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FABRICATION OF MULTILAYER Cu/Ni SYSTEMS WITH NANOMETRIC LAYERS BY ELECTROLYSIS METHOD

The paper presents research results of multilayer systems composed of alternate Cu/Ni layers. The layers thickness obtained by the galvanic treatment was determined by using the transmission electron microscopy and X-ray diffraction method in the grazing incidence diffraction geometry. The surface morphology was observed using scanning electron microscope with EDS microanalysis. Observation of the surface topography of systems using the atomic force microscope was also carried out.

Keywords: Cu/Ni multilayer systems, galvanic method, thickness measurement, surface morphology and topography

1. Introduction

One of the constantly developing faculties in science are issues related to the problem of thin layers deposited on inorganic substrates. As a layer, an area with a certain thickness is defined, which differs in properties from the deeper part of the material being the core. Initially, layers with thickness lower than 0.01 mm were considered as thin. When manufacturing and testing techniques were improved a layer thickness less than 1000 nm and now thinner than 100 nm was considered as thin [1].

In the thin layers category, one of the most interesting for the research and applications of metal layers are thin magnetic layers, which can be used to obtain multilayer systems. These layers, for example, show the effect of giant magnetoresistance (GMR) [2,3]. Currently available modern techniques allow to largely form and shape the properties of layers with nanometric dimensions to specific needs [4,5], but often their disadvantage remains high cost and complicated manufacturing processes. There are various methods used to obtain multilayer systems [6,7]. Currently, the nanostructured systems needed for prepare GMR sensors on an industrial scale are produced by magnetic field sputtering methods and molecular beam epitaxy. These methods, although provide very precise results, require the use of high vacuum, but they are complicated and expensive. For this reason, the subject of current research is the application of thin layers using galvanic methods, which are much more economical. They do not require the use of expensive equipment and high vacuum [8].

The preparation of thin layers by the electrochemical method consists the galvanic deposition of layered coatings. The basis of this method is the flow of ions in solutions and the application of Faraday's laws. Factors which determine the properties of thin electrochemically deposited layers are: the type and composition of the electrolyte, the pH of the solution, the current density in the process, temperature, as well as the quality and properties of the metal from which the electrodes are made [9,10].

One of the important technological issues necessary to obtain layers is the desired thickness. That is why precise measurements of layer thicknesses are very important, especially in multilayer systems. Non-destructive X-ray methods can be used to determine the thickness of thin layers on the nanometer scale [11,12]. In this case, the thickness of the layer is determined by the effective depth of X-ray penetration at a constant angle of incidence. Layer thickness in thin-layer systems can also be effectively determined by using scanning transmission electron microscopy [13].

The aim of the paper is preparation of multilayer systems composed of alternate Cu/Ni nanometric layers by electrolysis method and then determining the thickness of deposited layers. The research results also include morphology observations and study of surface topography of multilayer systems.

2. Material and methods

The material for investigations was a copper foil with dimensions of 50×50 mm and a thickness of about 70 μm, on which Cu and Ni layers were alternately applied in the electrolysis process. The surface of the samples for deposition

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was cleaned by degreasing and etching. The copper layer was deposited from the cyanide bath. The copper plating operation was conducted at ambient temperature, the current was 0.0125 A. Nickel plating occurred from Watts's bath. The operation of nickel layer deposition was carried out at 50°C at a current of 0.1 A. In order to obtain layers of the assumed thickness, a differentiated time for copper plating and nickel plating operations was applied (Table 1). The thickness of deposited layers was determined based on the mass increment calculations, using the formula:

$$d = \frac{(m_1 - m_2) \times 10000}{D \times S} \tag{1}$$

where m_1 – sample weight after application of a nickel or copper layer [g], m_2 – sample weight before applying a nickel or copper layer [g], D – specific weight of copper or nickel [g/cm^3], S – sample surface [cm^2].

After the operations of surface preparation and the proper electrochemical treatment, the samples were rinsed using the ultrasonic method.

