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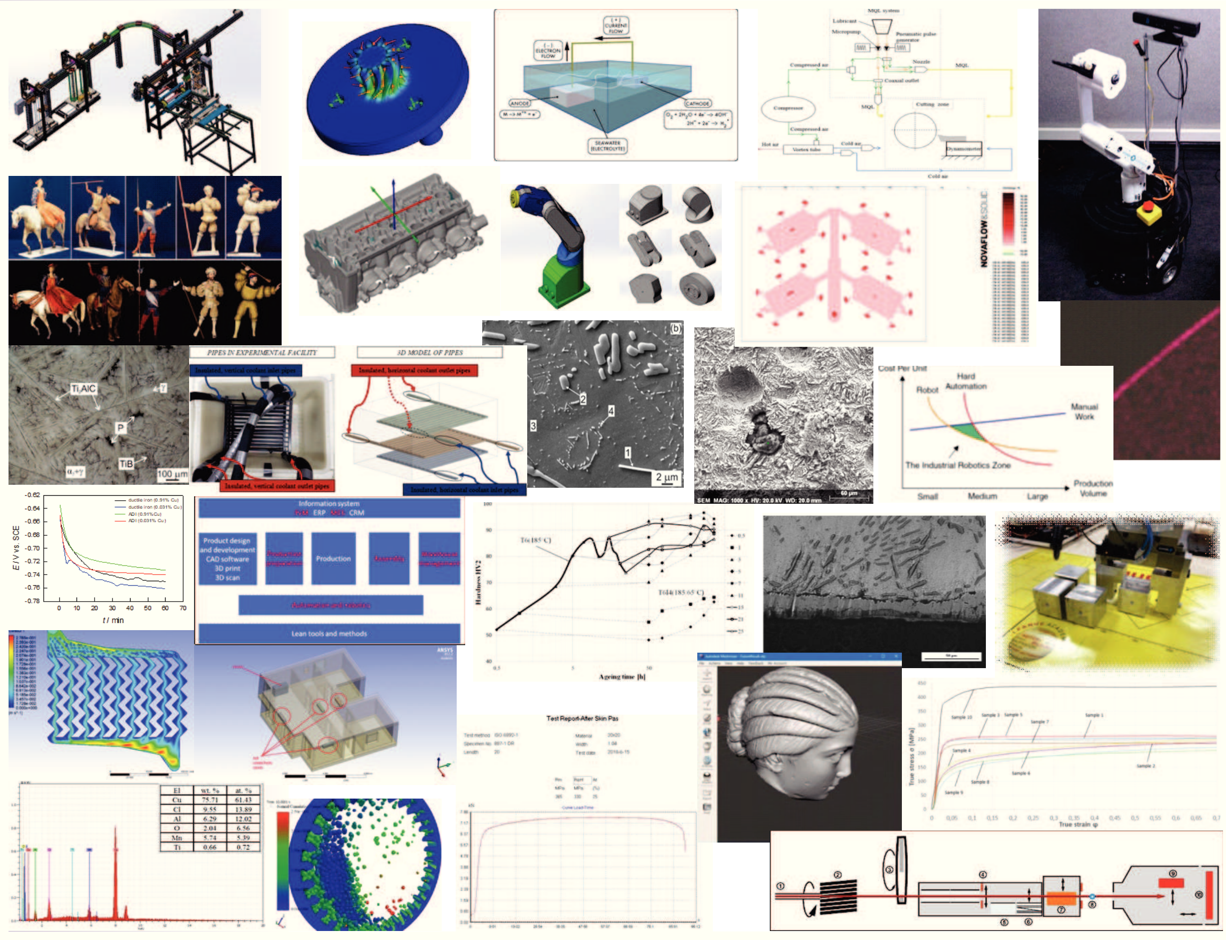

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The influence of pH and electrolyte temperature on corrosion behaviour of CuAlMnTi alloy ribbons in NaCl solution

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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. In 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.

