

# Influence of Mn on the corrosion behavior of CuAlMn alloy in NaCl solution

---

**Gudić, Senka; Rakuljić, Blanka; Vrsalović, Ladislav; Bizjak, Milan; Ivanić, Ivana; Kožuh, Stjepan; Gojić, Mirko**

*Source / Izvornik:* **Proceedings book 18th International Foundryman Conference, 2019, 227 - 236**

**Conference paper / Rad u zborniku**

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

*Permanent link / Trajna poveznica:* <https://urn.nsk.hr/urn:nbn:hr:115:656395>

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

*Download date / Datum preuzimanja:* **2024-07-23**



SVEUČILIŠTE U ZAGREBU  
METALURŠKI FAKULTET  
UNIVERSITY OF ZAGREB  
FACULTY OF METALLURGY

*Repository / Repozitorij:*

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



University of Zagreb  
Faculty of Metallurgy  
Sisak, Croatia



University of Ljubljana  
Faculty of Natural Sciences and Engineering  
Ljubljana, Slovenia



University North  
Koprivnica, Croatia



Technical University of Košice  
Faculty of Materials, Metallurgy and Recycling  
Košice, Slovakia



ELKEM ASA  
Oslo, Norway



## PROCEEDINGS BOOK

# 18<sup>th</sup> INTERNATIONAL FOUNDRYMEN CONFERENCE

**Coexistence of material science and sustainable  
technology in economic growth**



Sisak, May 15<sup>th</sup> – 17<sup>th</sup>, 2019

**ORGANIZERS**

University of Zagreb Faculty of Metallurgy, Sisak, Croatia

University of Ljubljana Faculty of Natural Sciences and Engineering, Ljubljana, Slovenia

University North, Koprivnica, Croatia

Technical University of Košice Faculty of Materials, Metallurgy and Recycling, Košice, Slovakia

ELKEM ASA, Oslo, Norway

**PROCEEDINGS BOOK****18<sup>th</sup> INTERNATIONAL FOUNDRYMEN CONFERENCE**

Coexistence of material science and sustainable technology in economic growth

**EDITORS**

Natalija Dolić, Zdenka Zovko Brodarac, Anita Begić Hadžipašić

**TECHNICAL EDITOR**

Anita Begić Hadžipašić

**PUBLISHER**

University of Zagreb

Faculty of Metallurgy

Aleja narodnih heroja 3

44000 Sisak

Croatia

**PRINT**

InfOmArt Zagreb d.o.o.

Nikole Tesle 10

44000 Sisak

Croatia

**ISSUE**

200 copies

**ISBN**

978-953-7082-34-5

-A CIP record is available in computer catalogue of the National and University Library in Zagreb under the number 001029655.

## **UNDER THE HIGH AUSPICES**

President of Croatia  
Kolinda Grabar – Kitarović

## **UNDER THE PATRONAGE**

Ministry of Science and Education of the Republic of Croatia  
Ministry of Economy, Entrepreneurship and Crafts of the Republic of Croatia  
University of Zagreb  
World Foundry Organization (WFO)  
Mittel Europäische Giesserei Initiative (MEGI)  
Chamber of Commerce of Republic of Croatia  
Sisak – Moslavina County  
City of Sisak

## **SPONSORED BY**

### **SILVER SPONSOR**

HEMOLAB Ltd, Beograd (RS)  
LABTIM ADRIA Ltd, Sesvete (HR)

### **BRONZE SPONSOR**

BENTOPRODUCT Ltd, Šipovo (BA)  
BITUS Ltd, Zagreb (HR)  
EBERT Ltd, Ljubljana (SI)  
FERRO-PREIS Ltd, Čakovec (HR)  
HAGI GmbH, Pyhra (AT)  
HEINRICH WAGNER SINTO MASCHINENFABRIK GmbH, Bad Laasphe (DE)  
LABEKO Ltd, Zagreb (HR)  
MECAS ESI s.r.o., Plzen (CZ) & TC LIVARSTVO Ltd, Ljubljana (SI)  
TROKUT TEST GROUP Ltd, Zagreb (HR)

### **MEDIA COVERAGE**

IRT 3000  
Foundry Lexicon  
Foundry Planet

### **SUPPORTING ASSOCIATION AND COMPANIES**

Croatian Foundry Association  
Slovenian Foundry Association

## **ORGANIZING COMMITTEE**

Zdenka Zovko Brodarac, president

Anita Begić Hadžipašić

Sandra Brajčinović

Damijan Cerinski

Natalija Dolić

Gordana Gojsević Marić

Martina Hrubovčáková

Franjo Kozina

Stjepan Kožuh

Ladislav Lazić

Jožef Medved

Marin Milković

Primož Mrvar

Tomislav Rupčić

Sanja Šolić

Iveta Vasková

## **PROGRAM COMMITTEE**

Hasan Avdušinović (BA)

Branko Bauer (HR)

Anita Begić Hadžipašić (HR)

Jaka Burja (SI)

Lidija Čurković (HR)

Mile Djurdjević (AT)

