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The resistance to general corrosion of series of zinc-aluminum alloys modified with silicon and strontium

ABSTRACT

The resistance to corrosion of the series of zinc-aluminum casting alloys modified with silicon and strontium was studied in a sodium chloride solution. It was shown that general corrosion was the main form of corrosion of Zn25Al-Si-Sr alloys in the test solution. The corrosion process takes place through the anodic dissolution of the alloys, while the cathodic reaction is controlled by diffusion of oxygen in the test solution. Three different electrochemical techniques were applied to determine the corrosion current density, which is the electrochemical indicator of corrosion rate. The value of corrosion current density for each Zn25Al-Si-Sr alloy was calculated using the value of polarization resistance, obtained by electrochemical impedance spectroscopy or by linear polarization resistance technique. The value of corrosion current density was also determined directly from Tafel plots, which were recorded by linear sweep voltammetry. As the content of silicon and strontium in the tested alloys increases, the value of corrosion current density increases gradually. The results obtained by different electrochemical techniques are in good agreement.

Keywords: zinc-aluminum alloys, corrosion rate, electrochemical techniques.

1. INTRODUCTION

ZA27 alloy belongs to the family of zinc-aluminum (ZA) casting alloys with high aluminum content. It has been widely used in the production of sliding bearings because of high strength and hardness and favorable tribological characteristics. The alloy usually contains 25 to 28 wt.% aluminum, 2 to 2.5 wt.% copper, and 0.01 to 0.02 wt.% magnesium. The presence of copper has a beneficial effect on the hardness and tensile strength of the alloy. However, during long-term aging at ambient or slightly elevated temperatures copper can lead to irreversible changes in the dimensions of the alloy castings [1]. This unfavorable feature of commercial ZA27 alloy can be overcome by replacing the copper in the alloy with silicon [2,3]. Silicon also shows a beneficial effect on the wear resistance of zinc-aluminum alloys [4-6]. The wear resistance of alloys with silicon was found to be approximately five times

higher than the wear resistance of ZA27 alloy [7]. Adding of strontium to Zn25Al-Si alloys resulted in further improvement of their wear resistance [7]. Thus, Zn25Al-Si-Sr alloys can be regarded as respectable tribological materials intended for use in complex tribo-mechanical systems. For a successful application of these alloys in real conditions of exploitation (atmosphere, natural waters) it is also necessary to take their corrosion resistance in the relevant corrosive environment into account.

Corrosion behavior of zinc-aluminum casting alloys is similar to that of pure zinc. General corrosion is the main form of zinc corrosion under atmospheric conditions, in natural waters, aqueous solutions and soil. General corrosion occurs as a more or less uniform dissolution of the metal/alloy surface, which results with a gradual decrease in the metal/alloy thickness. Due to the presence of aluminum, zinc-aluminum casting alloys have better resistance to general corrosion than zinc [8, 9]. The resistance to corrosion depends on the alloy composition and structure, as well as on the chemical composition, concentration, pH and temperature of the corrosive environment, i.e. on the corrosivity of atmospheres. Atmospheres are usually classified as industrial, urban, rural or

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marine. The presence of chlorides from the sea is characteristic for marine atmosphere [8, 9].

The corrosion behavior of binary zinc-aluminum alloys has often been studied in chloride solutions open to the atmospheric air because of a great influence of the dissolved oxygen on the corrosion kinetics [10-14]. Corrosion rate v_{corr} , which is a quantitative indicator of the general uniform corrosion, can be determined by the weight loss method or by various electrochemical techniques. The weight loss method is time-consuming and a large number of samples is needed to obtain reliable results. However, electrochemical techniques are fast and give an instantaneous rate of a corrosion process, which cannot be obtained by the weight loss method. Corrosion current density j_{corr} , determined by an electrochemical technique, is a quantitative electrochemical indicator of the corrosion rate [15,16]. Linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and extrapolation of Tafel lines [16,17] can be applied to obtain the value of corrosion current density of an electrochemical corrosion process. LPR technique and EIS technique are used to obtain the polarization resistance R_p of the electrochemical (corrosion) system [17]. The value of R_p is inversely proportional to the value of corrosion current density j_{corr} and to the value of corrosion rate v_{corr} . When the value of R_p is known, the corrosion current density j_{corr} can be calculated using the Stern-Geary equation [18]. The value of j_{corr} can also be determined from Tafel plots [19]. These plots are obtained by linear sweep voltammetry (LSV) technique.

