

# The influence of pH and electrolyte temperature on corrosion behaviour of CuAlMnTi alloy ribbons in NaCl solution

---

**Vrsalović, Ladislav; Jerčić, Radosna; Gudić, Senka; Ivanić, Ivana; Kožuh, Stjepan; Kosec, Borut; Bizjak, Milan; Gojić, Mirko**

*Source / Izvornik:* **Proceedings of 8th International Conference Mechanical Technologies and Structural Materials 2018, 2018, 193 - 198**

**Conference paper / Rad u zborniku**

*Publication status / Verzija rada:* **Published version / Objavljena verzija rada (izdavačev PDF)**

*Permanent link / Trajna poveznica:* <https://um.nsk.hr/um:nbn:hr:115:841958>

*Rights / Prava:* [In copyright](#)/[Zaštićeno autorskim pravom.](#)

*Download date / Datum preuzimanja:* **2025-01-29**



*Repository / Repozitorij:*

[Repository of Faculty of Metallurgy University of Zagreb - Repository of Faculty of Metallurgy University of Zagreb](#)





HRVATSKO DRUŠTVO  
ZA STROJARSKE TEHNOLOGIJE  
CROATIAN SOCIETY  
FOR MECHANICAL TECHNOLOGIES

In association with:



University of Split  
Faculty of Electrical Engineering,  
Mechanical Engineering and  
Naval Architecture



Slovak Academy of Science  
Institute of Materials and  
Machine Mechanics



Sveučilište u Splitu  
Sveučilišni  
odjel za stručne studije



Croatian Society for  
Materials and Tribology



Dublin Institute of  
Technology



Rogante Engineering  
Office

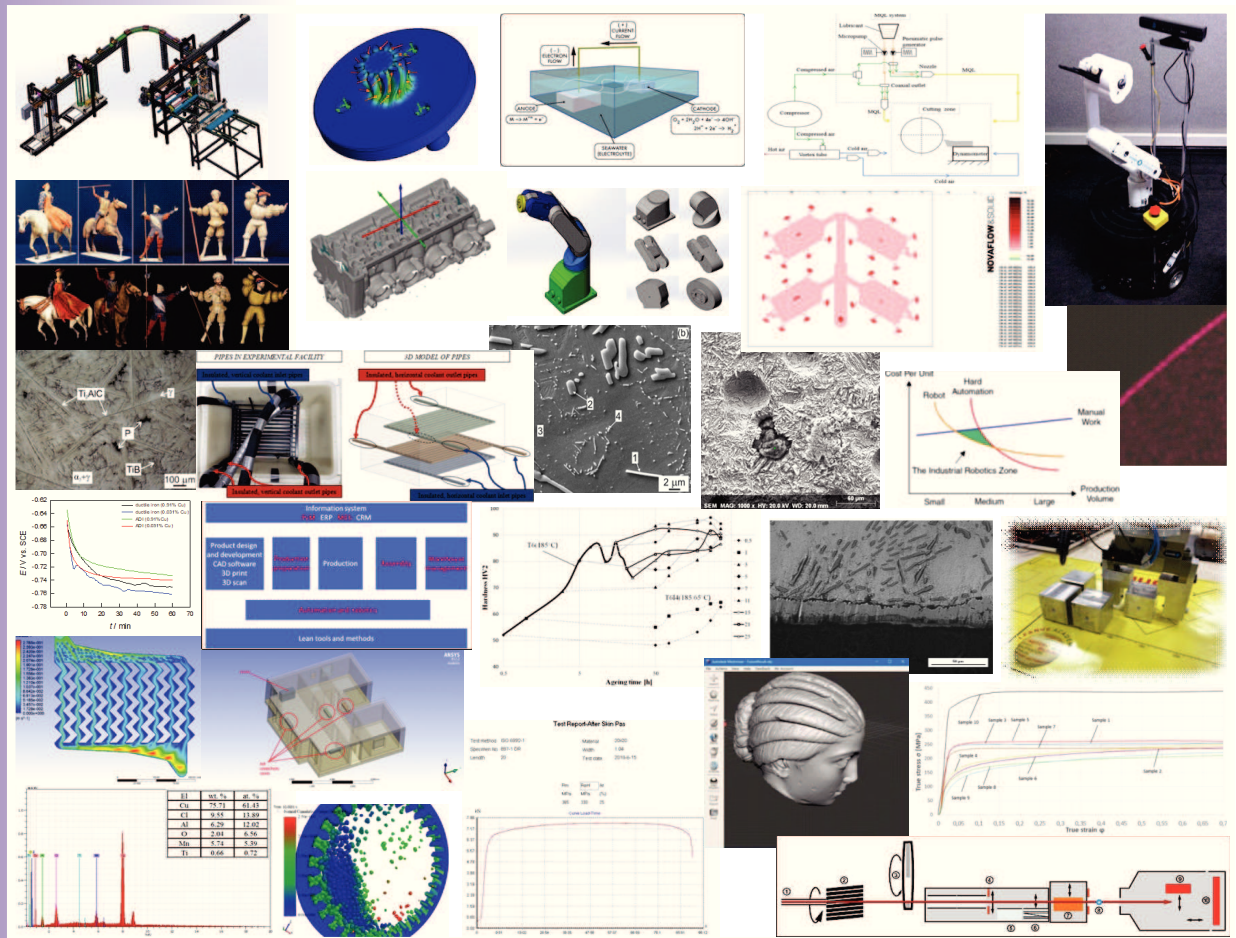
# 8<sup>th</sup> International Conference