Natalija Dolić (HR)

Peter Cvahte (SI)

Regina Fuchs-Godec (SI)

Dario Iljkić (HR)

Sebastjan Kastelic (SI)

Varužan Kervorkijan (SI)

Ivica Kladarić (HR)

Borut Kosec (SI)

Dražan Kozak (HR)

Stjepan Kožuh (HR)

Zoran Kožuh (HR)

Ladislav Lazić (HR)

Martina Lovrenić-Jugović (HR)

Srećko Manasijević (RS)

Dragan Manasijević (RS)

Jožef Medved (SI)

Daniel Novoselović (HR)

Mitja Petrič (SI)

Bojan Podgornik (SI)

Karlo T. Raić (RS)

Vera Rede (HR)

Zdravko Schauperl (HR)

Peter Schumacher (AT)

Ljerka Slokar Benić (HR)

Božo Smoljan (HR)

Tahir Sofilić (HR)

Davor Stanić (HR)

Sanja Šolić (HR)

Iveta Vaskova (SK)

Maja Vončina (SI)

Zdenka Zovko Brodarac (HR)

Irena Žmak (HR)

## REVIEW COMMITTEE

Vesna Alar (HR)	Ladislav Lazić (HR)
Ljubiša Balanović (RS)	Martina Lovrenić-Jugović (HR)
Jakov Baleta (HR)	Dragan Manasijević (RS)
Marko Ban (HR)	Ivana Marković (RS)
Branko Bauer (HR)	Adrijana Milinović (HR)
Anita Begić Hadžipašić (HR)	Aleš Nagode (SI)
Mile Djurdjević (AT)	Daniel Novoselović (HR)
Natalija Dolić (HR)	Vesna Ocelić Bulatović (HR)
Nikša Čatipović (HR)	Mitja Petrič (SI)
Vladan Ćosović (RS)	Zora Pilić (HR)
Stanisław Gil (PL)	Grzegorz Piwowarski (PL)
Vesna Grekulović (RS)	Milena Premović (RS)
Tamara Holjevac Grgurić (HR)	Žarko Radović (ME)
Dario Iljkić (HR)	Ankica Rađenović (HR)
Ivan Ivec (HR)	Matija Sakoman (HR)
Miće Jakić (HR)	Božo Smoljan (HR)
Ivan Jandrlić (HR)	Ivan Stojanović (HR)
Sebastjan Kastelic (SI)	Sanja Šolić (HR)
Zvonimir Katančić (HR)	Iveta Vasková (SK)
Witold Kazimierz Krajewski (PL)	Tatjana Volkov Husović (RS)
Varužan Kevorkijan (SI)	Darja Volšak (SI)
Ana Kostov (RS)	Maja Vončina (SI)
Stjepan Kožuh (HR)	Domagoj Vulin (HR)
Jure Krolo (HR)	Zdenka Zovko Brodarac (HR)
Dajana Kučić Grgić (HR)	Irena Žmak (HR)



**18<sup>th</sup> INTERNATIONAL FOUNDRYMEN CONFERENCE**  
**Coexistence of material science and sustainable technology in  
economic growth**

Sisak, May 15<sup>th</sup>-17<sup>th</sup>, 2019

<http://www.simet.hr/~foundry/>

**INFLUENCE OF Mn ON THE CORROSION BEHAVIOR OF CuAlMn ALLOY  
IN NaCl SOLUTION**

**Senka Gudić<sup>1\*</sup>, Blanka Rakuljić<sup>1</sup>, Ladislav Vrsalović<sup>1</sup>, Milan Bizjak<sup>2</sup>, Ivana Ivanić<sup>3</sup>, Stjepan  
Kožuh<sup>3</sup>, Mirko Gojić<sup>3</sup>**

<sup>1</sup> University of Split Faculty of Chemistry and Technology, Split, Croatia

<sup>2</sup> University of Ljubljana Faculty of Natural Sciences and Engineering, Ljubljana, Slovenia

<sup>3</sup> University of Zagreb Faculty of Metallurgy, Sisak, Croatia

**Poster presentation**  
*Original scientific paper*

**Abstract**

The corrosion behavior of different CuAlMn shape memory alloys (Cu-12%Al-4%Mn, Cu-12.3%Al-5.2%-Mn and Cu-12%Al-6%Mn) in 0.9% NaCl solution at pH = 7.4 and T = 37°C was investigated using open circuit potential measurements, polarization and electrochemical impedance spectroscopy methods. It has been found that the corrosion resistance of the tested samples at open circuit potential increases with increasing Mn content in the alloy, i.e. growing in the order of: Cu-12%Al-4% Mn < Cu-12.3%Al-5.2%Mn < Cu-12%Al-6% Mn. Namely, the corrosion current decreases in same order, while the polarization resistance and the resistance, thickness and compactness of the surface oxide layer increase. However, at high anodic potentials ( $E > 0.1$  V), the corrosion rate increases with Mn content in the alloy, and light microscopy investigations reveal pits on the surface of Cu-12.3%Al-5.2%-Mn and Cu-12%Al-6%Mn alloys, while Cu-12%Al-4%Mn surface is almost clear of any corrosion damage.

