Corrosion behavior of CuAlNiMn in 0.9% NaCl solution

Vrsalović, Ladislav; Gotovac, Ivan; Gudić, Senka; Ivanić, Ivana; Kožuh, Stjepan; Kosec, Borut; Bizjak, Milan; Pezer, Robert; Gojić, Mirko

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SADRŽAJ / CONTENTS

			str./page
1.	J. W. Erning	Release of heavy metals from alloys used in drinking water: How to test and evaluate materials *Otpuštanje teških metala iz legura korištenih u sustavima pitke vode: Kako ispitati i ocijeniti materijale* **(Predavanje na poziv / Invited lecture)**	1-6
2.	L. Vrsalović, I. Gotovac, S. Gudić, I. Ivanić, S. Kožuh, B. Kosec, M. Bizjak, T. Holjevac, R. Pezer, M. Gojić	Corrosion behavior of CuAlNiMn alloy in 0.9% NaCl solution *Korozijsko ponašanje legure CuAlNiMn u 0.9% NaCl otopini*	7-16
3.	L. Lokas, V. Alar	Influence of temperature on electrochemical properties of AA5083 aluminum alloy in seawater *Utjecaj temperature na elektrokemijska svojstva aluminijske legure AA5083 u morskoj vodi*	17-25
4.	M. Kurtela, I. Stojanović, V. Alar, T. Benković	Influence of $CeCl_3$ on the oxide coating properties of aluminum alloy AA2024-T3 *Utjecaj Cerij(III)-klorida na svojstva oksidne prevlake aluminijske legure AA2024-T3*	26-40
5.	Z. Keran, M. Mihaljević, A. Horvatić Novak, B. Runje	The impact of the grain size on the ultrasound velocity in the material *Utjecaj veličine zrna na brzinu ultrazvuka u materijalu*	41-47
6.	V. Grudić, S. Martinez, B. Knežević	Corrosion inhibition of steel in NaCl solution by propolis *Inhibicija korozije čelika u otopini NaCl pomoću propolisa*	48-57
7.	Zhi Feng LIN, Li Kun XU, Xiang Bo LI, Li Wang, Weimin GUO, Chuan Jie WU, Yi YANG	Corrosion resistance of composite coating used for fastener protection *Otpornost na koroziju kompozitne prevlake za zaštitu vijčanih spojeva*	58-69
8.	V. Šimunović, M. Kurtela, I. Stojanović, E. Zvonc	Corrosion properties of aluminum alloy AA2024-T3 after immersion in NaCl aqueous solution with $CeCl_3$ *Korozijska svojstva aluminijske legure AA2024-T3 nakon uranjanja u vodenu otopinu NaCl s Cerij(III)-kloridom*	70-81

9.	M. Lafta, M. Bratošević	Protection with corossion inhibitors on demaged coating in seawater *Zaštita inhibitorima korozije na oštećenim prevlakama u morskoj vodi*	82-88
10.	E. K. Mioč, B. Riautet, Z. Hajdari Gretić, H. Otmačić Ćurković	Corrosion protection in flow conditions by carboxylic and phosphonic acids *Korozijska zaštita u protočnim uvjetima primjenom fosfonskih i karboksilnih kiselina*	89-101
11.	S. Božović, S. Martinez, V. Grudić, A. Gezović	Synergetic effect of propolis, tannin and benzoate on corrosion behavior of metal in 0.5M NaCl *Sinergijsko djelovanje propolisa, tanina i benzoata na korozijsko ponašanje metala u 0.5M NaCl*	102-111
12.	K. Kekez, I. Rogan, L. Lokas, T. Madaoui	Corrosion inhibition of equipment under hydrstatic test – experience from Algeria *Inhibiranje korozije opreme pod hidrostatskom tlačnom probom – iskustva iz Alžira*	112-121
13.	M. Serdar, D. Bjegović	Application of nano- and micro-indentation in the analysis of mechanical properties of corrosion products *Primjena nano- i mikro-utiskivača u analizi mehaničkih svojstava korozijskih produkata*	122-129
14.	N. Pavić	Corrosion protection by hot deep galvanizing *Zaštita materijala vrućim pocinčavanjem*	130-136
15.	L. Pomenić	Corrosion in electronics *Korozija u elektronici*	137-146
16.	T. Šolić, D. Marić, I. Putnik, S. Muić, I. Samardžić, S. Aračić	Mechanical properties testing of steel 1.7131 after nitrocarburization *Ispitivanje mehaničkih svojstava čelika 1.7131 nakon nitrokarburiranja*	147-154
17.	M. Bilušić, B. Runje	The influence of coating on the accuracy of the optical 3D measurement system *Utjecaj premaza na točnost mjerenja optičkim 3D mjernim sustavom*	155-161

