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CORROSION, MATERIALS AND ENVIRONMENTAL PROTECTION

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Ecologically friendly corrosion inhibitor for low alloy steels and aluminium alloys

Ekološki prihvatljiv inhibitor korozije za nisko legirane čelike i aluminijumske legure

Bojana Radojković^{1,*}, Dunja Marunkić¹, Jovanka Pejić¹, Milena Milošević¹, Bore Jegdić¹, Aleksandar Marinković²

¹ University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Belgrade, Republic of Serbia.

² University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Republic of Serbia.

*bojana.radojkovic@ihtm.bg.ac.rs

Abstract

The corrosion protective properties of environmentally friendly Ce-citrate were analyzed on AISI 4130 low alloy carbon steel and AA7075 aluminum alloy in 0.05 M NaCl solution. For this purpose different concentrations of corrosion inhibitor were analyzed in the range of 0.1-0.5 mM. Electrochemical impedance spectroscopy and potentiodynamic polarization test were used for measurements of resistance to general corrosion. Pitting potential E_{pit} value was used for the determination of resistance to pitting corrosion. Additionally, corrosion resistance measurements and determination of pitting potential value were performed in Ce-chloride solution with the aim of comparison. SEM microscopy was used for the determination of changes on the surface of the specimens after corrosion testing. The XPS method was used for the analyses of the formed inhibitory layer on the steel specimen surface. It has been shown that significant amounts of cerium, as well as the citrate anions, are present in the inhibitory layer. Ce-citrates have proved to be an effective corrosion inhibitor for AISI 4130 steel as well as an effective pitting corrosion inhibitor for AA7075 aluminum alloy. The mechanism of action of Ce-citrate on AISI 4130 steel and AA7075 aluminum alloy has been proposed.

Keywords: Low alloy steel, aluminium alloys, corrosion, green corrosion inhibitor, electrochemical methods, XPS.

Izvod

Zaštitna svojstva ekološki prihvatljivog inhibitora korozije Se-citrata analizirana su na AISI 4130 nisko legiranom ugljeničnom čeliku i AA7075 leguri aluminijuma u 0,05 M rastvoru NaCl. U tu svrhu analizirane su različite koncentracije inhibitora korozije u opsegu od 0,1-0,5 mM. Za merenje otpornosti na opštu koroziju korišćene su metode elektrohemijske impedansne spektroskopije i potenciodinamičke polarizacije. Vrednost piting potencijala E_{pit} je korišćena za određivanje otpornosti na piting koroziju. Pored toga, na datim legurama su, radi poređenja, sprovedena merenja otpornosti na opštu i piting koroziju u rastvoru Se-hlorida. SEM mikroskopija je korišćena za određivanje promena na površini uzoraka nakon korozionih ispitivanja. XPS metoda je korišćena za analizu formiranog inhibitoranskog sloja na površini čeličnog uzorka. Pokazalo se da su u inhibitorskom sloju prisutne značajne količine cerijuma, kao i citrat anjona. Se-citrati su se pokazali kao efikasan inhibitor korozije za AISI 4130 čelik, kao i efikasan inhibitor korozije za AA7075 leguru aluminijuma. Predložen je mehanizam delovanja Se-citrata na čelik AISI 4130 i leguru aluminijuma AA7075.

Ključne reči: nisko legirani čelici, legure aluminijuma, korozija, zeleni inhibitori korozije, elektrohemijske metode, XPS

Introduction

AISI 4130 steel [1] (25CrMo4 steel according to EN standard) belongs to the group of low-alloy chromium-molybdenum steels. It has a good combination of properties: strength, toughness, and fatigue strength, and it is widely used in various branches of industry, including the automotive and aircraft industries. This steel can be welded using conventional welding procedures.

All microconstituents in the steel are dissolved in a solid solution of the austenite phase after austenitization at 820°C to 870°C. After quenching, the AISI 4130 steel has a martensitic microstructure. The martensitic microstructure is characterized by high strength and low toughness. Optimal values of strength and toughness of the AISI 4130 steel are achieved after the tempering process. AISI 4130 steel is tempered at 400°C to 565°C, depending on the desired strength level. The lower the tempering temperature the greater the strength level. However, tempering should not be carried out between 200°C to 420°C to avoid the danger of embrittlement [2].