**Keywords:** *shape memory alloys, CuAlMn alloy, corrosion, polarization, electrochemical methods*

\*Corresponding author (e-mail address): [senka@ktf-split.hr](mailto:senka@ktf-split.hr)

**INTRODUCTION**

Shape memory alloys (SMA) are significant and growing group of intelligent materials which have ability to “remember” their original shape and return to it by heating above a certain temperature due to its crystallographic structure changes between low temperature martensite and the high temperature austenite phase [1-4]. Mainly three alloy systems



## 18<sup>th</sup> INTERNATIONAL FOUNDRYMEN CONFERENCE

Coexistence of material science and sustainable technology in  
economic growth

Sisak, May 15<sup>th</sup>-17<sup>th</sup>, 2019

<http://www.simet.hr/~foundry/>

which are known to exhibit the shape memory phenomena have been in the focus of research and development: Ni-Ti, Cu-Al and Fe based alloys [5]. Nickel-titanium alloys (Nitinol) possess the unique thermal shape memory and superelasticity effects as well as excellent corrosion resistance and biocompatibility, that make these alloys very attractive for medical use [6,7]. However, their difficulty in production and processing, high cost and low transformation temperatures prohibit their use where Cu-based shape memory alloys fill in the need [5,8]. The main advantages of Cu-based shape memory alloys are their low price, relatively simple fabrication procedure, higher range of potential transformation temperatures, high thermal and electrical conductivity. Shortcoming of Cu-based shape memory alloys are brittleness and low mechanical strength which are close related to the microstructure characteristics of Cu-SMAs, such as coarse grain size, high elastic anisotropy and the segregation of secondary phases [9-11]. Some research has shown that CuAlMn alloy possess good strain recovery, better ductility, higher shape memory strain, larger recovery power, and higher damping capacity than CuAlNi [11-14]. Investigated CuAlMn alloys were produced by melt spinning methods which enables the formation of homogeneous solution and have unique advantages in refining the microstructure [15-17]. Most research on influence of alloying elements in CuAlMn shape memory alloys have focused on its microstructure and mechanical properties, however little attention has been devoted to their influence to the electrochemical behavior [5,8,18]. Thus some studies have shown that additions of Mn to the binary Cu-Al alloy stabilize the  $\beta$ -phase and widen the single-phase region to lower temperature and lower Al contents [18]. With the increase in the aluminum and manganese concentration of the alloy, the martensite morphology is modified and the transformation temperature decrease [8]. Also, increase in the Al:Mn ratio leads to increase in grain size as well as cast hardness [5]. This paper deals with the influence of Mn content on corrosion behavior of CuAlMn alloy in NaCl solution.

### MATERIALS AND METHODS

The CuAlMn alloys used in this study were Cu-12%Al-4%Mn (A), Cu-12.3%Al-5.2%-Mn (B), and Cu-12%Al-6%Mn (C). Alloy ribbons were manufactured with the single roll melt spinning apparatus. The cast precursors were inserted into the graphite crucible, inductively melted in Ar atmosphere and sprayed through the nozzle onto a rotating cooled copper wheel. The obtained ribbons were 4-5 mm wide and 30-100  $\mu$ m thick. The as-prepared specimens were cut at the proper dimensions and solder to an isolated copper wire to insure good electrical contact. Solder joints were isolated with polyacrilate resin and prepared electrodes were degreased ultrasonically in ethanol, rinsed in deionized water and immersed in 0.9% NaCl solution (pH = 7.4, T = 37 °C). Since melt-spin alloys are rather thin, the surface of the ribbons was not mechanically polished.

Experiments were performed with a PAR 273A potentiostat/galvanostat and a PAR M5210 lock-in amplifier. A double walled three-electrode glass cell was used, thermostated at 37 °C, with Pt-plate auxiliary electrode and saturated calomel electrode (SCE) as a reference





**18<sup>th</sup> INTERNATIONAL FOUNDRYMEN CONFERENCE**  
**Coexistence of material science and sustainable technology in  
economic growth**

Sisak, May 15<sup>th</sup>-17<sup>th</sup>, 2019

<http://www.simet.hr/~foundry/>

electrode. Prior the electrode immersion, solution was deaerated with Ar for a 20 min and the deaeration continued during the experiment.

The corrosion behaviour of CuAlMn alloys in 0.9% NaCl solution was performed by open circuit potential measurements ( $E_{OC}$ ) in 60 min time period, linear polarisation method in the potential region of  $\pm 20$  mV vs.  $E_{OC}$  with the scan rate of  $0.2 \text{ mV s}^{-1}$  and potentiodynamic polarisation method in the range of  $-0.250 \text{ V}$  from  $E_{OC}$  to  $0.7 \text{ V}$  with scan rate of  $0.5 \text{ mV s}^{-1}$ . Electrochemical impedance spectroscopy measurements were carried out at  $E_{OC}$  using the signal amplitude of  $10 \text{ mV}$  and a frequency interval from  $50 \text{ kHz}$  to  $30 \text{ mHz}$ . All electrochemical measurements were performed after 60 min electrode stabilisation on  $E_{OC}$ . After the potentiodynamic polarization measurements electrode surfaces were cleaned ultrasonically in deionized water, dry in desiccator and investigated with light microscope MXFMS-BD, Ningbo Sunny Instruments co., with magnifications of 100 times.