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CORROSION BEHAVIOR OF CuAlNiMn ALLOY IN 0.9% NaCl SOLUTION

KOROZIJSKO PONAŠANJE LEGURE CuAlNiMn u 0,9% NaCl OTOPINI

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Abstract

The corrosion behavior of the CuAlNiMn alloy in 0.9% NaCl solution at pH 7.4, and temperatures of 25, 37 and 50 °C, was investigated by electrochemical methods such as monitoring the open circuit potential, linear and potentiodynamic polarization methods. Investigations were also performed in 0.9% NaCl solution at 37 °C and different pH of solution (pH = 3.4, 5.4 and 7.4). Results of the investigations have shown that increasing the temperature leads to the shift of the open circuit potential values in the negative direction and also leads to increase of the corrosion current density and decrease of the polarization resistance values. Decreasing the pH of solution leads to the increase of the corrosion current density and decrease the values of polarization resistance.

After the polarization measurements, corroded electrode surfaces was examined using an optical microscope and SEM. Microscopic images have shown the significant corrosion damages on the CuAlNiMn alloy surface, which manifests itself in the form of a thin leaf, with a larger part of the surface being covered with sheets of corrosion products loosely bonded to the surface which were elevated from the surface of the electrode. SEM surface analysis revealed the existence of two layers on the surface of the alloy: the exterior is extremely damaged, which represent sheets of loosely bonded surface, and an inner layer that also shows significant corrosion damage. The elemental composition of corrosion products on the surface of the samples was determined by EDS analysis.

Keywords: CuAlNiMn alloy, corrosion, polarization, electrochemical methods

Sažetak

Korozijsko ponašanje legure CuAlNiMn u 0.9% NaCl otopini pri pH = 7.4 i temperaturi otopine od 25, 37 i 50 °C ispitano je elektrokemijskim metodama kao što su praćenje potencijala otvorenog strujnog kruga, metodama linearne i potenciodinamičke polarizacije. Ispitivanja su također provedena u 0.9% NaCl otopini pri 37 °C i različitim vrijednostima pH otopine (pH = 3.4, 5.4 i 7.4). Rezultati ispitivanja su pokazali da povećanje temperature elektrolita dovodi do negativiranja potencijala otvorenog strujnog kruga, a također i do povećanja vrijednosti gustoća korozijske struje i do smanjenja vrijednosti polarizacijskog otpora. Snižavanje pH otopine dovodi do povećanja gustoće korozijske struje i do smanjenja vrijednosti polarizacijskog otpora.

Nakon polarizacijskih mjerenja korodirane površine elektroda ispitane su optičkim mikroskopom i pretražnim elektronskim mikroskopom (SEM). Mikroskopske snimke su pokazale značajna korozijska oštećenja na površini CuAlNiMn legure koja se manifestiraju u vidu svojevrsnog listanja, pri čemu je veći dio površine prekriven s listićima korozijskih produkata labavo vezanim za površinu koji se uzdižu s površine elektrode. SEM analiza površine otkrila je postojanje dvaju slojeva na površini legure: vanjski izrazito oštećen, koji predstavlja listiće korozijskih produkata labavo vezane za površinu, i unutarnji sloj na kojem su također vidljiva značajna korozijska oštećenja. EDS analizom određen je elementarni sastav korozijskih produkata na površini uzoraka.