The main goal of this paper was to apply three electrochemical techniques to test the corrosion resistance of series of Zn25Al-Si-Sr alloys in the chloride solution. Until now there have been no data on the corrosion behavior of zinc-aluminum alloys modified with silicon and strontium in the corrosive environment containing chlorides, so that results of the tests performed should provide an insight into the possibility of using Zn25Al-Si-Sr alloys in the marine atmosphere.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The samples for electrochemical tests were made of Zn25Al-Si-Sr alloys. The designation and chemical composition of these alloys are given in Table 1.

Zn25Al-Si-Sr alloys were prepared by conventional melting and casting route in the Department of Materials Sciences at "Vinča" Institute of Nuclear Sciences. The alloys were melted in the laboratory electric resistance furnace.

Technically pure zinc and aluminum were used in the preparation of these alloys, with the addition of master alloys Al7Si and Al18Si to provide the specified content of silicon. The master alloy Al10Sr was also used, to add the desired strontium content to the alloys. The melted alloys (570 °C) were poured into steel molds preheated to 200 °C. Samples for corrosion tests (30 mm x 20 mm x 5 mm) were cut from the obtained castings.

Table 1. Chemical composition of Zn25Al-Si-Sr alloys

Tabela 1. Hemijski sastav Zn25Al-Si-Sr legura

Alloy	Chemical element [wt.%]			
	Al	Si	Sr	Zn
Zn25Al-1Si	25	1.0	0.00	balance
Zn25Al-1Si-0.03Sr			0.03	
Zn25Al-1Si-0.05Sr			0.05	
Zn25Al-3Si	25	3.0	0.00	balance
Zn25Al-3Si-0.03Sr			0.03	
Zn25Al-3Si-0.05Sr			0.05	

2.2. Methods

The values of corrosion current density of the prepared Zn25Al-Si-Sr alloys are determined by electrochemical techniques. Electrochemical measurements are carried out using a potentiostat/galvanostat BIOLOGIC SP-200 and a three-electrode electrochemical cell for flat samples. A sample with a surface of 1.0 cm² in contact with the test solution is used as a working electrode. The saturated calomel electrode (SCE) is the reference electrode, and a platinum foil is used as a counter electrode. Electrochemical measurements are performed at room temperature, in a solution of sodium chloride (3 wt.% NaCl, pH 6.3), in the presence of atmospheric oxygen. The test solution simulates the marine atmosphere that contains chloride ions, without the presence of acid gases. Before electrochemical tests the samples were wet ground using progressively finer abrasive SiC paper (600 grit to 1500 grit). Then, they were rinsed with ethanol and dried in the air. The test sample is held in the test solution on the open circuit potential until a stable corrosion potential E_{corr} is achieved. After that, the sample is electrochemically polarized depending on the applied electrochemical technique.

Linear polarization resistance (LPR)

This technique is used to obtain the value of polarization resistance R_p of tested electrochemical (corrosion) systems. After reaching stable corrosion potential E_{corr} , the working electrode (test sample) is electrochemically polarized in a small range of potential (± 10 mV) near E_{corr} and the corresponding polarization curve is recorded. The applied sweep rate is 1 mV/s. The value of R_p is

determined as the slope of the experimental E - j curve on the E_{corr} .

Electrochemical Impedance Spectroscopy (EIS)

The values of R_p for all Zn25Al-Si-Sr alloys are also determined by electrochemical impedance spectroscopy. This technique is usually performed by applying an AC potential to an electrochemical (corrosion) system and then measuring the corresponding AC current. The AC signal is applied over a wide range of frequencies (0.01 Hz to 100 kHz) to generate an impedance spectrum for the tested corrosion system. The value of R_p is determined from the so-called Nyquist plot, by reading the real axis value of the electrochemical impedance Z at high and low frequencies.

Three LPR tests and three EIS tests are performed for each test sample (Zn25Al-Si-Sr alloys), with good reproducibility. The value of corrosion current density j_{corr} is calculated using the experimental R_p value for each test sample.

Linear sweep voltammetry (LSV)

After LPR test and EIS test, the test sample is subjected to potentiodynamic polarization using a linear sweep voltammetry technique (LSV). The