ISSN 1847-7917

## Mechanical Technologies and Structural Materials 2018

General sponsors:

University of Split - Faculty of Electrical Engineering,  
Mechanical Engineering and Naval Architecture  
The Split - Dalmatia County  
EVN Croatia Plin d.o.o.



<http://www.strojarska-tehnologija.hr>

September, 27<sup>th</sup> - 28<sup>th</sup>, 2018.  
FESB, Ruđera Boškovića 32, Split

# **CONFERENCE PROCEEDINGS**

ZBORNIK RADOVA

## **MECHANICAL TECHNOLOGIES AND STRUCTURAL MATERIALS**

STROJARSKE TEHNOLOGIJE I KONSTRUKCIJSKI  
MATERIJALI

**Split**

**Croatia / Hrvatska**

27. - 28. September / rujan 2018.

### **ORGANIZED BY / ORGANIZATOR:**

CROATIAN SOCIETY FOR MECHANICAL TECHNOLOGIES, Croatia

HRVATSKO DRUŠTVO ZA STROJARSKE TEHNOLOGIJE, Hrvatska

### **CO-ORGANIZERS / SURGANIZATORI:**

UNIVERSITY OF SPLIT  
FACULTY OF ELECTRICAL ENGINEERING, MECHANICAL ENGINEERING  
AND NAVAL ARCHITECTURE

CROATIAN SOCIETY FOR MATERIALS AND TRIBOLOGY

DUBLIN INSTITUTE OF TECHNOLOGY

SLOVAK ACADEMY OF SCIENCE INSTITUTE OF MATERIALS AND MACHINE  
MECHANICS

ROGANTE ENGINEERING OFFICE

UNIVERSITY OF SPLIT  
UNIVERSITY DEPARTMENT OF PROFESSIONAL STUDIES

**SPONSORS / SPONZORI:**

UNIVERSITY OF SPLIT

SPLIT – DALMATIA COUNTY

EVN CROATIA PLIN d.o.o.

**PUBLISHER / IZDAVAČ:**

CROATIAN SOCIETY FOR MECHANICAL TECHNOLOGIES, Croatia

HRVATSKO DRUŠTVO ZA STROJARSKE TEHNOLOGIJE, Hrvatska

c/o FESB, Ruđera Boškovića 32, 21000 SPLIT

tel.: +385 21 305 910; fax.: +385 21 463 877

e-mail: [info@strojarska-tehnologija.hr](mailto:info@strojarska-tehnologija.hr)

<http://www.strojarska-tehnologija.hr>

**EDITORS / UREDNICI:**

PhD Sonja Jozić, Associate Professor

PhD Nikola Gjeldum, Assistant Professor

ISSN 1847-7917

ISSUE / NAKLADA: 70

**ORGANIZING COMMITTEE:**  
**ORGANIZACIJSKI ODBOR**

- Sonja JOZIĆ (Croatia) - Chairman
- Branimir LELA (Croatia) – Vice Chairman
  
- Ante ALUJEVIĆ (Croatia)
- Ante BAROVIĆ (Croatia)
- Nikša ČATIPOVIĆ (Croatia)
- Zvonimir DADIĆ (Croatia)
- Ivana DUMANIĆ (Croatia)
- Igor GABRIĆ (Croatia)
- Nikola GJELDUM (Croatia)
- Dario ILJKIĆ (Croatia)
- Jure KROLO (Croatia)
- Neven KUZMANIĆ (Croatia)
- Petar LJUMOVIĆ (Croatia)
- Zvonimir MRDULJAŠ (Croatia)
- Stipe PERIŠIĆ (Croatia)
- Slaven ŠITIĆ (Croatia)

**PROGRAMME AND REVIEW COMMITTEE:**  
**PROGRAMSKI I RECENZIJSKI ODBOR**

- Dražen ŽIVKOVIĆ (Croatia) – President
- Dražen BAJIĆ (Croatia) – Vice President
  