Ključne riječi: CuAlNiMn legura, korozija, polarizacija, elektrokemijske metode

1. INTRODUCTION

Copper and its alloys belongs to a group of technically most commonly used metal materials that have a large application in electrical engineering (electrical conductor manufacturing), heat exchanger manufacturing, boilers in the food and chemical industry, civil engineering, etc. [1-3]. The reason for their large application lies in desirable properties of these materials such as high electrical and thermal conductivity, good corrosion resistance, and favourable mechanical properties [1-2]. A special group of copper alloys are shape memory which has characteristic features such as superelasticity and shape memory effect owing to the reversible martensitic transformation [4-6]. Cu-based shape memory alloys are currently derived from three binary alloy systems *i.e.* Cu-Al, Cu-Zn and Cu-Sn [7]. Copper based shape memory alloys are less expensive compared to Ni-Ti alloy and are easier for preparation and processing [7,8].
The most important disadvantage of polycriystaline CuAlNi alloys is the small reversible deformation (one-way shape memory effect up to 4% and two-way effect around 1.5%) and their fragility at average stress levels [9]. The addition of alloying elements to Cu-Al-Ni alloy increases their mechanical properties and corrosion resistance, while the presence of the precipitates of Al/Ni-X (where X is alloying element) is essential to the passivation of Cu-Al-Ni alloys [6]. Several investigations have performed on Cu-Al-Mn-X alloys (X=Ni, Ag, Mg or Ti) and their results have shown that their various properties, damping and low critical stress to introduce martensitic transformation were improved through alloying [10-13].
Due to their very diverse applications, Cu-shape memory alloy are exposed to various corrosive environments, which can compromise their integrity. In this investigation the corrosion properties of Cu-Al-Mn-Ni alloy has been investigated in deaerated 0.9% NaCl solution at different temperatures of electrolyte and different pH of solution.

2. EXPERIMENTAL

Cu13-Al2.5-Ni2.5-Mn alloy was obtained by melting technically pure components (Cu, Al, Ni and Mn) in a vacuum induction furnace under a protective atmosphere of argon. The melting furnace is connected to a vertical continuous casting device and the entire process (melting and casting) is carried out in a protective atmosphere. The alloy is solidified in a water-cooled crystallizer to form an alloy rod of a certain diameter which coming out between the rollers that rotate in the direction of melt flow.
Working electrodes was obtained by cutting CuAlNiMn alloy into cylindrical samples and then they are connected by soldering with insulated copper wire to ensure good electrical contact. Samples are isolated with Polirepar S acrylate leaving only one base of cylindrical sample ($P = 0.502$ cm^2) to be exposed to the electrolyte. Before each experiment, the electrode surface was mechanically treated with different grit emery papers (from 400 to 1500), polished with Al_2O_3 polishing paste (particle size 0.05 μm), ultrasonically degreased in ethanol, rinsed with deionised water and immersed in electrolyte solution.
Measurements were undertaken in a double wall glass three-electrode electrochemical cell connected to a thermostatic bath to ensure adjusting and maintaining the constant temperature of the electrolyte during the measurements. Electrochemical cell was equipped with Pt-plate counter electrode and saturated calomel electrode as the reference electrode. Electrochemical measurements were performed with a PAR 273A potentiostat/galvanostat.

The evaluation of corrosion behaviour of CuAlNi alloy in 0.9% NaCl solution were perform by open circuit potential measurements (E_{OC}) in 60 min time period, linear polarization method in the potential region of ±20 mV around corrosion potential, with the scanning rate of mV s^{-1} and potentiodynamic polarization method in the potential region of −0.250 V from ope circuit potential to 1.100 V. with the scanning rate of 0.5 mV s^{-1}.
After the potentiometric polarization measurements the surface of the electrode were washed deionized water, dried in the desiccator and then visualized by Canon IXUS1000 camera macro mode and the light microscope with magnification of 100 times. A more detailed surfa analysis was performed with Scanning Electron Microscope Tescan Vega 5136 MM paired wit Energy Dispersive Spectroscopy Microscopy (SEM/EDS).

