ISSN 0543-5846
METABK 60(1-2) 39-42 (2021)
UDC – UDK: 620.193.002.61:66.065.087:546.56/73-532.6:620.197.6=111

CORROSION PROPERTIES OF ELECTRODEPOSITED Cu/Co MULTILAYERS

Received – Primljeno: 2020-07-17
Accepted – Prihvaćeno: 2020-10-20
Original Scientific Paper – Izvorni znanstveni rad

The paper presents the results of corrosion resistance of Cu/Co multilayer systems fabricated by using the electrolytic method. The systems obtained were composed of layers differing in number and thickness, which was determined by observing the cross-sections of the samples using scanning electron microscopy (SEM). The measurements of multilayer system corrosion properties carried out in 3,5 % NaCl solution showed different corrosion resistance depending on system thickness. The microscopic observations revealed the effect of the aggressive environment on the Cu/Co multilayer systems manufactured, adopting various forms of corrosion degradation.

Key words: corrosion properties, electrodeposition, Cu/Co multilayer systems, surface morphology and topography

INTRODUCTION

Multilayer systems have received increasing attention in recent years because of their special properties (mechanical, optical, electrical and magnetic) as compared to traditional materials. Magnetic multilayer systems consist of alternating layers of ferromagnetic and nonferromagnetic components with nanometric thickness. Ferromagnetic layers are ferromagnetic transition metals such as Co, Fe, Ni or their alloys (e.g. CoFe, NiFe and CoNi). These ferromagnetic layers are separated by nonferromagnetic metal intermediate layers, such as Cu, Cr, Au, Mn, etc [1].

Cu/Co multilayer systems are very popular due to their interesting current applications, depending on the substrate used. For example, when deposited on silicon, copper or platinum substrates, they can be used in the industry of data storage devices, sensors etc. In turn, when applied on other substrates they can be used mainly for catalytic purposes and as anticorrosive coatings [2]. But, first of all, the Cu/Co multilayers systems are used to study magnetic and magnetoresistive properties. An excellent magnetoresistance ratio was reported by Jiang et al. [3].

Among many physical and chemical deposition methods, the electrodeposition has proved to be an effective technique for preparing alternate micro or nanometric layers, because of its simplicity and low costs, as well as minimum interdiffusion and the formation of flat individual layers [4, 5]. However, the conditions of electrolytic deposition, such as: the type and composition of electrolyte, cathode electrical potentials, pH of the solution, current density used in the process and temperature, affect the thickness of layers obtained, and hence the total thickness of the system, which is reflected in the properties of the multilayer systems obtained [6-8].

The aim of this work is to produce multilayer systems with an alternate Cu/Co nanometric layers by using the electrolytic method, examine their surface morphology and topography as well as corrosion resistance.

EXPERIMENTAL DETAILS

The material used for the studies included steel plates 50 x 50 mm in size and 1 mm thick, on which copper and cobalt layers were alternately applied in different number and thickness by using the electrolytic method.

The copper layer was deposited in a cyanide bath. The copper plating operation was carried out at ambient temperature; the current intensity was 0,0125 A and the duration of the operation was variable, depending on the thickness of the layer to be obtained.

The deposition of cobalt layers was carried out in the electrolyte containing $CoSO_4$ at a temperature of 35 °C, with various current intensity and exposure time. The parameters of the copper and cobalt plating operations are presented in Table 1.

The thickness of Cu/Co systems was determined by observing the cross-sections of samples using a scanning electron microscope (SEM) Supra 35 Carl Zeiss equipped with an Energy dispersive spectrometer (EDS).

The study of sample surface topography was performed using atomic force microscope (AFM) provided by Park System XE-100.

