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ORIGINAL PAPER

Electrochemical and acoustic emission studies of aluminum pitting corrosion

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Abstract The potentiodynamic and acoustic emission studies were carried out in a typical three-electrode electrochemical cell. The working electrode was prepared from aluminum alloy 1050A. Cyclic polarization and acoustic emission investigations of pitting corrosion were carried out simultaneously. On the basis of acoustic and potentiodynamic (cyclic polarization) investigations pitting corrosion potential was determined and compared.

Keywords Pitting corrosion · Aluminum alloys · Acoustic emission

Introduction

Acoustic emission (AE) defined as a sudden release of energy in the form of elastic wave generated by the source placed inside the material, is widely used in investigating those types of corrosion, which are the result of both, mechanical factors, and an aggressive environment activity. AE is mainly applied to describing a process of corrosion cracking and fatigue corrosion [1–5].

The other applications of AE as a research method in corrosion measurements can be divided into several main areas. One of them is investigating reinforced concrete constructions. The formation of passive film on reinforcement steel under high alkaline condition of concrete, as well as its destruction by chloride ions, can be investigated with the use of AE. The results obtained with this method are well correlated to electrochemical tests' results [6].

With the use of AE method the corrosion process in concrete reinforcement can be detected before any significant changes occur in the concrete which covers rebar rod [7, 8]. Spasova and Ojovan [9] presented the results describing early stage and the character of evolution of the cracks caused by the corrosion of aluminum occluded in cement matrix.

Acoustic evaluation of corrosion processes, in which the corroding specimens are not subjected to mechanical stresses, was firstly proposed by Rettig and Felsen [10]. Mansfeld and Stocker investigated the corrosion of aluminum alloys in galvanic connections with other metals. The genesis of acoustical signals was not precisely explained, however, they assumed that the source of emission were hydrogen bubbles exuding from the pits during local corrosion of aluminum alloys [11].

The investigation of localized corrosion of stainless steels using AE method is widely described in literature [12, 13]. This concerns mainly pitting and crevice corrosion of stainless steels [14, 15]. In their investigation of pits initiation and growth, Fregonese et al. have pointed at hydrogen as a possible source of AE when considering the occluded cells type of pits. Furthermore, while analyzing the occurring acoustic emission signals, they found that the range of pits propagation is more emissive than the initiation of pitting. Also Darowicki et al. regarded hydrogen as the source of AE [16].

The results of studies that present the correlation between different parameters of registered acoustic emission signals and the degree of corrosion destruction of

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Table 1 Chemical composition of investigated alloy

	Al	Mg	Zn	Si	Other
1050	99.5	0.05 max	0.05 max	0.25 max	–

aluminum alloys exposed in different conditions can be found in literature. The described destructions are the result of corrosion cracking [17]. In [18] changes proceeding in passive film on aluminum alloys in stress conditions, measured with the use of DC and AC methods, were collated with the acoustic activity of specimens. Bellenger et al. [19] presented the results of examining the susceptibility of two aluminum alloys to exfoliation corrosion. The comparison was based on the analysis of registered acoustic emission signals as well as on the microscope images of the examined specimens. Two main sources of acoustical signals were indicated: the emission of gaseous hydrogen and the second one connected with IGSCC (inter-granular stress corrosion cracking). Fatigue cracking is also investigated with the use of AE method other types of aluminum alloys corrosion [20].

So far the AE method has not been used in aluminum alloys pitting corrosion investigation. The paper presents the results of investigating susceptibility of aluminum alloy 1050A to pitting corrosion with the use of AE method. The object of this study was to apply AE to monitoring the processes which lead to initiation and progress of pitting corrosion. The superior aim of the entire research is to verify the possibility to use AE method in cases, when the use of electrochemical methods is not possible.

Experimental procedure

The chemical composition of aluminum alloy 1050A used in this study is presented in Table 1. Alloy 1050A is commercially pure aluminum, very resistant to corrosion.

Tests were carried out in borate buffer solution admixed with 0.002 mol/dm^3 natrium chloride, prepared with the use of reagents pure for analysis and demineralized water.