TABLE 1

Parameters of nickel and copper plating processes

Deposited layer	Layer thickness, [nm]	Current density, [A/dm^2]	Duration of nickel and copper plating, [s]
Cu	25	0.0125	165
Cu	12	0.0125	79
Cu	5	0.0125	33
Ni	25	0.1	62.5
Ni	12	0.1	30

A copper and nickel layers formed by electrodeposition were tested to determine their thickness. The theoretical thickness was calculated using the weight method.

The thickness of deposited layers was also determined using high resolution scanning transmission electron microscope S/TEM TITAN 80-300 (FEI Company) and X-ray diffraction method in the grazing incidence diffraction geometry.

The high resolution transmission electron microscope (S/TEM) is equipped with scanning mode STEM, scanning and transmission detectors BF (Bright Field), DF (Dark Field) and HAADF (High Angle Annular Dark Field), energy dispersion spectrometer EDS.

Sample for S/TEM observations were prepared in accordance with the methodology of cutting and thinning using a focused ion beam (FIB). The lamella was taken from the cross section of the sample, which was thinned with gallium ions.

The diffraction investigations were performed on a Siemens D500 diffractometer using Cu K$_\alpha$ radiation ($\lambda k\alpha$ = 0.154 nm). The X-ray examinations included Bragg-Brentano symmetrical geometry (XRD) and grazing-incidence X-ray diffraction (GIXRD) measurements in the diffraction angle (2Θ) range of 40°-54° comprising reflections from the planes (111) and (200).

The thickness of layers constituting the Cu/Ni multilayer systems was calculated using the formula [14]:

$$\Lambda = \frac{\lambda}{2(\sin\theta_i - \sin\theta_{i-1})} \tag{2}$$

where: Λ – multilayer period thickness [nm], λ – X-ray wavelength [nm], i – main peak, i–1 – satellite peaks.

The period (bilayer) size is the sum of thickness of two layers constituting the multilayer system (Fig. 1).

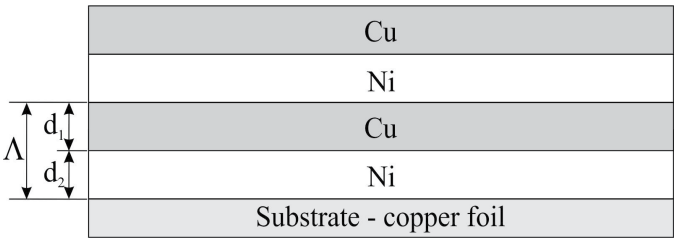


Fig. 1. Schematic representation of Cu/Ni multilayer system

X-ray examinations were carried out by using the Rigaku MiniFlex600 X-ray diffractometer with Cu K$_\alpha$, radiation. The diffraction patterns for the samples were collected by the "step-scanning" method in the 2Θ range from 30° to 80°.

Observation of the surface morphology of prepared multilayer systems was conducted using a scanning electron microscope (SEM) Zeiss SUPRA 25 with an EDS (energy dispersive spectrometer) equipped.

The topography of the samples was examined using an atomic force microscope by Park System XE 100.

3. Results and discussion

On the basis of preliminary investigations and the calculations of the current efficiency, the parameters of nickel plating and electrolysis copper plating processes were determined in order to obtain layers with thicknesses of 25, 12 and 5 nm. The thickness of individual layers constituting the multilayer systems was confirmed by X-ray diffraction methods. The measurements of layer thickness at the nanometer scale were obtained using the grazing-incidence and Bragg-Brentano method (appropriate angles of incidence α). X-ray diffraction analysis was carried out in Bragg-Brentano geometry and for constant incidence angles α = 0.5 and 1 degree. Table 2 shows the description of samples and assumed thicknesses of multilayers, while Table 3 presents the penetration depth of X-rays calculated for Ni and Cu using the X-ray source with copper anode.