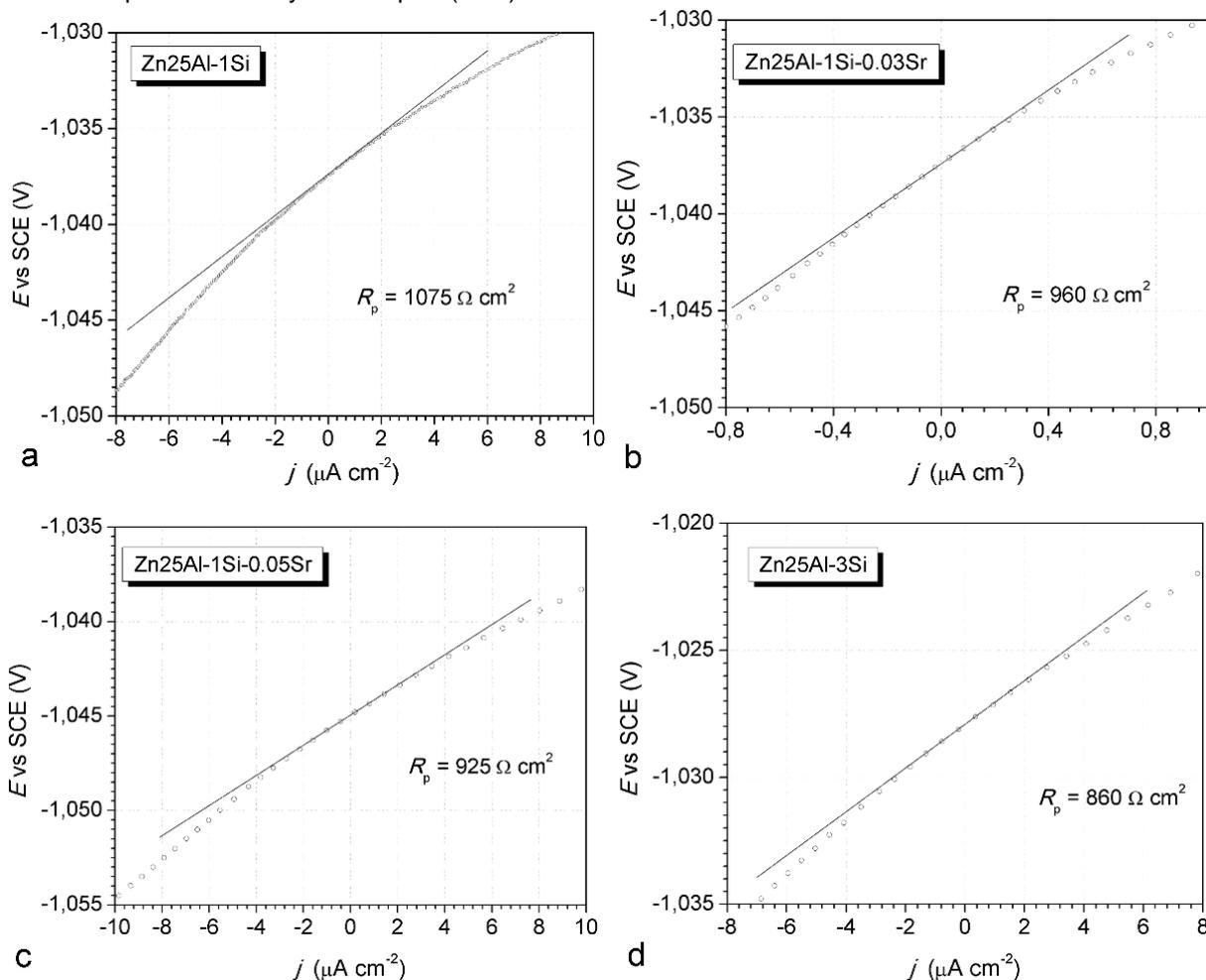
sample is polarized in a wide potential range (± 0.150 V vs E_{corr}) at a sweep rate of 1 mV/s, and the corresponding polarization curve was recorded. The value of corrosion current density j_{corr} is determined directly from the obtained E - $\log j$ plot (Tafel plot), by extrapolation of the linear part of the anodic polarization curve to the corrosion potential E_{corr} .

3. RESULTS AND DISCUSSION

3.1. E - j graphs

Experimental E - j graphs for Zn25Al-Si-Sr alloys are obtained by linear polarization resistance technique. The graphs are shown in Figure 1.

The current density j on the corrosion potential E_{corr} is $j = 0$. The negative current densities correspond to the cathodic current densities, while the positive current densities correspond to the anodic current densities. The slope ($\Delta E/\Delta j$) on the corrosion potential E_{corr} is the polarization resistance R_p . The value of R_p , which is obtained from experimental E - j graphs for each Zn25Al-Si-Sr alloy (Figure 1 a-f), is given in Table 2.



