X-Ray Spectral Microanalysis of Copper-Nickel Thin Films Alloys

V.B. Loboda*, V.M. Zubko, S.M. Khursenko, V.O. Kravchenko, A.V. Chepizhnyi

Sumy National Agrarian University, 160, Gerasim Kondratyev st., 40021 Sumy, Ukraine

The article presents the results of studying the elemental composition of films of CuNi alloys by X-ray microanalysis (an X-ray microanalyzer based on an energy-dispersive spectrometer, which is part of the REM-103-01 scanning electron microscope). Alloy films 30-150 nm thick were obtained by simultaneous separate evaporation of the components (copper and nickel) in a vacuum of 10^{-4} Pa. Copper was evaporated from a tungsten foil ribbon 0.05 mm thick. Nickel was evaporated by the electron beam method using an electron diode gun. The condensation rate was 0.5-1.5 nm/s. The purity of the evaporated metals was no less than 99.98 %. The calculated composition of the concentrations of the sample components varied over a wide range. The characteristic X-ray spectrum of the film substance was excited by scanning a section of the film with dimensions of 300×300 µm with an electron beam; for thicker films, the size of the scanning area was 1×1 µm. Thin Ni films of the same thickness were used as standards for quantitative measurements of the elemental composition of alloy films of a certain thickness. The results of X-ray microanalysis indicate a high purity of the films. Comparison of the calculated concentrations of alloys and the results of measurements by X-ray microanalysis showed that in the region of film thicknesses $d < 100$ nm, the discrepancy is about 10 %, decreasing to $1 - 3$ % for sample thicknesses $d > 100$ nm.

Keywords: X-Ray Spectral Microanalysis, Thin Films, Copper-Nickel Alloys.

1. INTRODUCTION

The study of the physical properties of thin metal films is due both to obtaining results that contribute to the solution of a number of fundamental problems in solid state physics and to the prospects for their practical application. The use of thin metal films has led to significant progress in microelectronics, high-frequency technology, optoelectronics, optics and many other areas of modern science and technology, and a special branch of solid-state physics has emerged – the physics of thin films.

A special place in the physics of thin films is occupied by films of magnetically ordered metals Ni, Fe, Co and alloys based on them. This is connected both with purely scientific questions (their study allows solving a number of fundamental problems for "two-dimensional magnetism") and applied ones (nanoelectronics, spintronics). In recent years, a number of new fundamental effects have been discovered in film objects based on these metals (giant magnetoresistance, colossal magnetoresistance, spin-polarized tunneling, etc.). This creates a basis for the development of miniature magnetoelectronic devices, new methods for recording and storing information, new types of highly sensitive sensors and sensors.

Along with studies of films of pure magnetic metals (Ni, Co, Fe) and Cu, it is promising to study films of metal alloys [1-5] and film multilayer structures [6-8] which include these metals. Alloy films (as well as bulk alloys) have a number of advantages over pure metal films: by changing the composition of the alloy, materials with other electrophysical, physicochemical, and operational properties can be obtained. Along with the traditional film directions, in recent decades, a scientific direction has been formed related to the improve-ment of the service properties of massive metal samples by methods of creating layered structures in modified near-surface layers [9-10].

The properties of thin films differ significantly from those of bulk samples. Limiting the size of film objects in one of the directions leads to the appearance of the so-called size effects, which in a massive state are either weakly expressed or not observed at all. This paper presents the results of studying the elemental and chemical composition of CuNi alloy films in a wide range of component concentrations.

2. EXPERIMENTAL METHODOLOGY AND TECHNIQUE

2.1 Preparation of the Alloy Film Samples

The method of obtaining metallic films by evaporation of the initial metal and its condensation in a vacuum (see, for example, [11]) has been widely used for many years in various fields of science and technology due to the versatility of the technology, high productivity of the process, low energy consumption, the absence of environmental pollution, etc. These and a number of other indicators determine the competitiveness of this method in comparison with other methods of film production (electrodeposition, cladding, metallization, sputtering, etc.). The quality of the formed films, the reproducibility and stability of their characteristics under different operating conditions significantly depend on the characteristics of evaporation and condensation.