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 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 β-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, μAcm^{-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, Ωcm^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 ±20 mV around corrosion potential, with the scanning rate of 0.2 mV s^{-1} and potentiodynamic polarization method in the potential region of −0.250 V from open circuit potential to 0.7 V, with the scanning rate of 0.5 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 ^{o}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 (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 pH = 7.4 and 5.4 have similar values, and the value of E_{oc} for the measurement in NaCl solution 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 lover 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 (pH = 37 ^{o}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 ^{o}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

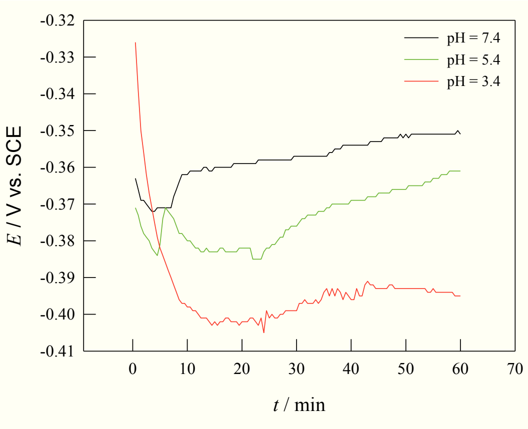


Figure 1. Variation of the open circuit potentials with time for the CuAlMnTi alloy in 0.9% NaCl solution at different pH values of solution

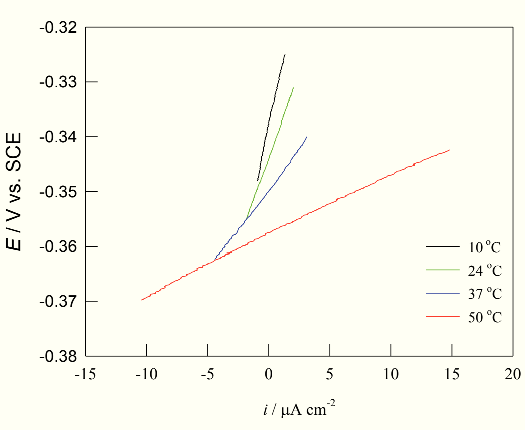


Figure 2. Results of linear polarization measurements for CuAlMnTi alloy in 0.9% NaCl solution (pH = 7.4) at different electrolyte temperatures

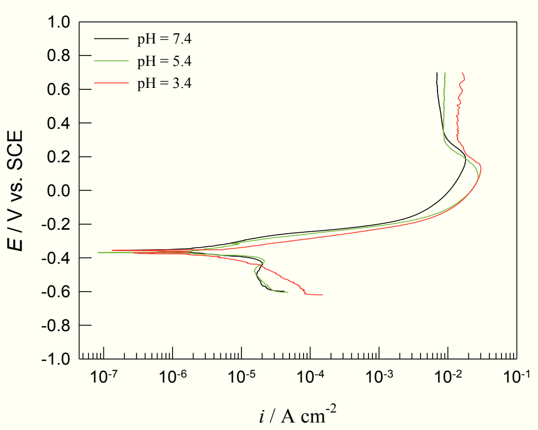


Figure 3. Potentiodynamic polarization curves for CuAlMnTi alloy in 0.9% NaCl solution (T = 37 °C) at different pH values

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

Measurement conditions	E_{corr} / V	i_{corr} / µA cm^{-2}	R_p / kΩ 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 reviled 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.