## RESULTS AND DISCUSSION

Figure 1 shows the variation of  $E_{OC}$  of investigated alloys with time in the NaCl solution. The open circuit potential reflects the composite results of the electrochemical reactions which take place at the electrode/solution interface. As can be seen, all investigated samples shows similar changes of  $E_{OC}$ . Namely, immediately after immersing each electrode in NaCl solution, values of  $E_{OC}$  were shifted towards negative values due to the adsorption of chloride ions on the surface of the electrode [19]. After the initial drop,  $E_{OC}$  for all alloys increases gradually towards positive values which indicate the formation and thickening of the protective passive film on their surfaces during the immersion. The stabilization of  $E_{OC}$  for all alloys occurs in period of 20 minutes. It can also be noted that by increasing the Mn content in alloy, the final  $E_{OC}$  value become more negative.

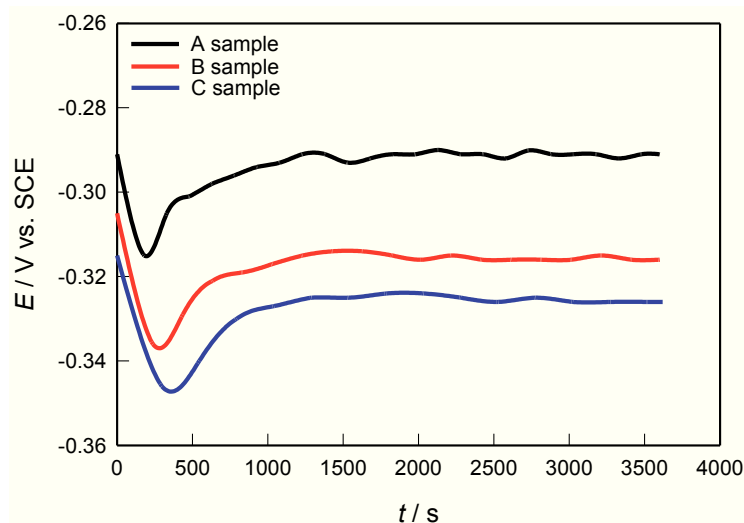


Figure 1. Evolution of open circuit potential as a function of time for investigated CuAlMn alloys in a 0.9% NaCl solution



**18<sup>th</sup> INTERNATIONAL FOUNDRYMEN CONFERENCE**  
**Coexistence of material science and sustainable technology in  
 economic growth**

Sisak, May 15<sup>th</sup>-17<sup>th</sup>, 2019

<http://www.simet.hr/~foundry/>

The general corrosion behavior of tested CuAlMn alloys in NaCl solution was investigated by recording the polarization curves in wide potential range. The purpose of these measurements was to evaluate influence of Mn on anodic and cathodic behaviour of alloy and determination of corrosion current density ( $i_{corr}$ ) and corrosion potential ( $E_{corr}$ ). Obtained results are presented on Figure 2 and Table 1.

Significant differences in corrosion behavior of tested samples can be noticed. The slight increases of the anodic current density in Tafel region and gradually reduction of cathodic current density along with the slight changes the values of corrosion potential in the cathodic side can be observed with increasing Mn content in alloy. This direction of change ultimately leads to a reduction in the corrosion rate.

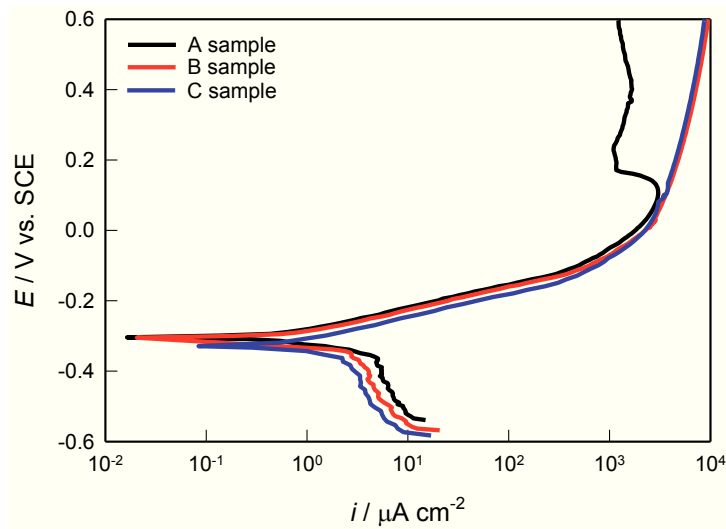


Figure 2. Potentiodynamic polarization curves for investigated CuAlMn alloys in 0.9% NaCl solution

