Srpsko hemijsko društvo

Serbian Chemical Society

58. Savetovanje Srpskog hemijskog društva

KRATKI IZVODI RADOVA

KNJIGA RADOVA

58th Meeting of the Serbian Chemical Society

Book of Abstracts
Proceedings

Beograd 9. i 10. jun 2022. godine
Belgrade, Serbia, June 9-10, 2022

CIP - Каталогизација у публикацији - Народна библиотека Србије, Београд
54(082)
577.1(082)
66(082)
66.017/.018(082)
502/504(082)
СРПСКО хемијско друштво. Саветовање (58 ; 2022 ; Београд)
Kratki izvodi radova ; [i] Knjiga radova / 58. savetovanje Srpskog hemijskog društva, Beograd 9. i 10. jun 2022. godine = Book of Abstracts [end] Proceedings = 58th meeting of the Serbian Chemical Society, Belgrade, June 9-10, 2022 ; [glavni i odgovorni urednik, editor Bogdan Šolaja]. - Beograd : Srpsko hemijsko društvo = Serbian Chemical Society, 2022 (Beograd : Razvojno-istraživački centar grafičkog inženjerstva TMF). - 226 str. : ilustr. ; 25 cm
Radovi na srp. i engl. jeziku. - Tekst ćir. i lat. - Tiraž 30. - Bibliografija uz pojedine radove.
ISBN 978-86-7132-079-5
a) Хемија - Зборници b) Биохемија - Зборници c) Технологија - Зборници d) Наука о материјалима - Зборници e) Животна средина - Зборници
COBISS.SR-ID 67900169

58. SAVETOVANJE SRPSKOG HEMIJSKOG DRUŠTVA,
Beograd, 9. i 10. jun 2022.
KRATKI IZVODI RADOVA/KNJIGA RADOVA
58th MEETING OF THE SERBIAN CHEMICAL SOCIETY
Belgrade, Serbia, 9-10 June 2022
BOOK OF ABSTRACTS/PROCEEDINGS

Izdaje/Published by
Srpsko hemijsko društvo/Serbian Chemical Society
Karnegijeva 4/III, 11000 Beograd, Srbija
tel./fax: +381 11 3370 467; www.shd.org.rs, E-mail: office@shd.org.rs
Za izdavača/For Publisher
Dušan Sladić, predsednik Srpskog hemijskog društva

Glavni i odgovorni urednik/ Editor
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Uređivački odbor/Editorial Board
Ivana Ivančev-Tumbas, Suzana Jovanović-Šanta, Aleksandra Tubić, Melina Kalagasidis Krušić

Priprema za štampu i štampa/Prepress and printing
Razvojno-istraživački centar grafičkog inženjerstva Tehnološko-metalurškog fakulteta, Beograd / Research and Development Centre of Printing Engineering, Belgrade

Godina izdanja: 2022.

Tiraž/ Circulation
30 primeraka/ 30 copies printing

ISBN 978-86-7132-079-5

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Savetovanje je podržalo /*Supported by*

Ministarstvo prosvete, nauke i tehnološkog razvoja Republike Srbije
Ministry of Education, Science and Technological Development of Republic of Serbia

Hemijsko inženjerstvo/Chemical Engineering

Knjiga radova/Proceedings

Analitička hemija/Analytical Chemistry

Elektrohemija/Electrochemistry

R-EH-1

Synergistic effect of Neodymium and Cysteine as inhibitors for AA7075 alloy in NaCl solution

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Abstract

The synergistic effect of neodymium chloride and cysteine in NaCl solution was investigated. The concentration ratio of these two inhibitors was 1: 3 (neodymium: cysteine). The corrosion resistance of AA7075 alloy was tested electrochemically using electrochemical impedance spectroscopy (EIS). Significantly higher polaryzation resistance in inhibitor containing solution, along with phase angle peak shift to more negative values, indicate good corrosion inhibition by Nd-cysteine. The morphology, analyzed by scanning electron microscopy (SEM/EDS), shown that the surface of the AA7075 alloy was wholly protected from corrosion after 24h in NaCl solution.

Introduction

Aluminum alloy AA7075 belongs to alloys that have extremely high strength, and are used in various industries, mostly in the aircraft industry. However, in the presence of chloride ions it is prone to corrosion, which is one of its main disadvantages [1,2]. The simplest and most economical way of its protection is by inhibitors. The most effective inhibitors were chromates, but due to their harmfulness and carcinogenicity, they were banned by European regulations [3]. Recently, so-called green or eco-friendly inhibitors have been used as not harmful ones to humans and nature. Lanthanides, either alone or in combination with organic compounds, are good inhibitors in NaCl solution [4].

