

Branimir N. Grgur*, Lazar Marunčić

University of Belgrade, Faculty of Technology and Metallurgy,
Belgrade, Serbia

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The influence of chloride anions on the pitting corrosion of aluminum alloy EN 46000

ABSTRACT

The corrosion behavior of AlSi9Cu3 aluminum alloy, which is commonly used for manufacturing radiators of remote central heating systems, is investigated. The tendency for pitting corrosion is investigated in the phosphate buffer solution at pH = 7, in the sodium chloride anion concentration range 10-300 mg dm⁻³. The critical pitting potentials are estimated. The behavior of aluminum alloy and copper corrosion couple is also investigated.

Keywords: Corrosion, Central heating systems, Radiators, Critical potential

1. INTRODUCTION

In the modern remote central heating systems in the past twenty years, the use of the aluminum alloys based radiators practically replaced the old ones based on cast iron. Today, the most commonly used aluminum alloys for radiator manufacturing are based on AlSi9(11)Cu3(2)(Fe) alloy (EN 46000 and EN46100), due excellent mechanical, thermic and corrosion properties. Aluminum-silicon castings constitute 85% to 90% of the total aluminum-cast parts produced; aluminum alloys containing silicon as the major alloying element offer excellent castability, good corrosion resistance, and can be machined and welded [1,2]. Corrosion of these alloys is practically suppressed in the pH range of 6 to 8 in the de-aerated and low chloride containing water [3]. Nevertheless, in the open to air solutions containing halide ions, with Cl⁻ being the most common, aluminum alloys are susceptible to pitting corrosion [4]. This process occurs, because in the presence of oxygen, the metal is readily polarized to its pitting potential and because chlorides contribute to the formation of soluble chlorinated aluminum(hydro)oxide which

interferes with the formation of a stable, protective, oxide on the aluminum surface [5-7].

In these days, the most commonly used piping, especially in buildings, are made from copper. Copper in contact with the aluminum alloys act as a cathode and can polarized anode significantly, in some cases to the critical pitting potentials. In the presence of chloride, with limiting concentrations of <300 mg dm⁻³ [8].

Therefore, in this paper, we investigated the influence of chloride ion concentrations on the corrosion behavior of aluminum alloy AlSi9Cu3(Fe) - EN 46000 alloy.

2. EXPERIMENTAL

The chemical composition of the used aluminum alloy according to the European norm EN 1706 [9] is shown in Table 1.

Electrodes made from aluminum alloy plate with dimensions of 2 cm × 10 cm and exposed area of 5 cm² are used. Before experiments, the electrode is mechanically grinded with fine sandpaper and degreased in acetone. Electrochemical glass cell, with the volume of 200 cm³, equipped with reference and counter electrode compartments is used. Saturated calomel and platinum mesh are used as reference and counter electrode respectively. As a corrosion medium, the phosphate buffer with pH = 7.0 (commonly used in the conditioning of the pH of the circulating water)

Corresponding author: Branimir N. Grgur

E- mail: BNGrgur@tmf.bg.ac.rs

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is used, with the following composition: $6,81 \text{ g dm}^{-3}$ KH_2PO_4 + $1,868 \text{ g dm}^{-3}$ NaOH . The adequate volume of the chloride anions is added to the investigated solutions using different micro-burettes (10, 100 and 5000 μl) from starting sodium chloride stock solutions of 15 g dm^{-3} . The corresponding sodium chloride (chloride anions) concentrations is

investigated: 10(6); 50(30); 100(60) and 300(180) mg dm^{-3} . The polarization measurements at room temperature are conducted after 55 min of expose to corrosion potential, according to ASTM Designation: G 59 – 97 [10]. Optical micrographs are obtained with an optical microscope Olympus CX41 connected to the personal computer.