The corrosion resistance studies of Cu/Co multilayer systems were conducted in 3,5 % NaCl solution at room temperature using an Autolab 302 N potentiostat controlled by the NOVA software (version 1.11). The

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Table 1 **Operation parameters of copper and cobalt plating**

Sample number	Copper layers			Cobalt layers		
	Current intensity / A	Time / s	Number of layers	Current intensity / A	Time / s	Number of layers
1	0,0125	79	20	0,1	60	20
2	0,0125	33	20	0,1	30	20
3	0,0125	79	10	0,025	60	10
4	0,0125	33	10	0,025	90	10
5	0,0125	79	20	0,025	90	20

Table 2 **The roughness parameters of Cu/Co systems**

Sample	*Ra* / nm	*RMS* / nm	Max. / nm
3	159,4	201,5	815,7
5	164,1	219,3	530,2

measurements were performed in a three-electrode cell with a water jacket using a saturated calomel electrode (SCE) as a reference electrode, a platinum rod as a counter electrode, and the sample as a working electrode. The corrosion resistance was evaluated by recording the open circuit potential (E_{OCP}) variation. The corrosion potential (E_{corr}) and corrosion current density (j_{corr}) were determined by using the Tafel extrapolation method.

The observation of surface morphology of fabricated multilayer systems and the changes in the surface morphology of samples after electrochemical tests were analyzed using a Zeiss SteREO Discovery V12 stereoscopic microscope (SM).

RESULTS AND DISCUSSION

The surface morphology of fabricated Cu/Co multilayer systems is shown in Figure 1.

Observations carried out using a stereoscopic microscope did not reveal the occurrence of cracks, crevices or places where the copper and cobalt layers did not cover the substrate, which means that the layers were applied continuously.

Depending on the sample topography, differences in Cu/Co system thickness can be observed (Figure 2).

After observing the cross-sections of samples using the scanning electron microscope it was found that the thickness of system sample No. 1 ranged from approx. 220 to 500 nm, sample No. 2 had a thickness of approx. 240-510 nm, while sample No. 3 had a thickness of approx. 50-400 nm.

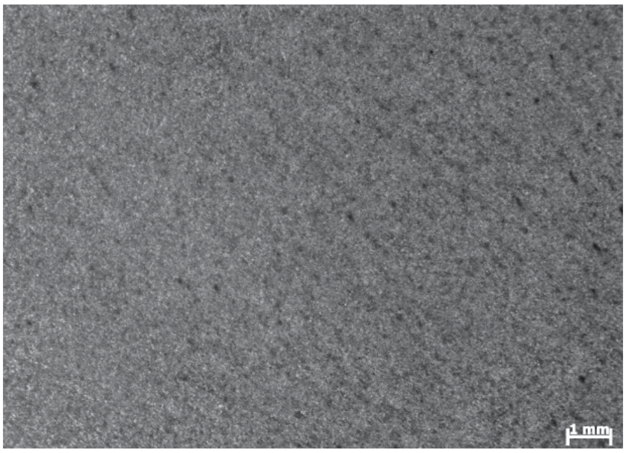

Figure 1 Surface morphology of sample No. 3 in as prepared state (ring lighting), 10 x

An EDS analysis confirmed the presence of deposited elements. Figure 3 presented the linear profile of EDS analysis, while the distribution of elements on the analytical line is shown in Figure 4.

An image of the surface topography to define the surface morphology was presented for a selected area (10 x 10 mm) of the sample (Figure 5).

Based on test results, the following roughness parameters: mean roughness (roughness average – Ra), root mean square (RMS), and maximum profile height (*Max.*) for Cu/Co systems were determined (Table 2). It was found that the surface roughness increases expo-