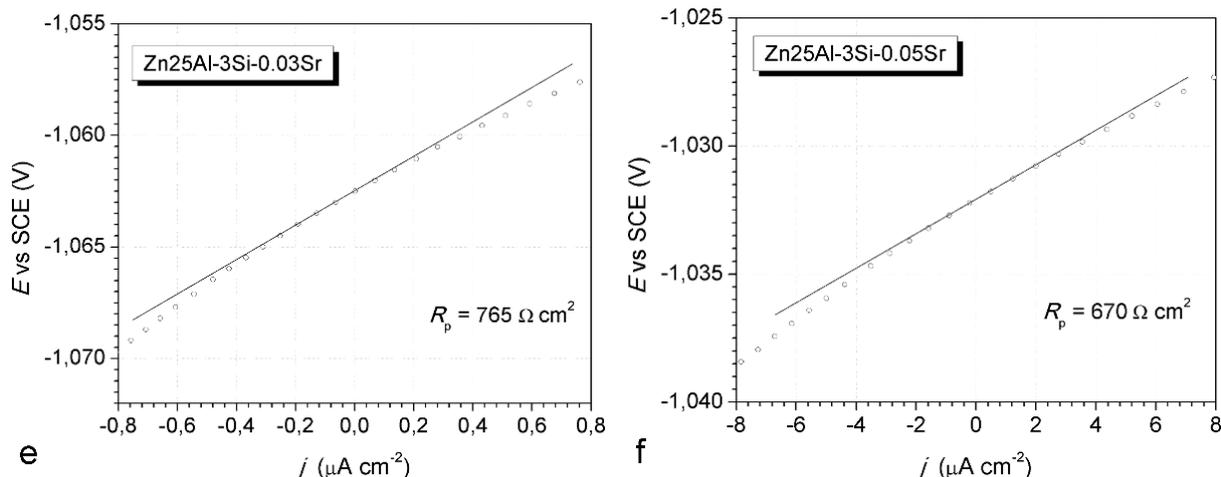


Figure 1. *E-j* graphs for Zn25Al-Si-Sr alloys in sodium chloride solution (3 wt.% NaCl).
Slika 1. *E-j* dijagrami za Zn25Al-Si-Sr legure u rastvoru natrijum hlorida (3 wt.% NaCl).

3.2. Nyquist plots

Experimental data obtained using Electrochemical Impedance Spectroscopy are shown in Figure 2 a-f. The data are presented in the form of

Nyquist plots. A Nyquist plot shows the dependence of the real impedance component (Z_{Re}) and the imaginary impedance component (Z_{Im}) on frequency f , in linear coordinates.