Table 1. The chemical composition of aluminum alloy EN 46100 [9]

Tabela 1. Hemijski sastav legure aluminijuma EN 46100 [9]

	Al %	Si %	Cu %	Mn %	Mg %	Fe %	Ni %	Zn %	Pb %	Sn %	Ti %	Cr %
EN 46100	ost.	10-12	1,5-2,5	0,55	0,3	0,45-1	0,55	1,7	0,25	0,15	0,2(5)	0,15

3. RESULTS AND DISCUSSION

In Fig. 1 the polarization curve of the aluminum alloy in the $\text{pH} = 7$ solution without the presence of chloride is shown. The value of the corrosion potential is around -0.53V , with corrosion current density of $2 \times 10^{-7} \text{ A cm}^{-2}$. Aluminum is practically in the passive state up to $\sim 0.3 \text{ V}$, with a passive current density value of $\sim 10 \mu\text{A cm}^{-2}$. In the reverse scan, the current additionally decrease, and the protective potential (E_{rp}) is about -0.35V [11]. We can see that the protective potential of aluminum (E_{rp}) in solution $\text{pH} = 7$ without chloride is more positive than the corrosion potential (E_{corr}), which means that aluminum is protected in this case, i.e. will not succumb to the eventual pitting corrosion, due to the presence of oxygen, on the corrosion potential [12,13].

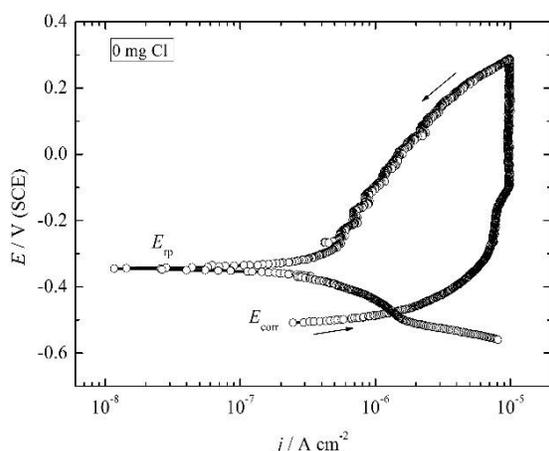


Figure 1. Polarization curve ($v = 1 \text{ mV s}^{-1}$) of aluminum alloy in solution $\text{pH} = 7$ without the presence of chloride

Slika 1. Polarizaciona kriva ($v = 1 \text{ mV s}^{-1}$) legure aluminijuma u rastvoru $\text{pH} = 7$ bez prisustva florida

Figure 2, shows the dependence of the current density on the potentials at different concentrations of sodium chloride in the range of 10 to 300 mg dm^{-3} . It can be seen that for the chloride concentrations 0 and 10 mg dm^{-3} there is practically no change in the current density (no pitting corrosion) to the potential of $\sim 0.3 \text{ V}$. With a sodium chloride concentration of 50 mg dm^{-3} and more, there is a rapid increase in the current density at lower potentials, indicating a pitting corrosion. The more chloride is in the solution, the larger is the current density at lower potentials.

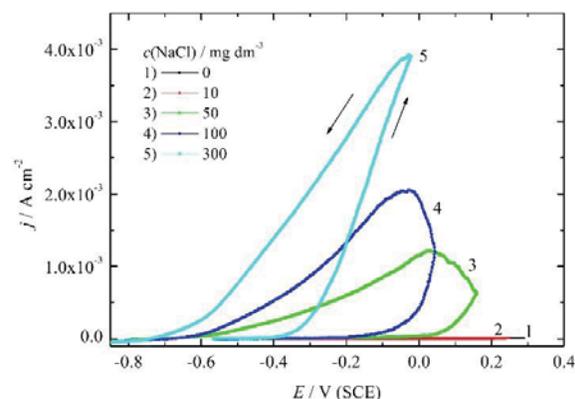


Figure 2. Polarization curve ($v = 1 \text{ mV s}^{-1}$) of aluminum alloy in solution $\text{pH} = 7$ for different concentrations of sodium chloride

Slika 2. Polarizaciona kriva ($v = 1 \text{ mV s}^{-1}$) legure aluminijuma u rastvoru $\text{pH} = 7$ za različite koncentracije natrijum-hlorida

In order to determine the characteristic values of the aluminum alloy corrosion (indicated in the diagram) in chloride containing solutions [11], Fig. 3 shows the dependence of the potential on the logarithm of current density.