AA7075 aluminium alloy belongs to a series of high-strength aluminium alloys which, in addition to zinc and magnesium, contain copper as alloying elements. They are widely used in various industries, including the aircraft industry due to their high strength and low density, which is more than three times lower than the density of steel [3,4]. In chloride solutions, these alloys are very susceptible to localized types of corrosion, such as pitting corrosion, intergranular corrosion, exfoliation corrosion, and stress corrosion cracking [3]. As a result, adequate corrosion protection is of great importance for this series of alloys.

The susceptibility of AA7075 aluminium alloy to different types of corrosion depends to a large extent on the heat treatment process (alloy aging) [5,6]. The aging of AA7075 alloys is usually one-step and/or two-step aging. Aging primarily improves the mechanical properties of this aluminium alloy. However, after aging (one-step and two-step) AA7075 alloy has low resistance to general and pitting corrosion. By applying two-step aging, the resistance of this aluminium alloy to stress corrosion cracking is improved, while the alloy maintains relatively good tensile characteristics [7,8]. Chromates have traditionally been used as effective corrosion inhibitors of many metals and alloys, including steels and aluminium alloys. However, due to the high toxicity and carcinogenicity of hexavalent chromium, which is part of chromate inhibitors, the use of chromates is prohibited. In recent decades, much attention has been paid to finding ecologically-friendly corrosion inhibitors that have a high protective ability, similar to chromates.

In the 1990s, Hinton [9] showed that rare earth metal chlorides (Y, Nd, Ce, La, etc.) are effective corrosion inhibitors of many metals and alloys in NaCl solutions, including steels and aluminium alloys. The mechanism of their protective action consists of the formation of poorly soluble oxides and hydroxides of rare earth metals on the metal surface, especially on the cathodic parts. These oxides and hydroxides of rare earth metals significantly reduce the rate of cathodic reaction of the corrosion process, and thus the rate of the overall corrosion process [9-11].

In this work, the inhibitory effect of the new ecologically-friendly Ce-citrate inhibitor for corrosion protection of low-alloy chromium-molybdenum AISI 4130 steel and AA7075 aluminium alloy in NaCl solution was investigated. Citrates (salts of citric acid such as Na-citrate) are very affordable salts. Citrates are used to passivate stainless steel, instead of HNO₃, when the steel items are used in the pharmaceutical or food industry [12]. Citrates are used for food canning in the food industry and in the household. The citrate anion contains three carboxyl groups in its molecule, so it can be expected that with cerium cations on the steel surface a protective inhibitory layer forms.

2. EXPERIMENTAL

2.1 Materials

The inhibitory effect of Ce-citrate was tested on chromium-molybdenum low-alloy steel AISI 4130 and on AA7075 aluminum alloy. The tests were performed in NaCl solution without and in the presence of Ce-citrate as a corrosion inhibitor. The concentration of Ce-citrate was in the range of 0.1 mM to 0.5 mM in boat cases, on the AISI 4130 steel and AA7075 alloy. Ce-chloride and Na-citrate solutions were used with the aim of comparison and their concentrations were 0.3 mM in the boat cases.

Analyzed AISI 4130 steel specimen contains 0.28-0.33 wt. % C, 0.4-0.6 wt. % Mn, 0.80-1.1 wt. % Cr, 0.15-0.25 wt. % Mo, 0.035 wt. % P, 0.040 wt. % S, 0.15-0.35 wt. % Si as alloying elements. Chemical composition of AA7075 alloy is 5.35 wt. % Zn, 2.09 wt. % Mg, 1.44 wt. % Cu, 0.20 wt. % Cr, 0.14 wt. % Si, 0.13 wt. % Fe, 0.030 wt. % Mn, 0.024 wt. % Ti, 0.020 wt. % Zr and rest is Al.