- Boris ANZULOVIĆ (Croatia)
- Frane BARBIR (Croatia)
- Franjo CAJNER (Croatia)
- Goran CUKOR (Croatia)
- Vinko IVUŠIĆ (Croatia)
- Zlatko JANKOSKI (Croatia)
- Jaroslav JERZ (Slovakia)
- Sonja JOZIĆ (Croatia)
- David KENNEDY (Ireland)
- Branimir LELA (Croatia)
- Zoran PANDILOV (Macedonia)
- Mladen PERINIĆ (Croatia)
- Massimo ROGANTE (Italy)
- Zdravko SCHAUPERL (Croatia)
- František SIMANČIK (Bratislava)
- Božo SMOLJAN (Croatia)
- Goran ŠIMUNOVIĆ (Croatia)
- Katica ŠIMUNOVIĆ (Croatia)
- Matej VESENJAK (Slovenia)
- Ivica VEŽA (Croatia)

# The influence of pH and electrolyte temperature on corrosion behaviour of CuAlMnTi alloy ribbons in NaCl solution

Ladislav VRSALOVIĆ<sup>1)</sup>, Radosna JERČIĆ<sup>1)</sup>, Senka GUDIĆ<sup>1)</sup>, Ivana IVANIĆ<sup>2)</sup>, Stjepan KOŽUH<sup>2)</sup>, Borut KOSEC<sup>3)</sup>, Milan BIZJAK<sup>3)</sup> and Mirko GOJIC<sup>2)</sup>

1) University of Split, Faculty of Chemistry and Technology, Ruđera Boškovića 35, 21000 Split, Croatia

2) University of Zagreb, Faculty of Metallurgy, Aleja narodnih heroja 3, 44103 Sisak, Croatia

3) University of Ljubljana, Faculty of Natural Science and Engineering, Aškerčeva cesta 12, 1000 Ljubljana, Slovenia

ladislav@ktf-split.hr

senka@ktf-split.hr

iivanic@simet.hr

kozuh@simet.hr

borut.kosec@ntf.uni-lj.si

milan.bizjak@ntf.uni-lj.si

gojic@simet.hr

## Keywords

CuAlMnTi alloy

NaCl solution

corrosion

polarization

SEM/EDS

## 1. Introduction

Cu-based shape memory alloys (SMA) are considered to be commercially attractive alloys for technological applications due to their shape memory effect (SME) and pseudoelasticity (PE). Their important advantage over Ni-Ti alloys lies in their lower production cost and the possibility of using at higher temperatures (around 200 °C) [1-4]. Cu-based SMA-s are currently derived from three binary alloy systems i.e. Cu-Zn, Cu-Al and Cu-Sn [5]. Cu-Zn based alloy containing alloying elements such as Al, Si, Sn, Ga or Mn as ternary alloy and Cu-Al based ternary alloys containing Ni, Be, Zn and Mn as alloying elements have been explored for their potential use [6-10]. One of the major drawback of CuAlNi and CuZnAl shape memory alloy are their brittleness and susceptibility to intergranular fracture due to its coarse grain structures and high elastic anisotropy [11, 12]. To overcome these particular problems, several ways have been identified by the researcher so far such as thermomechanical procession, use of micro-alloy elements for grain refinement and use rapid solidification

*Original scientific paper*

**Abstract:** The influence of pH and temperature of 0.9% NaCl solution on corrosion behaviour of CuAlMnTi alloy ribbons, produced by rapid solidification using melt spinning method, were investigated by electrochemical methods. Open circuit potential measurement, linear and potentiodynamic polarization were employed during the investigation, and the measurements were conducted in the electrolyte temperature of 10, 24, 37 and 50 °C and in solution pH of 7.4, 5.4 and 3.4. It has been found that corrosion rate generally increase with increasing the temperature of the electrolyte while the influence of pH change on CuAlNiTi ribbon corrosion is little less pronounced. After polarization measurements CuAlNiTi ribbon surfaces were investigated with light microscope and with SEM/EDS analysis.

*Izvorni znanstveni rad*

**Sažetak:** U radu je elektrokemijskim metodama ispitan utjecaj pH i temperature 0.9% NaCl otopine na korozijsko ponašanje legure CuAlMnTi koja je proizvedena u obliku trake naglim hlađenjem melt spinning metodom. Tijekom ispitivanja primijenjene su metode mjerenja potencijala otvorenog strujnog kruga, linearne i potenciodinamičke polarizacije a ispitivanja su provedena na temperaturama 10, 24, 37 i 50 °C i pri pH vrijednostima otopine od 7.4, 5.4 i 3.4. Nađeno je da se brzina korozije povećava s povećanjem temperature elektrolita dok je utjecaj promjene pH na koroziju CuAlMnTi traka nešto manje izražen. Nakon polarizacijskih mjerenja površine CuAlMnTi traka su ispitane pomoću svjetlosnog mikroskopa a također je napravljena i SEM/EDS analiza.

process in alloys production [12-15]. Generally there are four advantages of rapid solidification over the slow conventional solidification techniques. These are an ability to form metastable phases, increasing the solubility above the equilibrium solubility, decreasing the segregation of additions and refining the microstructure [13-15]. Introduction of a less soluble forth alloying element in CuAlNi or CuAlMn alloy can improve ductility of the alloy. For example Ti has proved to be an effective  $\beta$ -grain growth inhibitor that inhibits the grain coarsening of the alloy during annealing [4]. Adachi et al. [16] revealed that the Ti-doped in Cu-Al-Ni SMA can reduce grain size and leads to enhancing the mechanical properties, while Morris and Gunter [17] refer in their study to the fact that the addition of boron and zirconium can lead to an improvement in the mechanical properties. This paper aims to investigate corrosion behaviour of CuAlMnTi alloy ribbons, produced by rapid solidification using melt spinning method in NaCl solution of different temperatures and different pH values of electrolyte.