3. RESULTS AND DISCUSIONS

Figure 1 illustrates the influence of electrolyte temperature on the value of open circuit curre potential of CuAlNiMn alloy in 0.9 % NaCl solution at 37 °C, while Figure 2 shows th influence of solution pH on the value of E_{OC}.

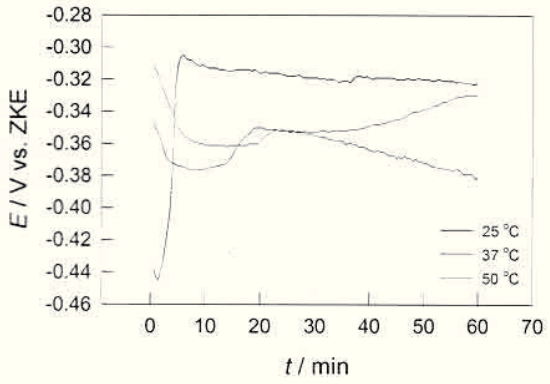

Figure 1. Variation of the open circuit potential with time for the CuAlNiMn alloy in 0.9% NaCl solution at different temperatures of electrolyte.

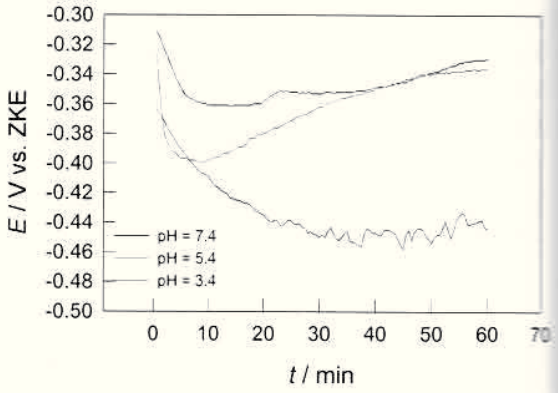

Figure 2. Variation of the open circuit potential with time for the CuAlNiMn alloy in 0.9% NaCl solution at different pH values of electrolyte.

It is apparent that the rise in electrolyte temperature leads to the changes of the E_{OC} CuAlNiMn alloy in the negative direction, which is particularly evident for the measurement at 50 °C. The influence of the solution pH on the value E_{OC} is shown in Figure 2. Lowering the pH values of the electrolyte leads to the negation of the open circuit potential of the CuAlNiMn alloy, which is particularly pronounced at the beginning of the measurements. Values of E_{OC} for the CuAlNiMn alloy in the NaCl solution at pH = 5.4 changes in negative direction in the first 10 minutes after the electrode immersion in the electrolyte solution, and after that have positive changes and after 60 minutes the values of E_{OC} is almost the same as the values of E_{OC} of the alloy in NaCl solution at pH = 7.4. Different behavior shows the investigated alloy in a NaCl solution at pH = 3.4, where the value of the open circuit potential changes in negative direction within the first 35 minutes of immersion in the solution and then the potential stabilization is followed by a certain fluctuation of the open circuit potential values which was not observed in the measurements at higher pH values of the solution.

The reason for this behaviour is probably due to the fact that at the lower pH of the NaCl solution there is a higher adsorption of chloride ions on the alloy surface, which causes higher changes of the values of open circuit potential to the negative direction, while potential fluctuations are results of the initial surface dissolution of the alloy.

A linear polarization measurement were undertaken immediately after E_{OC} measurements in order to determine polarization resistance values (R_p) which represent the resistance of metal to corrosion, and is defined by the slope of the polarization curve near the corrosion potential, by the equation (1):

$$R_p = \frac{\Delta E}{\Delta i} (\Omega\ \mathrm{cm}^2) \qquad (1)$$

The influence of the temperature on the slope of the linear parts of the polarization curves is shown in Figure 3, while the influence of the pH of the solution is shown in Figure 4.