2.2 Methods

2.2.1 Electrochemical impedance spectroscopy (EIS)

Measurements by the EIS method were performed in 0.05 M NaCl solution without and with the addition of corrosion inhibitors Ce-chloride, and Ce-citrate. Ce-citrate was not commercially available, so solutions were made by mixing appropriate amounts of Na-citrate and Ce-chloride (1: 1). EIS measurements were performed at room temperature using an electrochemical device GAMRY Reference 1010E Potentiostat/Galvanostat/ZRA. A classic three-electrode cell with a volume of ~ 200 cm³ was used. The working electrode was AISI 4130 steel and AA7075 aluminium alloy (the examined area was 1 cm²). The reference electrode was a saturated calomel electrode, and the counter electrode was a platinum mesh. Measurements were performed in a Faraday cage on the corrosion potential of E_{corr} in the frequency range from 10 000 to 0.01 Hz using a sinusoidal voltage with an amplitude of ± 10 mV vs. E_{corr} . Results were fitted using Gamry Echem Analyst software. The experiments were performed twice, and representative diagrams are presented in the paper.

2.2.2 Potentiodynamic polarization measurements

Polarization measurements were performed at room temperature on the same electrochemical device GAMRY Reference 1010E Potentiostat/Galvanostat/ZRA, in NaCl solution in the presence of corrosion inhibitor Ce-chloride or Ce-citrate, in the same concentrations as when using the EIS method. After a relatively stable corrosion potential E_{corr} was established (up to 10 min), a polarization curve was recorded, starting from the cathodic potential (-0.25 V vs. E_{corr}). The sweep rate was 1 mV s⁻¹. Polarization measurements were completed at anodic potential +0.25 V vs. E_{corr} . The experiments were performed twice, and representative diagrams are presented in the paper.

2.2.4 SEM/EDS analysis

To perform SEM/EDS analysis of AA7075 alloy specimens, a JEOL JSM-6610LV scanning electron microscope (SEM), equipped for energy dispersive spectroscopy (EDS) measurements, was used. Before starting the SEM/EDS analysis, the specimens were grinded with abrasive paper to a fineness of 1500, and then polished with Al₂O₃ paste with a fineness of 5 μm , 1 μm , and 0.3 μm respectively. Several specimens were held in NaCl solution for 24 h before SEM/EDS analysis to determine the surface appearance of the AA7075 alloy after the corrosive action of NaCl solution.

2.2.5 XPS analysis

Before XPS analysis, the specimens made from AISI 4130 chromium-molybdenum steel, with dimensions 7 mm x 7 mm x 1.5 mm, were immersed in inhibitor solution (0.05 M NaCl + 0.3 mM Ce-citrate) for 48 h. The specimens were removed from the inhibitor solution, washed with bidistilled water, and air-dried. XPS analysis was performed using SPECS Systems with XP50M X-ray source for Focus 500 and PHOIBOS 100/150 analyzer. Survey spectra (0–1000 eV binding energy) were recorded in the FAT mode, using an AlK α source (1486.74 eV).

The specimens which have been previously immersed in Ce-citrate inhibitive solution were also sputtered for the 20 s with PU IQE 12/38 argon beam to remove surface impurities and thin surface inhibitory layer. Spectra were collected by SpecsLab data analysis software supplied by the manufacturer and analyzed with a commercial CasaXPS software package.

3. RESULTS AND DISCUSSION

3.1 Corrosion behavior of steel in neutral NaCl solution with and without Na-citrate

Figure 1a shows Nyquist diagrams for AISI 4130 steel after 96 h testing in NaCl solution without and in the presence of Na-citrate. As can be seen the Na-citrate to some extent reduces the value of the polarization resistance R_p . A similar tendency was obtained after shorter periods of testing.