2-channel Vallen AMSY 4 measuring set was used to register AE signals. It was composed of analog/digital measuring card with DSP processor and specialized software for on-line signal recording and analysis. High sensitivity piezoelectric transducer VS75-V (Vallen Systeme) was used for tests. The sensor was connected to the card through AEP3 pre-amplifier. The applied gain was 60 dB with threshold value set to 27 dB. As a coupler between the sensor and the examined specimen mineral grease was used.

Cyclic polarization measurement was carried out by application of electrochemical, digital system Gamry Instruments. Scan rate of potential was 1 mV/s. The test determined the susceptibility of the alloy to pitting corrosion and they were carried out in a three-electrode system. The working electrode was a double-sided specimen. One side of the specimen which was in contact with the electrolyte was examined to pitting corrosion. The second one was connected to the piezoelectric transducer. The auxiliary electrode was platinized titanium gauze and the reference electrode was a silver wire covered with silver chloride and placed directly in the solution used for tests. The scheme of experimental set-up is presented in Fig. 1, where: 1—AE transducer, 2—double-sided specimen, and 3—solution.

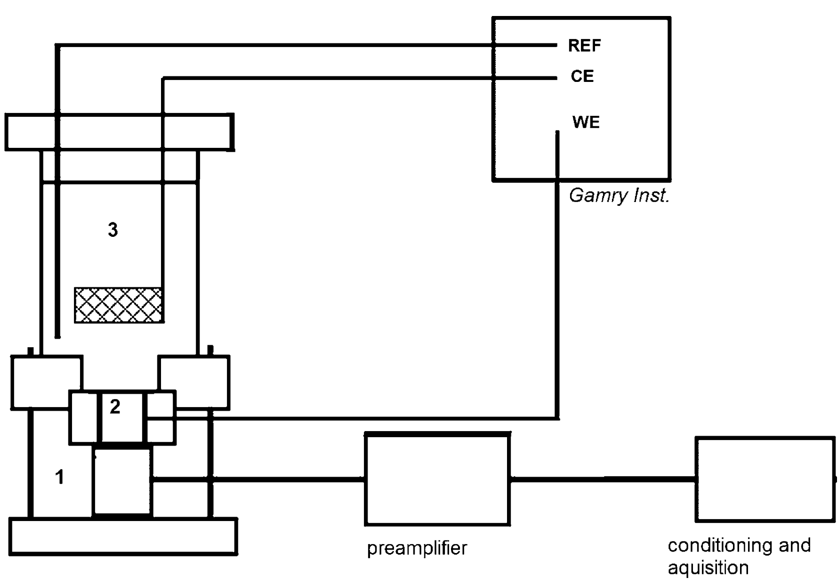

Fig. 1 Experimental set-up

Results and discussion

Cyclic polarization and acoustic emission investigations were carried out simultaneously. The polarization curve (solid line) and the run of events (dashed line) obtained during the measurements of aluminum alloy 1050A are plotted in Fig. 2. We show the typical potentiodynamic polarization curve of aluminum alloy in neutral solution at room temperature. It can be noticed that the 1050A alloy exhibited stable passive state. Following range of those intensive current fluctuations connected with processes destructions and rebuilding of passive layer. Sudden current increase described pit growth on the surface. As can be observed in Fig. 2, the run of events of AE is well correlated to the current plot. It is also worth noticing that, before a significant number of events appear, the polarization curve has a shape characteristic for stable passive state, whereas along with the first current fluctuations the number of events increases. First current perturbations are the result of metastable pitting corrosion, viz. the simultaneous formation and repassivation of pits on the specimen's surface.

The analysis of potential values for which first acoustical signals appear as well as the relation between the sum of acoustical events and the potential indicate that the results are not repeatable. This observation corresponds to the statistical nature of pitting corrosion process, which is described in literature [21–23]. As a result, statistical analysis of the obtained data becomes necessary. Therefore, for each of the examined specimens of 1050A alloy, 19 polarization tests were conducted with simultaneous registration of acoustical activity.

Presented in Fig. 3 are the chosen plots of sum of registered acoustical events in standardized form as a function of potential.