**Symbols/Oznake**

$E_{oc}$	- open circuit potential, V - potencijal otvorenog strujnog kruga	$SCE$	- saturated calomel electrode - zasićena kalomel elektroda
$i_{corr}$	- corrosion current density, $\mu Acm^{-2}$ - gustoća korozijske struje	$wt. \%$	- maseni postotak, - weigh percentage
$E_{corr}$	- corrosion potential, V - korozijski potencijal	$at. \%$	- atomski postotak - atomic percentage
$R_p$	- polarization resistance, $\Omega cm^2$ - polarizacijski otpor		

**2. Experimental setup**

Rapidly solidified ribbons of CuAlMnTi with the composition of 82.3 wt.% Cu, 8.3 wt.% Al 9.4 wt.% Mn and 1 wt.% Ti were manufactured with the single roll melt spinning apparatus. The cast precursors were inserted into the graphite crucible and inductively melted in Ar atmosphere and sprayed through the nozzle into the cooled rotating copper wheel. The CuAlMnTi alloy ribbon samples for the electrochemical measurements were prepared by cutting to the appropriate dimensions and then soldered on an insulated copper wire to gain proper electrical contact. Soldered joint points are insulated with Polirepar S protective mass to prevent the evaluation of galvanic corrosion in contact with the electrolyte. Due to its small thickness, mechanical treatment by grinding and polishing of the CuAlNiTi ribbons could not be performed, so the surface of the electrode was processed by ultrasonic degassing in ethanol, washed with deionized water and immersed in the electrolyte.

Experiments were performed with a PAR 273A potentiostat/galvanostat in a double walled three-electrode glass cell thermostated at 37°C, with Pt-plate auxiliary electrode and saturated calomel electrode (SCE) as a reference electrode, which was located in the Luggin capillary. The evaluation of corrosion behaviour of CuAlMnTi alloy in 0.9% NaCl solution was performed by open circuit potential measurements (EOC) in 60 minutes time period, linear polarization method in the potential region of  $\pm 20$  mV around corrosion potential, with the scanning rate of  $0.2 \text{ mV s}^{-1}$  and potentiodynamic polarization method in the potential region of  $-0.250 \text{ V}$  from open circuit potential to  $0.7 \text{ V}$ , with the scanning rate of  $0.5 \text{ mV s}^{-1}$ .

After corrosion testing the surface of investigated samples was photographed by a Canon Ixus 1000 HS digital camera and with light microscope MXFMS-BD, Ningbo Sunny Instruments co.. Detailed surface morphology of the samples after the potentiodynamic measurements was examined by scanning electron microscope (SEM) Tescan Vega TS5136LS. The quantitative analysis of the elements on the electrode surface was determined by energy dispersive spectroscopy (EDS).

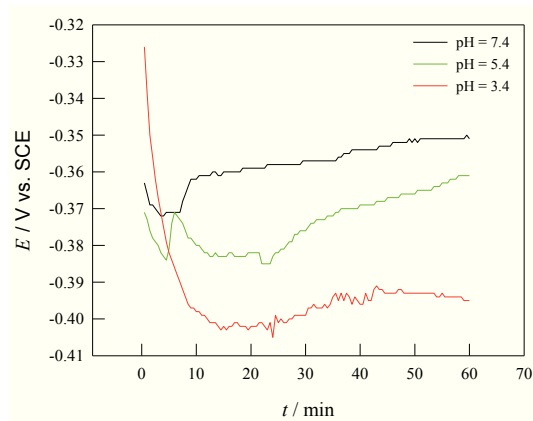
**3. Results**

Figure 1 shows the open circuit potential  $E_{oc}$  measurements for the CuAlMnTi alloy in 0.9% NaCl solution ( $T = 37 \text{ }^\circ\text{C}$ ) at different pH of the solution. Immediately after immersion in the solution  $E_{oc}$  was shift towards negative potential due to the adsorption of the chloride ions on the electrode surface. The highest negative drop of potential was recorded in the NaCl solution with the lowest pH value ( $\text{pH} = 3.4$ ). The initial decline in potential is followed by its stabilization and change in the positive direction indicating formation of protective surface layer. From the Figure 1 it can be seen that  $E_{oc}$  for the CuAlMnTi alloy in NaCl solution at  $\text{pH} = 7.4$  and  $5.4$  have similar values, and the value of  $E_{oc}$  for the measurement in NaCl solution  $\text{pH} = 3.4$  have the most negative values. Increasing the electrolyte temperature also leads to the displacement of the open circuit potential value towards negative values.