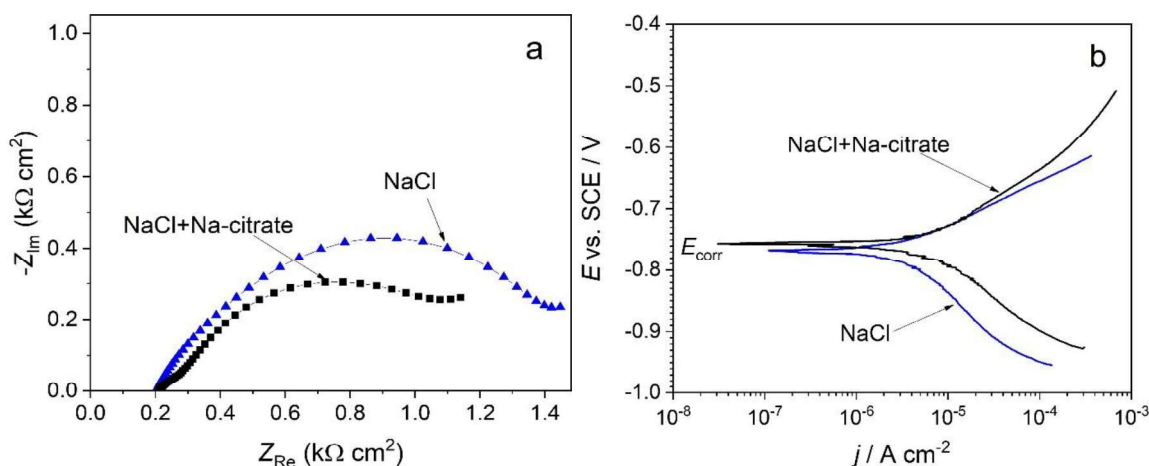


Figure 1. a) Nyquist diagrams and b) Polarisation diagrams for AISI 4130 steel after 96 h testing in NaCl solution without and in the presence of Na-citrate.

The results of polarization measurements are in good agreement with the results of EIS measurements. Figure 1b shows the polarization diagrams for 0.05 M NaCl without and in the presence of 0.3 mM Na-citrate. It can be observed that the value of the corrosion current density j_{corr} is lower in NaCl solution than in NaCl solution in the presence of Na-citrate. This means that the presence of Na-citrate causes an increase in the corrosion rate of AISI 4130 steel.

3.2 Corrosion behavior of steel in neutral NaCl solution in the presence of Ce-citrate

3.2.1 EIS measurement results

Figure 2 shows the Bode diagrams for AISI 4130 steel obtained after 48 h of testing in 0.05 M NaCl solution in the presence of 0.3 mM Ce-citrate, and 0.3 mM Ce-chloride, respectively. The value of the polarization resistance R_p in NaCl solution (without the inhibitors) has a relatively small value. A significantly higher value of polarization resistance was obtained in the presence of Ce-chloride and particularly Ce-citrate (Figure 2a).

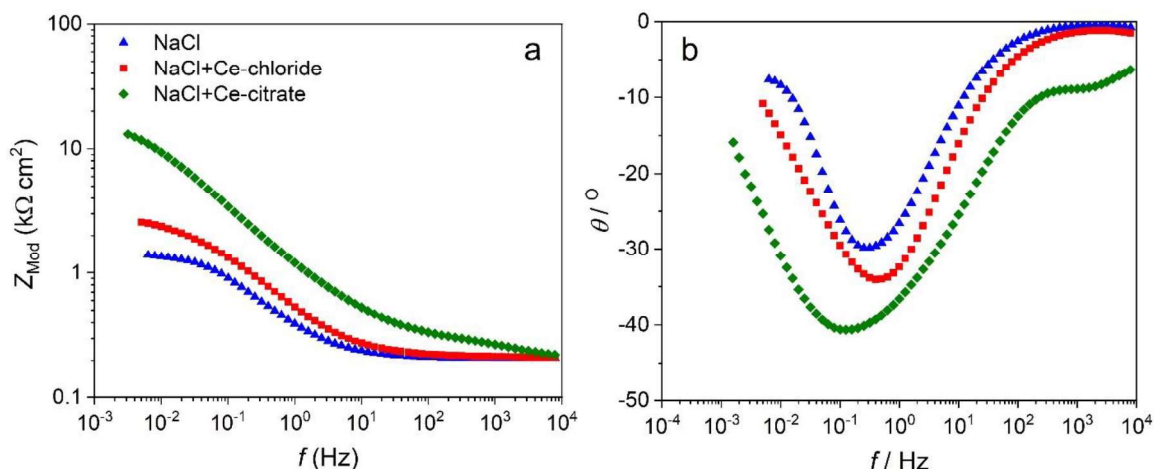


Figure 2. a) Bode modulus, and b) Bode phase diagrams for AISI 4130 steel after 48 h testing in 0.05 M NaCl solution in the presence of 0.3 mM Ce-chloride and 0.3 mM Ce-citrate.

