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ELECTROCHEMICAL ANALYSIS OF THE PASSIVE LAYER CRACKING PROCESS ON A95052 ALUMINIUM ALLOY PERFORMED BY MEANS OF DC AND AC TECHNIQUES

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The following paper presents comparative results of electrochemical analysis of the passive layer cracking process occurring on A95052 aluminium alloy during tensile process under anodic polarization conditions performed by means of DC and AC techniques.

As a result evident advantage of AC technique over the DC one was determined. Moreover, the application of dynamic electrochemical impedance spectroscopy (DEIS) and acoustic emission (AE) allows detecting the threshold strain value that reflects the exact moment of the passive layer cracking process.

Keywords: acoustic emission, DEIS, DC, non-stationary electrochemical process, tensile stresses.

INTRODUCTION

Aluminium-magnesium alloys (5xxx series) are well-known and excellent materials for a variety of applications in various branches of industry due to their excellent mechanical and exploitation properties, and corrosion resistance [1-5]. Many of these properties depend strongly on magnesium content in the alloy. In general, mechanical properties increase proportionally to magnesium content in the range of 0,5-5 wt.% Mg [3]. On the other hand, corrosion resistance of aluminium alloys highly depends on constitutions, and decreases with addition of magnesium [6-9]. Enhanced magnesium content above 3 wt.% can be precipitated at grain boundaries and can diminish such properties, for it leads to the formation of relatively thick and friable surface oxides. Such passive films effectively cause reduced corrosion resistance, especially to stress corrosion cracking [7-8,10].

Aluminium alloys as construction materials are subjected to tensile stresses in many cases. Rupture of the passive layer under tensile stresses conditions is considered as one of the most important aspects causing faster dissolution of metal in aggressive corrosion environments due to exposure of a bare metal substrate to electrolyte, and so initiating the SCC cracks [11,12].

Researches involved with the SCC processes are well-known and widely perform all around the world. Classical stress corrosion cracking researches are based on electrochemical and mechanical measurements, and metallographical studies [13,14]. The use of potentiostatic techniques developed the knowledge of the SCC mechanism [15-17] and allowed the determination of the SCC characteristic potentials [14-17]. Classical electrochemical impedance spectroscopy (EIS) also makes possible receiving information concerning the SCC process, but only before and after the moment of cracking, when investigated system is in the stable state [18-20]. Basic backgrounds of such measurements were widely discussed by Gabrielli [21], Macdonald [18], Mansfeld and Lorenz [22] and Stoyanova et al. [23].

However, as for now, detailed determination of the moment of the passive layer cracking in time/strain domain was not possible using any electrochemical technique or mechanical test. Dynamic electrochemical impedance spectroscopy (DEIS) and acoustic emission (AE) techniques give such opportunity. Studies performed by Darowicki *et al.* on 304L stainless steel and A95056 in chlorides solution confirm that fact [24-27].

The major aim of this paper was to compare the application of AC techniques with the DC ones for the examination of passive layer cracking on A95052 aluminium alloy during tensile process under anodic polarization conditions.

Utilization of the AC methods allows the performance of more detailed analysis of dynamic changes of investigated electrochemical system compared to DC measurements. Accordingly, the authors focused on estimation of proper criterion concerning the moment of the passive layer cracking on the basis of DC and AC techniques as the selection methods used for determination of initiation stage of the SCC.

EXPERIMENTAL

Experiments were composed of cyclic polarization measurements, AC measurements performed using DEIS and AE techniques afterwards.

Examined samples were made of A95052 according to ASTM standard in the form of bars. Detailed chemical composition of investigated material based on the UNS Number (Unified Numbering System for Metals and Alloys) has been presented in Table 1.

Table 1: Chemical composition according to the UNS Number

Type of alloy	Chemical composition, wt.%						
	Al	Mg	Cr	Fe	Mn	Cu	Other
A95052	95.7 -97.7	2.2 - 2.8	0.15-0.35	max. 0.4	max. 0.05	max. 0.05	bal.

Samples were mounted in a measurement cell and then in a tensile testing machine MTS 81012. Tensile tests and samples preparations were performed according to EN 10002-1 +AC1 standard at room temperature. Scheme of the investigated specimens together with the measurement cell was the same as in the case of previous experiments [27]. Examinations were carried out in a three-electrode electrochemical cell in which silver / silver chloride electrode was used as a reference electrode and the auxiliary electrode was made of platinum net.