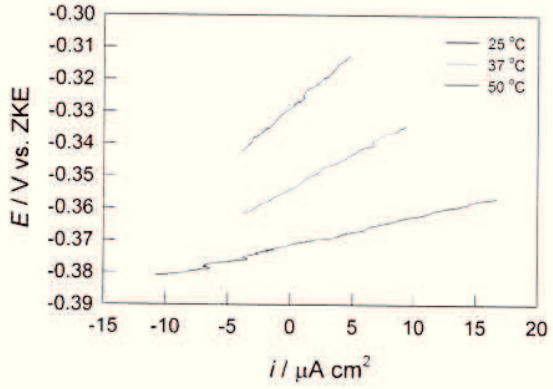

Figure 3. Results of the investigation by linear polarization method for CuAlNiMn alloy in 0.9% NaCl solution at 25 °C (-), 37 °C (-) and 50 °C (-).

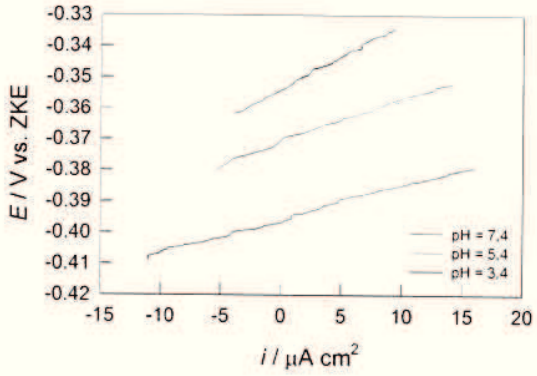

Figure 4. Results of the investigation by linear polarization method for CuAlNiMn alloy in 0.9% NaCl solution at pH = 7.4 (-), 5.4 (-) and 3.4 (-).

From the Figures 3 and 4 it is apparent that elevation of the electrolyte temperature as well as lower electrolyte pH value have a negative impact on the corrosion stability of the CuAlNiMn alloy and lead to a decrease in the slope of the linear curve parts indicating a lowering the polarization resistance values.

Potentiodynamic polarization curves were recorded in wide potential area from -250 mV vs. E_{OC} up to 1.1 V and the results are shown in Figure 5 and 6.

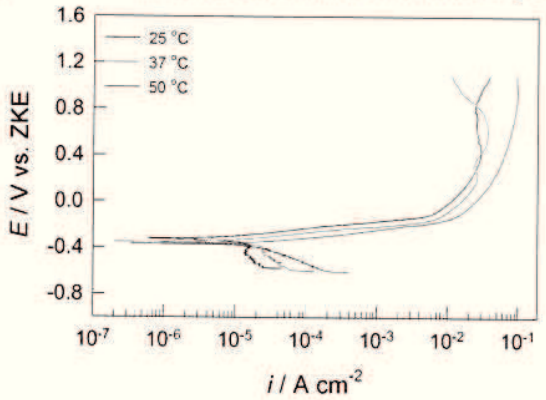

Figure 5. Potentiodynamic polarization curves for CuAlNiMn alloy in 0.9% NaCl solution at 25 °C (-), 37 °C (-) and 50 °C (-).

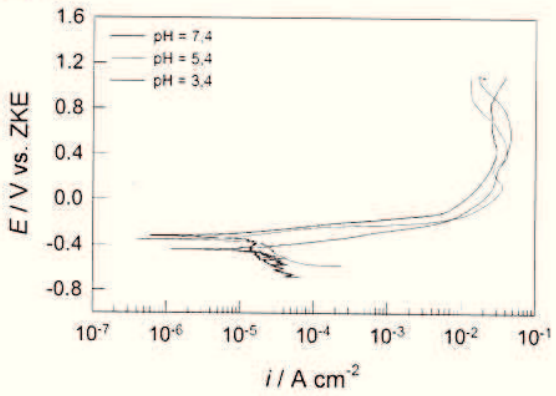

Figure 6. Potentiodynamic polarization curves for CuAlNiMn alloy in 0.9% NaCl solution at pH = 7.4 (-), 5.4 (-) and 3.4 (-).

Figure 5 shows the influence of electrolyte temperature on the potentiodynamic polarizati curve for CuAlNiMn in 0.9% NaCl solution. Increase in electrolyte temperature leads to a increase in the anodic and cathodic current density resulting in higher corrosion density, i. greater corrosion attack on the CuAlNiMn alloy. There is also a negative correlation of corrosi potential with an increase in electrolyte temperature.