The inhibitory effect of Ce-citrate can be observed on the Bode Phase diagram. The characteristic peak on the Bode Phase diagram in the case of Ce-citrate widens to lower frequency values. Also, the lowest value of the phase angle was obtained in the case of Ce-citrate and the highest value in the case of NaCl without the corrosion inhibitors (Figure 2b).

Previously [13] it was shown that the widening or narrowing of the characteristic phase peak at low frequencies indicates an increase or decrease of the inhibitor layer compactness or the inhibitor efficiency.

3.2.2 Results of polarization measurements

The polarization diagrams for AISI 4130 steel in 0.05 M NaCl solution without and in the presence of the corrosion inhibitors 0.3 mM Ce-chloride and 0.3 mM Ce-citrate are shown in Figure 3. The corrosion current density value j_{corr} is lowest in the presence of Ce-citrate and highest in NaCl solution without the corrosion inhibitors (Figure 3).

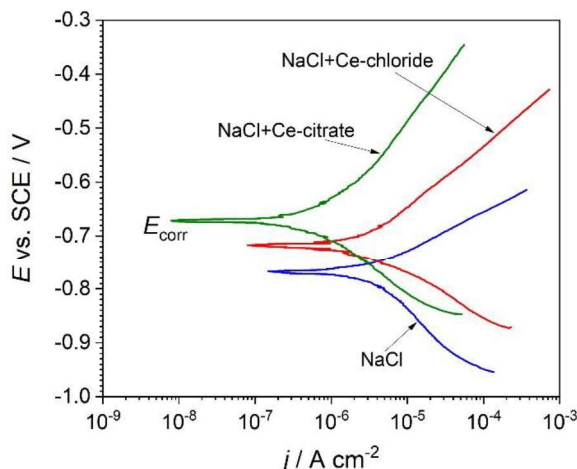


Figure 3. The polarization diagrams for AISI 4130 steel after 96 h testing in 0.05 M NaCl solution without and in the presence of the corrosion inhibitors 0.3 mM Ce-chloride and 0.3 mM Ce-citrate.

3.3 Results of XPS analysis inhibitive layer on AISI 4130

The results of XPS analysis show that a significant amount of cerium is present in the inhibitive layer in the oxidation states CeIII and CeIV, as well as citrate anions and iron oxides, hydroxides, and oxyhydroxides (Figure 4). Oxides, oxy-hydroxides, and hydroxides of iron are formed during the formation of the inhibitive layer, as a consequence of corrosion reactions (dissolution of the base metal-steel). The iron compounds were incorporated in the inner parts of the inhibitive layer and probably in the parts of the inhibitive layer which is directly next to the metal surface.