The obtained diffraction patterns (Fig. 1) are not typical for multilayer systems, presented in [15,16]. The principal reflection should be flanked by additional satellite reflections, which are characteristic of the multilayer structure. In case of multilayer systems manufactured, different effects were obtained in the form of satellites come from multilayers. For samples which total thickness is higher than the depth of radiation penetration, clear

TABLE 2

Data of multilayer systems subjected to diffraction investigations

Sample	Thickness of the period Λ, [nm]	The number of period repetitions Λ	Total thickness of the system, [nm]
Cu/Ni 5/12	17	20	340
Cu/Ni 12/25	37	30	1110
Cu/Ni 25/25	50	25	1250

TABLE 3

Calculated depth of radiation penetration for copper and nickel ($\lambda_{k\alpha Cu}$ = 0.154 nm)

Element	BB geometry	$\alpha = 1^o$	$\alpha = 0.5^o$
Ni	11.17-29.82 μm θ = 20-60°	1.18 μm	0.6 μm
Cu	11.12-28.17 μm θ = 20-60°	1.12 μm	0.56 μm

satellites appeared in the form of peak asymmetry (Fig. 2). In other cases, when the thickness of all layers was lower than the depth of radiation penetration, there is a strong effect from the substrate, which is a copper foil, because X-rays penetrate the Cu + Ni multilayer and penetrate into the substrate. Based on the obtained diffraction records, an attempt was made to determine the thickness of the layers constituting the multilayer systems with the largest total thickness.

The multilayer period thickness for the sample designated as Cu/Ni 25/25×25 is equal to 51.36 nm as determined for the reflection (200). The results of period measurement are very similar to the assumed theoretical thickness of single layers (25 nm).

The thickness of the deposited layers was also verified by means of the high-resolution electron microscope for a sample consisting of 50 layers of copper and nickel. The thickness obtained by calculations should be 25 nm. The image obtained in the HAADF mode provided information about the arrangement of Cu and Ni layers in the multilayer system (Fig. 3). The distribution of Cu and Ni elements through 16 measurement layers at 330 nm is shown in Fig. 5. The STEM image of the multilayer system with marked measuring points to determine the content of copper and nickel in the study area is shown in Fig. 4.

On the basis of results presented in Fig. 3, an average thickness of copper and nickel layers was obtained, which is 17 nm (Cu) and 18 nm (Ni), respectively. The thicknesses of individual layers are significantly different (Table 4). Taking into account the obtained layer thickness, the minimum and maximum difference is about 25 nm. The atomic content of elements constituting the multilayer system at selected points in the studied area