Table 1. Corrosion parameters of investigated CuAlMn alloys in 0.9% NaCl solution

sample	$E_{corr} / V$	$i_{corr} / \mu A \text{ cm}^{-2}$	$R_p / k\Omega \text{ cm}^2$
A	-0.29	3.17	5.24
B	-0.31	2.54	6.53
C	-0.33	2.09	7.18

As can be seen from Table 1 the lowest  $i_{corr}$  and the most negative  $E_{corr}$  have been obtained for C sample (alloy with the largest Mn content) which also have the highest polarization resistance,  $R_p$  (i.e. resistance of metal to corrosion). The  $R_p$  data were determined from the slope of linear part of polarization curves obtained by measurements in the potential range close to  $E_{oc}$  (Figure 3). Thus, it can be concluded that the corrosion resistance of the tested samples at open circuit potential increases with increasing Mn content in the alloy (i.e. growing in the order of: A < B < C).

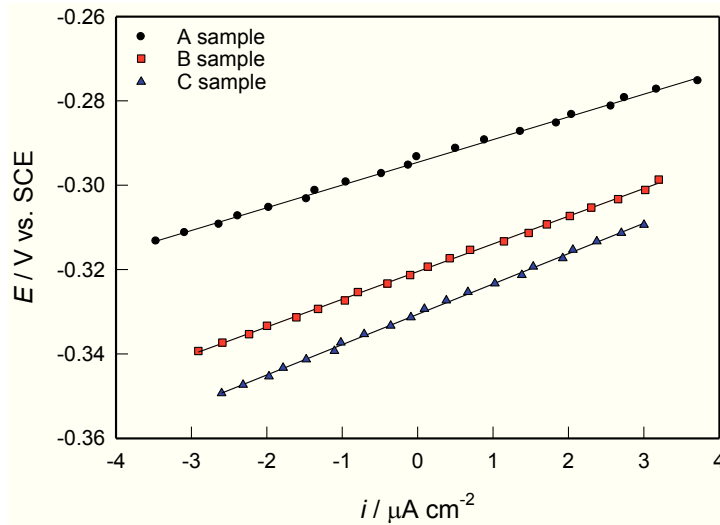


Figure 3. Linear parts of polarization curves for investigated CuAlMn alloys in 0.9% NaCl solution

However, at high anode potentials (after passing through Tafel area,  $E > 0.1$  V) the opposite trend is noticed. Anodic current density, and thus the corrosion are increased with the increase of Mn content in the alloy. After polarization measurement (which ended at 0.7 V) electrode surfaces were examined with light microscope with magnification of 100 times, and obtained results have shown on Figure 4 (a-c). Pits are visible on the surface of samples C and B, while surface of sample A is almost clear of any pitting corrosion damages.

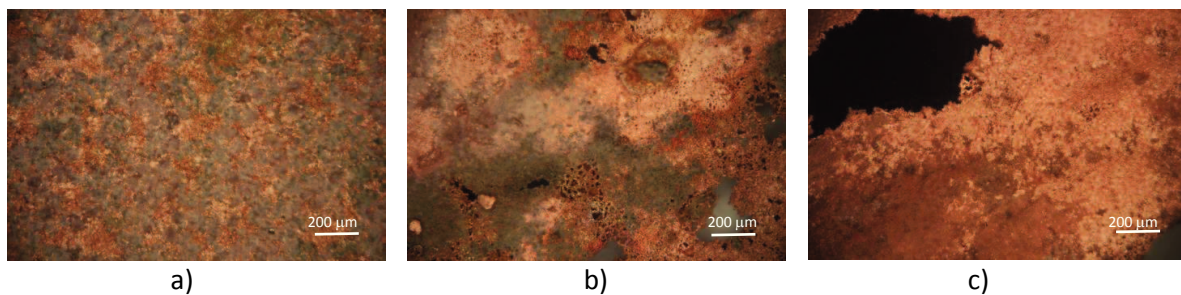


Figure 4. Light microscopy images of the electrode surfaces after potentiodynamic polarization measurements for a) sample A, b) sample B and c) sample C

Impedance measurements were undertaken in order to obtain physical insight into the processes occurring at the CuAlMn alloys/solution phase boundary. Figure 5 shows the Nyquist plots for CuAlMn electrodes in NaCl solution obtained after 60 minutes stabilization at  $E_{OC}$ . The response of the systems in the Nyquist complex plane was a semicircle that can be correlated with the dielectric properties of the naturally formed oxide film on alloy surface, which mostly consists of aluminum and manganese oxides [20,21]. The diameter of capacitive loop increases with the increase of the Mn content in the alloy.