Lowering the pH value of the electrolyte (Figure 6) greatly influences on the increase in t anodic current density and also leads to a shift of the corrosion potential to a negative direct

Corrosion parameters which are determined from potentiodynamic polarization measure and are presented in Table 1, along with the values of the polarization resistance obtained fr linear polarization measurements.

Table 1. Corrosion parameters for CuAlNiMn alloy in 0.9 % NaCl solution

Measurement conditions	i_{corr} ($\mu A\ cm^{-1}$)	E_{corr} (V)	R_p ($k\Omega\ cm^2$)
25 °C, pH = 7.4	7.3	-0.320	3.420
37 °C, pH = 7.4	10.7	-0.354	2.120
37 °C, pH = 5.4	11.2	-0.354	1.739
37 °C, pH = 3.4	14.6	-0.441	1.204
50 °C, pH = 7.4	22.1	-0.391	0.914

After polarization measurements, the surface of the CuAlNiMn electrode was examined usin light microscope, and the results of investigations have shown in Figure 7.

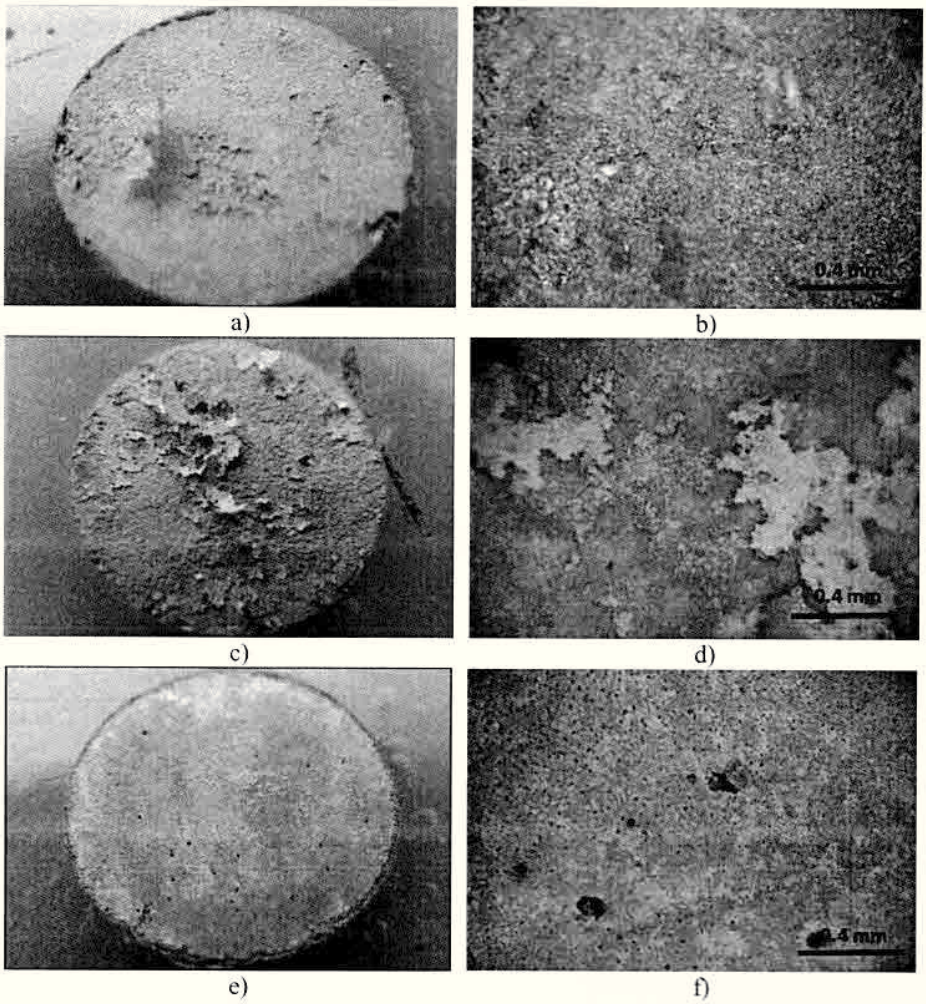

Figure 7. CuAlNiMn alloy surface images after polarization measurements 0.9% NaCl solution (pH=7.4 at diferent temperatures of electrolyte: a) 25 °C, macro image b) 25 °C, with magnification of 100 times, c) 37 °C, macro image d) 37 °C, with magnification of 100 times, c) 50 °C, macro image d) 50 °C, with magnification of 100 times.