In Fig. 3 one can observe the spread of the obtained plots. That confirms the statistical character of pitting corrosion of aluminum alloys. In the early stage of measurements, the number of registered events changes insignificantly. It is related to the stable passive state existing on the surface of aluminum. Slight increase and then rapid rise of registered events number correspond to metastable corrosion and the progress of pitting on the alloy surface respectively.

In order to analyze dependencies of acoustic events it was necessary to perform statistical evaluation of obtained results. By analyzing the obtained acoustical registers one obtains the data which help to characterize the acoustical activity of material subjected to different processes, including corrosion. The proposed method eliminates the need to analyze parameters such as: signal duration, rise time, amplitude or the number of AE events in register. On the other hand, based on the number of registered AE hits for which the times of appearance can be directly referred to potential, one can determine the cumulative distribution function (CDF) of probability of pitting corrosion occurrence.

With this in view, the number of events was presented in cumulated form and it was arbitrarily assumed that pitting corrosion occurs when 10% of all events are registered. Based on the acoustical signals obtained for individual examined specimens, potentials, for which the overall

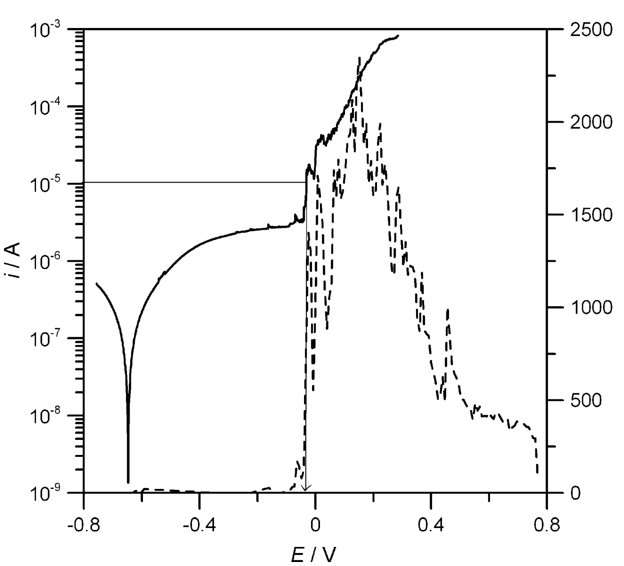

Fig. 2 An exemplary anodic polarization curve and the acoustic emission activity of alloy 1050A

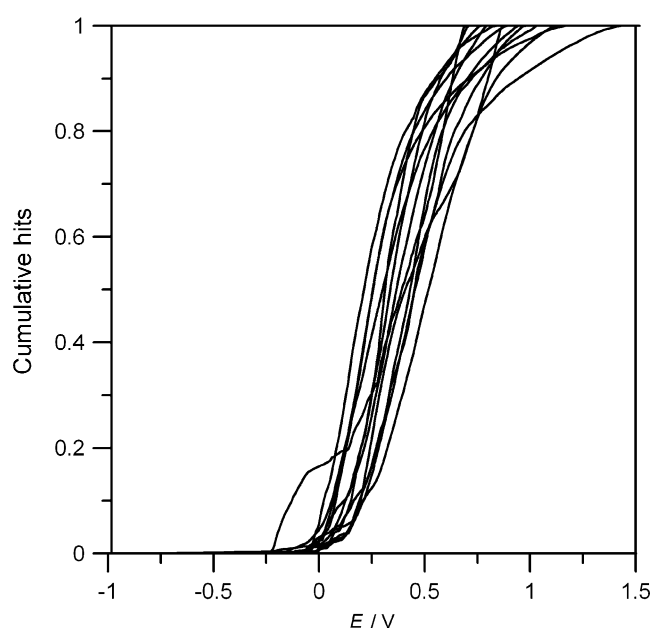

Fig. 3 Evolution of the cumulative of AE signals number vs. potential

number of registered events reached 10% of all recorded events, were determined. The values of these potentials were used for calculating the CDF of pitting corrosion occurrence (see Fig. 4).