**18<sup>th</sup> INTERNATIONAL FOUNDRYMEN CONFERENCE**  
**Coexistence of material science and sustainable technology in**  
**economic growth**

Sisak, May 15<sup>th</sup>-17<sup>th</sup>, 2019

<http://www.simet.hr/~foundry/>

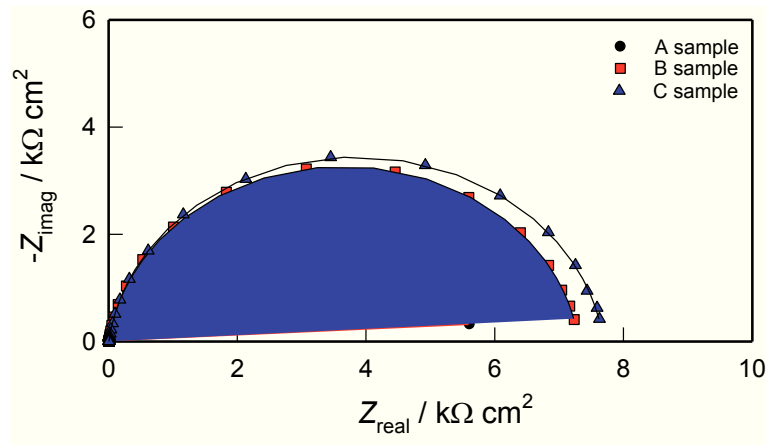


Figure 5. Nyquist plots for investigated CuAlMn alloys in 0.9% NaCl solution

In mathematical analysis of impedance diagrams the constant phase element, CPE, was used instead of an "ideal" capacitor to account for the deviations observed as capacitive loops are depressed. The impedance,  $Z_{CPE}$ , of CPE is described by the expression [22]:

$$Z_{CPE} = [Q(j\omega)^n]^{-1} \quad (1)$$

with  $n$  and  $Q$  constants, that can be used in data fitting when interpreting frequency dispersions. When the value of  $n$  is close to 1, the CPE behaves like an ideal capacitance. The equivalent circuit, shown in the Figure 6 was used to fit the experimental data.  $R_{el}$  represents the resistance of electrolyte.  $R$  is the resistance and  $Q$  is the capacitance of the surface oxide film ( $n \approx 1$ ;  $Q \approx C$ ).

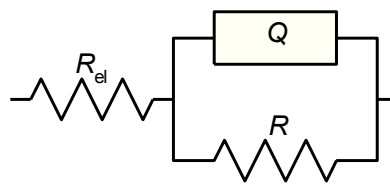


Figure 6. Proposed equivalent circuits for modeling the impedance data

The parameters of the equivalent circuit  $R_{el}$ ,  $R$  and  $Q$  were evaluated using a simple least square fit procedure and are presented in Table 2.



**18<sup>th</sup> INTERNATIONAL FOUNDRYMEN CONFERENCE**  
**Coexistence of material science and sustainable technology in**  
**economic growth**

Sisak, May 15<sup>th</sup>-17<sup>th</sup>, 2019

<http://www.simet.hr/~foundry/>

Table 2. Impedance parameters of investigated CuAlMn alloys in 0.9% NaCl solution

sample	$R_{el} / \Omega \text{ cm}^2$	$Q \times 10^6 / \Omega^{-1} \text{ s}^n \text{ cm}^{-2}$	$n_1$	$R / \text{k}\Omega \text{ cm}^2$
A	8.31	44.75	0.91	5.24
B	8.04	38.62	0.93	6.53
C	7.78	34.21	0.93	7.18

Increase in Mn content lead to the increase in alloy surface film resistance ( $R$ ), while the surface layer capacity ( $Q$ ) decreases. This is attributed to the increase of protective properties of the surface oxide layer on the electrode.

According to the plate capacitor model, the surface film capacity,  $C$ , is inversely proportional to its thickness,  $d$  (according to  $C = \varepsilon_0 \varepsilon / d$ ;  $\varepsilon_0$  is the permittivity of vacuum; and  $\varepsilon$  the relative permittivity of the film). Hence, the reduction of  $Q$  (from 44.75 to 34.21  $\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$ ), with the increase of Mn content matches the corresponding increase in the thickness of the surface layer, which additionally corresponds to an enhancement in the protective properties of the surface layer. This indicates that Mn (with constant content of Al) increases the stability of oxide layer on the surface and effectively prevents alloy corrosion at  $E_{OC}$ .

Properties of the oxide films which are formed on the alloy surfaces primarily depend on the chemical composition of the based metal, i.e. the content of the individual alloying elements in the investigated samples. If the alloying element facilitates alloy passivation, the properties of the oxide film will be better (higher resistance and thickness, more compact structure), which will ultimately increase the corrosion resistance of the metal, i.e. less corrosion currents and greater polarization resistance.

Cu-Al alloys represent the base material for production of copper shape-memory alloys. The role of Al is primarily in reducing weight and increasing corrosion resistance of the alloy. High corrosion resistance of Cu-Al alloys is primarily due to the presence of a protective layer which, according to the data in the literature, has a two layer structure and consists of an inner thin, compact layer (mainly containing  $\text{Cu}_2\text{O}$  and  $\text{Al}_2\text{O}_3$ ) and an exterior enriched porous layer [23]. Inner compact layer decelerate the passage of  $\text{Cu}^+$  cations and prevent surface alloy dissolution [24,25]. It should be emphasized that Al has an extremely high affinity for oxygen and that  $\text{Al}_2\text{O}_3$  is one of the most stable oxides found in nature. At standard conditions,  $\text{Al}_2\text{O}_3$  has more than 11 times high stability over  $\text{Cu}_2\text{O}$ .