The aim of this paper is to analyse the combination of cysteine and neodymium, as green corrosion inhibitors, for AA7075 alloy. Inhibitory behavior was evaluated by electrochemical impedance spectroscopy (EIS), and the surface of the specimens before and after the experiments was examined using a scanning electron microscopy (SEM / EDS).

Materials and methods

The chemical composition of AA7075 alloy, determined by XRF method (Olympus Vanta C Series Handheld XRF Analyzer) is shown in Table 1. For electrochemical testing the specimens were mechanically polished with SiC paper up to 1200 grit, and for SEM /EDS analysis, they were additionally polished by water based Al_2O_3 suspension (5 μm and 1 μm). The following chemicals were used for the preparation of the solutions: 0.1M NaCl (p.a. grade, Sigma Aldrich), 0.3mM cysteine (≥98%, Sigma Aldrich), 0.1mM $NdCl_3$ (99 %, Across Organics), high-purity water (Millipore, 18 MΩ cm resistance, using Milli-Q Water Purification Systems).

Table 1. Chemical composition of AA7075 alloy, wt.%

Zn	Mg	Cu	Mn	Cr	Si	Fe	Al
6.90	2.64	1.62	0.27	0.24	0.20	0.09	Rest

The EIS measurements were carried out by GAMRY Reference 1010E Potentiostat/Galvanostat/ZRA in a standard three-electrode cell setup. The working electrode was the aluminum alloy, the counter electrode was Pt mesh, and the reference electrode was saturated calomel electrode (SCE). Measurements were performed in triplicate at the corrosion potential over the frequency range: 100 kHz – 10 mHz, ±10 mV amplitude of the sinusoidal voltage.

Microstructural analyses of samples before and after corrosion measurements were performed using field emission scanning electron microscopy (FE-SEM) JEOL JSM-6610LV, 20 kV working voltage, with Energy Dispersive X-Ray Spectroscopy (EDS).

Results and Discussion

SEM/EDS analysis- The surface morphology and chemical composition of polished, bare AA7075 specimen were analyzed by SEM-EDS technique (Fig. 1).

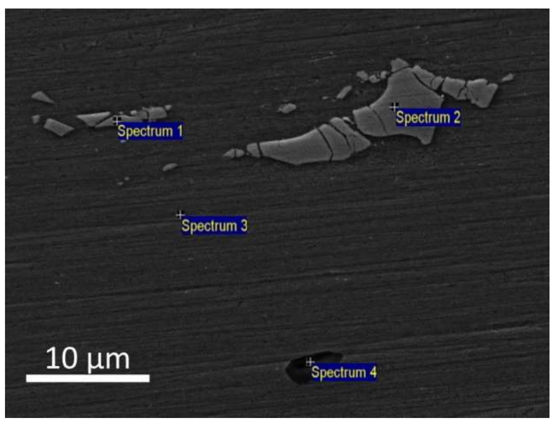

Figure 1. SEM microphotograph of AA7075 alloy

AA7075 alloy contains intermetallic particles (IMP) of micrometer dimensions, which can be anodic or cathodic. IMPs containing Mg, Zn, and Si are of an anodic character, they dissolve in the initial period of the corrosion process but they do not significantly deteriorate the corrosion properties of aluminum alloy, and they are darker than matrix (Fig. 1, Spectrum 4: 6.8 % Zn, 12.6 % Mg, 1.5 % Cu, 12.8 % Si). IMPs containing Fe and Cu are cathodic and lighter than matrix, as shown in Fig. 1 by Spectrums 1 (2.1 % Zn, 3.8 % Cu, 4.5 % Si, 16.4 % Fe, 5.7 % Mn) and 2 (2.7 % Zn, 0.2 % Mg, 3.5 % Cu, 4.3 % Si, 15.8 % Fe, 5.1 % Mn). A cathodic oxygen reduction reaction occurs on the surface of cathodic IMPs during the corrosion process in neutral chloride solutions. As a result, these particles significantly deteriorate the corrosion properties of AA7075 alloy. In Fig. 1, Spectrum 3 refers to an aluminium matrix.

Bode-Phase diagrams for AA7075 alloy obtained in NaCl solution without and in the presence of Nd-cysteine inhibitor are shown in Figure 2. A significant increase in the polarization resistance in inhibitor containing solution was obtained. The phase angle peak in the presence of Nd-cysteine shifts to more negative values (Figure 2b), and it is expanded over greater frequency range as compared with the inhibitor-free NaCl solution.

