

Corrosion behaviour of an AlZnSnSrGa alloy in aqueous solutions of NaCl and Na₂SO₄

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The alloy composed of Al(95.53%), Zn(2.85%), Sn(0.515%), Ga(0.1%) and Sr(0.009%), with the weight percents in the parentheses, was prepared by melting, using Al(99.84%), a product of the Aluminium Plant-Podgorica, as the base material. The corrosion behaviour of this alloy was tested in relation to the behaviour of the base metals, by both open circuit potential and polarization resistance methods, in aqueous solutions of both NaCl and Na₂SO₄, the concentration of which varied within the range 0.00051–0.51 mol dm⁻³. Over the whole salt concentration ranges, the corrosion parameters indicate that the corrosion rate of the alloy is significantly higher than the rate of the base material. For instance, for the concentration range 0.00051–0.51 mol dm⁻³, the stationary open circuit potentials, related to SCE, in NaCl solutions were –1.200 to –1.460 V for the alloy and –0.693 to –0.920 V for Al, while in Na₂SO₄ solutions, the stationary open circuit potentials were –1.190 to –1.465 V for the alloy and –0.780 to –0.860 V for Al. At the same time, the corrosion current density in NaCl solutions varied within 11–89 mA cm⁻² for the alloy and 0.35–0.80 for Al, while in Na₂SO₄ solutions it amounted to 5.7–52 mA cm⁻² for the alloy and 0.28–0.88 mA cm⁻² for Al.

Keywords: corrosion, Al, Al alloys, neutral solutions.

Corrosion of both pure Al and its alloys has been the subject of numerous investigations. In both air and aqueous solutions, aluminium is covered by a protective oxide layer, causing its open circuit potential in approximately neutral water solutions to become much more positive in comparison to that of bare metal. Solutions which do not allow oxide formation, for instance HF solution,^{1–4} enable the potential of Al to achieve its most negative values. The stability of the protecting oxide layer depends on both pH^{5–7} and surface mechanical treatment.^{8,9} In non-aggressive media, the oxide layer is very stable, and protects the base metal from corrosion, permitting the magnitude of the corrosion current density to amount to the order of 1 mA cm⁻².

When oxide formation on Al is undesirable, for instance, when it was intended to prepare a material for cathodic protection, an alloying was undertaken. In this

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sense, Shirkhazadeh *et al.*¹⁰ investigated an Al–Ga alloy. Despić *et al.*¹¹ reported that small additions of In, Tl and Ga cause, for Al in NaCl solutions a decrease of the open circuit potential by even 0.7 V, in relation to the one of the pure base metal. Valand *et al.*¹² and Krstulović *et al.*¹³ investigated the corrosion of AlSn alloys in chloride solutions and pointed out the activating role of Sn. Many other additives to aluminium have also been investigated, for instance, Mg, Ba, Zn, Cd, Hg, Mn^{14,15} in order to prevent oxide layer formation and to enlarge the rate of anodic dissolution. The activation mechanism depends on the nature of the additive. Under corrosion conditions additives having positive redox potentials (Sn, Hg) separate themselves as metallic phases, enabling electronic conduction between the base alloy and the solution. Additives with negative redox potentials corrode together with the base metal, but do not permit the formation of a protective oxide film.

The alloys Al–Zn(5.03%)–Mg(1.67%)–Cu(0.23%)¹⁶ and Al–Cu(4%)–Mg(1.5%)–Mn(0.6%)¹⁷ present important construction materials, and, as such, they were the subject of corrosion investigations. The effect of the addition of small quantities of Cu, Cr and Zr to these alloys was also investigated.^{18–27}

The solubility of additives is an important property. There are highly soluble (up to 10 %) additives, such as Mg, Si, Zn and Cu, while others, such as Sn (up to 0.1%) are significantly less soluble. However, in a multicomponent alloy, a synergistic effect of the components might increase mutual solubilitis.