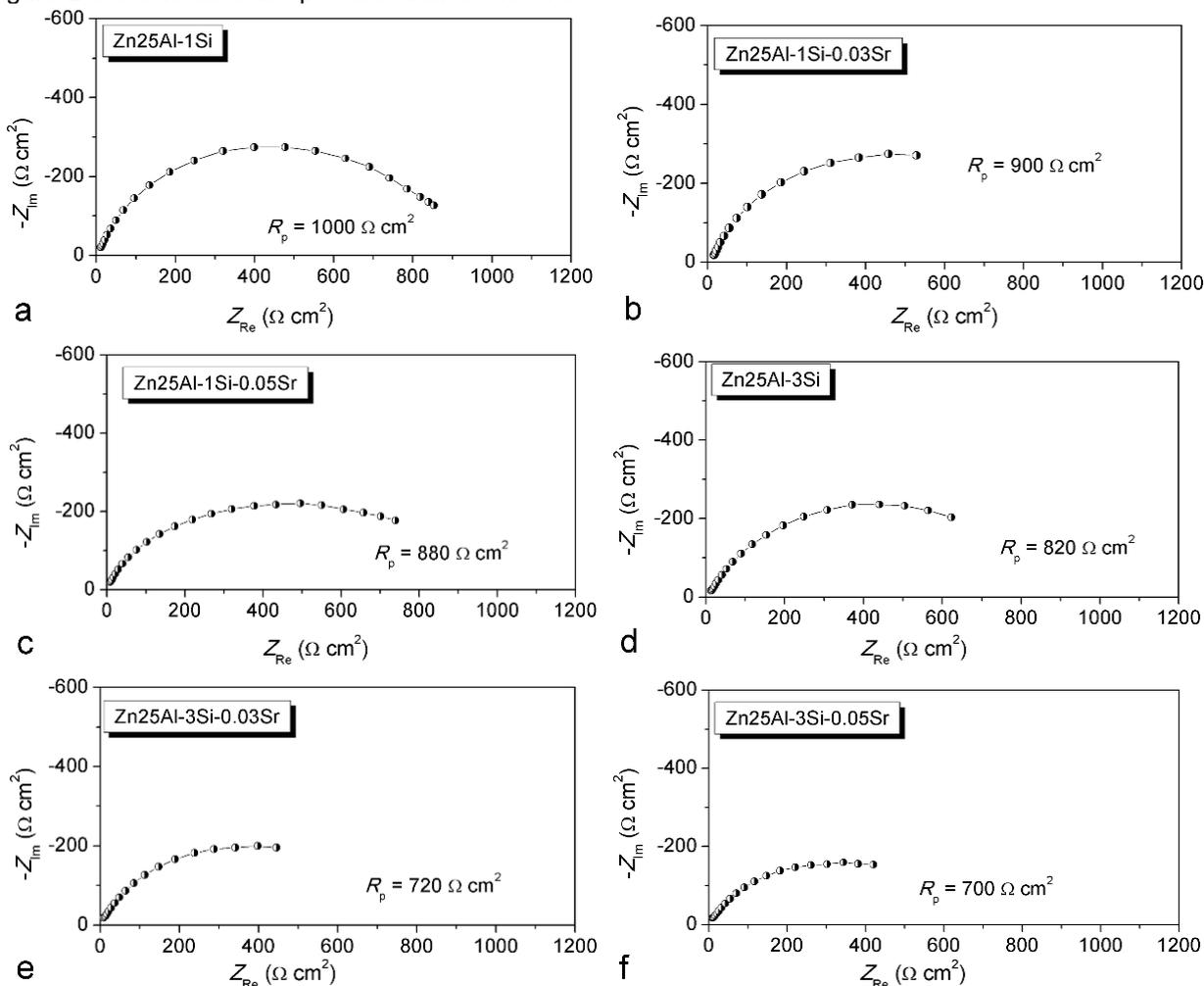


Figure 2. Nyquist plots for Zn25Al-Si-Sr alloys in sodium chloride solution (3 wt.% NaCl).
Slika 2. Nyquist dijagrami za Zn25Al-Si-Sr legure u rastvoru natrijum hlorida (3 wt.% NaCl).

Resistance of test solution can be obtained by reading the real axis value at the high frequency intercept (left side of the plot). The real axis value at the low frequency intercept (right side of the plot) is the sum of the polarization resistance R_p and the resistance of test solution. Therefore, the diameter of the semicircle in the Nyquist plot is equal to the value of polarization resistance R_p . The values of R_p determined by EIS technique for all Zn25Al-Si-Sr alloys are shown in Figure 2 a-f and they are also given in Table 2.

When the value of polarization resistance R_p is known, the value of corrosion current density j_{corr} can be calculated using the Stern-Geary equation [18]:

$$j_{corr} = \frac{B}{R_p} \quad (1)$$

B is a constant that depends on the values of the anodic and cathodic Tafel slope b_a and b_c :

$$B = \frac{b_a \times b_c}{2.3 \times (b_a + b_c)} \quad (2)$$

Equation (2) applies when both cathodic and anodic reactions are activation controlled. If the anodic reaction is under the charge-transfer control while the cathodic reaction is controlled by diffusion, the modified Stern-Geary equation is used [15]:

$$j_{corr} = \frac{b_a}{2.3 \times R_p} \quad (3)$$

Corrosion of each Zn25Al-Si-Sr alloy in the test solution takes place through anodic dissolution of the alloy. The anodic reaction is under the charge-transfer control with anodic Tafel slope $b_a = 30$ mV/decade (Figure 3). The cathodic reaction is controlled by diffusion of oxygen in the test solution [15, 17]. In that case, the value of cathodic Tafel

slope $b_c \rightarrow \infty$ and Equation (3) should be used to calculate the value of corrosion current density j_{corr} .

R_p values are experimental values, obtained when using LPR and EIS techniques. Calculated values of the corrosion current density for tested Zn25Al-Si-Sr alloys are given in Table 2.

3.3. E-log j graphs (Tafel plots)

Potentiodynamic polarization curves for the tested zinc-aluminum alloys with silicon and strontium are obtained by LSV technique. Experimental anodic and cathodic polarization curves for each Zn25Al-Si-Sr alloy are shown in Figure 3.

The anodic polarization curves in Figure 3 a-f show an increase in the current density when the applied polarization increases, indicating the anodic dissolution of Zn25Al-Si-Sr alloys. The curves are linear in the marked current region and the value of anodic Tafel slope $b_a \sim 30$ mV/decade for all Zn25Al-Si-Sr alloys. On the other hand, in the cathodic region, the current density plateau is clearly visible. This behavior is a characteristic of the process controlled exclusively by diffusion. In neutral solutions open to the atmosphere, dissolved oxygen is the main cathodic reactant [16]. The transport of oxygen to the electrode surface (test sample) is limited due to a low solubility of oxygen in the test solution. The cathodic reaction (the reduction of oxygen) is controlled by diffusion and the value of cathodic Tafel slope $b_c \rightarrow \infty$.