To obtain thin alloy films, two main groups of methods are used: 1) formation of multicomponent films directly on a substrate (separate evaporation of components, diffusion annealing of multilayer structures, vapor

---

* loboda-v@i.ua

saturation); 2) the use of finished alloys as initial metallizers (evaporation of the final weighed portions of the alloy, stationary mode of evaporation, explosive evaporation).

Direct evaporation of finished alloys is widely used in technologies for obtaining multicomponent films and coatings due to the simplicity of the design solution of this method. However, with this method, there is a discrepancy between the composition of the alloy film and the composition of the initial bulk alloy due to fractionation of the alloys during their evaporation.

Films of CuNi alloys were obtained by us by the method of condensation of initial materials (Cu and Ni) during their simultaneous evaporation from two independent evaporators according to the Vekshinskii method. This made it possible to obtain alloy films of arbitrary composition on the substrate.

The choice of methods for the evaporation of metal components was determined by such physical properties of the starting materials as the melting temperature and saturated vapor pressure. For copper, the thermal evaporation of Cu from a tungsten foil ribbon 0.05 mm thick was used. For more refractory nickel, the method of electron beam evaporation of Ni using an electron diode gun was used. The purity of the evaporated metals was no less than 99.98 %. The rate of condensation was determined from the time of condensation and the final thickness of the sample. During the condensation process, it remained constant and amounted to $0.5 - 1.5$ nm/s.

The design of the substrate holder made by us made it possible to obtain four film samples of different concentrations of components with almost the same thickness in one technological cycle of deposition.

The substrates used were polished optical glasses with preliminarily deposited contact pads (study of electrophysical and magnetoresistive properties), NaCl single crystals, and carbon films (structural studies).

The film thickness was measured using a modernized MII-4 microinterferometer with a laser light source and digital processing of the interference pattern. As a result, it is possible to reduce the error in measuring the film thickness, especially in the thickness range $d < 50$ nm. The thickness measurement error was $5 - 10$ % for thicknesses $50 - 200$ nm and $10 - 15\%$ for thicknesses $d < 50$ nm.

The calculation method and X-ray microanalysis were used to determine the concentration of the alloy film components.

The essence of the calculation method is illustrated by the diagram shown in Fig. 1.

Based on the geometry of the "substrate-evaporators" system, the thickness of individual components d_1 and d_2 at the point M of the substrate can be calculated from the relations [11]:

$$d_1 = d_{01}\left[1 + \left(\frac{l_1}{h}\right)^2\right]^{-\frac{3}{2}} , \quad d_2 = d_{02}\left[1 + \left(\frac{l_2}{h}\right)^2\right]^{-\frac{3}{2}}, (2.1)$$

where d_0 – the film thickness at the point above the evaporator; d_{01}, d_{02} – the thicknesses of the "witness" films; l_1, l_2 – the distance from the middle of the "witness" to the point M; h – the distance from the plane of the evaporators to the plane of the substrate.

To find the concentration of the C_1 and C_2 components

of the alloy at the M point of the substrate, one can use the obvious relations:

$$C_1 = \frac{D_1 d_1 \mu_1^{-1}}{D_1 d_1 \mu_1^{-1} + D_2 d_2 \mu_2^{-1}} , \quad C_2 = \frac{D_2 d_2 \mu_2^{-1}}{D_1 d_1 \mu_1^{-1} + D_2 d_2 \mu_2^{-1}}, \quad (2.2)$$

where D_1 and D_2 are the film densities of each of the materials; μ_1 and μ_2 are the molar masses of evaporated metals.