In order to synthesize an alloy suitable for cathodic protection purposes, two of the authors of the present work^{28,29} used Zn, Ga, an Sn as additives to aluminium, having in mind literature reports^{10–15} that these additives suppress the passivation of Al. A relatively large amount of Zn (2.85%) enabled, in comparison to pure Al, an improved mechanical stability of the alloy, as well as an enlarged solubility of the second additive, Sn (0.515 %). Since all these additives, in comparison to Al, have more positive redox potentials, Sr (0.009 %), having a more negative redox potential, was added too. This alloy appear to be homogeneous in both the molten and the solid state. In this work, its corrosion behaviour was investigated in usual media for corrosion measurements, namely in aqueous solutions of NaCl and Na₂SO₄.

EXPERIMENTAL

For the corrosion measurements, the PAR 332 device consisting of a Potentiostat Galvanostat Model 273 and of a cell MK-0.47 designed particularly for corrosion investigations, was used. The cell was a three-electrode type, with a large graphite cylinder as the counter electrode. A standard saturated calomel electrode, equipped with a Luggin capillary, was used as the reference electrode. The base metal Al(99.84%) and its alloy under investigation (AlZnSnSrGa), formed as discs, were used as the working electrodes. The surface of the working electrode was polished mechanically in a unique way, by the finest emery paper No. 1200, prior to each measurement.

The solutions used as corroding media were aqueous NaCl solutions, the concentration of which amounted to 0.00051 (6.96), 0.0051(6.86), 0.051(6.50) and 0.51(6.08) M, as well as aqueous Na₂SO₄ solutions, the concentration of which amounted to 0.00051(6.92), 0.0051 (6.89), 0.051(6.80) and 0.51(6.57) M. The numbers in parentheses give the respective pH values. When placed into the cell, the solutions were deaerated. The cell was thermostated at 20–0.05 °C, by a thermostat VEB-Prüfgeräte, Model U-15.

The open circuit potential and corrosion current densities were observed. The open circuit potential was read directly from the device display. Its change with time was observed and recorded. In all cases, a time of 1 h was long enough to achieve a stationary value. For the corrosion current measurements, software aimed to determine the slope of the j - E curve, at the corrosion potential (polarization resistance) was used. This method is based on the use of the following equation:³⁰

$$dE/dj = b_a b_c / [2.3 j_{\text{corr}} (b_a + b_c)] \quad (1)$$

where dE/dj presents the slope of the j - E curve at the corrosion potential, determined by a small perturbation of the DC potential, namely -10 mV, in respect to the stationary value of the corrosion potential, b_a and b_c present the slopes of the anodic and cathodic Tafel lines, determined at large enough overpotentials (more than 100 mV) in respect to the corrosion potentials, and j_{corr} presents the corrosion current density. It can be expressed in an explicit form as follows:

$$j_{\text{corr}} = b_a b_c / [2.3 (b_a + b_c) (dE/dj)]. \quad (2)$$

The corrosion current was measured on freshly polished electrodes, immediately after the stationary potential value was attained.

RESULTS AND DISCUSSION

The corrosion behaviour of both the starting metal, Al(99.84%), and its alloy AlZnSnGaSr, in the corroding media used, are presented in Figs. 1–6.

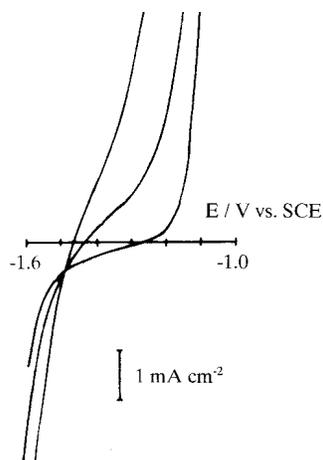


Fig. 1. Potentiodynamic j - E curves of AlZnSnGaSr alloy in 0.51 M NaCl solution at 20 °C. Polarization rate was 10 mV s⁻¹. Curves (from right to left) were recorded 1) immediately after immersion, 2) after 3 min, 3) after 10 min.

