

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

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

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

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#### 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

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#### 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



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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



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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.

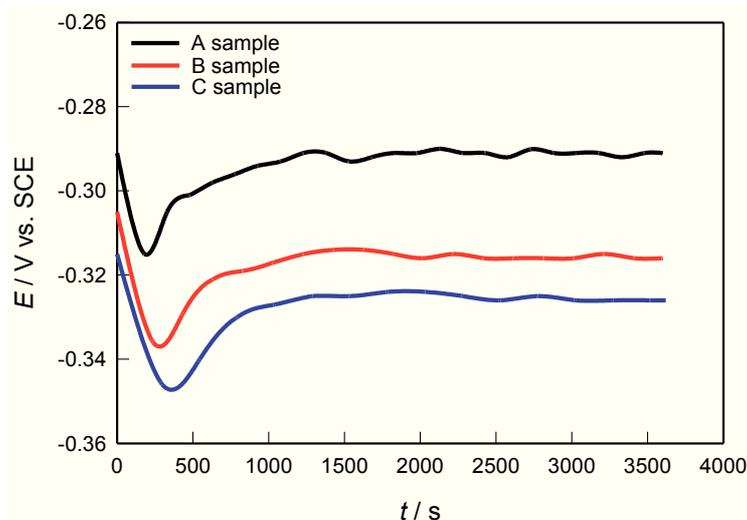


Figure 1. Evolution of open circuit potential as a function of time for investigated CuAlMn alloys in a 0.9% NaCl solution



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.

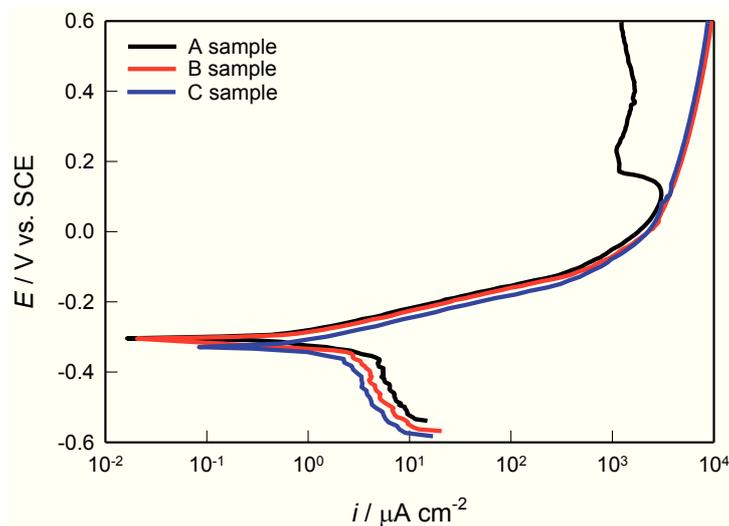


Figure 2. Potentiodynamic polarization curves for investigated CuAlMn alloys in 0.9% NaCl solution

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:  $A < B < C$ ).

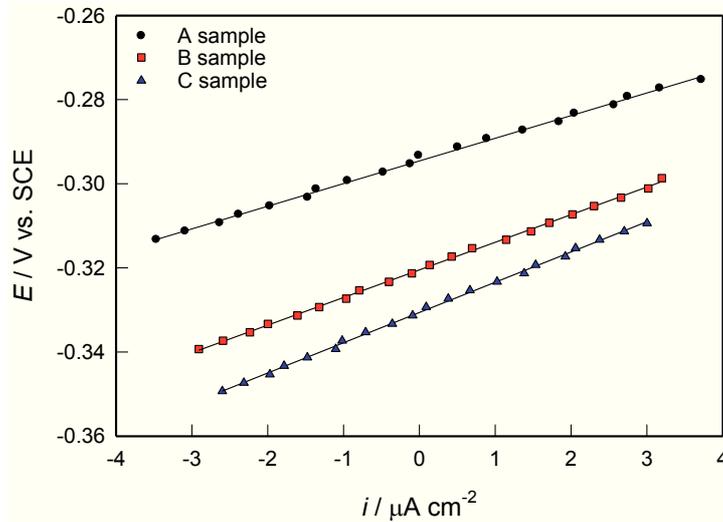


Figure 3. Linear parts of polarization curves for investigated CuAlMn alloys in 0.9% NaCl solution

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.

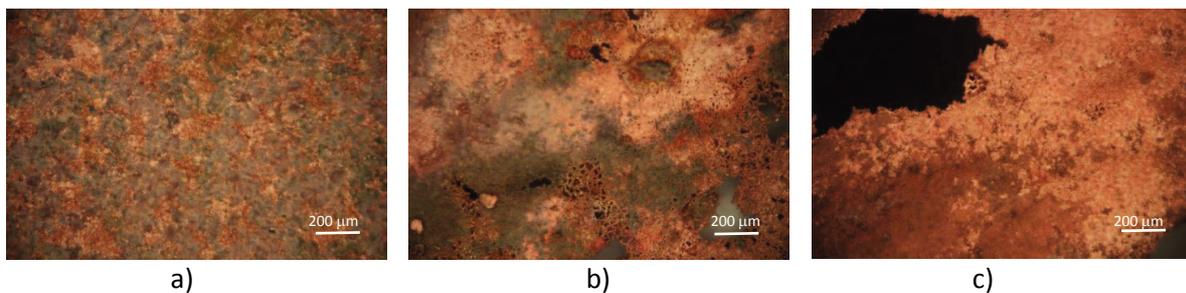


Figure 4. Light microscopy images of the electrode surfaces after potentiodynamic polarization measurements for a) sample A, b) sample B and c) sample C

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.



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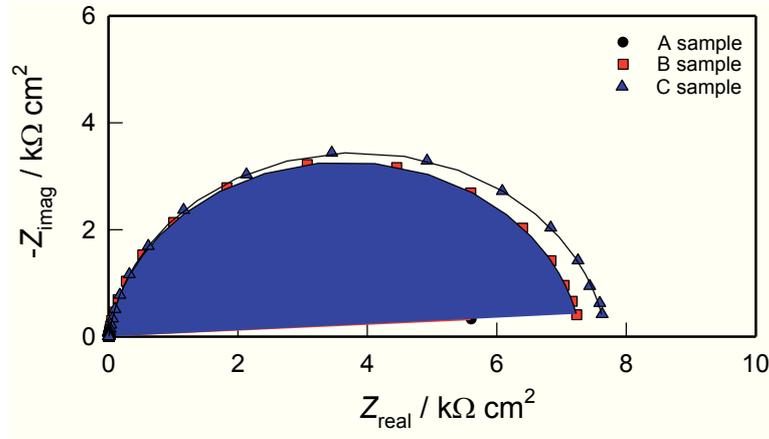


Figure 5. Nyquist plots for investigated CuAlMn alloys in 0.9% NaCl solution

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 ( $n \approx 1$ ;  $Q \approx C$ ).

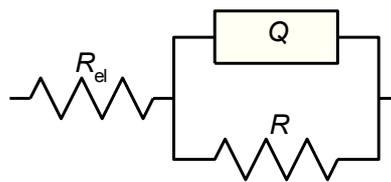


Figure 6. Proposed equivalent circuits for modeling the impedance data

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.



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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



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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.

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