When analyzing the obtained CDF vs. potential one can distinguish three ranges of potential. For potentials lower than −0.125 V pitting corrosion of alloy 1050 practically does not occur in testing condition. From −0.125 V to 0.210 V the CDF increases. For potentials higher than 0.210 V alloy 1050A is subjected to pitting corrosion surely (Fig. 5).

For probability equal to 0.5 the value of pitting potential, E_{np}, was determined. It is mean value of the distribution for obtained results, in practice. In this case, this value characterizes the distribution and is simply called the pitting potential. The pitting potential obtained from CDF calculated on the basis of AE method equals to $E_{np}^{acu} = 0.118$ V.

The next step was involved with the analysis of anodic polarization curve and the number of acoustic events vs. potential for the events registered between the first recorded acoustical signal and the moment when 10% of all AE signals occurred. The first significant number of events that occurred before the assumed 10% threshold can be related to the initial current fluctuations on the polarization curve. These perturbations are usually associated with metastable pitting corrosion, viz. with formation and repassivation of pits. In order to describe this stage of corrosion of aluminum alloy 1050A, an analysis was performed, identical to the one carried out for the potentials for which the number of registered acoustic emission events reached the 10% threshold. Only this time, the obtained CDF referred to the potentials for which the number of registered acoustical events was equal to 1% of all recorded signals. Determined for probability equal to 0.5 the value of potential for which metastable pitting corrosion occurred was −0.025 V.

In order to determine the acoustical activity related to the changes proceeding in the passive film and the progress of

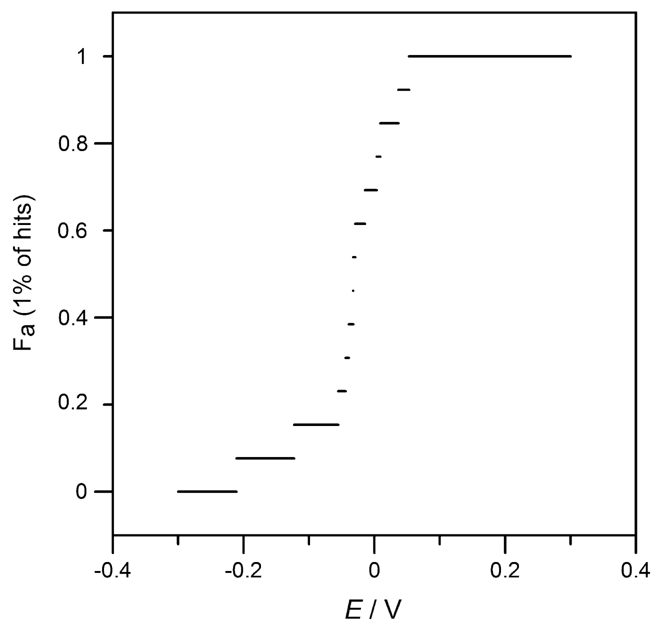

Fig. 5 The potential range for metastable corrosion determined on the basis of acoustical CDF (1% of all registered signals)

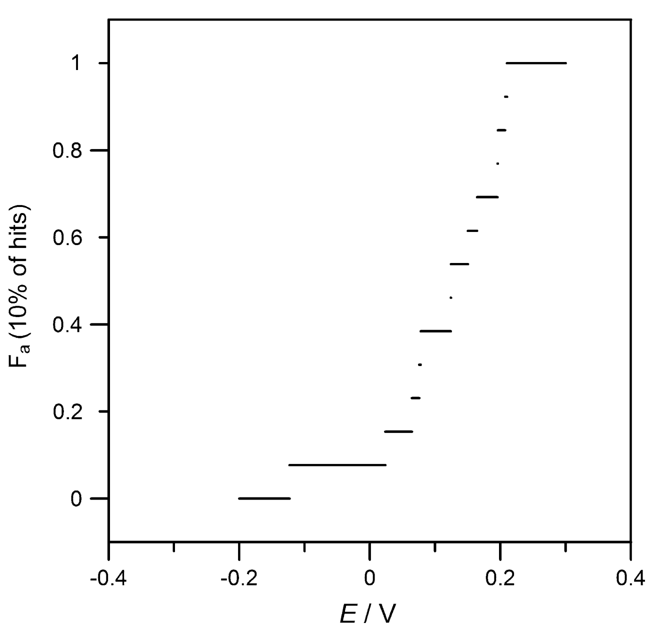

Fig. 4 Cumulative distribution function of the probability of pitting corrosion occurrence obtained with the use of acoustical data

