

COMPARISON OF THE FUNCTIONAL PROPERTIES OF SELECTED MULTILAYER SYSTEMS

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Electrodeposition of multilayers continues to grow and diversify. Research is still underway on the adaptation of multilayer systems to new applications in various industries. Cu/Ni multilayers are still very commonly used for practical purposes. In this work, the functional properties of selected multilayer systems with different layers quantity and thicknesses in nanoscale were investigated. The Cu and Ni layers were electrolytically deposited on a low carbon steel substrate and obtained systems were subjected to structural and anticorrosion properties study. The electrochemical parameters were determined by potentiodynamic method and the surface evaluation of the systems after corrosion tests was also carried out.

Key words: Cu/Ni system, galvanic treatment, multilayer systems, corrosion resistance, x-ray research

INTRODUCTION

Cu/Ni multilayer systems are popular and have been extensively studied in terms of their structure, thermal stability, mechanical and magnetic properties, especially the demonstrated effect of giant magnetoresistance (GMR) [1-4]. The thickness of the layers was also determined using various measurement methods and the influence of the thickness of the ferro and non-ferromagnetic layers on the properties obtained by these systems was investigated [5, 6]. However, very little work has been devoted to studying the corrosion properties of these materials. Considering that corrosion resistance is extremely important in the practical application of multilayer systems as engineering materials, this paper attempts to investigate the corrosion behavior of multilayer copper/nickel systems obtained by electrolytic deposition, depending on the number and thickness of the layers.

EXPERIMENTAL DETAILS

A sample of low-carbon steel foil with dimensions of 50 x 50 mm and a thickness of about 0,1 mm was used for the tests, on which alternate layers of copper and nickel were applied in the process of electrolytic deposition. The copper layer was deposited from a cyanide bath at room temperature and a current intensity of 0,0125 A. The nickel plating operation was carried out in a nickel bath at 50 °C with a current intensity of 0,1 A (Table 1).

Microanalysis of the chemical composition of the Cu/Ni multilayers was carried out using an Energy Dis-

Table 1 **The parameters of the copper and nickel plating operations**

Sample no.	Cu layer Time / s	Ni layer Time / s	Quantity of layers
1	165	62,5	40
2	79	30	40
3	79	62,5	40
4	165	30	40
5	165	62,5	20
6	79	30	20
7	79	62,5	20
8	165	30	20

persive X-ray fluorescence spectrometer (EDX-7000 by SHIMADZU).

The thickness of the obtained systems was determined based on the observation of cross-sections of samples made in liquid nitrogen using a Scanning Electron Microscope (SEM) Supra 35 Carl Zeiss.

Surface topography studies were conducted using an atomic force microscope (AFM) provided by Park System XE-100.

The anticorrosion properties of the systems were determined using the potentiodynamic method. The investigations were conducted in 3,5 % sodium chloride solution at room temperature with the use of Autolab 302 N potentiostat, by NOVA software (version 1.11) controlled. The measurements were performed in a cell containing three electrodes (reference electrode – saturated calomel electrode (SCE); counter electrode – platinum rod; working electrode – sample). The corrosion resistance was evaluated by recording the open circuit potential (E_{OCP}) variation on time (3 600 s). Corrosion current density (j_{corr}), the polarization resistance (R_p), and the corrosion potential (E_{corr}) were determined by extrapolating Tafel curves. The scan rate was 1 mV s⁻¹.

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The evaluation of the samples surface after corrosion tests was carried out using the Supra 35 scanning electron microscope (SEM) by Carl Zeiss, and the chemical composition of the surface layer was determined with the Energy Dispersive Spectrometer (EDS) by EDAX.

RESULTS AND DISCUSSION

Analysis of the chemical composition of the Cu/Ni multilayer systems was carried out by energy dispersive X-ray fluorescence spectrometer (Figure 1). The obtained XRF spectra showed a varied presence of copper and nickel depending on the time of individual layers deposition.

After the cross-sections observation of the samples with the use of a scanning electron microscope and the local measurement of the multilayer systems thickness, it turned out that the thickness of the samples varies depending on the location of the measurement (Figure 2). This may be due to the deformation of the layers during the preparation of the samples for testing.

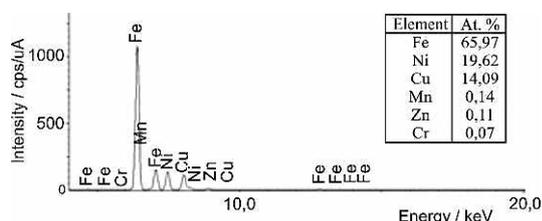


Figure 1 XRF spectrum of the Cu/Ni multilayers (sample no. 1)

Based on the AFM test results, the following roughness parameters were determined: mean roughness (average roughness – Ra), root mean square (RMS), and maximum profile height (Max.) (Table 2).