Figure 1 presents examples of the j - E curves recorded for the alloy in 0.51 M NaCl solution. The j - E curves follow, in general, the form published by Øvári *et al.*³¹ for pure Al in NaCl solution, as well as that published by Jamakosmanović *et al.*³² for technical Al in NaCl solution. Øvári *et al.*³¹ concluded that a sweep rate within the interval 0.1–10 mV s⁻¹, which was also used in this work, presents the optimum one for voltammetric investigations of corrosion. Freshly polished alloy electrode displays the highest polarizability. However, this behaviour becomes less expressed with increasing time the electrode was in contact with the electrolyte. Along with the polarizability decrease, the open circuit potentials shift in a negative direction. This electrode shows quite similar behaviour in Na₂SO₄ solution.

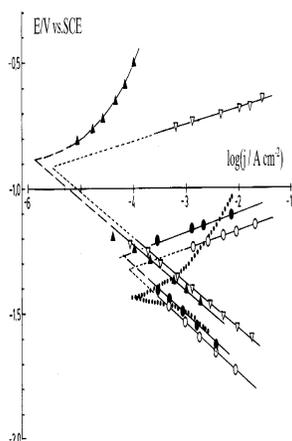


Fig. 2. Tafel diagrams of Al(99.84%) (triangles) and alloy AlZnSnGaSr (circles) in 0.51M NaCl (empty triangles, full circles) and 0.51 M Na₂SO₄ (full triangles, open circles), obtained potentiodynamically at a polarization rate of 10 mV s⁻¹. All the diagrams relate to freshly polished electrode, with exception of that given by small full circles, which relates to an alloy electrode kept 10 min in 0.51 M NaCl.

The j - E curve for Al in NaCl solution looks like the starting curve of the alloy electrode, and practically does not differ from the ones for technical aluminium in 3% NaCl solution published elsewhere.³² Its form does not change remarkably with time. However, the j - E curve of the Al electrode is much more sensitive to the nature of the electrolyte than the j - E curve of the alloy. Namely, the anodic passivation of Al is much more expressed in Na₂SO₄ than in NaCl solution, which causes an abrupt change of the corresponding Tafel dependence presented in Fig. 2.

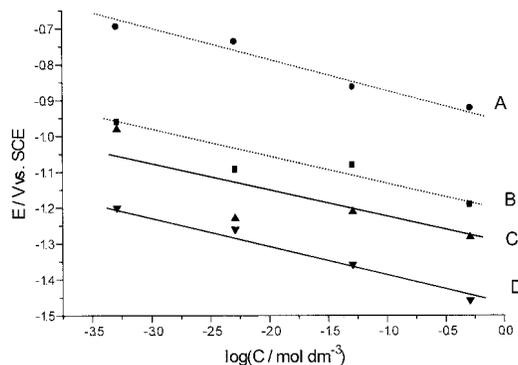


Fig. 3. Initial and stationary corrosion potentials of Al (A, B) and AlZnSnGaSr alloy (C, D) in NaCl solutions as a function of concentration, A-stationary, B-initial, C-initial, D-stationary.

The j - E curves, registered in both chloride and sulphate solutions of the same molarity, 0.51 M, for both technical Al(99.84%) and the alloy under investigation, are presented in Tafel coordinates in Fig. 2. Similar to the results of Hurlen *et al.*³³ for pure aluminium in weak acidic solutions, established on the basis of both galvanostatic and potentiostatic transients, the Tafel lines in Fig. 2 are mostly linear. With the exception of Al in Na₂SO₄ solution, the crossing of the anodic and cathodic Tafel lines define unique value of the corrosion current density. The slopes of the cathodic Tafel lines in both electrolytes amount to approx. 160 mV per decade. Similarly, for Al of high purity in 2 M NaCl solution, Despić *et al.*³⁴ found by the method of galvanostatic transients slopes amounting to 110 – 175 mV per decade in the corresponding potential region. These potential regions, namely, corresponds to hydrogen evolution over oxide