At macro image of the CuAlNiMn alloy surface, after polarization measurement in NaCl solution at 25 °C (Figure 7 a), significant corrosive damage is observed. There is a rupture of thin layers of corrosion products from the surface, while on the edges of the electrode there are indication of the appearance of pitting corrosion. This behaviour differs from the behaviour of the CuAlNi alloy which was investigated under the same conditions and where the dominant corrosion attack was pitting corrosion without the appearance of these poorly attached surface layers [14].

Figure 7 c) and d) shows the state of CuAlNiMn alloy surface after potentiodynamic polarization measurement in 0.9% NaCl solution at 37 °C and in Figure 7 e) and f) at 50 °C. After polarization at 37 °C, intense corrosion damages is seen on the surface of the electrode in the form of a thin leaf (exfoliation), with a large part of the surface covered with sheets of corrosion products loosely bonded to the surface which were elevated from the surface of the electrode.

After polarization measurements at 50 °C, the surface of CuAlNiMn alloy are completely hollowed out as a result of pitting corrosion (Figure 7 e) and f)).

More detailed information on the surface condition of the samples was given by the SEM / EDS analysis, the results of which are shown in Figure 8 a)-d). Figure 8 shows the surface of CuAlNiMn alloy after potentiodynamic polarization measurement in a 0.9% NaCl solution at 50 °C.

Two layers of corrosion products are visible on the electrode surface, porous outer surface layer and also highly damage interior layer. The elemental composition of the surface layer shows that the dominant element Cu along with the detected presence small amount of Al, Mn and Cl.