Before the experiment execution investigated specimens were exposed for 24 hours in buffered solution ($H_3BO_3 + Na_3BO_3$; pH = 7.4) in order to receive stable passive layer. Afterwards, the measurements were performed in the same solution with additional content of 0.002 M sodium chloride.

The rate of stress increment was equal to $4 \cdot 10^{-5} s^{-1}$ (according to the standard EN 10002-1 +AC1) in order to detect such a rapid electrochemical process as the passive layer cracking. Additionally, electrochemical examinations were carried out under tensile stresses in such a way that time of DEIS and AE measurements was correlated with the strain process. Total measurement time was equal to 240 seconds. The measurement had been stopped when the sample was broken. Maximal recorded strain value for A95052 was of 18% (0.18).

The measurement set-up consisted of electrochemical measurement software Gamry International, an ELPAN EP20A potentiostat and a National Instruments PCI 6120 card generating the perturbation signal, registering voltage perturbation and current response signals. Impedance measurements were carried out for the frequency range: 20 kHz – 3 Hz. Sampling frequency of 50 kHz resulted from measurement card settings being at our disposal. In our investigations the multi-sinusoidal signal composed of 20 sinusoids was utilized. The papers [28,29] contain detailed description of this method.

Acoustic emission measurements were executed using the two-channel system Mistras 2001. Analysis of obtained data was performed on the basis of Mistras standard software.

RESULTS AND DISCUSSION

Application of DEIS method during the tensile tests for various anodic polarization made possible receiving sets of instantaneous impedance spectra reflecting the dynamic changes of examined system in relation to strain values (Figure 1). Impedance values were dropping together with increasing strain. Recorded decrease in impedance could be explained by the decay in barrier properties of the passive layer. Additionally, the effect of potential could be observed in spectrograms, particularly for higher strain values. However, it was not possible to determine threshold strain value related to the passive layer cracking precisely.

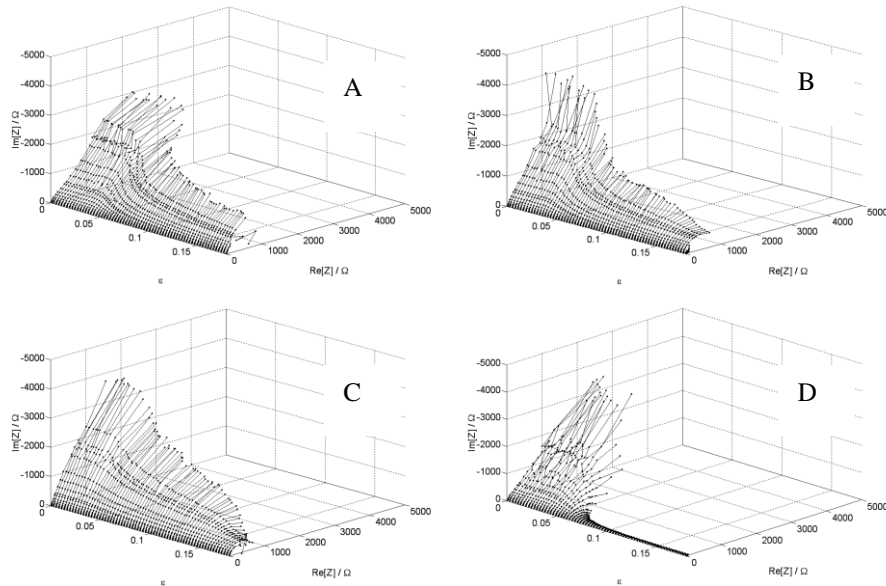


Fig. 1.: DEIS spectrograms recorded during the tensile process for examined A95052 aluminium alloy at various potentials: A) $E = -0.525\text{V}$, B) $E = -0.460\text{V}$, C) $E = -0.430\text{V}$, D) $E = -0.390\text{V}$.

From each impedance spectrum the DC current component was filtered. As a result the dependencies between DC current and strain for different potential levels were obtained and have been illustrated in Figure 2. Stable passive layer on the A95052 aluminium alloy surface existed for low strain values ($0.00 < \varepsilon < 0.04$). After exceeding the strain $\varepsilon = 0.04$ distinct increase in DC current values was observed. It is diversified in a characteristic way according to applied anodic potential levels with the maximum increase for the highest anodic polarization of -0.390V . Accordingly, above $\varepsilon = 0.04$ the barrier properties of investigated passive film started to decay. Summing up the potentiostatic results the threshold strain value for which the passive layer cracking was detected was determined as $\varepsilon = 0.04$.