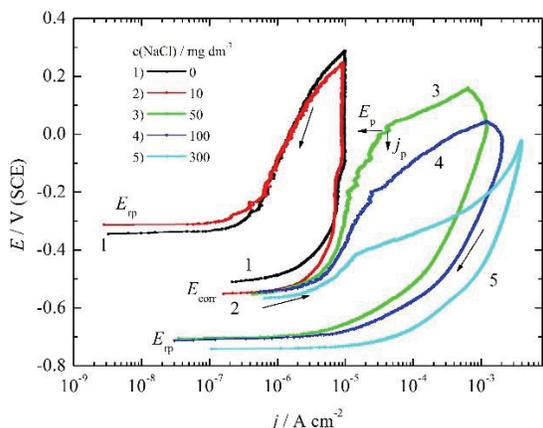


Figure 3. Polarization curve ($v = 1 \text{ mV s}^{-1}$) of aluminum alloy in $\text{pH} = 7$ for different concentrations of sodium chloride (E_{corr} -corrosion potential, E_{rep} -potential of repassivation or protective potential, E_p -pitting potential, j_p -pitting current density)

Slika 3. Polarizaciona kriva ($v = 1 \text{ mV s}^{-1}$) legure aluminijuma u rastvoru $\text{pH} = 7$ za različite koncentracije natrijum-hlorida (E_{corr} -korozijski potencijal, E_{rep} -potencijal repasivacije ili zaštitni potencijal)

From Fig. 3 the values of the corrosion and protection potential are determined and shown in Fig. 4. Because pitting occurs at potentials more positive than the protective potential, it can be seen that pitting corrosion, theoretically, can occur at chloride concentrations greater than $\sim 20 \text{ mg dm}^{-3}$ (or $\sim 33 \text{ mg dm}^{-3}$ NaCl).

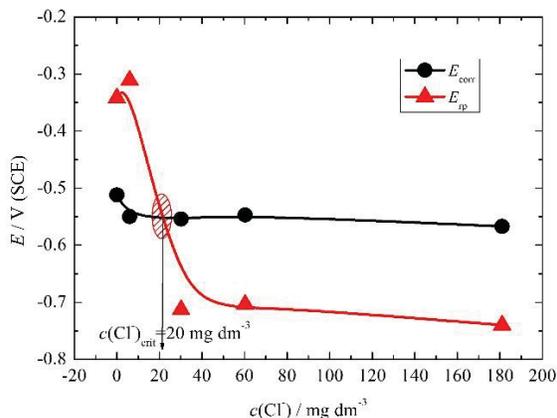


Figure 4. The determined values E_{corr} -corrosion potential and E_{rep} -protection potential, depending on the chloride concentration of

Slika 4. Određene vrednosti E_{corr} -korozijskog potencijala i E_{rep} -zaštitnog potencijala u zavisnosti od koncentracije hlorida

In Fig. 5, in order to more precisely determine the pitting potential and current density, Fig. 2 is shown for the lower values of the current densities. It can be seen that the critical pitting potentials (E_p) are shifted to more negative potentials by the increase in chloride concentration. In addition, the critical current density decrease with increasing chloride concentration and it is only $15 \mu\text{A cm}^{-2}$ for the sodium chloride concentration of 300 mg dm^{-3} . Fig. 6 shows the characteristic values of the critical pitting potential while the pitting current densities are shown in Fig. 7. It should be mentioned that for the concentration of 10 mg dm^{-3} NaCl the metastable pitting occurred up to the potentials of 1 V without reaching the critical pitting potentials [14].