Taking into account that in bulk samples $D_{Ni} \approx D_{Cu}$, ($D_{Ni} = 8.897$ g/cm^3, $D_{Cu} = 8.932$ g/cm^3 [12]) and assuming that the same is true for films, relations (2.2) are transformed to the form:

$$C_1 = \frac{d_1 \mu_2}{d_1 \mu_2 + d_2 \mu_1} , \quad C_2 = \frac{d_2 \mu_1}{d_1 \mu_2 + d_2 \mu_1}, \quad (2.2')$$
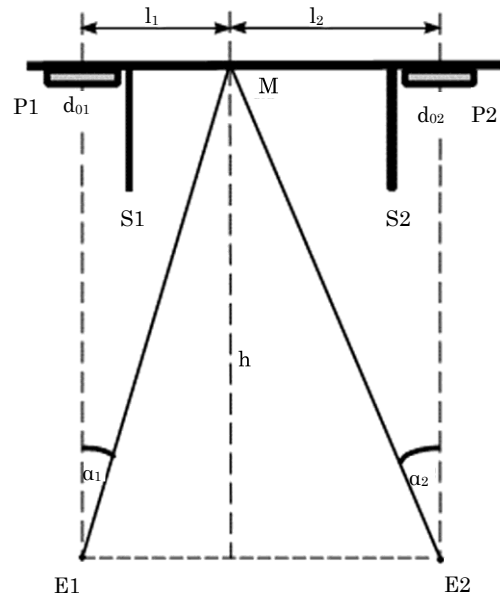

Fig. 1 – Geometry of the «substrate-evaporators» system for calculating the concentration of the alloy components: $S1$, $S2$ – screens; $E1$, $E2$ – evaporators; $P1$, $P2$ – glass plates "witnesses" of thickness

Since the concentration of the alloy components was determined by the thicknesses d_1 and d_2, the error in determining the concentration of the components is the same as for the thickness.

2.2 Method for Studying the Elemental Composition of Film Samples by X-ray Microanalysis

The study of the elemental composition of thin films of the CuNi alloy was carried out using an X-ray microanalyzer based on an energy dispersive spectrometer (EDS) included in the REM-103-01 scanning electron microscope. The main advantages of X-ray spectral microanalysis are its high local sensitivity, depth and transverse locality, and non-destructive effect on the sample. The possibility of local determination of the elemental composition of a substance is realized through the use of an electron beam of a microscope focused into a narrow zone. Thus, it is possible to isolate a certain micro-section of the sample, obtain (if necessary) its electron microscopic image in reflected electron beams, and at the same time record the generated X-ray radiation from this section [13].

The characteristic X-ray radiation of the atoms of the elements of the sample was measured using the EDS with subsequent processing of the information using the software of the X-ray microanalyzer. The EDS scheme is shown in Fig. 2.
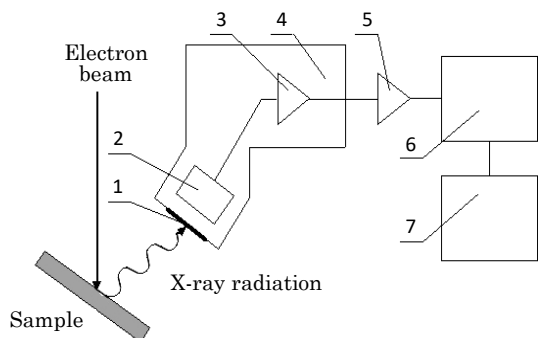

Fig. 2 – Scheme of the spectrometer with EDS

The characteristic X-ray radiation, which is generated in the sample when its surface is probed with a high-energy electron beam, passes through a thin beryllium window (1) into the cryostat (4), where a cooled (to reduce the noise level) detector (2) is located in vacuum. Further, the signal is amplified in amplifiers (3) and (5) and enters the multichannel pulse analyzer (6). Information is extracted from it using special computer software (7) and presented in the form of a spectrum of dependence of the number of pulses (X-ray intensity) on the energy of X-ray photons. Methods of X-ray spectral analysis using EDS can determine the concentration of almost any element from beryllium to californium in the concentration range up to tenths of an atomic percent.

Since the amount of substance in the film samples studied by us is extremely small, especially for films with effective thicknesses $d \sim 10$ nm, the characteristic X-ray spectrum of the film substance was excited by scanning a film section with dimensions of 300×300 µm with an electron beam. This made it possible to obtain integrated data on the elemental composition of the film without overheating it with an electron beam. For thicker films, it was possible to reduce the size of the film section to 1×1 µm.