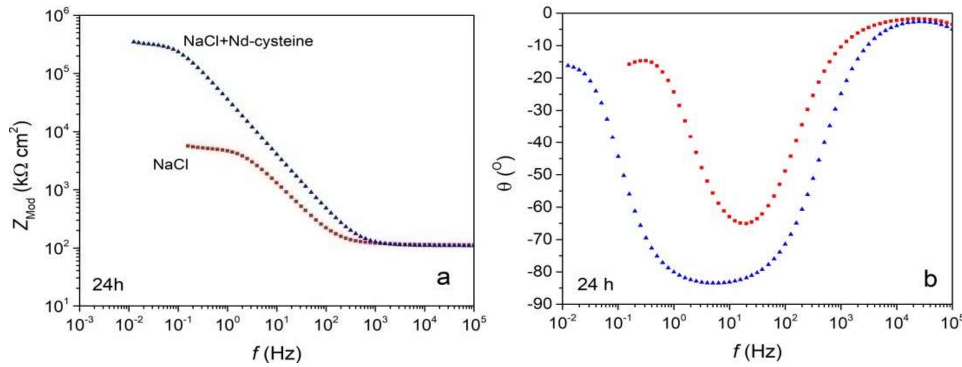

Figure 2. a) Bode modulus and b) Bode phase diagram for AA7075 alloy in NaCl solution without and in presence of Nd-cysteine.

After immersing the specimens in the inhibitor-free NaCl solution, trenches along cathodic IMPs edges were formed (Figure 3a), denoting a form of pitting corrosion of AA7075 alloy. SEM micrograph of the AA7075 alloy surface after immersion for 24 h in the inhibitory solution is shown in Figure 3b. Figure 3b, unlike Figure 3a, does not show any trenches or other corrosion damage around the IMPs. The surface of the AA7075 alloy is protected against corrosion when an inhibitor is present.

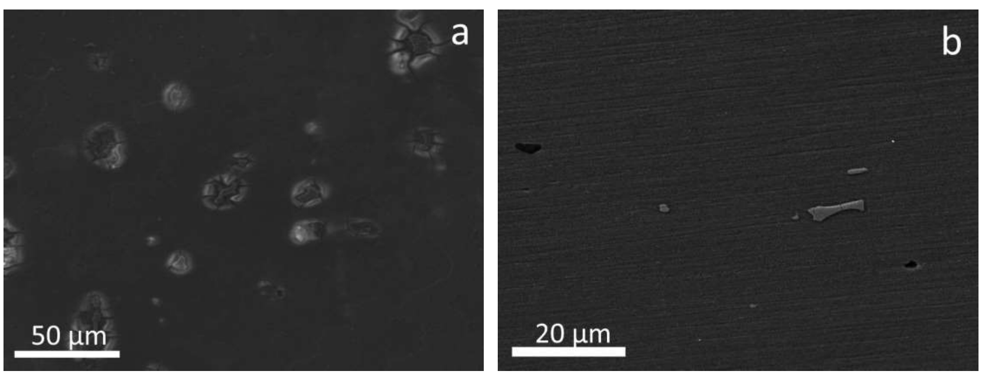

Figure 3. SEM micrograph of the surface AA7075 alloy after immersion for 24 h in: a) NaCl solution, b) NaCl solution + inhibitor.

Conclusion

Electrochemical measurements have shown that $NdCl_3$ in combination with cysteine, acting in synergy, plays a significant role in protecting the AA7075 alloy in 0.1M NaCl solution. Bode phase diagrams confirmed that the synergetic effect of cysteine and $NdCl_3$ showed good inhibitor protection. SEM analysis confirmed that tested corrosion inhibitors provide satisfying corrosion protection in NaCl solution after 24h, compared to inhibitor-free NaCl solution.

Acknowledgment: This study was financially supported by the Ministry of Education, Science, and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2022-14/200026, Grant No. 451-03-68/2022-14/200135).

Sinergetsko dejstvo neodimijuma i cisteina na leguri AA7075 u rastvoru NaCl

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Ispitano je sinergetsko dejstvo neodijumhlorida i cisteina u rastvoru NaCl. Odnos koncentracija ova dva inhibitora je bio 1:3 (neodijum:cistein). Otpornost na koroziju legure AA7075 ispitana je elektrohemijski pomoću spektroskopije elektrohemijske impendancije (EIS). Znatno veća otpornost u rastvoru inhibitora i manje vrednosti faznog ugla ukazuju na dobro inhibitorsko dejstvo neodimijuma i cisteina. Analiza površina uzoraka pre i posle korozionih ispitivanja, snimljenih pomoću skenirajuće elektronske mikroskopije (SEM/EDS), pokazuje da se posle 24h delovanja agensa korozije ne javljaju oštećenja AA7075 legure, što potvrđuje dobru zaštitu postignutu ispitivanim inhibitorima.

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