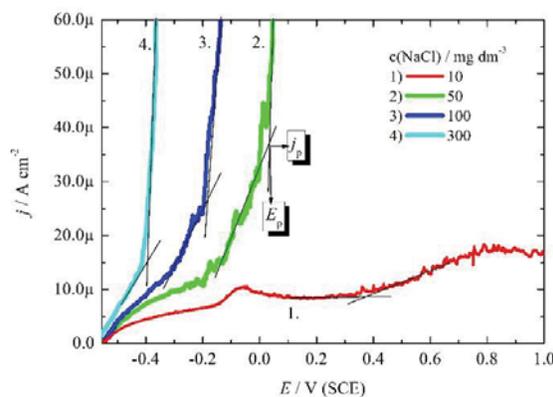


Figure 5. Determination of critical pitting potentials and current densities

Slika 5. Određivanje kritičnog piting potencijala i gustine struje

Figure 6 shows the dependence of the critical pitting potentials on the concentration of chloride ions. As can be seen, there is a linear relationship between the potentials and the concentration of chloride ions:

$$E_p = a + b \log c(\text{Cl}^-) \quad (1)$$

where a is 0.758 V and b is $-0.511 \text{ V dec}^{-1}$. Extrapolating the line to the corrosion potential (-0.55 V) has shown that pitting corrosion can occur at the corrosion potential, for the chloride ions concentration of $\sim 400 \text{ mg}$.

For the investigated alloy, the pitting corrosion at low level of chloride anions are rarely investigated and presented in the literature. The corrosion ability of the investigated alloy can be compared with reported results for pure aluminum and some aluminum alloys. For example, for the pure aluminum the pitting potentials of -0.61 V (SCE) in the solution containing 0.355 g dm^{-3} of chloride ions is reported [15], while Lee and Pyun

reported the pitting potentials of -0.65 V (SCE) under the same conditions [16]. Mazhar et al. reported that aluminum alloy containing 11 wt.% of Si, undergoes to pitting corrosion at pH = 7, at potential of -0.5 V for chloride ions concentration of 0.35 g dm⁻³ and at -0.65 V for chloride ion concentration of 3.55 g dm⁻³, which is in an agreement with our results [17]. Zaid et al. [18] reported that at pH = 6, aluminum alloy AA6061 undergoes to pitting corrosion at -0.55 V (SCE) even with sodium chloride concentration of 3 mg dm⁻³. Younis et al. [19] determined pitting potential of AA7075 aluminum alloy at pH = 7 in ~ 3 g dm⁻³ of sodium chloride to be -0.6 V (SCE).

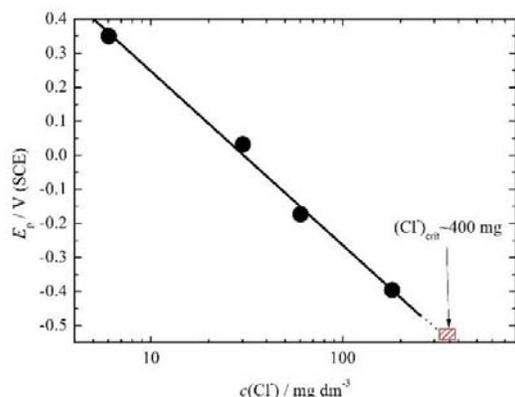


Figure 6. The dependence of critical pitting potential on the concentration of chloride ion. $(Cl)_{crit}$ critical concentration of chloride ion to reach the pitting already on the corrosion potential of ~ -0.55 V

Slika 6. Zavisnost kritičnog piting potencijala od koncentracije jona hlorida. $(Cl)_{crit}$ kritična koncentracija jona hlorida da do pitinga dođe već na korozionom potencijalu od $\sim -0,55$ V

Figure 7 shows the dependence of the pitting current density on the concentration of chloride ion, where extrapolation also determines the critical concentration of chloride ion in which pitting will occur without the subsequent polarization of aluminum, of about 450 to 500 mg dm⁻³. The dependence of the current density on the concentration of chloride can be given as:

$$j_p = a' + b' \log c(Cl) \quad (2)$$

where a' is ~ 78 $\mu\text{A cm}^{-2}$, and b' is -28 $\mu\text{A cm}^{-2} \text{dec}^{-1}$.

Figure 8 shows the current density dependency over time. After 200 s in chloride-free solution at corrosion potential, electrode is polarized anodically for 300 mV (200 - 700 s) without the chloride and after the addition of 180 mg dm⁻³ of

chloride. It can be seen that aluminum is up to 700 s in a passive state even after polarization. After adding 180 mg dm⁻³ of chloride ions, the rapid increase of the current density is observed indicating the development of the pitting corrosion.