Although the theory of quantitative elemental X-ray spectral analysis of thin films is based on the same prerequisites as for bulk samples (model ideas about the physical processes of the interaction of electrons with matter), the X-ray spectral microanalysis of thin films has its own characteristics due to differences in the absorption and transmission of X-rays in bulk samples and samples in the form of thin films.

In quantitative measurements of the elemental composition of thin films of binary CuNi alloys, we used a thin Ni film as a standard in accordance with the recommendations set forth in [13]. Nickel is included in the alloy films under study, and the densities of copper and nickel are close.

3. RESULTS AND DISCUSSION

On Fig. 3 shows the characteristic X-ray spectra of CuNi sample film alloys of various thicknesses and component concentrations. The left side of the spectrum is

the characteristic X-ray emission corresponding to the composition of the glass substrate, since the depth of X-ray generation when the sample is probed by an electron beam with an energy of 20 keV or more is on the order of µm [13], which is much greater than the thickness of the films under study. The right part of the spectrum corresponds to the composition of the alloy film sample.
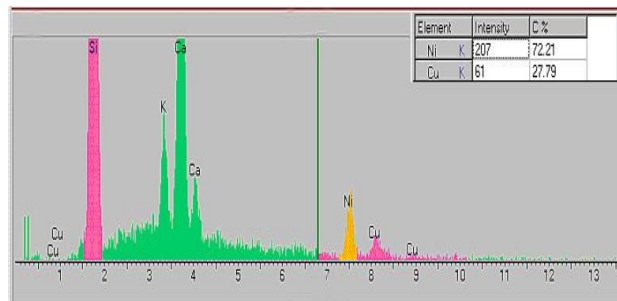
a)
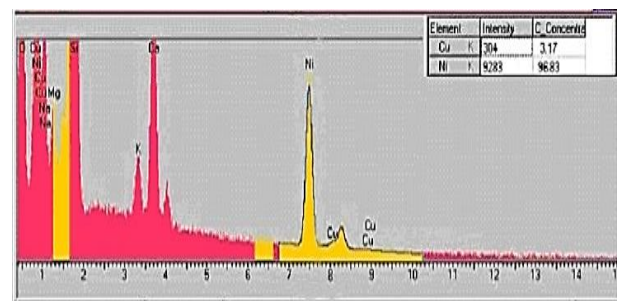
b)
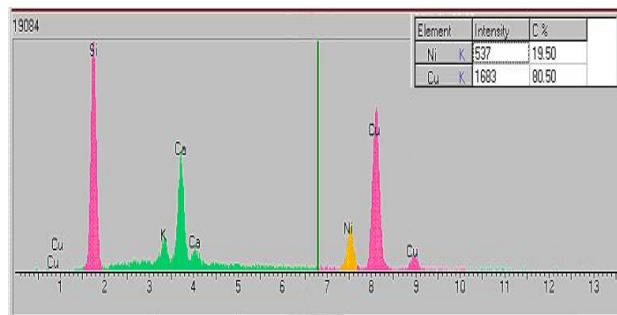
c

Fig. 3 – Characteristic X-ray spectra from film samples of the CuNi alloy: $d = 34$ nm, $C_{Cu} = 27.79$ at.% (a); $d = 54$ nm, $C_{Cu} = 3.17$ at.% (b); $d = 127.5$ nm, $C_{Cu} = 80.5$ at.% (c)

The results of such an analysis indicate a rather high purity of the film samples (the absence of impurity atoms of other metals), and allowed us to evaluate the accuracy of determining the concentration of the alloy components by the calculation method. In Table 1 shows for comparison the concentrations of CuNi film alloys of different thicknesses and compositions, calculated using relation (2.2), and the results of X-ray microanalysis of these samples.

An analysis of the data presented in the table shows that, in the range of film alloy thicknesses $d < 100$ nm, the discrepancy between the concentrations calculated using relations (2.2) and the measured values is about 10 %. For sample thicknesses $d > 100$ nm, the discrepan-

cy decreases to $1 - 3$ %. The decrease in the discrepancy between the calculated and experimentally measured results of determining the concentration of the components is fully explained by the fact that with an increase in the film thickness d, measured with the MII-4 micro-interferometer and included in relation (2.2), the relative error of its measurement decreases.

