

DEIS assessment of AISI 304 stainless steel dissolution process in conditions of intergranular corrosion

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Abstract

Results presented in this paper are first that demonstrate instantaneous impedance changes versus reactivation potential detected by means of dynamic electrochemical impedance spectroscopy (DEIS) technique for AISI 304 stainless steel dissolution process proceeding during intergranular corrosion (IG) in 0.5 M SO_4^{2-} + 0.01 M KSCN solution of different pHs. Application of DEIS method made it possible to evaluate dynamic changes of the examined system's impedance in conditions of IG. As a result, controlling stage of the overall rate of AISI 304 SS dissolution process was determined. Moreover, the paper proposes an alternative way of assessment of AISI 304 SS dissolution rate during intergranular corrosion based on approximation to theory of iron dissolution in sulfuric acid medium. Simultaneously, on the basis of the DEIS measurements it was possible to obtain information about the degree of sensitization (DOS) of the examined material. Accordingly, performed researches revealed the advantage of the DEIS technique over the electrochemical potentiokinetic reactivation (EPR) tests when investigating intergranular corrosion process.

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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]. Exposure to a high-temperature range of 500–800 °C, during welding or service, leads to precipitation of chromium-rich carbides (type Cr_{23}C_6) 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 [1–3].

Intergranular corrosion of austenitic stainless steels has been explained by the chromium depletion theory [4,5]. 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 [6].

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) [7–11]. 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 [12–13]. Among these methods, anodic polarization tests [14] were the most commonly used approaches. Nevertheless, ac impedance for the evaluation of DOS has not been reported yet.

A search for a rapid, quantitative and non-destructive test method, lead many researchers to develop double-loop electrochemical potentiokinetic reactivation (DL-EPR) tests [15–20]. 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

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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. Such possibility can be achieved by using dynamic electrochemical impedance spectroscopy (DEIS) due to its joint time–frequency procedure [21–25]. 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 [26–28], organic coatings [29], passive layer cracking process on austenitic stainless steels and aluminum alloys [30–34], and to investigate the mechanism and kinetics of pickling of high-temperature oxidized 304 SS in HF–H₂SO₄ [35].

The object of this paper is to assess dynamic changes of the impedance of AISI 304 stainless steel dissolution process in conditions of intergranular corrosion in electrolyte solution of various pH by means of DEIS technique including determination of controlling stage of the overall rate.

2. Experimental

Chemical composition of austenitic stainless steel used in the researches is given in Table 1. Examined specimens were prepared according to the instructions provided by the ASTM G108-94 standard [36]. Specimens were sensitized at 675 °C for 36 h. Corrosion potential of the sensitized specimens in the examined electrolyte solution was about $E_{CORR} = -0.900 \text{ V}_{\text{Hg,Hg}_2\text{SO}_4|\text{H}_2\text{SO}_4}$ independently of pH. 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. Thirty specimens of each type were investigated. In the case of all examined specimens the exposed area was equal to 0.5 cm².

DEIS measurements were performed in a three-electrode cell, in which mercury/mercury sulphate Hg, Hg₂SO₄|H₂SO_{4 mol/dm³} 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

Table 2

Composition of the investigated solutions

pH	Composition of the solution
0.2	0.5 M H ₂ SO ₄ + 0.01 M KSCN
0.5	0.4 M H ₂ SO ₄ + 0.1 M Na ₂ SO ₄ + 0.01 M KSCN
0.8	0.3 M H ₂ SO ₄ + 0.2 M Na ₂ SO ₄ + 0.01 M KSCN
1.1	0.2 M H ₂ SO ₄ + 0.3 M Na ₂ SO ₄ + 0.01 M KSCN

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 SO₄²⁻ + 0.01 M KSCN solution of various pHs to determine controlling stage of AISI 304 stainless steel dissolution process proceeding during intergranular corrosion. Composition of the investigated solutions is given in Table 2.

Each measurement was followed by chemical analysis of the solution performed by means of Atomic Absorption Spectrometer Sens AA GBC in order to determine concentrations of ions dissolved from the examined samples.

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 [36] to guarantee conditions equivalent with the DL-EPR tests performed on AISI 304 stainless steel: temperature of electrolyte was of 30 °C ± 1; the polarization was from $E_{CORR} = -0.900 \text{ V}_{\text{Hg,Hg}_2\text{SO}_4|\text{H}_2\text{SO}_4}$ to $E = -0.200 \text{ V}_{\text{Hg,Hg}_2\text{SO}_4|\text{H}_2\text{SO}_4}$ (maintained for 2 min in the passive state) – activation scan; and back to corrosion potential $E_{CORR} = -0.900 \text{ V}_{\text{Hg,Hg}_2\text{SO}_4|\text{H}_2\text{SO}_4}$ – reactivation scan.

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 to 7 Hz. Averaged 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 the measurement 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 et al. [21–25].

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	Bal.

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