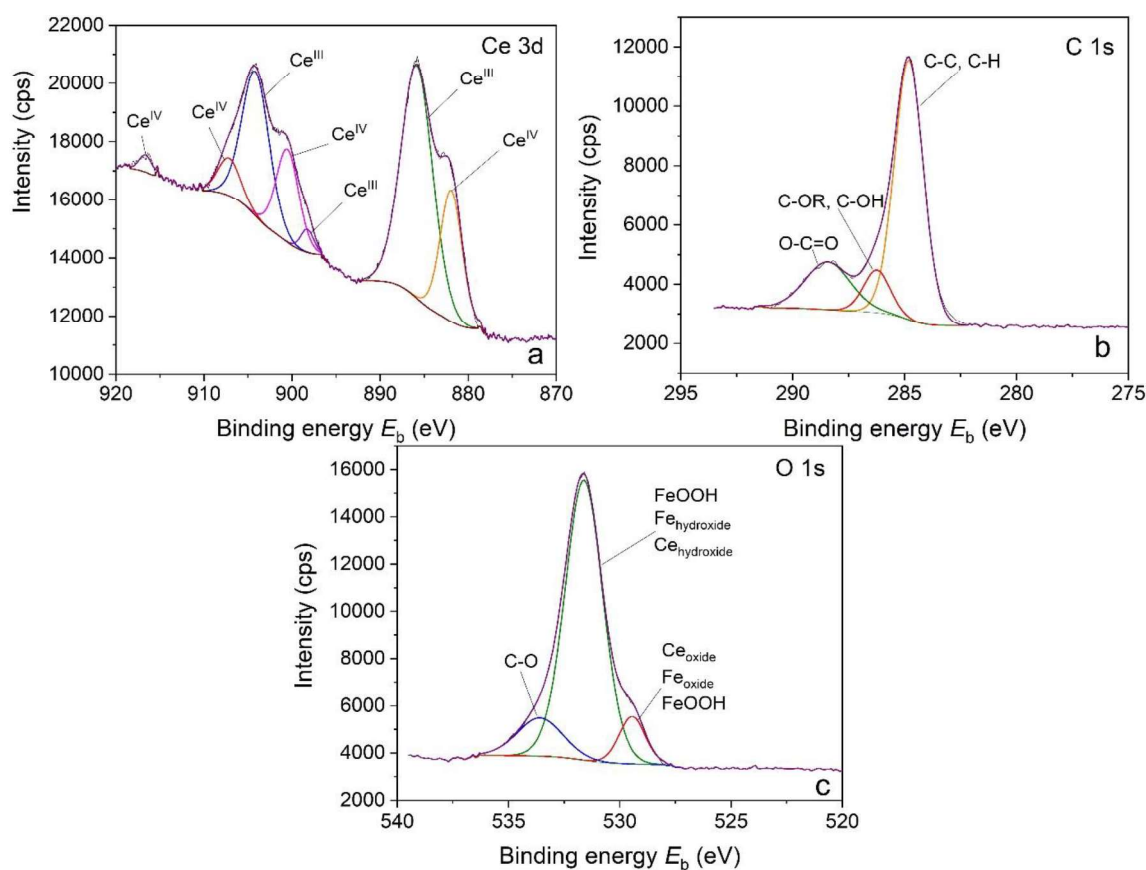


Figure 4. XPS diagrams: a) Ce 3d, b) C 1s and c) O 1s for AISI 4130 steel specimens previously immersed in 0.05 M NaCl solution containing 0.3 mM Ce-citrate for 48 h.

Citrate anions are known to be good complexants for many metals, especially in the presence of OH⁻ ions. It can be assumed with high probability that during the corrosion process (i.e. the cathodic reaction of oxygen reduction) formation and precipitation of the cerium complex with citrate anion occurred on the steel surface, as a consequence of the formation of OH⁻ ions in the near-electrode layer. In this complex, cerium cations are bound to citrate anions via oxygen atoms from carboxyl groups (citrate anion). The formed inhibitive layer becomes more compact and more resistant over time to the action of surrounding corrosive agents (chloride ions). The Ce-citrate complex is bound to the steel surface via oxygen atoms from the remaining carboxyl groups of the citrate anion. XPS analysis did not detect the presence of chloride ions in the inhibitor layer, which indicates the compactness and high corrosion resistance of the formed inhibitive layer.

The results presented in this paper confirm the correctness of the proposed mechanism, as well as the high compactness and corrosion resistance of the formed inhibitive layer.

3.4 SEM/EDS analysis AA7075 aluminium alloy

Figure 5a shows the microstructure of the polished AA7075 aluminium alloy obtained by SEM microscopy. Lighter IMCs are rich in copper and iron and represent cathodic IMC. A cathodic reaction of oxygen reduction takes place on these IMCs in a neutral NaCl solution, resulting in the formation of hydroxyl anions. Cathodic IMCs do not dissolve, and pits are formed along their border in NaCl solution. Dark-colored IMCs are rich primarily in magnesium and represent anodic IMCs. These IMCs dissolve in the neutral NaCl solution in the initial period of testing and thus do not significantly affect the overall corrosion resistance of the aluminium alloy.

Figures 5b and 5c show SEM microphotographs of the AA7075 aluminium alloy after 24 h in NaCl solution. It can be seen (Figures 5b and 5c) that channels have formed around the cathodic IMCs, which are suitable places for the pit formation.