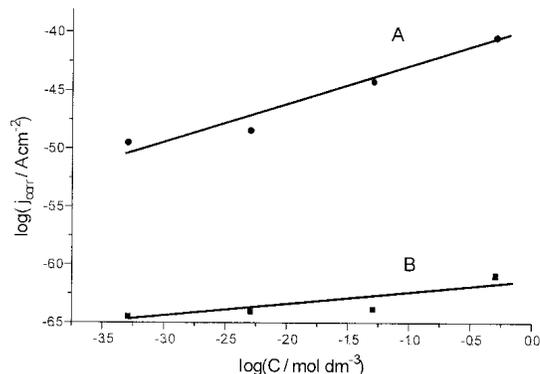


Fig. 4. Corrosion currents of Al(B) and AlZnSnGaSr alloy (A) in NaCl solutions in dependence of concentration.

covered metal surface. It is worth mentioning that the cathodic Tafel lines for the alloy are shifted toward lower currents in comparison to the lines for Al, indicating that the cathodic process is somewhat slower on the alloy than on Al.

For the alloy, the Tafel slopes of the anodic parts of the j - E curves depend largely on the time that the electrode had spent in the solution. In Fig. 2 plots are presented for contact times 0 min and 10 min that the alloy electrode had spent in 0.51 M NaCl solution. With increasing time, along with an open circuit potential decrease, the anodic Tafel slopes increase from the initial 40 mV per decade to about 350 mV per decade. This behaviour is typical of both corrosion media under investigation. Similarly, Stevanović *et al.*,³⁵ by galvanostatic transients, found very high anodic Tafel slopes, 750–1000 mV dec⁻¹ in NaClO₄ + NaCl solutions. The difference in the slopes may be caused by both the high purity of the Al and the electrolyte composition they used.

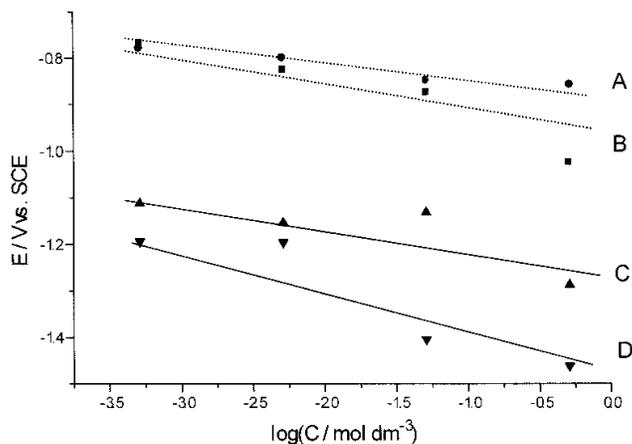


Fig. 5. Initial and stationary corrosion potentials of Al (A, B) and AlZnSnGaSr alloy (C, D) in Na₂SO₄ solutions as a function of concentration, A–stationary, B–initial, C–initial, D–stationary.

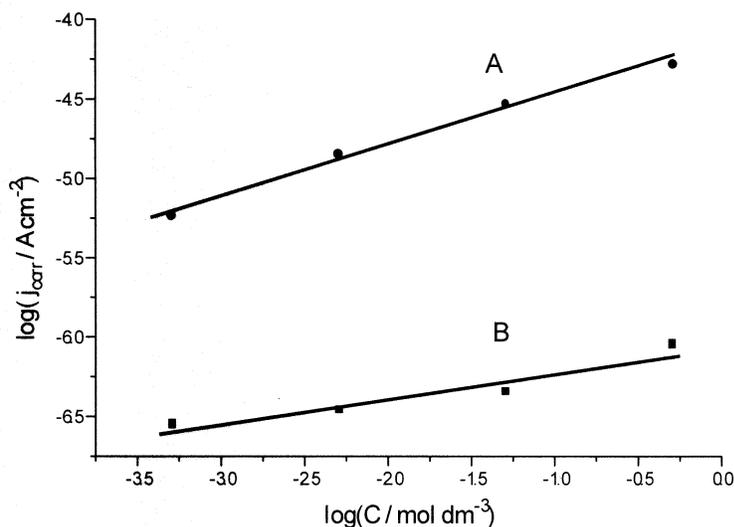


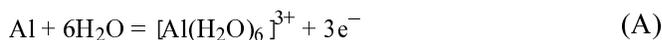
Fig. 6. Corrosion currents of Al(B) and AlZnSnGaSr alloy (A) in Na₂SO₄ solutions in dependence of concentration.

