or condemnation of the material for specific technological applications.

Figure 3 presents a fitted curve obtained with 0.56 mV/s and 0.05 mol/L KSCN. It is clearly possible to distinguish small DOS via I_r/I_a, which would be more realistic in industrial practice.

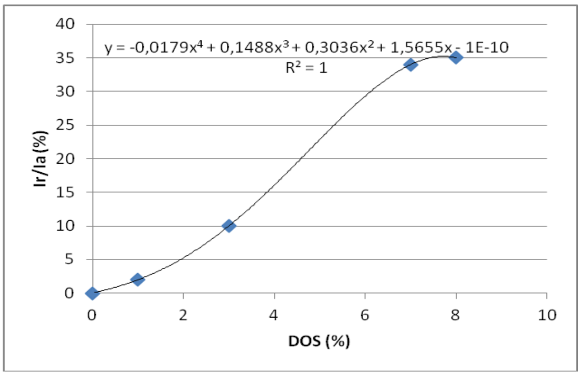


Figure 3: Fitted curve to the condition 0.56 mV/s and 0.05 mol/L of KSCN

Conclusions

The DL-EPR method is sensitive to the DOS of AISI 304 austenitic steel. However, its use based on the values of I_r/I_a suggested by ISO 12732 cannot be reliable unless considering the experimental parameters employed. As shown, the classification of materials with different DOS depends greatly on these conditions. The evaluation of the potential scan rate influence showed that slower scan rates can distinguish better small differences in DOS of 304 steel. Increasing the concentration of KSCN also enhances the sensitivity of the technique. The results indicate the need of an experimental protocol including standard curves previously established in lab. Another point to be considered is the DOS limit which determines acceptance of the material for a specific technological application.

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