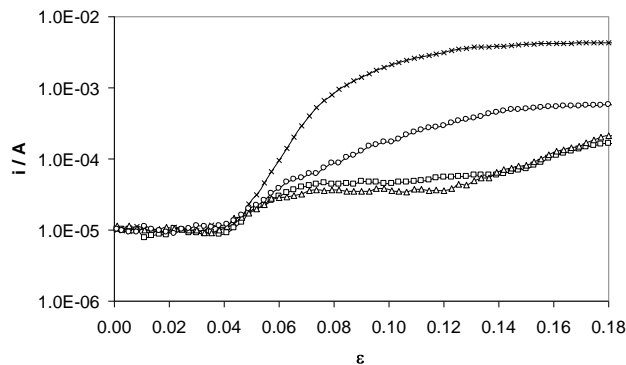


Fig. 2.: Dependencies of DC current as a function of strain recorded for A95052 aluminium alloy at various potentials: $E = \times -0.390\text{V}$, $\circ -0.430\text{V}$, $\square -0.460\text{V}$, $\triangle -0.525\text{V}$.

In order to determine explicitly the threshold strain value for which the passive layer cracking was registered, analysis of impedance spectra had to be performed based on the equivalent circuit presented in Figure 3. Proposed equivalent circuit constituted simplified form of the circuit used by Barbucci and de Witt [30,31].

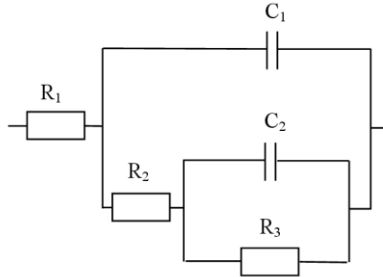


Fig. 3.: Equivalent circuit used in electrochemical analysis of impedance spectra recorded for A95052 aluminium alloy passive layer: R_1 – the electrolyte resistance, R_2 – resistance of oxide film, C_1 – capacitance of oxide film, R_3 – charge transfer resistance, C_2 – electric double layer capacitance.

Particular dependencies of electrochemical parameters versus strain have been depicted in Figure 4.

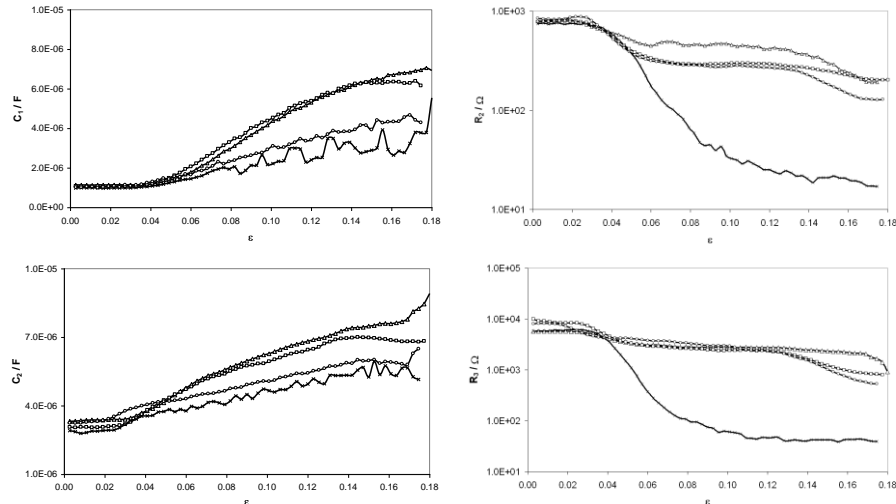


Fig. 4.: Electrochemical parameters of A95052 aluminium alloy passive film received on the basis of employed equivalent circuit versus strain under various potential conditions: $E = \times -0.390V$, $\circ -0.430V$, $\square -0.460V$, $\Delta -0.525V$.

Depicted results indicated the variability of individual electrochemical parameters with strain. Starting from the oxide film capacitance (C_1) recorded threshold strain value was determined as 0.04. In the case of C_2 , R_2 and R_3 parameters this value was lower $\varepsilon = 0.028$. Thus, it could be concluded that for $\varepsilon < 0.028$ stable passive layer on the A95052 aluminium alloy surface existed, as it was in the case of impedance spectra (see Figure 1). Different situation was recorded for the oxide film capacitance (C_1), which was stable up to $\varepsilon = 0.040$.