However, Cu-Al alloys manufactured by conventional procedures are often very fragile that is related to their large anisotropy and a crushed microstructure [1,2,4]. The microstructure can be affected by micro-alloying and by applying a rapid cooling process (resulting in a large number of limited-diameter crystal chips) [10].

As already noted, the addition of Mn to the binary Cu-Al alloy further increases the corrosion resistance of the alloy (Table 1 and 2). According to literature, addition of Mn in small amounts influences the microstructure of the alloy, i.e. reduces the size of the crystal grain. Specifically, Mn diffuses easily and rapidly disperses through the mass of alloy, and accumulates on the grain boundaries and thus prevents further growth of grain [21,26]. Studies have shown that such refining of microstructures, with the improvement of



## 18<sup>th</sup> INTERNATIONAL FOUNDRYMEN CONFERENCE

Coexistence of material science and sustainable technology in  
economic growth

Sisak, May 15<sup>th</sup>-17<sup>th</sup>, 2019

<http://www.simet.hr/~foundry/>

mechanical properties, significantly increases corrosion resistance of alloys [21]. This fine microstructure positively affects the compactness and stability of the passive oxide film formed on the alloy.

### CONCLUSIONS

In this paper, corrosion behavior of different CuAlMn shape memory alloys (Cu-12%Al-4%Mn, Cu-12.3%Al-5.2%-Mn and Cu-12%Al-6%Mn) was studied in 0.9% NaCl solution. From the analysis of the obtained results can be concluded as follows:

- By increasing the Mn content in alloy, the final  $E_{OC}$  value becomes more negative.
- Significant differences in corrosion behavior of tested samples at open circuit potential and at high anodic potentials can be noticed by polarization measurements.
- The corrosion resistance of the tested samples at open circuit potential is following the order: Cu-12%Al-4%Mn < Cu-12.3%Al-5.2%-Mn < Cu-12%Al-6%Mn. Namely, the corrosion current decreases in same order, while the polarization resistance increases.
- The corrosion resistance of the CuAlMn alloys is a consequence of the oxide layer formation whose properties depend on the Mn content in the samples. Namely, impedance measurements carried out on open circuit potential have shown that Mn facilitates passivation of tested alloys and improve surface film properties (higher resistance and thickness, more compact structure).
- At high anodic potentials (after passing Tafel's region,  $E > 0.1$  V), the corrosion rate increases with Mn content in the alloy, and light microscopy investigations reveal pits on the surface of Cu-12.3%Al-5.2%-Mn and Cu-12%Al-6%Mn alloys, while Cu-12%Al-4%Mn surface is almost clear of any corrosion damage.

### Acknowledgements

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

### REFERENCES

- [1] I. Ivanić, M. Gojić, S. Kožuh, Slitine s prisjetljivosti oblika (I. dio): najznačajnija svojstva, Kem. Ind., 63(2014), pp. 323-330.
- [2] I. Ivanić, M. Gojić, S. Kožuh, Slitine s prisjetljivosti oblika (II. dio): podjela, proizvodnja i primjena, Kem. Ind., 63(2014), pp. 331-344.
- [3] M. Čolić, R. Rudolf, D. Stamenković, I. Anžel, D. Vučević, M. Jenko, V. Lazić, G. Lojen, Relationship between microstructure, cytotoxicity and corrosion properties of Cu-Al-Ni shape memory alloy, Acta Biomater., 6(2010), pp. 308-317.