The value of corrosion current density j_{corr} for each Zn25Al-Si-Sr alloy is obtained directly from the characteristic Tafel plot (Figure 3 a-f), by extrapolating the linear part of the anodic polarization curve to the corresponding E_{corr} value. The experimental values of j_{corr} for the tested Zn25Al-Si-Sr alloys are given in Table 2. Table 2 summarizes all quantitative results of the performed electrochemical tests.

Table 2. Indicators of resistance to general corrosion for Zn25Al-Si-Sr alloys, obtained by various electrochemical techniques

Tabela 2. Pokazatelji otpornosti na opštu koroziju Zn25Al-Si-Sr legura, dobijeni različitim elektrohemijskim tehnikama

Alloy	LPR technique		EIS technique		LSV technique
	R_p [Ω cm ²]	j_{corr} [μ A cm ⁻¹]	R_p [Ω cm ²]	j_{corr} [μ A cm ⁻¹]	j_{corr} [μ A cm ⁻¹]
ZA27	1250	10.4	1220	10.7	8
Zn25Al-1Si	1075	12.1	1000	13.0	10
Zn25Al-1Si-0.03Sr	960	13.6	920	14.2	13
Zn25Al-1Si-0.05Sr	925	14.1	880	14.8	14
Zn25Al-3Si	860	15.2	820	15.9	15
Zn25Al-3Si-0.03Sr	765	17.0	720	18.1	17
Zn25Al-3Si-0.05Sr	670	19.4	700	18.6	20