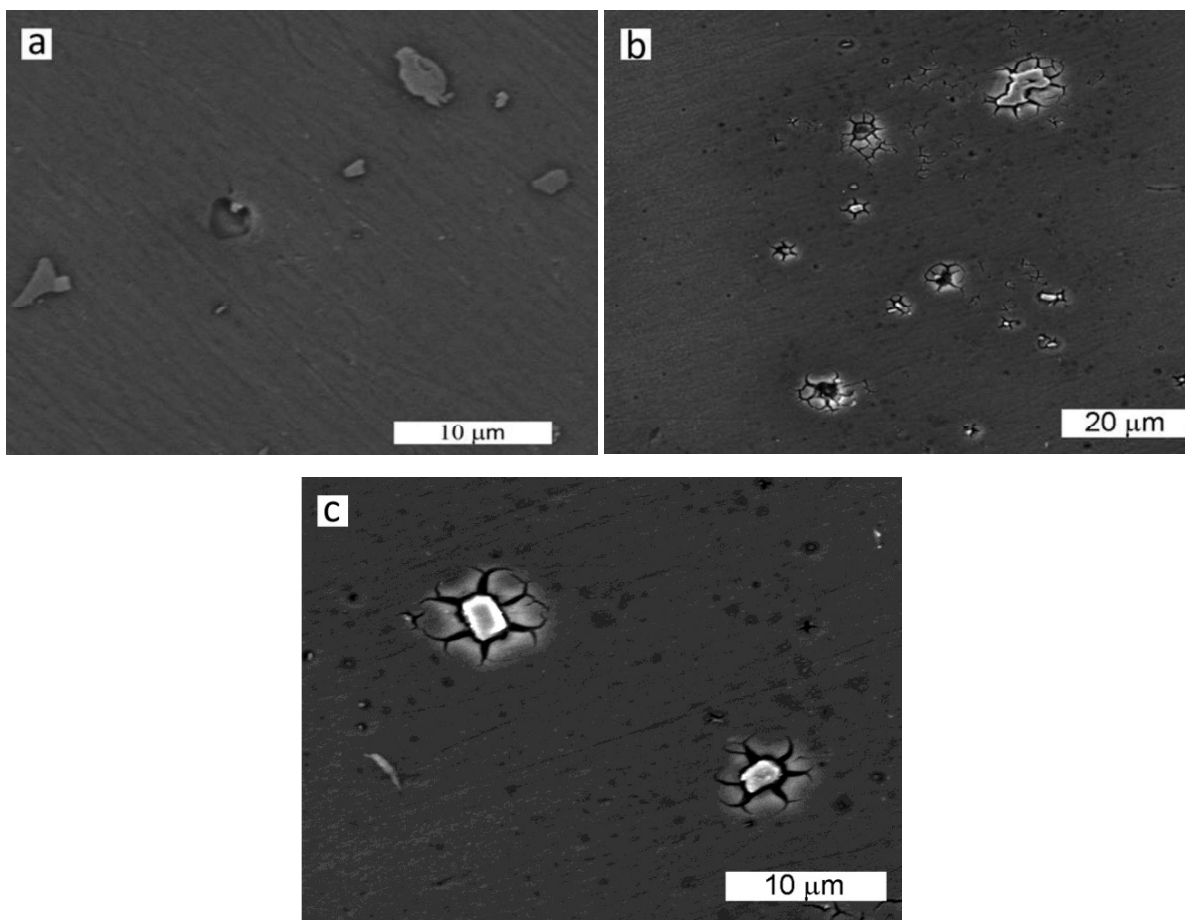


Figure 5. SEM microphotographs of the a) polished AA7075 aluminium alloy, b) and c) AA7075 aluminium alloy after 24 h in NaCl solution.

3.5 Comparison of inhibition effect of Ce-citrate with Ce-chloride on AA7075 alloy

Figure 6a shows the time dependence of E_{corr} for the AA7075 alloy in NaCl solution in the presence of Ce-chloride and Ce-citrate, respectively. In the presence of Ce-chloride, significant fluctuations of the corrosion potential occurred over time (Figure 6a). In the case of Ce-citrate, the corrosion potential had a constant value throughout the measurement period. Also, in the case of Ce-citrate, the value of E_{corr} had a lower value ($E_{\text{corr}} = -0.80$ V) than in the case of Ce-chloride ($E_{\text{corr}} = -0.68$ V), which indicates the cathodic character of the Ce-citrate as a corrosion inhibitor.