Figures 3 and 5 present the dependences of the initial and stationary open circuit potentials on electrolyte concentration. Figures 4 and 6 present the dependences of the corrosion current density on electrolyte concentration. These dependences were obtained from polarization resistance measurements, performed at stationary open circuit potentials. To calculate the current densities, a cathodic Tafel slope of 160 mV dec⁻¹ and an anodic Tafel slope of 50 mV dec⁻¹ for Al and 350 mV dec⁻¹ for the alloy were used, as being representative of most of the experimental data. The corrosion current densities obtained by means of formula (2) are not in full agreement with the data obtained from Tafel plots in Fig. 2. This is probably due to the difference between steady state and potentiodynamic measurements, having in mind primarily the fact that the real surface area may change in an irregular way with increasing time. Figures 3 and 4 relate to NaCl-solutions, while Figs. 5 and 6 relate to Na₂SO₄ solutions. One can clearly distinguish between the behaviour of Al and of its alloy. For Al in both solutions, the stationary value of the open circuit potential is more positive than the starting one, with this behaviour being remarkably expressed in NaCl solution, but very little in Na₂SO₄ solution. This indicates that the oxide layer, formed spontaneously in air, becomes thicker after immersing the Al-sample in the solution. As is known from the literature, in Cl⁻ containing media, the spontaneously formed oxide layer does not protect the corrosion surface enough, thus the open circuit potential is initially more negative than in sulphates. However, the corrosion produces a thicker oxide layer which renders the shift of the open circuit potential towards more positive values. The stationary value is approx. 0.3 V higher compared to the initial value. The oxide layer formed spontaneously in air appears to be stable in sulphate solutions, and the open circuit potential appears to be

practically independent on time. Contrary to Al, the open circuit potential of the alloy, after immersing in any of the investigated solutions, shows a continuous drop towards more negative values, indicating that the spontaneously formed oxide layer becomes destroyed and cannot reform itself. To illustrate these facts numerically, for increasing concentrations in the range $0.00051\text{--}0.51\text{ mol dm}^{-3}$, the stationary open circuit potentials in NaCl solutions on Al amount to -0.693 , -0.737 , -0.862 and -0.920 , and on the alloy to -1.200 , -1.260 , -1.358 and -1.460 V; in Na₂SO₄ solutions the stationary open circuit potentials on Al amount to -0.780 , -0.801 , -0.849 and -0.860 V, and on the alloy to -1.190 , -1.196 , -1.405 and -1.465 V.

The difference between the base metal and its alloy is also expressed if the corrosion current is considered. Figures 4 and 6 show that in both corrosion media under investigation, the corrosion currents of Al and that of its alloy differ mutually by 1.5 – 2 order of magnitude, that of the alloy being higher. To illustrate this numerically, the corrosion current densities in NaCl on Al amount to 0.35, 0.39, 0.49 and 0.80 mA cm⁻², and on the alloy amount to 11, 14, 37 and 89 mA cm⁻² and in Na₂SO₄ solutions on Al amount to 0.28, 0.34, 0.45 and 0.88 mA cm⁻², and on the alloy amount to 5.7, 14, 29 and 52 mA cm⁻².