## 18<sup>th</sup> INTERNATIONAL FOUNDRYMEN CONFERENCE

Coexistence of material science and sustainable technology in  
economic growth

Sisak, May 15<sup>th</sup>-17<sup>th</sup>, 2019

<http://www.simet.hr/~foundry/>

- [4] S. Sathish, U. S. Mallik, T. N. Raju, Microstructure and shape memory effect of Cu-Zn-Ni shape memory alloys, *JMMCE*, 2(2014), pp. 71-77.
- [5] A. K. Jain, S. Hussain, P. Kumar, A. Pandey, Effect of varying Al/Mn ratio on phase transformation in CuAlMn shape memory alloys, *Trans. Indian Inst. Met.*, 69(2016), pp. 1289-1295.
- [6] S. Shabalovskaya, J. Anderegg, J. Van Humbeeck, Critical overview of nitinol surfaces and their modifications for medical applications, *Acta Biomater.*, 4(2008), pp. 447-467.
- [7] S. Kožuh, L. Vrsalović, M. Gojić, S. Gudić, B. Kosec, Comparison of the corrosion behavior and surface morphology of NiTi alloy and stainless steels in sodium chloride solution, *J. Min. Metall. Sect. B-Metall.*, 52(2016), pp. 53-61.
- [8] U. S. Mallik, V. Sampath, Influence of aluminium and manganese concentration on the shape memory characteristics of Cu-Al-Mn shape memory alloys, *J. Alloy Compd.*, 459(2008), pp. 142-147.
- [9] A. O. Moghaddam, M. Ketabchi, R. Bahrami, Kinetic grain growth, shape memory and corrosion behavior of two Cu-based shape memory alloys after thermomechanical treatment, *Trans. Nonferrous Mat. Soc. China*, 22(2013), pp. 2896-2904.
- [10] K. K. Alaneme, E. A. Okotete, M. O. Bodunrin, Microstructural analysis and corrosion behavior of Fe, B, and Fe-B-modified Cu-Zn-Al shape memory alloys, *Corros. Rev.*, 35(2017), pp. 3-11.
- [11] S. Kožuh, M. Gojić, I. Ivanić, T. Holjevac Grgurić, B. Kosec, I. Anžel, The effect of heat treatment on the microstructure and mechanical properties of Cu-Al-Mn shape memory alloy, *Kem. Ind.*, 67(2018), pp. 11-17.
- [12] M. R. Rezvani, A. Shokuhfar, Synthesis and characterization of nano structured Cu-Al-Mn shape memory alloy by mechanical alloying, *Mater. Sci. Eng. A*, 532(2012), pp. 282-286.
- [13] U. S. Mallik, V. Sampath, Influence of quaternary alloying additions on transformation temperatures and shape memory properties of Cu-Al-Mn shape memory alloy, *J. Alloys Comp.*, 469(2009), pp. 156-163.
- [14] J. Chen, Z. Li, Y. Y. Zhao, A high-working-temperature CuAlMnZr shape memory alloy, *J. Alloys Comp.*, 480(2009), pp. 481-484.
- [15] H. Morawiec, J. Lełątko, D. Stróż, M. Gigla, Structure and properties of melt-spun Cu-Al-Ni shape memory alloys, *Mat. Sci. Eng. A*, 273-275(1999), pp. 708-712.
- [16] M. Izadinia, K. Dehghani, Structure and properties of nanostructured Cu-13.2Al-5.1Ni shape memory alloy produced by melt spinning, *Trans. Nonferrous Met. Soc. China*, 21(2011), pp. 2037-2043.
- [17] G. Lojen, I. Anžel, A. Kneissl, A. Križman, E. Unterweger, B. Kosec, M. Bizjak, Microstructure of rapidly solidified Cu-Al-Ni shape memory alloy ribbons, *J. Mater. Process. Technol.*, 162-163(2005), pp. 220-229.
- [18] R. Kainuma, S. Takahashi, K. Ishida, Thermoelastic martensite and shape memory effect in ductile Cu-Al-Mn alloys, *Metal. Mater. Trans.*, 27(1996), pp. 2187-2195.
- [19] L. Vrsalović, E. Oguzie, M. Kliškić, S. Gudić, Corrosion inhibition of CuNi10Fe alloy with phenolic acids, *Chem. Eng. Comm.*, 198(2011), pp. 1380-1393.



## 18<sup>th</sup> INTERNATIONAL FOUNDRYMEN CONFERENCE

Coexistence of material science and sustainable technology in  
economic growth

Sisak, May 15<sup>th</sup>-17<sup>th</sup>, 2019

<http://www.simet.hr/~foundry/>

- [20] L. Vrsalović, M. Matulić, S. Kožuh, I. Ivanić, M. Gojić, Effect of pH on corrosion of CuAlMn alloy in 0.9% NaCl solution, Proceedings of the MTSM 2017, (S. Jozić, B. Lela), Croatian society for mechanical technologies, 21.-22. September, 2017., Split, Croatia, 159-163.
- [21] S. N. Saud, E. Hamzah, T. Abubakar, H. R. Bakhsheshi-Rad, Correlation of microstructural and corrosion characteristics of quaternary shape memory alloys Cu-Al-Ni-X (X=Mn or Ti), Trans. Nonferrous Met. Soc. China, 25(2015), pp. 1158-1170.
- [22] D. D. Raistrick, J. R. Macdonald, D. R. Franceschetti, in: J. R. Macdonald (Ed.), Impedance Spectroscopy, J. Wiley & Sons, New York, 1987.
- [23] W. A. Badawy, M. El-Rabeiee, N. H. Hilal, H. Nady, Electrochemical behavior of Mg and some Mg alloys in aqueous solutions of different pH, Electrochim. Acta, 55(2010), pp. 1880-1887.
- [24] H. Nady, N. H. Hilal, M. M. Rabeiee, W. A. Badawy, The role of Ni content on the stability of Cu-A-Ni ternary alloy in neutral chloride solutions, Mater. Chem. Phys., 134(2012), pp. 945-950.
- [25] W. A. Badawy, M. El-Rabeiee, N. H. Hilal, H. Nady, Effect of nickel content on the electrochemical behavior of Cu-A-Ni alloys in chloride free neutral solutions, Electrochim. Acta, 56(2010), pp. 913-918.
- [26] G. N. Sure, L. C. Brown, The mechanical properties of grain refined  $\beta$ -CuAlNi strain memory alloys, Metall. Trans. A, 15A(1984), pp. 1613-1621.