The lowest value of the corrosion current density j_{corr} was obtained on AA7075 alloy in the presence of Ce-chloride (Figure 6b). However, in the case of Ce-chloride, a sudden increase in corrosion current density occurs immediately after the transition from the cathodic to the anodic region, which indicates the pit formation. This means that the AA7075 alloy in the presence of cerium-chloride has negligible resistance to pitting corrosion.

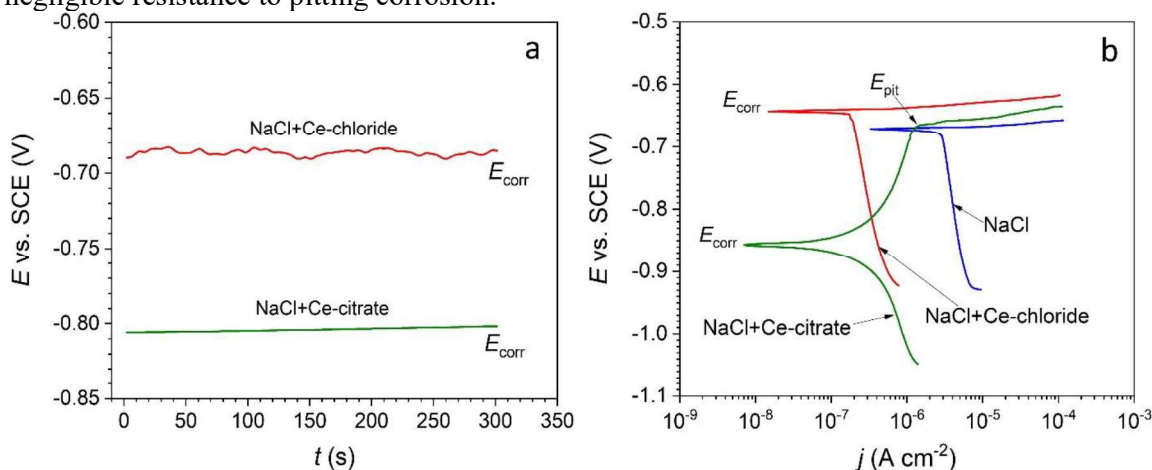


Figure 6. a) Time dependence of E_{corr} and b) Polarization diagrams for AA7075 alloy after 24 h testing in NaCl solutions without and in presence of 0.5 mM Ce-citrate or 0.5 mM Ce-chloride.

In contrast to Ce-chloride, which has a sharp increase in corrosion current density after the transition from the anodic to the cathodic region, in the case of Ce-citrate after the transition from the cathodic region there is a relatively wide pseudo-passive area in which the alloy is in a passive state (pseudo-passive area width is ~ 0.20 V and pitting potential E_{pit} is around -0.67 V). In addition to the native passive film, an inhibitory film is also present on the surface of the AA7075 alloy, so that is why it is more correct to call this area a pseudo-passive area. With a further increase in the potential, only after crossing the passivation area, the current increase, i.e., pits are formed. This indicates that Ce-citrate is an effective inhibitor of general and especially pitting corrosion even at very low concentrations (0.5 mM).

CONCLUSION

On the basis of the presented results, following conclusion can be formed:

- Na-citrate, without the cerium ions, did not show an inhibitory effect in NaCl solution, at a concentration of 0.3 mM. Na-citrate to some extent acted as an activator of steel corrosion.
- Ce-citrate at the optimal concentration had a significantly higher inhibitory effect than Ce-chloride.
- The results of XPS analysis show that a significant amount of cerium is present in the inhibitory layer in the oxidation states CeIII and CeIV, as well as citrate anions and iron oxides, hydroxides, and oxy-hydroxides.
- The results of polarization measurements (pitting potential, E_{pit}) showed that the resistance of AA7075 alloy to pit formation in the presence of Ce-citrate is far higher than in the presence of Ce-chloride. A wide pseudo-passive area between the corrosion potential and the pitting potential was obtained in the presence of Ce-citrate. No pseudo-passive area was obtained in the presence of Ce-chloride.
- The mechanism of the inhibitory effect of Ce-citrate in NaCl solution on the corrosion resistance of AISI 4130 steel and AA7075 aluminium alloy has been proposed.

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