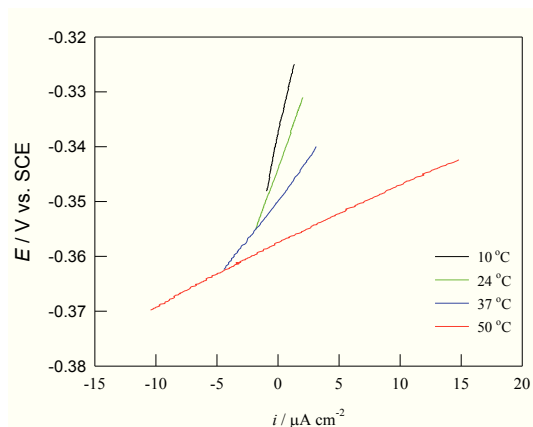
Linear polarization measurements were conducted in order to determine the influence of temperature and pH of the NaCl solution on polarization resistance values. In a linear polarization measurement, the potential vs. current density is measured in a narrow area around the  $E_{oc}$  and the slope of the potential-current density curve is then calculated and equal to  $R_p$  value. As  $R_p$  value is reverse proportional to the corrosion current density ( $i_{corr}$ ), higher value of  $R_p$  means lower value of  $i_{corr}$  i.e. lower corrosion.

Figure 1 shows the results of linear polarization measurements for CuAlMnTi alloy in 0.9% NaCl solution ( $\text{pH} = 37 \text{ }^\circ\text{C}$ ) at different electrolyte temperature. The slopes of the linear parts of the curves decreased with increasing electrolyte temperature indicating higher corrosion of CuAlMnTi in NaCl solution. Lowering the pH of the solution has a similar effect on the values of polarization resistance.

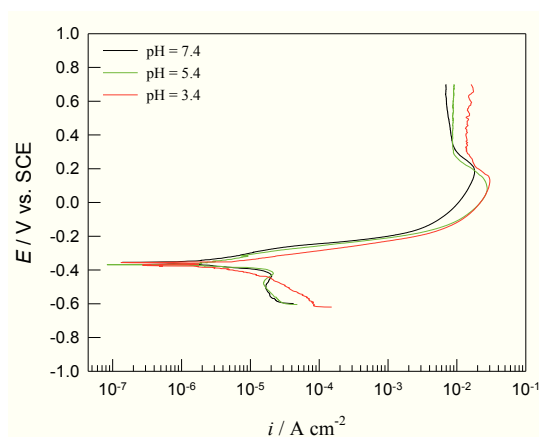
The potentiodynamic polarization behaviour of the alloy in 0.9 % NaCl solution ( $T = 37 \text{ }^\circ\text{C}$ ) with different pH values are presented in Figure 3. Lowering the pH values of NaCl solution lead to the increase in anodic and cathodic current density resulting in the higher value of the corrosion current density. Corrosion parameters for CuAlMnTi alloy obtained by polarization measurements, are given in Table 1



**Figure 1.** Variation of the open circuit potentials with time for the CuAlMnTi alloy in 0.9% NaCl solution at different pH values of solution



**Figure 2.** Results of linear polarization measurements for CuAlMnTi alloy in 0.9% NaCl solution (pH = 7.4) at different electrolyte temperatures



**Figure 3.** Potentiodynamic polarization curves for CuAlMnTi alloy in 0.9% NaCl solution ( $T = 37\text{ }^{\circ}\text{C}$ ) at different pH values

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

Measurement conditions	$E_{\text{corr}} / \text{V}$	$i_{\text{corr}} / \mu\text{A cm}^{-2}$	$R_p / \text{k}\Omega \text{cm}^2$
10 °C; pH = 7.4	-0.314	1.17	9.440
24 °C; pH = 7.4	-0.339	1.62	4.214
37 °C; pH = 7.4	-0.357	1.94	2.909
37 °C; pH = 5.4	-0.365	2.16	2.456
37 °C; pH = 3.4	-0.362	4.03	1.194
50 °C; pH = 7.4	-0.352	2.80	1.395