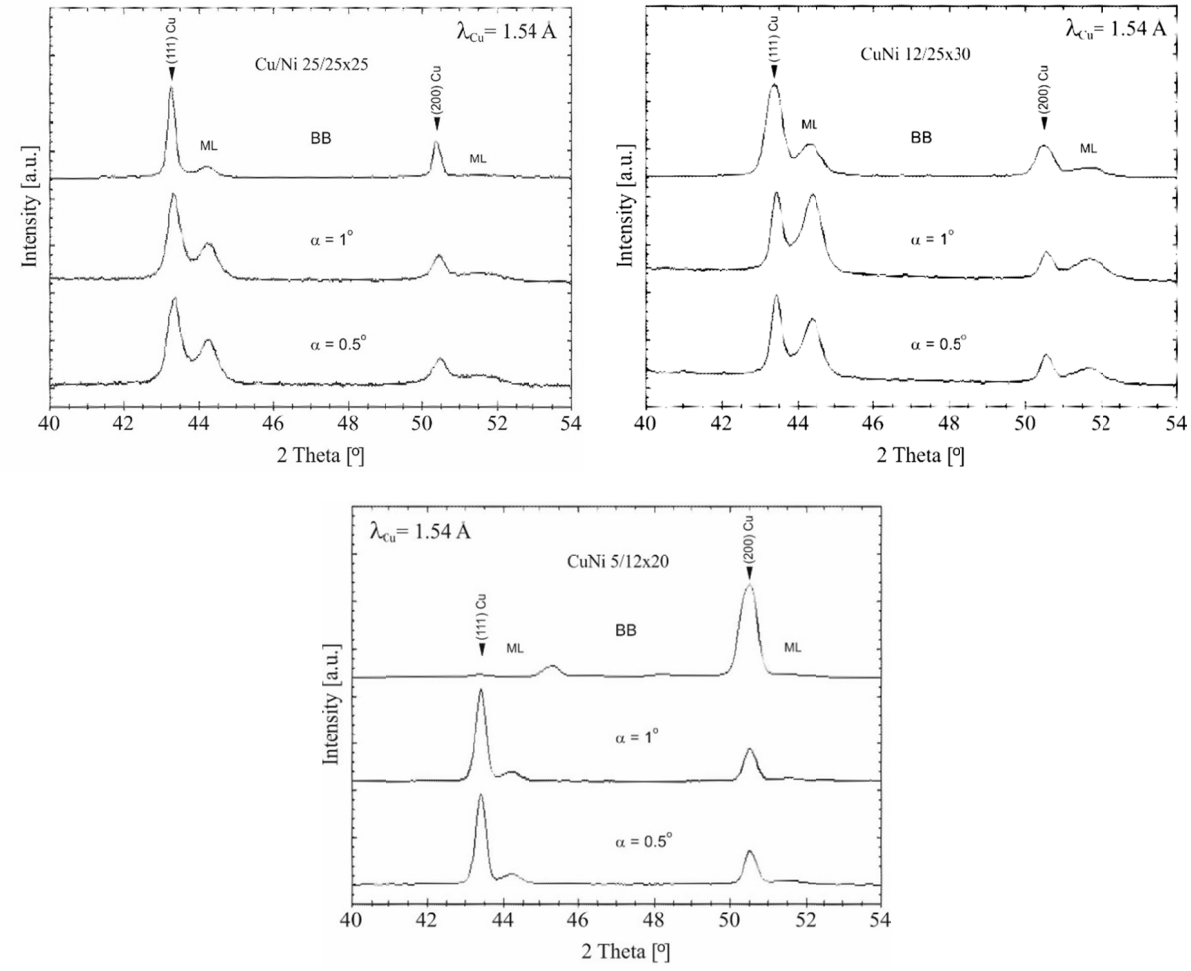


Fig. 2. X-ray diffraction patterns of Cu/Ni multilayer systems obtained by XRD and GIXRD techniques

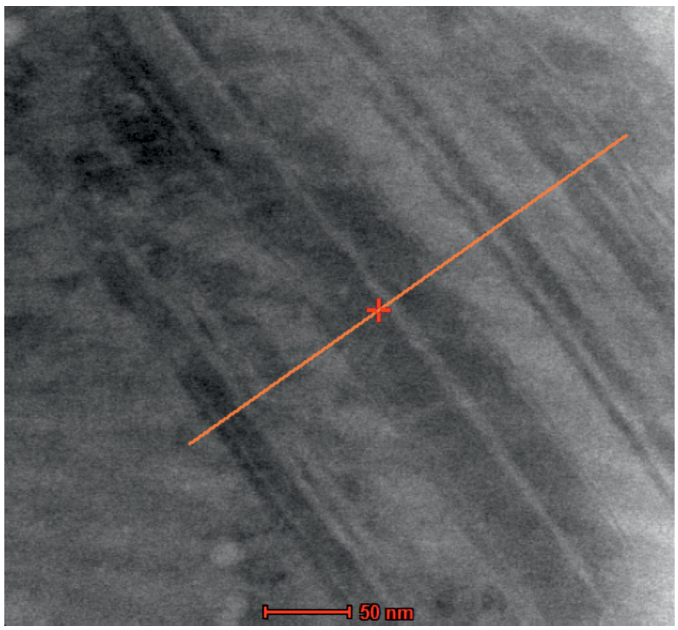


Fig. 3. HAADF-STEM image of Cu and Ni layers with the chemical composition profile shown in Fig. 4