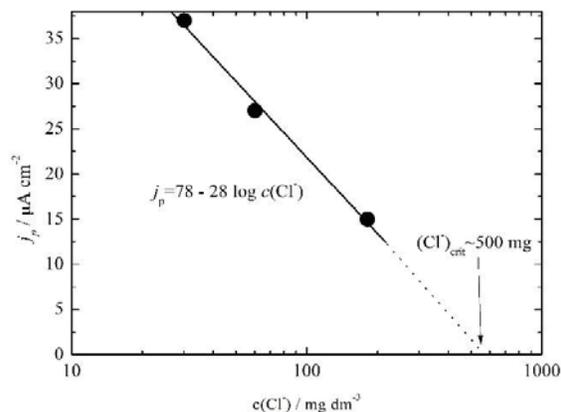


Figure 7. Dependence of the pitting current density on the concentration of chloride ion, $(Cl)_{crit}$ - critical concentration of chloride ion to provoke pitting without polarization

Slika 7. Zavisnost gustine struje pitinga od koncentracije jona hlorida, $(Cl)_{crit}$ kritična koncentracija jona hlorida da do pitinga dođe bez polarizacije

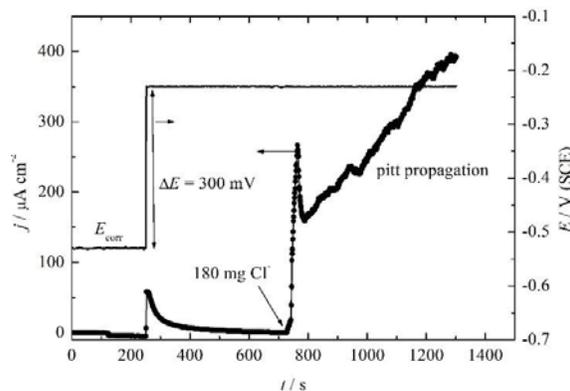


Figure 8. Dependence of the current density over 200 s without chloride, on the corrosion potential, after electrode polarization anodically for 300 mV (200 - 700 s) without the presence of chloride and after the addition of 180 mg dm⁻³ of chloride

Slika 8. Zavisnost gustine struje od vremena tokom 200 s bez hlorida na korozionom potencijalu, polarizacije elektroda anodno za 300 mV (200 - 700 s) bez prisustva hlorida i nakon dodatka 180 mg dm⁻³ hlorida

Figure 9 shows the micrographs of the aluminum surfaces before and after the experiment shown in Figure 8. From the images developed pits, with a diameter of ~ 100 μm can be easily

seen, even the electrode is polarized in the presence of chloride only for 600 s.

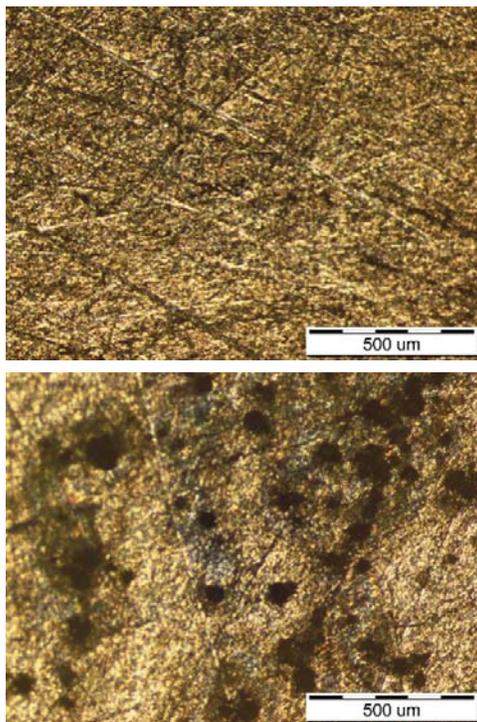


Figure 9. Micrograph images of the aluminum alloy before and after the experiment shown in Figure 8

Slika 9. Mikrografski snimci legure aluminijuma pre i posle eksperimenta prikazanog na slici 8