As widely accepted for neutral solutions, the primary anodic reaction during corrosion of aluminium and its alloys in the electrolytes under consideration, can be expressed by the formula:



A theoretical value of the Tafel slope of 39 mV corresponds to this reaction, and therefore, this reaction appears to be predominant at least in the early stages of corrosion. Namely, the experimental values of the Tafel slopes for freshly prepared electrodes have the relatively small values of 50 – 60 mV dec⁻¹ (Fig. 2). Jamakosmanović *et al.*³² for technical Al in HCl-acidified NaCl solutions, established even lower values of about 30 mV dec⁻¹. Although, the successive electron transfer of three electrons is kinetically much more probable, the reaction behaves like it involves a one step three-electron transfer.

Hexahydrated aluminium ions transform quickly into pseudoboehmite, (AlOOH)₄·H₂O, boehmite AlOOH, and bayerite Al(OH)₃, and thus a mixed oxide – hydroxyde layer grows up. If one deals with the alloy, the other components: Zn, Ga and Sn, at highly negative actual corrosion potentials separate themselves as a metallic foam at the corroding surface. In their presence, the electronic current can permanently cross the metal/electrolyte boundary, *i.e.*, a protective oxide layer cannot cover the metal surface completely.

For both the investigated materials in all solutions, the corrosion current on a logarithmic scale depends almost linearly on the logarithm of the concentration. From the aspect of chemical kinetics, this fact indicates that the anions under investigation participate as reactants in the corrosion reaction. Tomcsányi *et al.*³⁶ explained this effect assuming that the anions react chemically with the aluminium

oxides, pseudoboehmite, boehmite and bayerite, making more soluble anionic species. For instance, if chlorides are under consideration, the following reactions may occur:



The dissolution aggravates the formation of a protective layer over aluminium, enabling the primary reaction (A) to proceed faster. If the alloy is under consideration, the formation of the protecting layer is additionally hindered by metallic islands to the more noble additives.

Optical microscopy of the alloy surface after a 24 h long corrosion treatment in both of the investigated media, indicated uniform corrosion over the whole surface. Displaying exceptionally high negative open circuit potentials and high corrosion currents, the alloy under investigation widens the possibilities of search for aluminium based materials being most suitable for cathodic protection purposes.

ИЗВОД

КОРОЗИОНО ПОНАШАЊЕ ЛЕГУРЕ AlZnSnGaSr У ВОДЕНИМ РАСТВОРИМА NaCl и Na_2SO_4

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Легура састава $\text{Al}(95,53\%)$, $\text{Zn}(2,85\%)$, $\text{Sn}(0,515\%)$, $\text{Ga}(0,1\%)$ and $\text{Sr}(0,009\%)$ са тежинским процентима назначеним у заградама, добијена је ливењем користећи алуминијум чистоте 99,84% производ Алуминијумског комбината у Подгорици као основни метал. Корозионе особине легуре су испитане у корелацији са корозионим особинама основног метала, мерењем потенцијала отвореног кола и корозионих струја у воденим растворима NaCl и Na_2SO_4 концентрација у интервалу $0,00051\text{--}0,51 \text{ mol dm}^{-3}$. За све концентрације легура је показала израженије корозионе карактеристике у односу на основни метал. Ради илустрације, за испитивани низ концентрација у опсегу $0,00051\text{--}0,51 \text{ mol dm}^{-3}$ стационарни потенцијали отвореног кола (мерени у односу на ЗКЕ) у растворима NaCl износе за легуру $-1,200$ до $-1,460 \text{ V}$, а за алуминијум $-0,693$ до $-0,920 \text{ V}$, а у растворима Na_2SO_4 за легуру $-1,190$ до $-1,465 \text{ V}$ и за алуминијум $-0,780$ до $-0,860 \text{ V}$. У исто време за исти низ концентрација корозионе струје износе за растворе NaCl $11\text{--}89 \text{ mA cm}^{-2}$ за легуру и $0,35\text{--}0,80 \text{ mA cm}^{-2}$ за алуминијум, а за растворе Na_2SO_4 , $5,7\text{--}52 \text{ mA cm}^{-2}$ за легуру и $0,28\text{--}0,88 \text{ mA cm}^{-2}$ за алуминијум.

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