



## DEIS evaluation of the relative effective surface area of AISI 304 stainless steel dissolution process in conditions of intergranular corrosion

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### ABSTRACT

The results presented in this paper contribute further information concerning examinations of AISI 304 stainless steel dissolution process in conditions of proceeding intergranular corrosion (IG) which have been determined on the basis of dynamic electrochemical impedance spectroscopy (DEIS) measurements. For the first time changes of the relative effective surface area versus time of AISI 304 stainless steel dissolution process in conditions of proceeding intergranular corrosion (IG) in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M KSCN solution within the range of reactivation polarization scan have been demonstrated. The assessment of the effective surface area of the investigated process was based on approximation to theory of iron dissolution in sulfuric acid medium according to the shape of instantaneous impedance spectra recorded by means of DEIS technique. As a result, it was possible to evaluate that initially changes of the employed equivalent circuit parameters are not only caused by the changes of the relative effective surface area but also by the changes of the AISI 304 SS dissolution process kinetics. Further progress of the examined process implied that changes of the equivalent circuit parameters are only affected by the changes of the relative effective surface area during proceeding IG. Moreover, it was found that the character of changes of the relative effective surface area in conditions of proceeding IG can be described by exponential function.

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### 1. Introduction

Austenitic stainless steels (containing 18% chromium–8% nickel) are widely used engineering materials in many branches of industry due to their good mechanical properties and corrosion resistance at elevated temperatures. Nevertheless, the precipitation of intermetallic compounds at grain boundaries affects this resistance [1–3]. Exposure to a high-temperature range of 500–800 °C, during welding or service, leads to precipitation of chromium rich carbides (type Cr<sub>23</sub>C<sub>6</sub>) or sigma phase (Fe–Cr–Mo) at grain boundaries and formation of chromium depletion regions adjacent to these carbides. Stainless steels with chromium depleted regions at grain boundaries having chromium less than 12–13 wt.% are known to have undergone sensitization [1–5].

Intergranular corrosion of austenitic stainless steels has been explained by the chromium depletion theory [6,7]. It has been shown that the extent of chromium-depleted zones at grain boundaries is a direct indication of the material's susceptibility to IG process, and in the presence of residual stresses and strain to IGSCC as well in the final stage [8].

According to the ASTM standard, metallographic etching and weight-loss tests are regularly performed to assess degree of sensitization (DOS) of austenitic stainless steels (SS) [7–15]. These evaluation techniques suffer from either a long testing period or requirement of a large amount of etchant. Since anodic dissolution of austenitic SS in an electrolyte is an electrochemical process, electrochemical methods should be able to estimate DOS of austenitic stainless steels. Many electrochemical methods were proposed to determine DOS of stainless steels in the literature [16,17]. Among these methods, anodic polarization tests [18] were the most commonly used approaches.

A search for a rapid, quantitative and non-destructive test method, lead many researchers to develop double-loop electrochemical potentiokinetic reactivation (DL-EPR) tests [2,3,19–25]. The DL-EPR technique has especially found the application for detecting DOS of AISI 304 stainless steels. However, it is worth to emphasize certain disadvantages of this method. Among the most important are high-amplitude perturbation signal, determination of DOS only, and finally lack of information related to the mechanism and rate of IG.

Classical electrochemical impedance spectroscopy (EIS) also provides information concerning the IG, but only before and after the corrosion process, when investigated system is in the stable state. Therefore, EIS cannot provide detailed characteristic of proceeding corrosion processes. Nevertheless, AC impedance for the

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evaluation of DOS has not been reported yet. The more important is the fact that any information concerning the impedance assessment of the effective surface area of AISI 304 stainless steel dissolution process during the proceeding intergranular corrosion cannot be found in the literature sources.

Such possibility can be achieved by using dynamic electrochemical impedance spectroscopy (DEIS) due to its joint time-frequency procedure [26–30]. DEIS allows the investigation of corrosion process progressing in time what results in determination of very detailed characteristic of the examined system. So far DEIS was successfully applied to examination of pitting corrosion [31–33], organic coatings [34], passive layer cracking process on austenitic stainless steels and aluminum alloys [35–39], and to investigate the mechanism and kinetics of pickling of high-temperature oxidized 304 SS in HF–H<sub>2</sub>SO<sub>4</sub> [40]. Recently, this measurement technique was successfully applied to the evaluation of AISI 304 stainless steel dissolution process in conditions of intergranular corrosion [41].

The object of this paper is to assess effective surface area of AISI 304 stainless steel dissolution process in conditions of intergranular corrosion based on approximation to theory of iron dissolution in sulfuric acid medium.