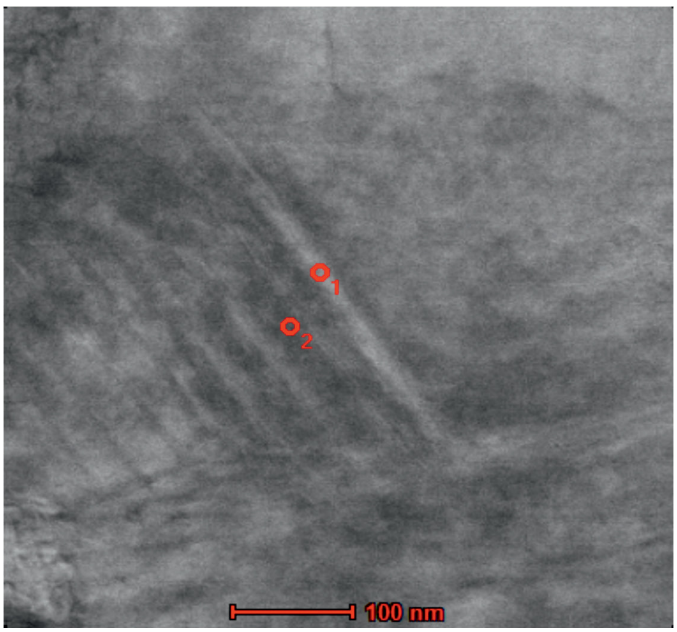


Fig. 4. BF-STEM image of a multilayer system with marked measuring points for EDS analysis

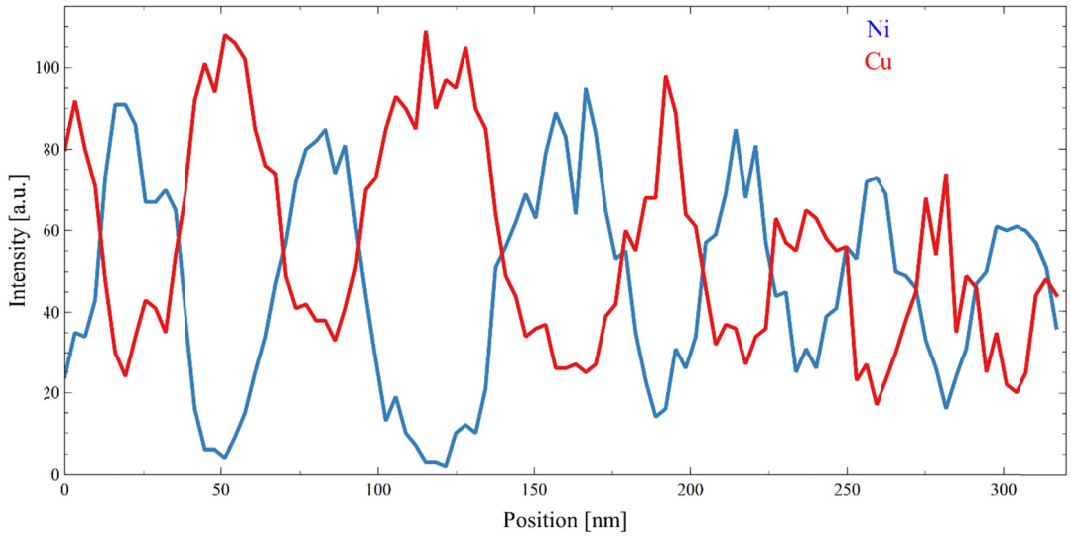


Fig. 5. Distribution of Cu and Ni elements by 16 layers at 330 nm

is also variable (Table 5). In Figure 4, in the first point, marked by O1, the dominant content is nickel (65%), visible in the form of lighter bands. In the second measurement point (O2), copper (in the form of dark bands) has a higher atomic content (54%), which may indicate diffusion mixing of the layers.

The use of a BF detector made it possible to observe the cross-section of a multilayer system as shown in Figs. 6 and 7. Fig. 6 shows an uniform expansion of layers from the substrate.