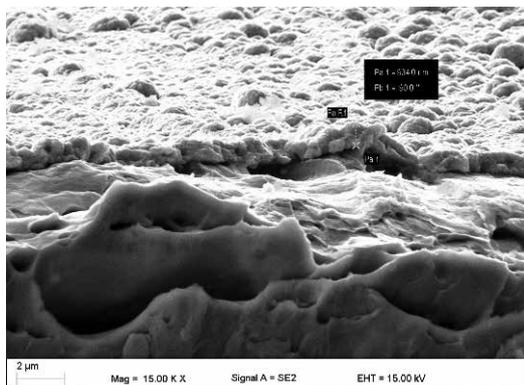


Figure 2 Local measurement of the of multilayer system thickness (sample no. 1)

The results of the tests showed that systems with a smaller number of deposited layers showed a higher surface roughness (Figure 3).

Changes in the open circuit potential as a function of time showed the variable corrosion resistance of the tested materials (Figure 4 a, b). After 3 600 s, the best E_{OCP} value was recorded for sample no. 4, consisting of 40 layers, where the copper layer was deposited for the longest time and constituted the top layer of the system. At the beginning of the test, sample no. 2 showed relatively good resistance to the aggressive environment,

while after 500 s the potential of the sample reached the lowest value, which was maintained until the end of the test and was the worst among the tested samples.

The analysis of the polarization curves of samples of Cu/Ni multilayer systems shows an increase in the corrosion potential (E_{corr}) from -0,35 V for sample no. 4 to -0,52 V for sample no. 2 (Figure 4 c, d). Therefore, the best and lowest E_{corr} values were recorded for the system with more single layers but with a thinner nickel

Table 2 The roughness parameters of Cu/Ni systems

Sample	Ra / nm	RMS / nm	Max / nm
substrate	92	115	595
1	113	152	776
6	180	237	1 289

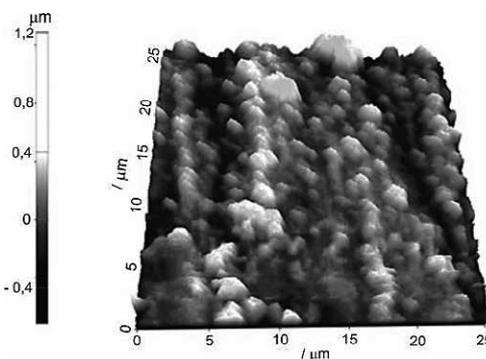


Figure 3 AFM image of three-dimensional visualization of Cu/Ni system topography (sample no. 6)

layer. In turn, the highest value of the corrosion current density was shown for systems with a smaller number of single layers, namely for samples no. 7 ($j_{corr} = 118,92 \mu\text{A}/\text{cm}^2$) and no. 5 ($j_{corr} = 80,69 \mu\text{A}/\text{cm}^2$). The lowest value of $j_{corr} = 7,36 \mu\text{A}/\text{cm}^2$ and the highest polarization resistance ($R_p = 12,25 \text{ k}\Omega\text{cm}^2$) were obtained for sample no. 1, which consisted of 20 layers of copper and 20 layers of nickel, applied in the longest time (Table 3).

On the sample no. 1 surface, there are visible residues of corrosion tests in the form of sodium chloride crystals, but the layer has maintained continuity and has not undergone significant degradation. EDS analysis also showed the presence of oxygen, indicating that a passive oxide layer had probably formed on the surface of the sample (Figure 5).

CONCLUSIONS

Electrochemical tests of the samples showed a varied corrosion resistance of the systems depending on the number and thickness of the layers. The discrepancy between the E_{corr} and j_{corr} values indicates a better corrosion resistance of sample no. 1, because the potential is a thermodynamic value, while the corrosion current density is kinetic and related to the corrosion rate.

SEM images did not reveal traces of pitting, which may indicate the formation of a passive oxide layer on the surface and the corrosion resistance of systems with the largest number and thickness of layers in the sodium chloride environment.