## 2. Experimental

Chemical composition of austenitic stainless steel used in the researches is given in Table 1. Examined specimens were prepared according to instructions provided by the ASTM G108-94 standard [42]: they were wet grinded with the use of abrasive paper (SiC) of increasing fineness (240, 400, 600 and 1000), washed and dried in a stream of hot air; then polished in MgO suspension, washed with distilled water, degreased, washed with ethanol and finally dried once again. Afterwards, specimens were sensitized at 675 °C for 36 h. Corrosion potential of the sensitized specimens in the examined electrolyte solution was about  $E_{\text{CORR}} = -0.900 \text{ V}_{\text{Hg, Hg}_2\text{SO}_4 | \text{H}_2\text{SO}_4}$ . Non-sensitized (reference) specimens were also examined in order to make adequate comparison. The corrosion potentials of non-sensitized and sensitized specimens were the same. 30 specimens of each type were investigated. In the case of all examined specimens the exposed area was equal to 0.5 cm<sup>2</sup>.

DEIS measurements were performed in a three-electrode cell, in which mercury/mercury sulphate [Hg, Hg<sub>2</sub>SO<sub>4</sub>|H<sub>2</sub>SO<sub>4</sub> (0.5 mol/dm<sup>3</sup>)] electrode was used as a reference electrode and the auxiliary electrode was made of platinum net. The employed reference electrode is not in accordance with the ASTM G 108-94 standard where saturated calomel electrode with controlled leakage rate was recommended. However, to avoid a risk of pitting corrosion due to the presence of chloride ions, which might be transported to the solution from the electrolytic bridge filled with potassium chloride, it was decided to use the reference electrode with electrolytic bridge filled with sulphuric acid of the same concentration as the one used in the investigated electrolyte solution. The experiments were realized in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M KSCN solution.

**Table 1**  
Normalized chemical composition of the investigated AISI 304 SS (averaged values)

C	≤0.08%
Mn	≤2.0%
Si	≤1.0%
P	≤0.045%
S	≤0.03%
Cr	18–20%
Ni	8–10.5%
Fe	Balance

DEIS measurements were carried out “on-line” while the samples were polarized in agreement with the measurement procedure presented in the ASTM G108-94 standard [42] to guarantee conditions equivalent with the DL-EPR tests performed on AISI 304 stainless steel: temperature of electrolyte was of  $30 \pm 1$  °C; the polarization was from  $E_{\text{CORR}} = -0.900 \text{ V}$  to  $E = -0.200 \text{ V}$  (maintained for 2 min in the passive state), activation scan; and back to corrosion potential  $E_{\text{CORR}} = -0.900 \text{ V}$ , reactivation scan. However, to estimate the effective surface area of proceeding AISI 304 SS dissolution process in conditions of intergranular corrosion it was demanded to perform DEIS measurements as a function of time for different potential values within the reactivation range. Therefore, during the reactivation scan the polarization was maintained for about 10 min at two different potentials:  $E = -0.675 \text{ V}$  and  $E = -0.700 \text{ V}$ , at which the investigated process was activation controlled. For potentials other than those examined there was no active state with activation control, the grain boundaries were passivated and the system was changing too rapidly. In this case higher frequencies would be demanded to reflect dynamics of such a fast process.

A complete time register in DEIS measurement can be described by the following equation:

$$T = N \Delta t \quad (1)$$

where  $N$  is the number of instantaneous impedance spectra,  $\Delta t$  is the length of the analyzing window. One can assume that within  $\Delta t$  the investigated system is in quasi-stationary state, whereas in the classical EIS in the entire register time  $T$  the system is assumed to be in the quasi-stationary state. In our calculation  $T = 600 \text{ s}$  and  $\Delta t = 0.44 \text{ s}$ , thus, at each investigated reactivation potential one can obtain 1364 instantaneous impedance spectra. However, presentation of such a number of spectra would be very difficult. Therefore, the paper contains only exemplary spectra, which have been additionally extracted from the registered DEIS spectrograms.

The measurement set-up consisted of a high-frequency potentiostat; a National Instruments PCI 6120 card generating the perturbation signal, and registering voltage perturbation and current response signals. Impedance measurements were executed for the frequency range 20 kHz–7 Hz. Average number of points per decade in the DEIS measurements was 5.

Sampling frequency of 100 kHz resulted from the measurement card settings being at our disposal. Proper selection of the sampling frequency in the DEIS measurements enables to reflect the highest measurement frequencies with very good precision. In the investigations the multi-sinusoidal perturbation signal composed of 20 sinusoids was utilized. Diversified amplitudes of the perturbation signal (a set of 20 sinusoids) ranging from 5 mV to 28 mV were applied in order to make it possible measuring of DC current by means of only one resistor with acceptable accuracy both for low and high frequencies. In the case of low frequencies higher amplitudes of the perturbation signal were applied, as opposed to the high frequency range in which lower amplitudes were selected.

Backgrounds and more detailed description of the DEIS technique can be found in papers written by Darowicki and co-workers [26–29].

## 3. Results and discussion

Dependencies between DC current and potential, both in the activation and reactivation range, were obtained on the basis of proper filtering procedure, which is strictly connected with the DEIS technique [26–29]. As it is presented in Eq. (2) both voltage perturbation and current response signals are composed of a DC term and the other one used for impedance characterization

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