Increasing anodic polarization, has led to significant decrease in both resistance parameters R_2 and R_3 , especially for $E = -0.390V$. At this potential level, while the passive layer cracking process took place the electrolyte penetrated to ruptured passive film causing the increase in capacitance of the passive layer C_1 . It is connected with direct proportionality of the capacitance to dielectric properties of the passive film, and inverse proportionality to the film thickness. Capacitance of the oxide film increases with strain due to electrolyte penetration to micropores and microcrevices in the passive film. The effect of reduced passive layer thickness during the tensile process was slight. On the other hand, substantial fluctuations of both capacitance parameters C_1 and C_2 , observed particularly at $E = -0.390V$ for $\varepsilon > 0.028$ resulted from the Le Chatelier–Portevin effect (PLC effect) [32].

Simultaneously with mechanical and electrochemical examinations the acoustic emission amplitude was recorded. Figure 5 presents exemplary diagram concerning the comparison of AE amplitude, C_1 and C_2 parameters and DC current versus strain at $E = -0.460V$.

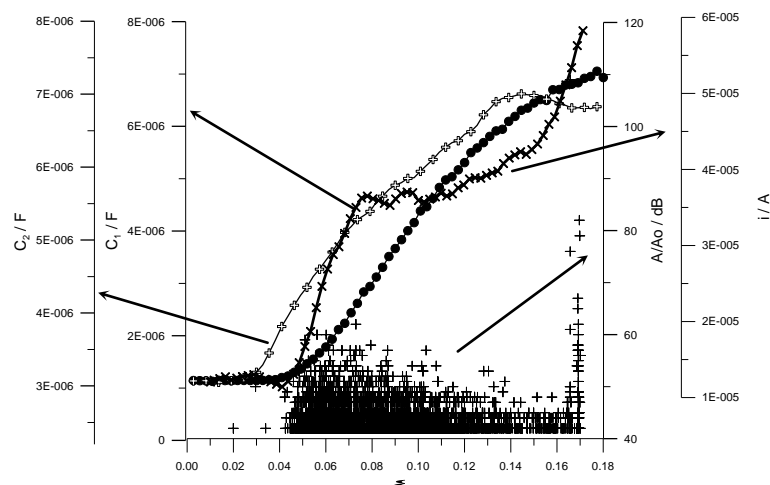


Fig. 5.: Diagram comparing the AE amplitude, C_1 and C_2 parameters and DC current as a function of strain for A95052 aluminium alloy at $E = -0.460V$.

Maximal value of acoustic emission amplitude was estimated at level of 40 dB, in a manner that allowed the elimination of registration of signals originated in the metal structure. It was achieved by comparison of AE results received for exposed and not exposed to electrolyte environment specimens. Therefore, AE data recorded during these examinations could be related to electrochemical processes occurring in the A95052 aluminium alloy passive film. The first symptoms of passive layer cracking were visible under the form of single acoustic signals registered for $\epsilon = 0.020$. Further significant increase in acoustic activity was correlated with growing C_1 parameter and DC current for $\epsilon = 0.040$. Therefore for this strain value one could state the initiation of corrosion processes on the A95052 aluminium alloy surface. Threshold strain value obtained on the basis of DC measurements was not correlated with the one from DEIS and AE examinations, what implies the application of AC techniques makes possible detection of passive layer cracking earlier than DC measurements. DC measurements allow the registration of corrosion processes on the metal surface, however, do not allow determining changes of electrochemical parameters of examined passive film. As a result, it is clearly visible that passive layer cracking process undergoes for lower strain as compared to the initiation of corrosion processes on the metal surface.

SUMMARY

Detection of the passive layer cracking process can be achieved more precisely based on acoustic emission activity and analysis of electrochemical parameters registered by means of DEIS. Registered threshold strain value, for which the passive layer cracking process was detected, differs depending on the application of DC and AC measurements. Detailed analysis points out that the threshold strain value obtained from the DC measurements is not correct, because it was determined on the basis of proceeding corrosion processes of aluminium alloy substrate, not from the dynamic changes of examined electrochemical parameters of the passive layer. Acoustic emission technique confirmed the results received from DEIS measurements.

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