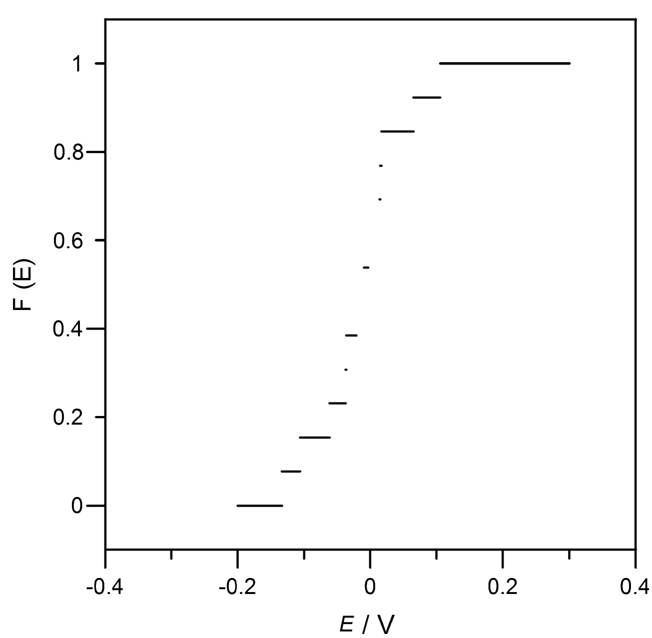

Fig. 6 CDF of pitting corrosion occurrence obtained on the basis of cyclic polarization data

pitting in examined aluminum alloy simultaneously to AE investigation the corrosion process was induced with the use of anodic polarization method. Having the data obtained from the parallel investigation with the use of polarization and AE methods one can perform two independent analyses. It is possible to calculate CDF of pitting corrosion occurrence based on the values of the obtained pitting potentials. Probability of pitting corrosion occurrence was estimated for 13 polarization curves. The threshold current density value was established arbitrary as j=10 μA. It was recognized that for a given potential, pitting corrosion process proceeded at given electrode, if determined current value was greater than or equal to threshold current density value. In connections with above the CDF of pitting corrosion occurring is estimates by equation:

$$\mathrm{CDF}(E) = n \times N^{-1}$$

where: CDF(E)—cumulative distribution function of pitting corrosion obtained on the basis of potentiodynamic measurements, N—number of all obtained curves, n—the number of this polarization curves for which current density for a given potential is equal to (or greater) than 10 μA.

The method for pitting potential determination and the description of evaluating the susceptibility to pitting corrosion based on the CDF was given in the previous papers [16, 23]. CDF obtained with the use of polarization technique is plotted in Fig. 6.

CDFs obtained with both methods are similar. Taking into consideration the assumptions that were the basis for CDF calculation, it can be stated that in laboratory conditions pitting corrosion can proceed on the surface of aluminum alloy 1050A in potential equal or higher to −0.13 V. For all potentials lower than −0.13 V investigated aluminum alloy does not undergo pitting corrosion. Above potential 0.11 V, initiation and growth of pits is a sure event.

For probability equal to 0.5 pitting potential, E_{np}, was determined on the basis of electrochemical CDF. The obtained value was $E_{\mathrm{np}}^{\mathrm{el}} = -0.025\,\mathrm{V}$.

Conclusions

AE method provides the possibilities of pitting potential determination which are comparable to those obtained by means of anodic polarization technique. One can therefore try to apply AE method to investigation of pitting process and determination of characteristic pitting corrosion potential. Moreover, since AE is a non-destructive method which does not require any excitation signals, it can be successfully used for monitoring pitting processes in industrial environment. The advantage of AE method is the ability to detect pitting in its initial stage, before metastable corrosion occurs.

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