X-ray diffraction studies confirmed the deposition of copper and nickel layers in the galvanization process (Fig. 8). The

TABLE 4

Results of layer thickness measurement determined by STEM method

Layer type	Number of measuring layers	Average thickness of layers [nm]	Minimum layer thickness [nm]	Maximum layer thickness [nm]
Ni	8	18.2	9.2	34.8
Cu	8	17.0	6.1	30.6

TABLE 5

Results of the chemical point analysis of the multilayer system determined by EDS method

Point 1			Point 2		
Element	Atomic [%]	Uncert [%]	Element	Atomic [%]	Uncert [%]
Ni (K)	65.6	4.4	Ni (K)	45.5	1.7
Cu (K)	34.4	3.4	Cu (K)	54.5	1.9

Fig. 6. STEM-BF image of the cross-section of a Cu/Ni multilayer system (substrate with copper and nickel layers)

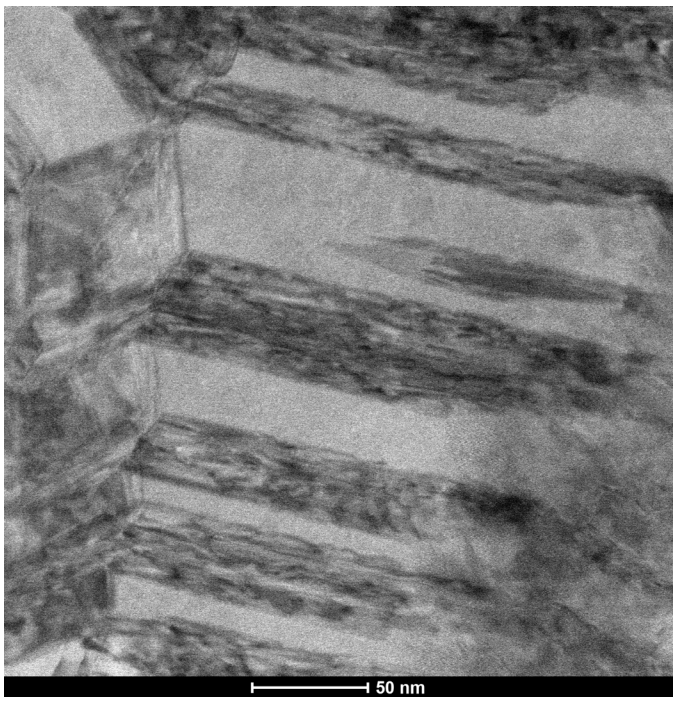


Fig. 7. STEM-BF image of the cross-section of a Cu/Ni multilayer system (visible layers under magnification)

sharp reflections come from copper are detected, however the intensity of the nickel is not prominent. Also in this case there is a strong effect from the substrate, which has an impact on the obtained X-ray diffraction pattern, which shows the dominant content of copper.

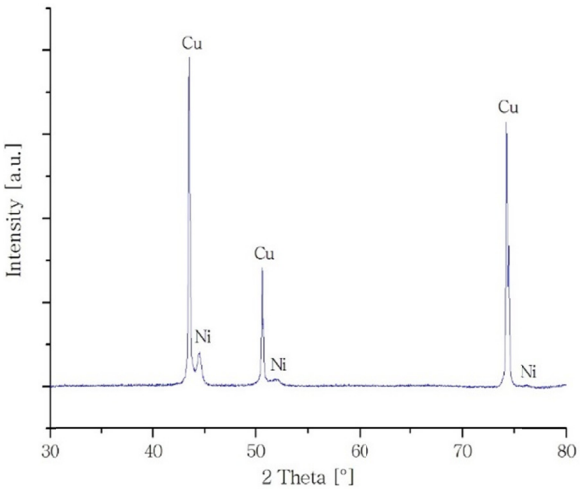


Fig. 8. X-ray diffraction pattern of the Cu/Ni system for a sample consisting of 50 copper and nickel layers

The observation of surface morphology of the obtained multilayer systems showed differences, which result from thickness of the deposited layer (Fig. 9).

In case of layers of the smallest thickness (Fig. 9 (a)) a structure with clear nucleation points of copper separated by ravines and craters is visible. With increasing deposition time, the copper layer increases in the form of spheroidal structures (Fig. 9 (b, c)). Analysis of the chemical composition of samples (Fig. 9 (d)) showed a variable concentration of elements constituting a multilayer system.

Depending on the accelerating voltage and the change of the sample area, the content of copper increased from 50 to 95 %. It was the result of using too high accelerating voltage in relation to the thickness of the layers, which resulted in the recording of strong signals of the spectra of the characteristic radiation of copper, which was the substrate material.