Table 1 – Calculated and measured concentrations C of the components of CuNi film alloys of different thicknesses

No	d, nm	Component concentration, at.%				Discrepancy, in % of the calculated
		Calculation		Measurements		
		Ni	Cu	Ni	Cu	
1.	34.0	62.0	38.0	72.2	27.8	10.2
2.	35.5	75.0	25.0	86.2	13.8	11.2
3.	37.0	63.0	37.0	67.2	32.8	4.2
4.	38.5	79.0	21.0	87.5	12.5	8.5
5.	41.0	73.0	27.0	80.1	19.9	7.1
6.	42.5	87.0	13.0	96.5	3.5	9.5
7.	43.0	81.0	19.0	89.0	11.0	8.0
8.	47.0	84.5	15.5	93.2	6.8	8.7
9.	51.0	86.0	14.0	99.8	0.2	13.8
10.	52.0	88.5	11.5	98.7	1.3	10.2
11.	52.5	86.0	14.0	94.9	5.1	8.9
12.	54.0	90.0	10.0	96.8	3.2	6.8
13.	60.0	85.5	14.5	95.9	4.1	10.4
14.	64.0	87.0	13.0	96.9	3.1	9.9
15.	64.5	86.5	13.5	96.0	4.0	9.5
16.	67.0	67.0	33.0	57.0	43.0	10.0
17.	68.0	89.0	11.0	97.3	2.7	8.3
18.	69.5	90.5	9.5	96.4	3.6	5.9
19.	70.0	70.0	30.0	59.0	41.0	11.0
20.	70.0	89.0	11.0	97.0	3.0	8.0
21.	72.0	73.0	27.0	63.6	36.4	9.4
22.	73.5	75.5	24.5	66.8	33.2	8.7
23.	75.0	61.0	39.0	51.5	48.5	9.5
24.	75.5	90.0	10.0	97.8	2.2	7.8
25.	78.5	68.0	32.0	60.0	40.0	8.0
26.	79.0	89.5	10.5	92.3	7.7	2.8
27.	80.0	65.0	35.0	59.0	41.0	6.0
28.	81.0	92.0	8.0	93.8	6.2	1.8
29.	87.0	74.0	26.0	65.5	34.5	8.5
30.	93.5	48.0	52.0	55.3	44.7	7.3
31.	95.0	59.0	41.0	65.9	34.1	6.9
32.	95.5	54.5	45.5	59.5	40.5	5.0
33.	103.5	42.5	57.5	45.3	54.7	2.8
34.	105.0	38.5	61.5	40.9	59.1	2.4
35.	118.5	56.5	43.5	54.0	46.0	2.5
36.	122.5	60.0	40.0	57.0	43.0	3.0
37.	125.0	65.0	35.0	64.1	35.9	0.9
38.	125.5	67.5	32.5	66.0	34.0	1.5
39.	127.5	17.5	82.5	19.5	80.5	2.0

Unfortunately, X-ray microanalysis does not allow obtaining information about the presence of chemical compounds (hydrides, oxides, nitrides, etc.) in the samples, the formation of which is possible during the condensation of samples during the interaction of the film material with gases of the residual atmosphere (H_2, O_2, N_2, etc.) as a result of their sorption on the film surface. The presence of such compounds can significantly affect the physical properties of film samples (electrical conductivity, phase composition, etc.).

4. CONCLUSIONS

1. The results of the study of the elemental composition of film alloys by X-ray microanalysis indicate the high purity of the films.

2. Evaluation of the accuracy of the calculation method for determining the concentration of film alloy components by comparing the results of calculations and the results of X-ray microanalysis showed that in the thickness range $d < 100$ nm, the discrepancy is about 10 %, decreasing to $1 - 3$ % at $d > 100$ nm.