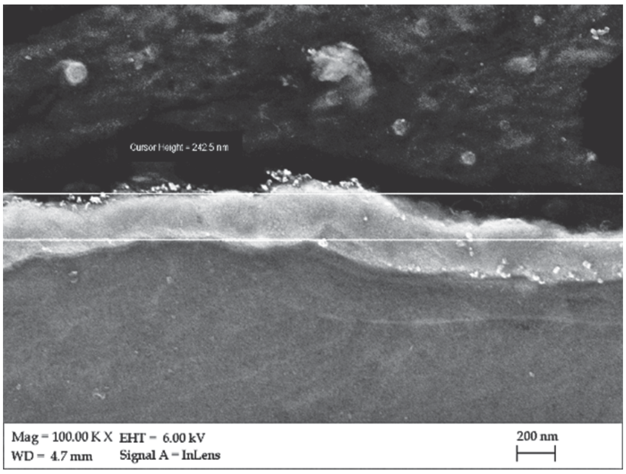

Figure 2 Measurement of system thickness (sample No. 2), 100 000 x

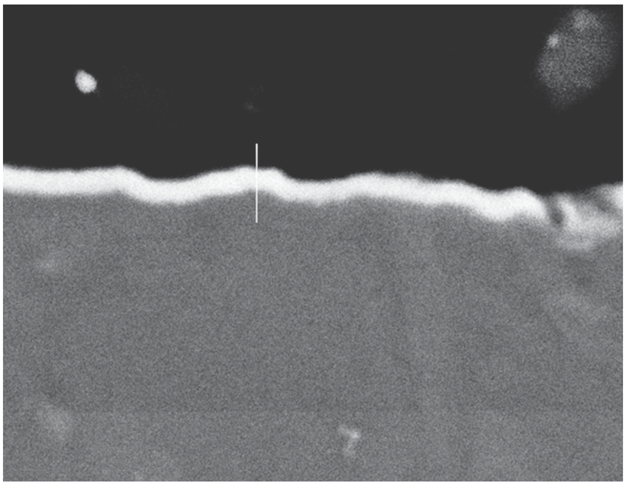

Figure 3 Linear profile of EDS analysis of sample No. 2

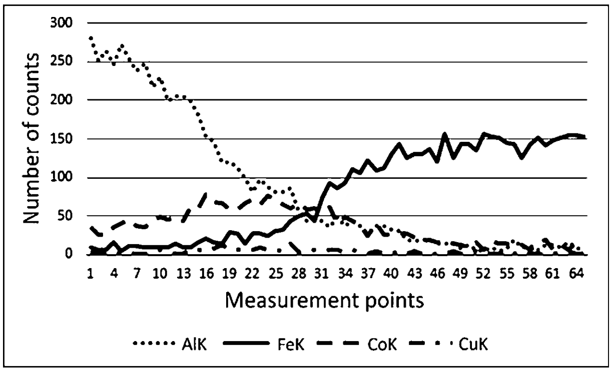

Figure 4 Distribution of elements on the analytical line (sample No. 2)

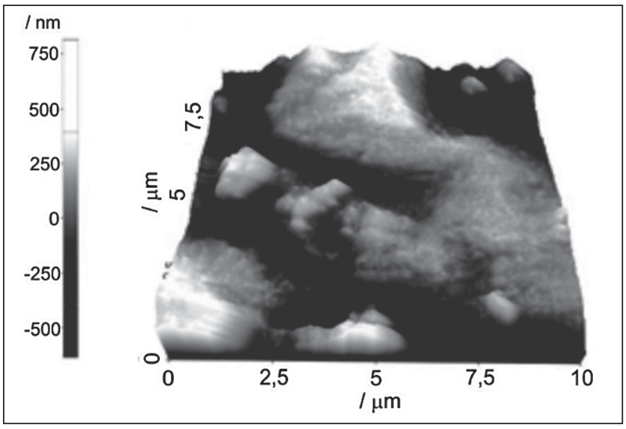

Figure 5 AFM image of three-dimensional visualization of Cu/Co system topography (sample No. 3)

nentially with the increase of total thickness of multilayer systems.

The electrochemical results obtained from measurements in 3,5 % NaCl solution at 25 °C for Cu/Co multilayer systems to determine their corrosion resistance are presented in Figures 6-7.

The open circuit potential (E_{OCP}) (Figure 6) for all samples shifts into negative values with immersion time, so they are not completely corrosion resistant. At the beginning of the test, sample No. 2 showed good resistance to an aggressive environment, while the potential of sample No. 2 decreased after finishing the test and was the lowest among the tested samples. Sample No. 5 had the best open circuit potential in comparison with other samples.