The surface topography investigations were conducted for selected area of the sample (15×15 mm) of multilayer Cu/Ni systems with different layer thicknesses. The AFM images of three-dimensional topography of samples confirm a globular type of layers deposited in the galvanic process (Fig. 10). However, no major defects in the surface of multilayer systems were found.

Based on the results it was found that the surface roughness increases with the increase of total thickness of multilayer systems. If the Cu layer is thicker, the surface roughness is higher.

4. Conclusions

The preparation of thin magnetic layers by electrochemical method exhibits many advantages. This method does not require complicated apparatus. It is relatively cheap. The time of deposition of layers with repetitive properties is often shorter than in the case of more complicated methods. However, the thin layers obtained by electrochemical method may be inhomogeneous due to the adsorption of impurities from the electrolyte. The disadvantage is also the need to deposit on conductive substrates, as well as the impossibility of perfect isolation of the individual layers

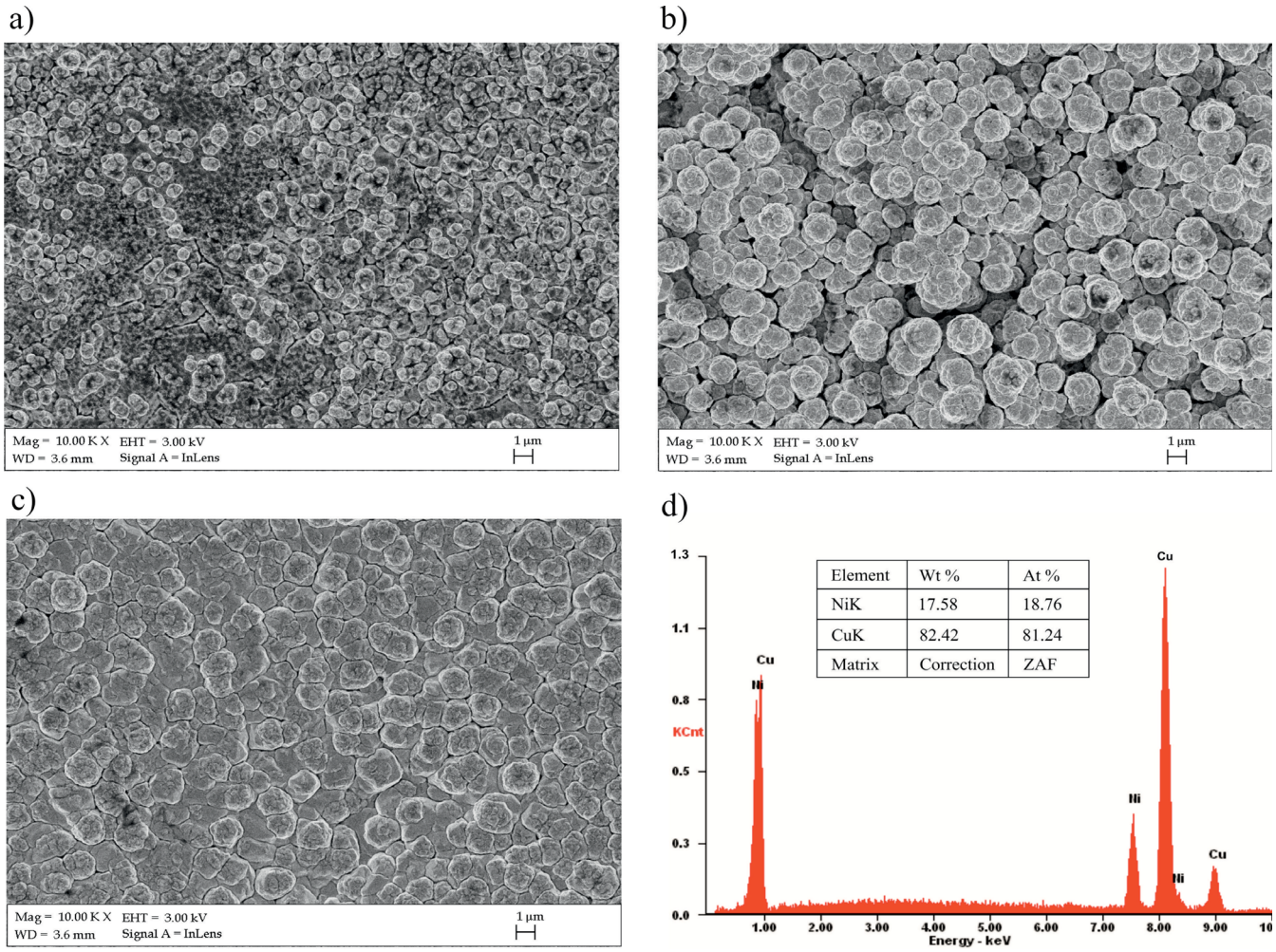
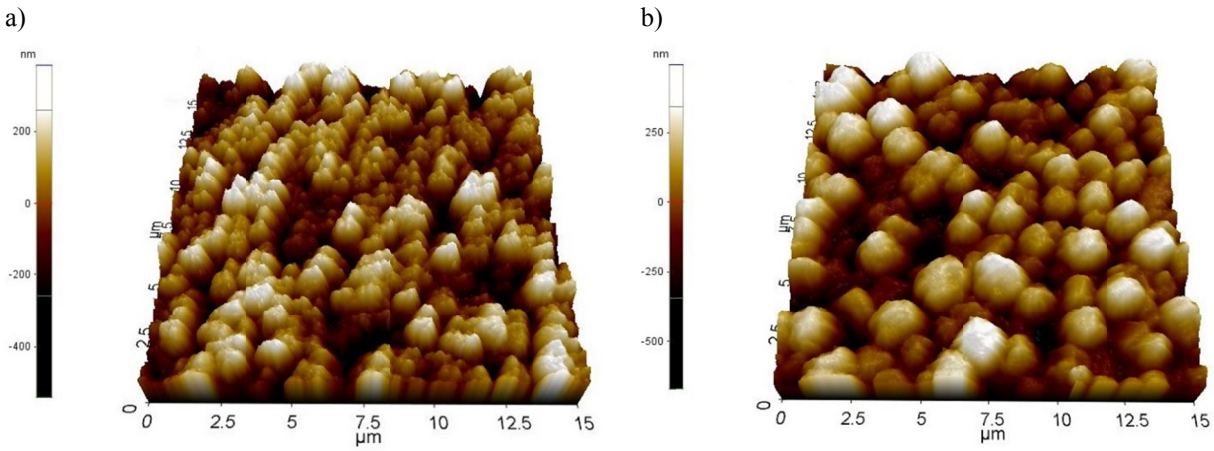