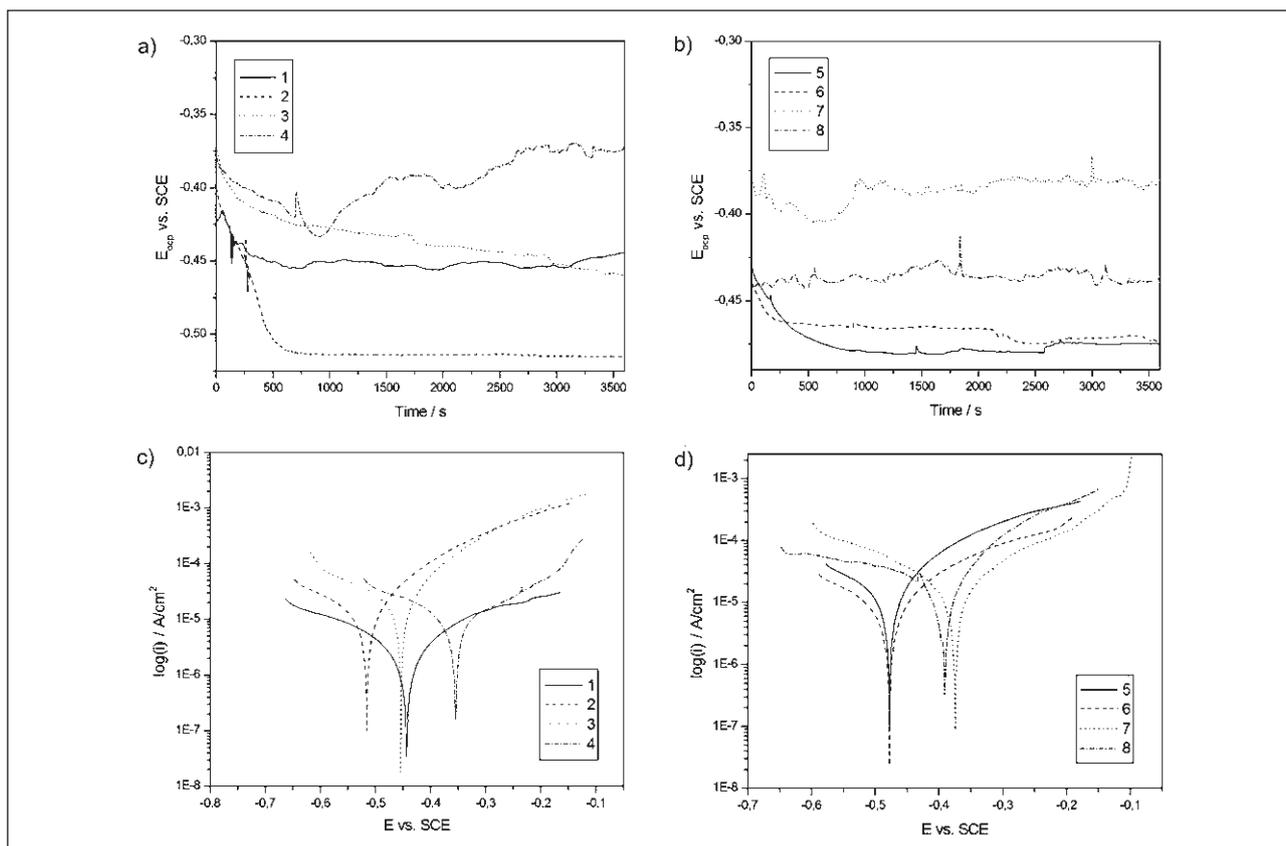


Figure 4 Variation of the E_{OCP} with time (a, b) and polarization curves (c, d) in 3,5 % NaCl solution of Cu/Ni multilayers with 40 layers (a, c) and 20 layers (b, d)

Table 3 Results of polarization tests of Cu/Ni multilayer systems

Sample no.	1	2	3	4	5	6	7	8
E_{corr} / V	-0,45	-0,52	-0,46	-0,35	-0,48	-0,48	-0,37	-0,44
$R_p / k\Omega cm^2$	12,25	2,17	1,26	3,06	1,81	3,39	1,77	1,88
$j_{corr} / \mu A/cm^2$	7,36	31,51	51,35	30,14	80,69	39,49	118,92	20,24

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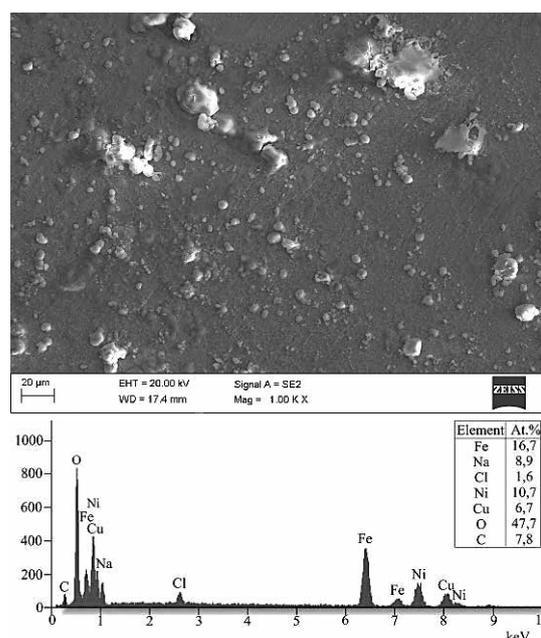


Figure 5 SEM images and EDS analysis of the surface morphology of sample no. 1 after electrochemical tests

Note: The responsible translator for English language is ITAMAR Group Sp. z o.o., Gliwice, Poland