In order to investigate the possibility of pitting corrosion of aluminum alloy in contact with copper, the following experiments are performed and shown in Fig. 10. Aluminum alloy is after reaching the stable corrosion potential of -0.55 V connected with a copper plate ($E_{\text{corr}} = -0.02$ V) with the same surface area. After connection, the potential of the aluminum is very fast shifted to the more positive potentials of ~ -0.15 V. At the same time current density after an initial jump to $\sim 20 \mu\text{A cm}^{-2}$, slowly decrease to very small values. After adding 30 mg dm^{-3} of chloride, potentials rapidly fall down almost to the corrosion potential followed by the rapid current increase. However, very fast, the repassivation of the surface occurred and only metastable pitting can be observed. On the other hand, the addition of the total chloride concentrations of 180 mg dm^{-3} , provoke the decrease of the potential to ~ -0.4 V, which corresponds to the critical pitting potential, see Fig. 5, with a stable pitting current density of $\sim 15 \mu\text{A cm}^{-2}$. Hereafter, with this simple experiment, is shown that aluminum alloy can undergo to pitting corrosion in contact with copper at the concentration of chloride 180 mg dm^{-3} , which is smaller than maximally allowed of 300 mg dm^{-3} [8].

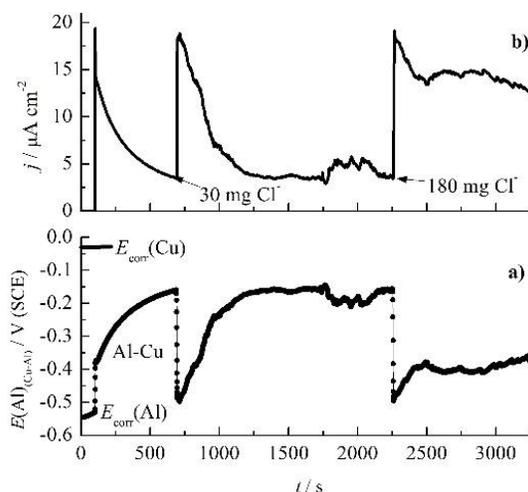


Figure 10. a) The time dependence of the polarization of the aluminum alloy electrode in connection with the copper of an equal surface area without and with the addition of 30 and 180 mg dm^{-3} of chloride. b) The time dependence of the corrosion current of the copper-aluminum cell.

Slika 10. a) Vremenska zavisnost potencijala legure aluminijuma tokom polarizacija elektrode od legure aluminijuma u spregu sa bakrom jednake površine bez i sa dodatkom 30 i 180 mg dm^{-3} hlorida. b) Zavisnost korozione struje od vremena sprega aluminijum bakar.

4. CONCLUSIONS

Based on the obtained results, it can be concluded that the critical concentration of chloride ions, which is theoretically necessary to induce a pitting corrosion of aluminum alloy, is $\sim 20 \text{ mg dm}^{-3}$. If not polarized, pitting corrosion of the aluminum alloy will certainly start at the corrosion potential if the concentration of chloride ions is $\sim 400\text{-}500 \text{ mg dm}^{-3}$. Under the anodic polarization, for example in contact with copper, it is possible that pitting corrosion starts at the chloride ions concentration of $\sim 180 \text{ mg dm}^{-3}$.

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IZVOD

UTICAJ HLORIDNIH ANJONA NA TAČKASTU KOROZIJU LEGURE ALUMINIJUMA EN 46000

Ispitano je korozivno ponašanje aluminijumske legure $AlSi9Cu3$, koje se obično koristi za proizvodnju radijatora u sistema daljinskog centralnog grejanja. U fosfatnom puferском rastvoru pri $pH = 7$, u opsegu koncentracije natrijum hlorida $10-300 \text{ mg dm}^{-3}$ ispitivana je tendencija ka tačkastoj koroziji. Procenjeni su kritični potencijali pri kojima može doći do tačkaste korozije. Ispitano je i ponašanje aluminijumske legure i bakarnog korozionog sprega.

Ključne reči: korozija, sistemi centralnog grejanja, radijatori, kritični potencijal.

Naučni rad

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