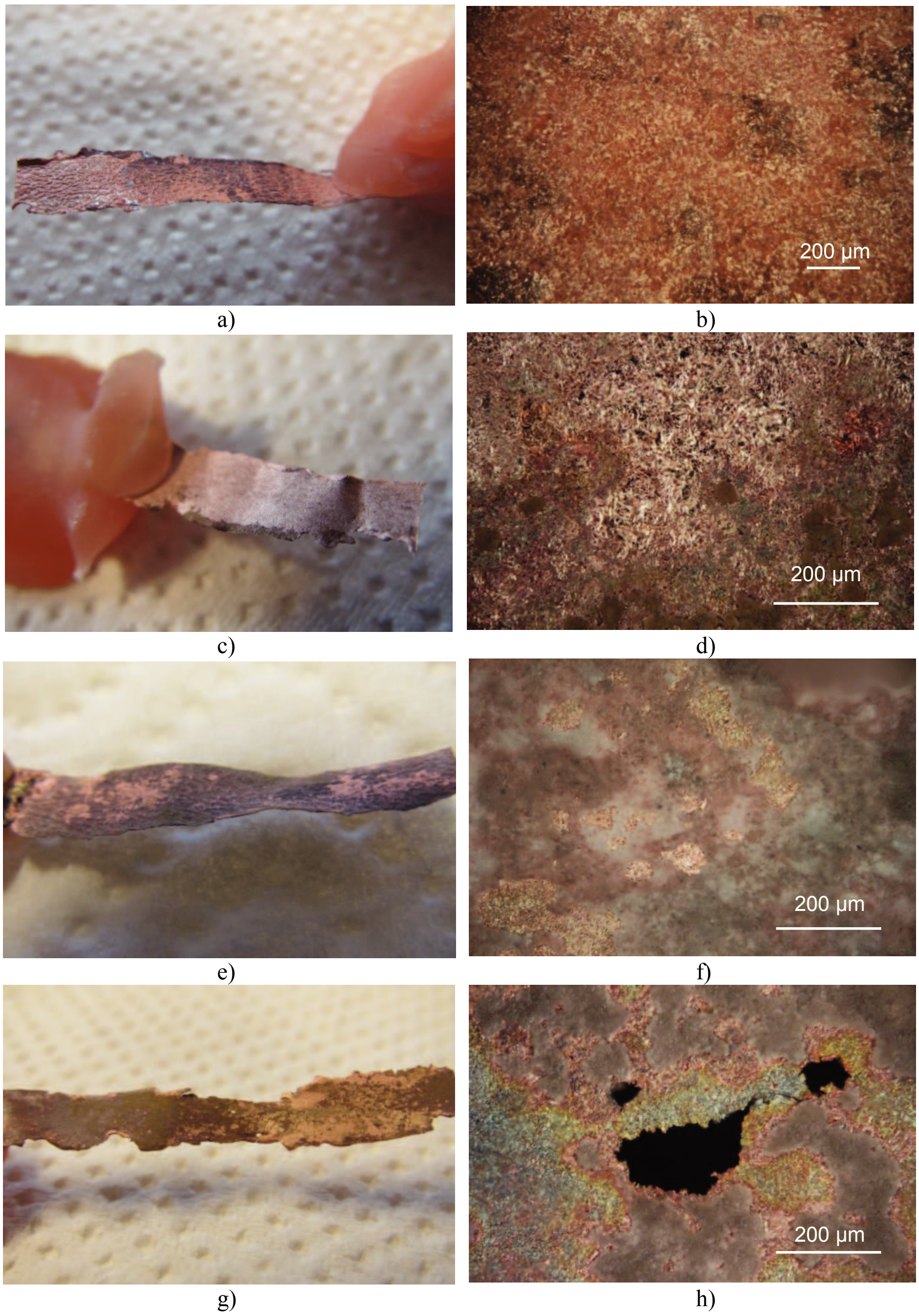
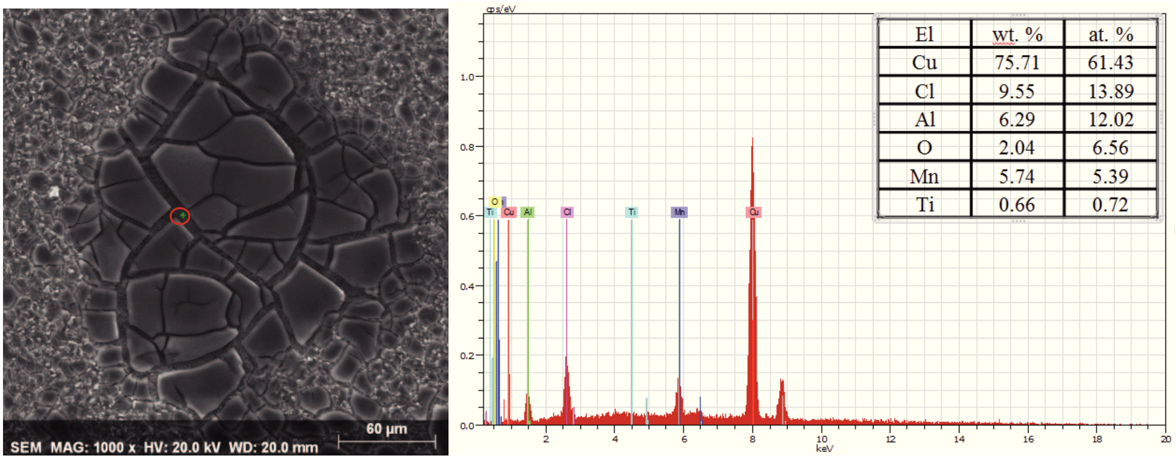