Figure 7 of the polarization curves shows the differences in corrosion potential for individual samples. The corrosion potential changed from -0,53 V for sample No. 2, -0,50 V for sample No. 4 to -0,47 V for sample No. 5. Thus, sample No. 5 has a higher corrosion resistance than samples No. 2 and 4. This is probably because sample No. 5 has the largest number of individual layers and the multilayer system of sample No. 5 is the

Table 3 **Results of corrosion tests of samples No. 2, 4, 5**

	Sample No. 2	Sample No. 4	Sample No. 5
E_{corr} / V	-0,53	-0,50	-0,47
j_{corr} / µA/cm^2	8,96	3,20	10,98
R_p / kΩcm^2	4,83	12,47	2,74

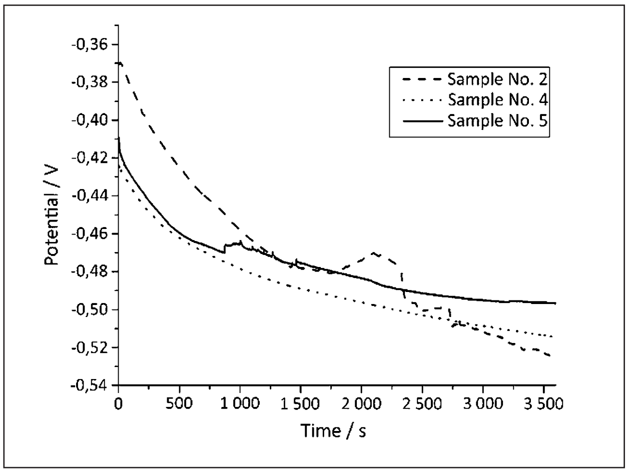

Figure 6 Changes of open circuit potential in time for samples No. 2, 4, 5

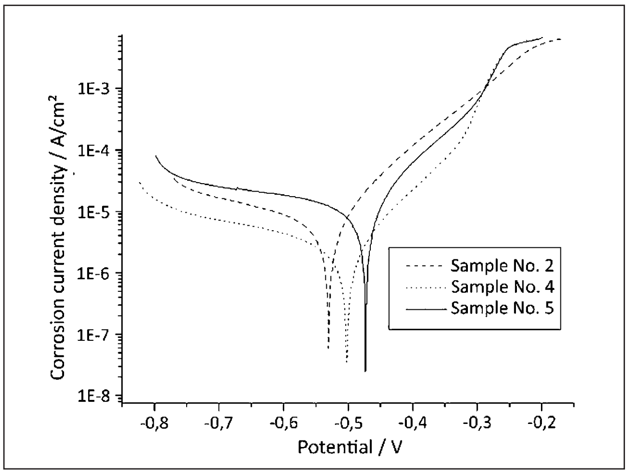

Figure 7 Polarization curves for samples 2, 4, 5 in 3,5 % NaCl solution

thickest. On the other hand, sample No. 2 shows the lowest corrosion resistance among the tested samples, due to the thinnest multilayer system in the set of samples.

The corrosion parameters including the corrosion current density (j_{corr}), corrosion potential (E_{corr}) and polarization resistance (R_p) are summarized in Table 3.

Microscopic observations show that the Cu/Co systems in an aggressive chloride environment undergo degradation (Figure 8).

CONCLUSIONS

The Cu/Co multilayer systems obtained by using the electrolytic method provide a relatively good quality. Morphology and topography surface tests have revealed no major defects.

The corrosion measurements of multilayer systems showed different corrosion resistance depending on system thickness.

The observation of samples surface morphology after electrochemical tests has revealed the occurrence of peeling layers and selective corrosion, which excludes the use of systems in the vicinity of chlorides.

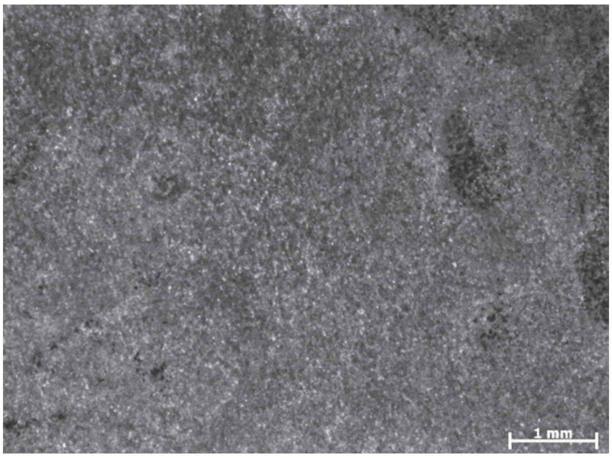

Figure 8 Surface morphology of sample No. 4 after electrochemical tests (ring lighting), 20 x

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