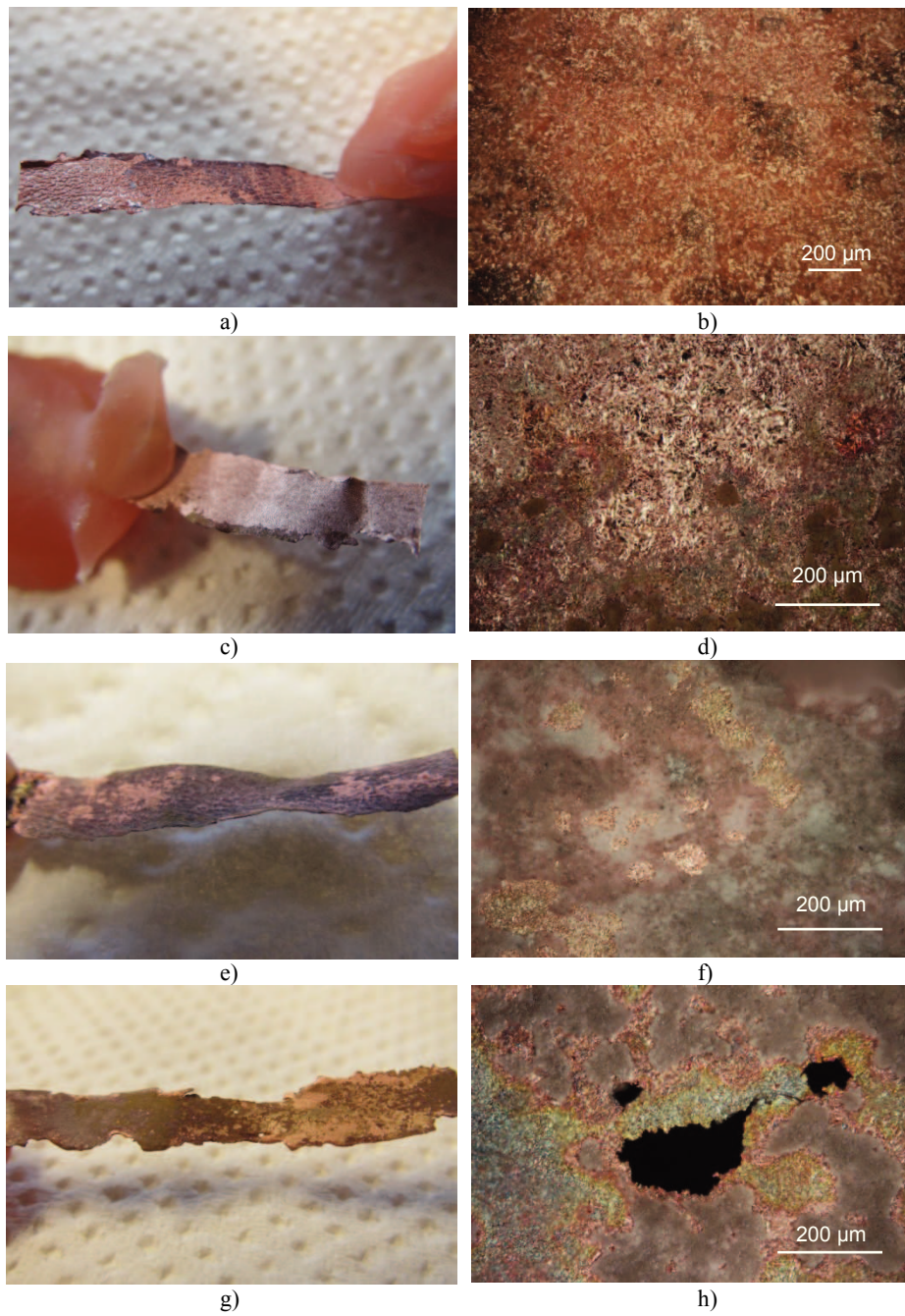
After polarization measurements, electrode surfaces were cleaned ultrasonically in deionized water, dried in desiccator and then photographed in macro mode with digital camera Canon Ixus 1000 and examined with light microscope. Results of these investigations are presented in Figure 4.

From the Figure 4 it can be seen that at higher electrolyte temperatures on the surface of the electrode there are more corrosion damages as well as more corrosion products. Pitting corrosion is observed at the highest investigated temperature (50 °C) while on lower temperatures uniform corrosion take place.