Fig. 9. SEM images of Cu layer in Cu/Ni multilayer system, a single layer thickness is (a) 5 nm, (b) 12 nm, (c) 25 nm, 10.000×; (d) EDS analysis



Ra (roughness average) = 106.71
RMS (root mean square) = 131.89
Max. (maximum profile height) = 383.96

Ra = 142.16
RMS = 175.14
Max. = 494.87

Fig. 10. AFM images of multilayer systems surface: (a) Cu/Ni 5/12×20, (b) Cu/Ni 25/25×25

of atoms between the coatings. The problem is with particles in the application process which can diffuse among themselves. Due to the specificity of the multilayer systems prepared (copper substrate) it is possible to use only a few methods of measuring the thickness of layers.

The differences between the thickness values for individual methods resulted from the irregular behavior of the examined layers, as well as from the X-ray diffraction measurement point, which does not exactly correspond to the cross-section area of the specimen examined by SEM method.

In the case of the weight method, the thickness of the calculated layers is burdened with an error resulting from the weight used to estimate a mass of the sample before and after an application of the layers. The scale has an error of 0.001 g. The thickness of the deposited layers determined by S/TEM method is ±0.5 nm, which is resulted from the resolution of the microscope and the resolution of the images taken.

It is recommended to prepare systems with a larger number of layers, so that their total thickness is higher than the penetration depth of X-radiation. Also, the use of a different substrate than the copper foil should give the expected results.

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