REFERENCES

1. V.K. Soni, S. Sanyal, S.K. Sinha, *Vacuum* **174**, 109173 (2020).
2. X. Hua, J. Li, H. Liu, Z. Yang, S.F. Liu, *Vacuum* **17485**, 109947 (2021).
3. G. Li, G. Song, N. Wang, *Surf. Interface.* **28**, 101651 (2022).
4. O.V. Pylypenko, I.M. Pazukha, A.S. Ovrutskyi, L.V. Odnodvorets, *J. Nano- Electron. Phys.* **8** No 3, 03022 (2016).
5. Y. Bereznyak, L. Odnodvorets, D. Poduremne, I. Protsenko, Yu. Shabelnyk, *Springer Proc. Phys.* **210**, 17 (2018).
6. O.V. Bezdidko, S.A. Nepijko, Y.O. Shkurdoda, Yu.M. Shabelnyk, *J. Nano-Electron. Phys.* **13** No 3, 03042 (2021).
7. V.B. Loboda, V.M. Kolomiets, S.M. Khursenko, Yu.O. Shkurdoda, *J. Nano-Electron. Phys.* **6** No 1, 01032 (2014).
8. V.B. Loboda, V.M. Kolomiets, Yu.O. Shkurdoda, V.O. Kravchenko, L.V. Dekhtyaruk, *Metallofiz. Noveishie Tekhnol.,* **34** No 8, 1043 (2012).
9. A.D. Pogrebnjak, A.G. Lebed, Yu.F. Ivanov, *Vacuum* **63** No 4, 483 (2001).
10. A.D. Pogrebnjak, I.V. Yakushchenko, G. Abadias, P. Chartier, O.V. Bondar, V.M. Beresnev, Y. Takeda, O.V. Sobol', K. Oyoshi, A.A. Andreyev, B.A. Mukushev, *J. Superhard Mater.* **35** No 6, 356 (2013).
11. H. Frey, H.R. Khan, *Handbook of Thin-Film Technology* (Berlin: Springer-Verlag: 2015).
12. W. Benenson, J.W. Harris, H. Stocker, H. Lutz, *Handbook of Physics* (New York: Springer-Verlag: 2002).
13. J.I. Goldstein, D.E. Newbury, P. Echlin, D.C. Joy, C.E. Lyman, E. Lifshin, J.R. Michael, *Scanning Electron Microscopy and X-ray Microanalysis* (New York: Springer Science + Business Media: 2003).

Рентгеноспектральний мікроаналіз тонких плівок мідно-нікелевих сплавів

В.Б. Лобода, В.М. Зубко, С.М. Хурсенко, В.О. Кравченко, А.В. Чепіжний

Сумський національний аграрний університет, вул. Герасима Кондратьєва, 160, 40021 Суми, Україна

У статті наведено результати дослідження елементного складу плівок сплавів CuNi методом рентгенівського мікроаналізу (рентгенівський мікроаналізатор на базі спектрометра з дисперсією з енергії, що входить до складу растрового електронного мікроскопа РЕМ-103-01). Плівки сплавів товщинами 30-150 нм були отримані одночасним роздільним випаровуванням компонент (мідь та нікель) у вакумі 10^{-4} Па. Мідь випаровувалася зі стрічки з вольфрамової фольги товщиною 0,05 мм. Нікель випаровувався електронно-променевим способом за допомогою електронної діодної гармати. Швидкість конденсації становила 0,5-1,5 нм/с. Чистота випаровуваних металів становила щонайменше 99,98 %. Розрахунковий склад концентрацій компонентів зразків змінювався в широкому діапазоні. Характеристичний рентгенівський спектр речовини плівки порушувався при скануванні електронним пучком ділянки плівки розмірами 300×300 мкм; для товстіших плівок розмір ділянки сканування становив 1×1 мкм. Як еталони при проведенні кількісних вимірювань елементного складу плівок сплавів певної товщини використовувалася тонкі плівки Ni такої ж товщини. Результати рентгенівського мікроаналізу свідчать про високу чистоту плівок. Зіставлення розрахункових концентрацій сплавів та результатів вимірювань рентгенівським мікроаналізом показало, що в області товщин плівок $d < 100$ нм розбіжність становить близько 10 %, знижуючись до 1-3 % при товщинах зразків $d > 100$ нм.

Ключові слова: Рентгеноспектральний мікроаналіз, Тонкі плівки, Мідно-нікелеві сплави.