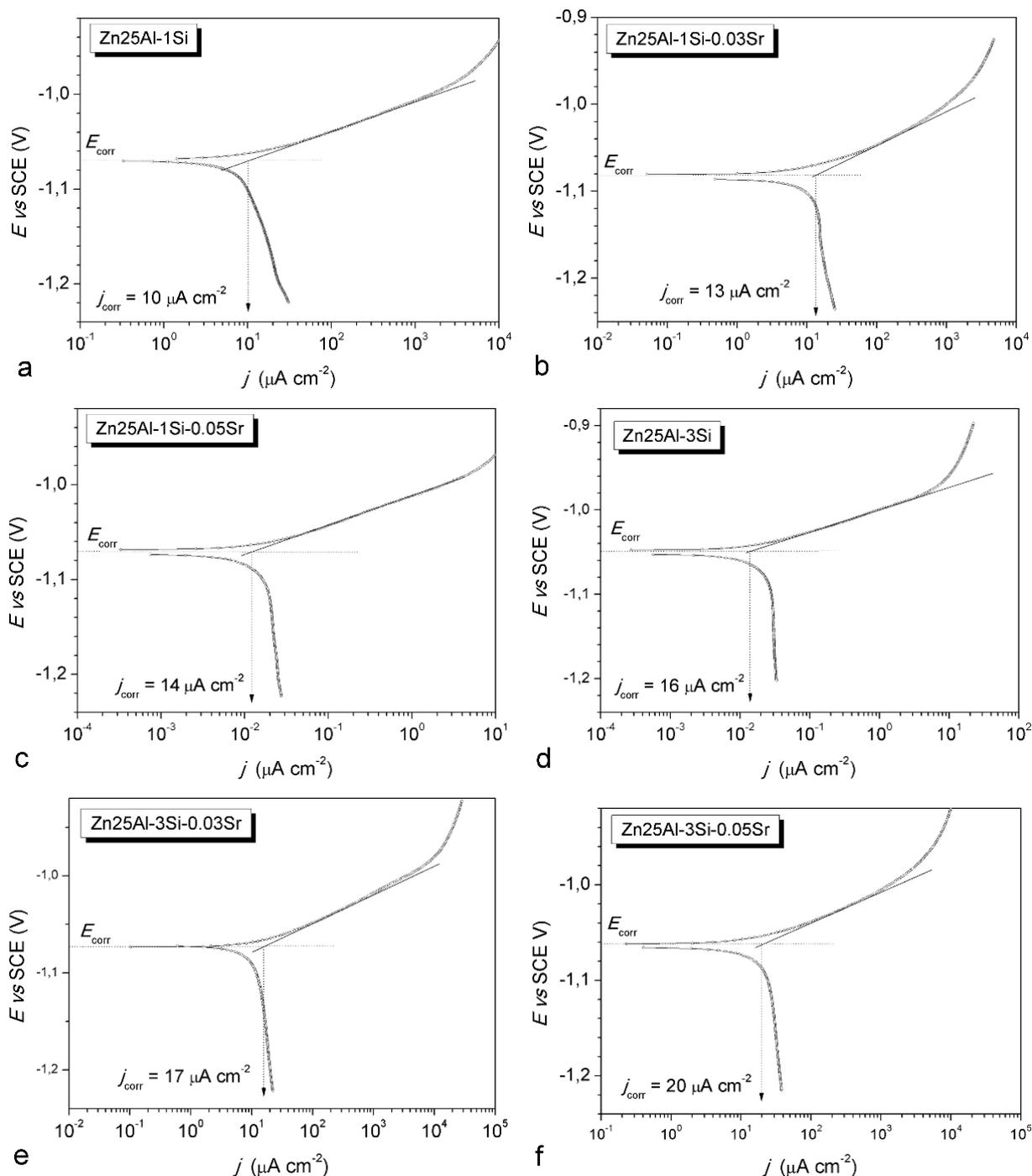


Figure 3. E - $\log j$ graphs (Tafel plots) for Zn25Al-Si-Sr alloys in sodium chloride solution (3 wt.% NaCl).

Slika 3. E - $\log j$ dijagrami (Tafelovi dijagrami) za Zn25Al-Si-Sr legure u rastvoru natrijum hlorida (3 wt.% NaCl).

The values of R_p and j_{corr} for the commercial ZA27 alloy are also given in Table 2, for the purpose of comparison. The alloy was supplied from the RAR[®] foundry, Batajnica. The same electrochemical techniques were used to determine the values of R_p and j_{corr} , as in the case of Zn25Al-Si-Sr alloys. The obtained results are given in Figure 4.

Table 2 shows that the highest value of polarization resistance R_p and the lowest value of corrosion current density j_{corr} are obtained in the case of commercial ZA27 alloy. A slightly higher value of j_{corr} is obtained for Zn25Al-1Si alloy without strontium. When the content of silicon and strontium increases in Zn25Al-Si-Sr alloys, the value of R_p slightly decreases, which leads to a small increase in the value of j_{corr} . Among all

Zn25Al-Si-Sr alloys, the alloy with the largest content of silicon and strontium i.e. Zn25Al-3Si-0.05Sr alloy, has the lowest value of polarization resistance R_p and the highest value of corrosion

current density j_{corr} . Accordingly, the presence of silicon and strontium in Zn25Al-Si-Sr alloys resulted in a lower resistance to corrosion of these alloys compared to the commercial ZA27 alloy.