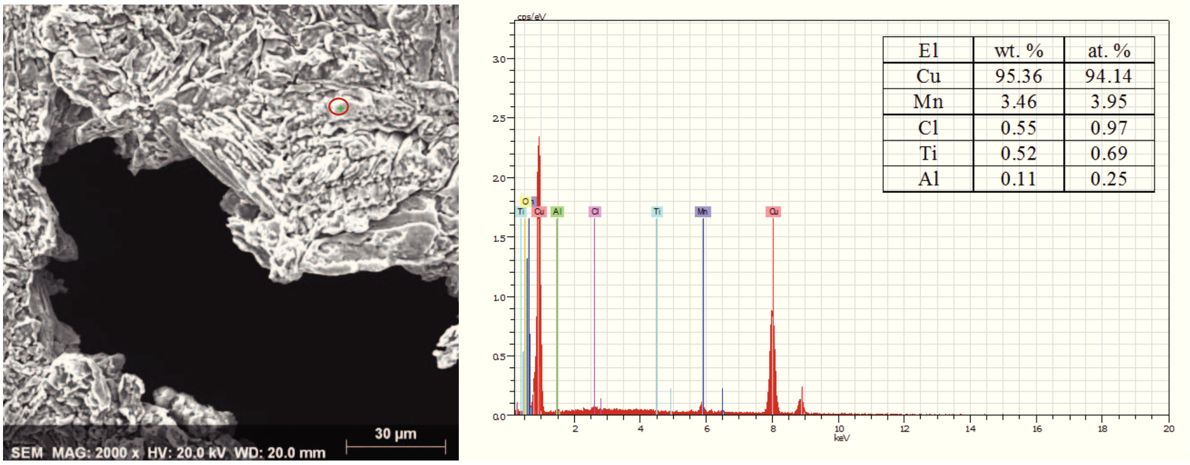
Figure 4. Macro images and optical micrographs of the corroded CuAlMnTi alloy surface in 0.9% NaCl solution at 10 ºC a) and b); 24 ºC c) and d); 37 ºC e) and f) and 50 ºC g) and h)



El	wt. %	at. %
Cu	75.71	61.43
Cl	9.55	13.89
Al	6.29	12.02
O	2.04	6.56
Mn	5.74	5.39
Ti	0.66	0.72

a) b)

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



El	wt. %	at. %
Cu	95.36	94.14
Mn	3.46	3.95
Cl	0.55	0.97
Ti	0.52	0.69
Al	0.11	0.25

a) b)

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.

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