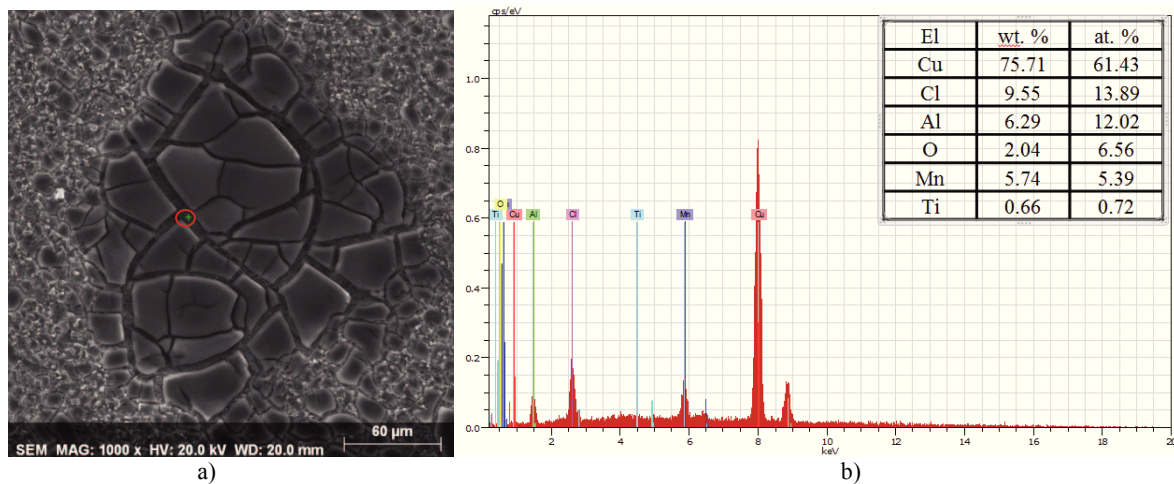
More detailed information on the electrodes surface condition after electrochemical measurement was obtained by scanning electron microscope, while the elemental composition was determined by XRD method, and the results are shown in Figures 5 and 6.

After potentiodynamic polarization measurements at 10 °C corrosion products can be found on the electrode surface which contains all of the alloying elements along with chloride and oxide (Figure 5 a) and b). Reduction in the percentage of alloying elements indicates its dissolution from the surface and the formation of chloride and oxide compounds. Potentiodynamic polarization measurements at 50 °C leads to significant corrosion damages on the electrode surface (Figure 6 a)). EDS analysis revealed significant reduction in % of all alloying elements (Figure 6 b)). The slightest reduction was noted for Ti, which is also the most stable element of this alloy.

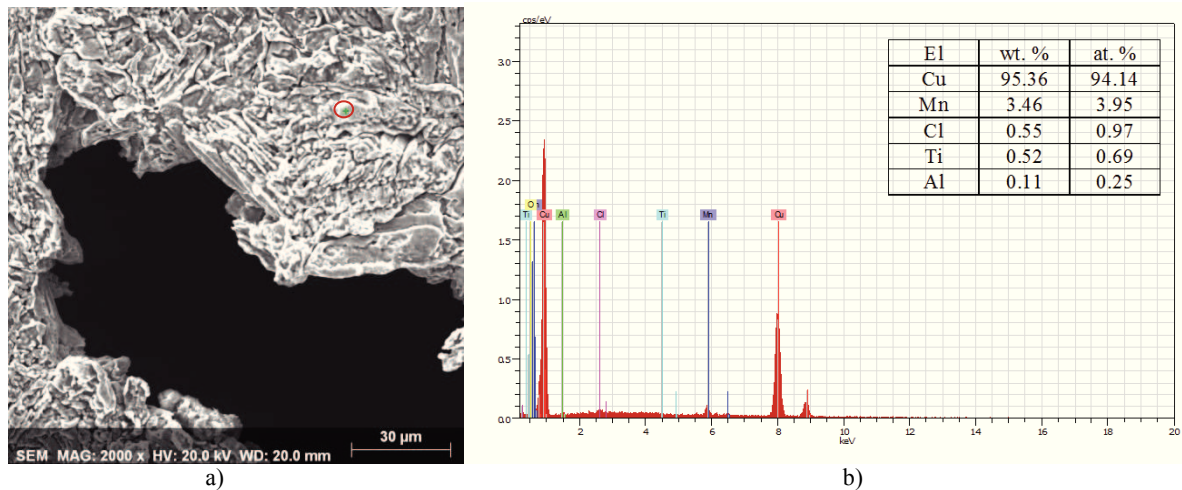




**Figure 4.** Macro images and optical micrographs of the corroded CuAlMnTi alloy surface in 0.9% NaCl solution at 10 °C a) and b); 24 °C c) and d); 37 °C e) and f) and 50 °C g) and h)



**Figure 5.** a) SEM images of the CuAlMnTi alloy surface after potentiodynamic polarization measurement in 0.9% NaCl solution (pH = 7.4, T = 10 °C); b) EDS analysis



**Figure 6.** a) SEM images of the CuAlMnTi alloy surface after potentiodynamic polarization measurement in 0.9% NaCl solution (pH = 7.4, T = 50 °C); b) EDS analysis

#### 4. Conclusions

- Open circuit potential for the CuAlMnTi alloy shifts in the negative direction by decreasing the pH value of the 0.9% NaCl solution. Increasing the electrolyte temperature also leads to the displacement of the open circuit potential value towards negative values.
- Increase in electrolyte temperature as well as decrease pH value of NaCl solution leads to decrease the polarization resistance values and increase the values of corrosion currents density, which indicates a more intense corrosion process.
- Macro images of the electrode surfaces after polarization measurements with a digital camera and an light microscope have shown that increasing the electrolyte temperature increases the surface damages of the electrode due to more intense corrosion. Pitting corrosion is observed at the highest investigated temperature while on lower temperatures uniform corrosion take place.
- SEM surface images of CuAlMnTi electrodes after polarization measurements have confirmed that with elevation electrolyte temperature a more intense corrosion attack occurs. EDS surface analysis indicated all alloying elements on the electrode surface along with oxygen and chlorine for the measurements at 10 °C. For the measurements at 50 °C dominant element on the surface is copper, while other elements are present in significantly less% than in initial composition of the alloy.