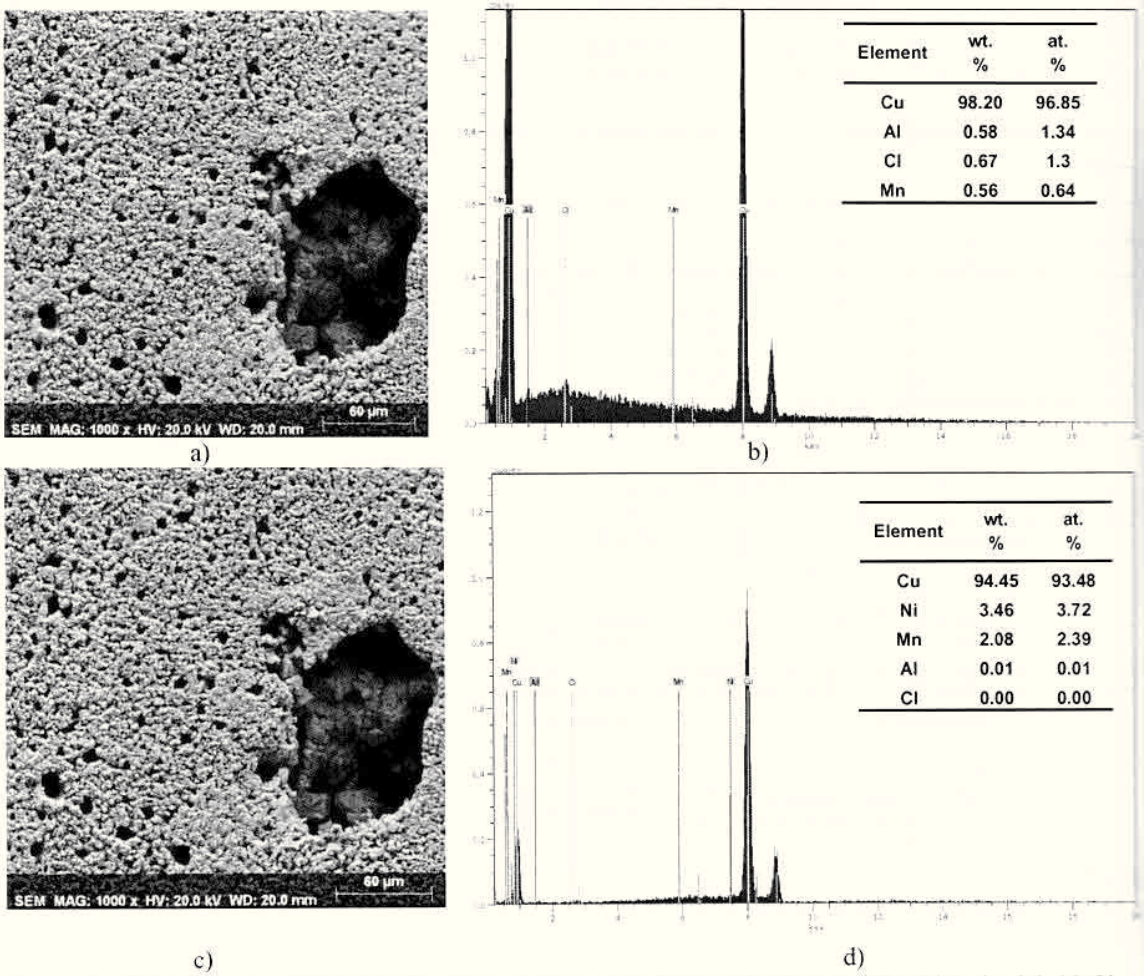

Figure 8. SEM images of CuAlNiMn alloy surface after potentiodynamic polarization in 0.9 NaCl solution (pH = 7.4 and T = 50 °C) with magnification of 1000 times a) and c) along with EDS surface analysis b) i d).

The elemental analysis of the inner surface layer revealed the presence of small quantities of Ni which is not detected in the outer surface layer. Also, the percentage of Mn is higher and the percentages of Al lower then in outer surface layer.

Unlike CuAlNi electrodes, where surface layers of corrosive products emerged in the form of raised "spikes" beneath which there were pits [15], the investigated CuAlNiMn alloy showed much greater corrosion destruction of the surface. These observations are contradicted by the literature findings in which alloying CuAlNi alloys with elements such as Mn or Ti leads to improved mechanical properties of the alloy and increases their corrosion resistance [6]. Sam end associates [6] have found that the addition of Mn as a alloying element to CuAlNi alloy in the amount up to 0.7% leads to the increased corrosion resistance of the alloy due to the reduction of the grain size in the material as well as the increase in the stability of the passive film on the alloy surface. However, further increase in Mn content in the alloy increases the grain size and reduces corrosion resistance. Since the content of Mn in the investigated alloy was relatively high (2.5%), this could be one of the reason for the worsening of corrosion resistance due to grain size growth.

4. CONCLUSIONS

- Increasing the electrolyte temperature as well as decreasing the pH leads to the shift*ing* open circuit potential of the CuAlNiMn alloy towards negative values, increasing the corrosion current density and reducing the polarization resistance values.
- Microscopic images show significant corrosion damages on t CuAlNiMn alloy surface, which manifests itself in thin layers like leaves, with a large part of the surface covered with corrosion-free slip sheets bonded to the surface that rises from the surface of the electrode. Electrode surfaces from which loosely bonded corrosion products are removed have visible damage caused by pitting corrosion.
- SEM surface analysis revealed the existence of two layers on the surface of the alloy: the exterior which is extremely damaged, and consist of thin layers of the corrosion products loosely bounded to the surface, and the inner layer which also shows significant corrosion damage.
- Using EDS surface analysis the elemental composition of the surface was determined. The dominant element in both layers was Cu along with the small quantities of Al, Mn and Cl in the upper layer of corrosion product, while in inner layer was found Ni and relatively higher percentage of Mn compared with upper layer.

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