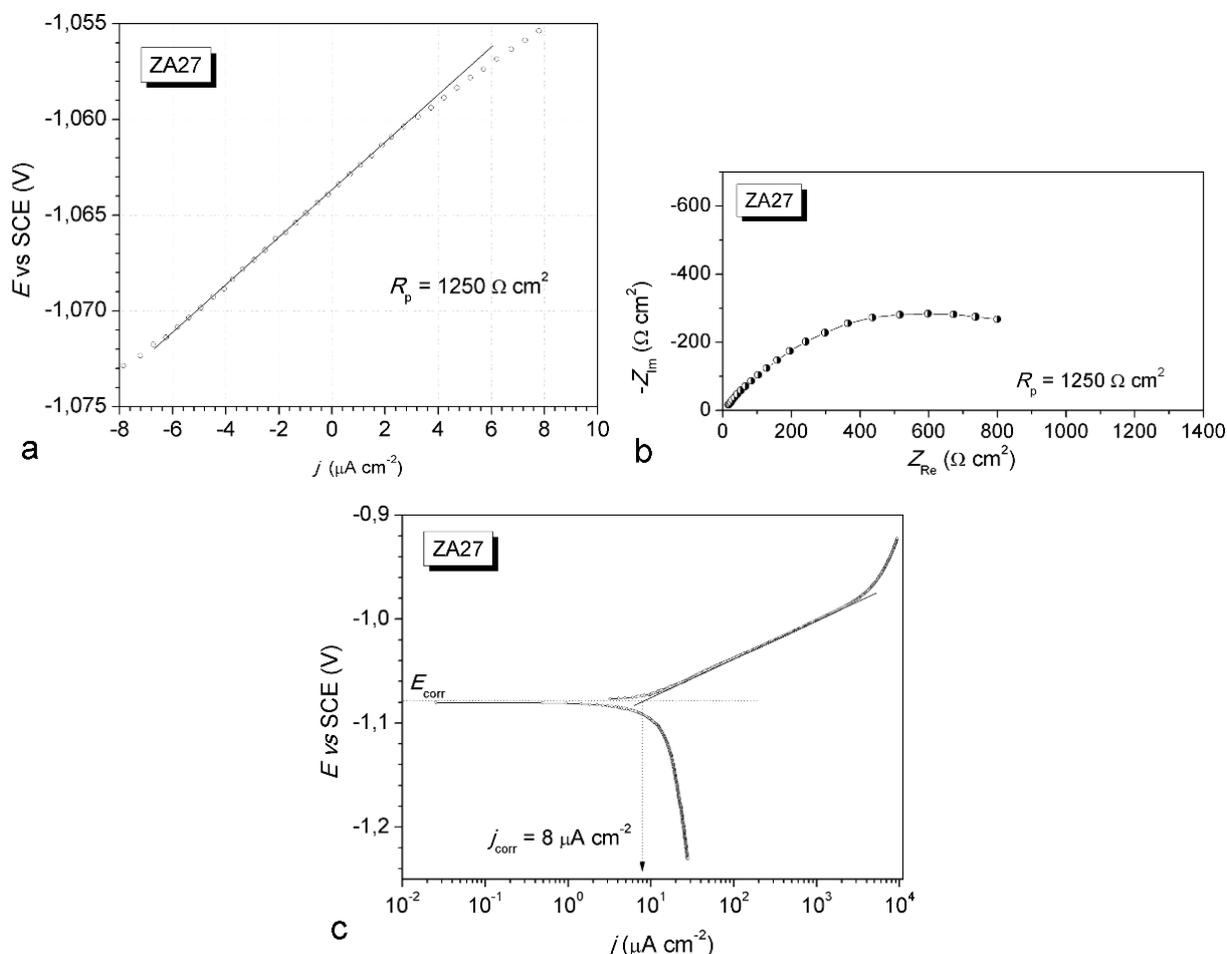


Figure 4. Results of electrochemical tests for commercial ZA27 alloy in sodium chloride solution (3 wt.% NaCl): a) E - j graph, b) Nyquist plot and c) E - $\log j$ graph (Tafel graph).

Slika 4. Rezultati elektrohemijskih ispitivanja komercijalne ZA27 legure u rastvoru natrijum hlorida (3 wt.% NaCl): a) E - j dijagram, b) Nyquist dijagram i c) E - $\log j$ dijagram (Tafelov dijagram).

The values of R_p obtained by LPR and EIS technique are very close. It can also be seen that the values of j_{corr} for all Zn25Al-Si-Sr alloys, determined by different electrochemical techniques, are in very good agreement.

4. CONCLUSIONS

The resistance to general corrosion of the series of zinc-aluminum alloys with silicon and strontium (Zn25Al-Si-Sr alloys) was tested in sodium chloride solution, using various electrochemical techniques. The process of corrosion occurs as anodic dissolution of the alloys. The anodic reaction is under the charge-transfer control while the cathodic reaction is controlled by

diffusion of oxygen in the test solution. With the increase in silicon and strontium content in the synthesized Zn25Al-Si-Sr alloys, the value of the corrosion current density j_{corr} increases gradually.

This indicates a lower resistance to general corrosion of Zn25Al-Si-Sr alloys, compared to the corrosion resistance of the commercial ZA27 alloy. However, the difference in the level of general corrosion is small, which can be significant for further development and wider application of zinc-aluminum alloys with silicon and strontium. The relatively low values of corrosion current density j_{corr} , obtained for Zn25Al-Si-Sr alloys in the sodium chloride solution, point to the potential use of these alloys in various tribo-mechanical systems designed to work in the marine atmosphere.

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IZVOD**OTPORNOST NA OPŠTU KOROZIJU SERIJE LEGURA CINK-ALUMINIJUM KOJE SU MODIFIKOVANE SILICIJUMOM I STRONCIJUMOM**

Otpornost na koroziju serije legura cink-aluminijum za livenje, koje su modifikovane silicijumom i stroncijumom, ispitana je u rastvoru natrijum hlorida. Pokazano je da je opšta korozija glavni oblik korozije Zn25Al-Si-Sr legura u navedenom rastvoru. Proces korozije odvija se kao anodno rastvaranje legura, dok je katodna reakcija kontrolisana difuzijom kiseonika u rastvoru. Tri različite elektrohemijske tehnike primenjene su za određivanje gustine struje korozije, koja je elektrohemijski pokazatelj brzine korozije. Vrednost gustine struje korozije za svaku Zn25Al-Si-Sr leguru izračunata je na osnovu vrednosti polarizacione otpornosti, koja je određenai spektroskopijom elektrohemijske impedanse ili tehnikom linearne polarizacije. Vrednost gustine struje korozije je takođe određena direktno iz Tafelovih dijagrama, koji su registrovani pomoću voltametrije sa linearnom promenom potencijala. Sa povećanjem sadržaja silicijuma i stroncijuma u ispitivanim legurama vrednost gustine struje korozije postepeno raste. Rezultati dobijeni različitim elektrohemijskim tehnikama su u dobroj saglasnosti.

Ključne reči: legure cink-aluminijum, korozija, brzina korozije, elektrohemijske tehnike.

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