## Acknowledgements

This work has been fully supported by the Croatian Science Foundation under the project HRZZ-IP-2014-09-3405.

## REFERENCES

- [1] Ivanić I., Gojić M., Kožuh S., (2014), *Slitine s prisjetljivosti oblika (I. dio): najznačajnija svojstva*, Kem. Ind. 63, p 323-330.
- [2] Ivanić I., Gojić M., Kožuh S., (2014), *Slitine s prisjetljivosti oblika (II. dio): podjela, proizvodnja i primjena*, Kem. Ind. 63, p. 331-344.
- [3] Saud S. N., Hamzah, E., Abubakar T., Bakhsheshi-Rad H. R., (2015), *Microstructure and corrosion behavior of Cu-Al-Ni shape memory alloys with Ag nanoparticles*, Materials and Corrosion 66, p. 527-534.
- [4] Sobrero C. E., Roca P. La., Roatta A., Bolmaro R. E., Malarria J. (2012), *Shape memory properties of high textured Cu-Al-Ni-(Ti) alloys*, Mater. Sci. Eng. A, 536, p 207-215.
- [5] Sathish S., Mallik U. S., Raju T. N., (2014), *Microstructure and shape memory effect of Cu-Zn-Ni shape memory alloys*, JMMCE, 2, p 71-77.
- [6] Kainuma, R., Takahashi, S., Ishida, K. (1996), *Thermoelastic Martensite and Shape Memory Effect in Ductile Cu-Al-Mn Alloys*, Metallurgical and Materials Transactions A, 27A, p 2187-2195.
- [7] Kainuma, R., Satoh, N., Liu, X. J., Ohnuma, I. and Ishida, K. (1998) *Phase Equilibria and Heusler Phase Stability in Cu-Rich Portion of the Cu-Al-Mn System*, Journal of Alloys and Compounds, 266, 191-200.
- [8] Gojić M., Vrsalović L., Kožuh S., Kneissl A., Anžel I., Gudić S., Kosec B., Klišković M., (2011), *Electrochemical and microstructural study of Cu-Al-Ni shape memory alloy*, J. Alloy. Compd. 509 p 9782-9790.
- [9] Rittapai A., Urapepon S., Kajornchaivakul J., Harniratsai C., (2014), *Properties of experimental copper-aluminium-nickel alloys for dental post and core applications*, J. Adv. Prosthodont, 6, p 215-223.
- [10] Yang S., Zhang F., Wu J., Lu, Y., Shi Z. Wang C. Liu X. (2017), *Superelasticity and shape memory effect in Cu-Al-Mn-V shape memory alloys*, Materials and Design 115, p 17-25.
- [11] Kožuh, S., Gojić, M., Ivanić, I., Holjevac Grgurić, T., Kosec, B., Anžel, I., (2018), *The Effect of heat treatment on the microstructure and mechanical properties of Cu-Al-Mn shape memory alloy*, Kem. Ind., 67, p 11-17.
- [12] Alaneme, K. K., Okotete, E. A. Bodunrin M. O., (2017), *Microstructural analysis and corrosion behavior of Fe, B and Fe-B-modified Cu-Zn-Al shape memory alloys*, Corros. Rev., 35, p 1-9.
- [13] Matsuoka, S., Hasebe, M., Oshima R., Fujita F. E., (1983) *Improvement of ductility of melt spun Cu-Al-Ni shape memory alloy ribbons by addition of Ti or Zn*, Japanese Journal of Applied Physics, 22, p L528-L530.
- [14] Bizjak, M., Karpe, B., Jakša, G., Kovač, J., (2013), *Surface precipitation of chromium in rapidly solidified Cu-Cr alloys*, Apply. Surf. Sci. 277, p 83-87.
- [15] Kim, Y-W., Yun, Y-M., Nam, T-H., (2006), *The effect of the melt spinning processing parameters on the solidification structures in Ti-30 at.% Ni-20 at.% Cu shape memory alloys*, Mat. Sci. Eng. A, 438-440, p 545-548.
- [16] Adachi K., Shoji K., Hamada Y., (1989), *Formation of (X) phases and origin of grain refinement effect in Cu-Al-Ni shape memory alloys added with titanium*, ISIJ Int., 29, p 378-87.
- [17] Morris MA, Gunter S., (1992), *Effect of heat treatment and thermal cycling on transformation temperatures of ductile Cu-Al-Ni-Mn-B alloys.*, Scripta Metallurgica et Materiala. 26, p 1663-1668.