*Materials Science-Poland, Vol. 26, No. 1, 2008*

# Comparative X-ray investigation of Ni/Cu systems heated in the 250–350 °C temperature range

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Results of investigation of structural properties of Cu/Ni multilayers have been presented. Samples were obtained by the electrochemical method and after deposition they were heated from 250 ºC to 350 ºC. The increase of the heating temperature and of the Cu thickness in multilayers caused a decrease of intensities of peaks corresponding to (111) planes. The phenomenon results from the formation of a solid solution in the interfaces. Heating of multilayers in the investigated temperature range resulted in the increase of tensile stresses in external layers and of compressive stresses in substrate adjacent layers.

Key words: *multilayers; electrochemical method; solid solution; tensile stress; compressive stress*

## 1. Introduction

For last few years, systems of thin metallic multilayers have been often used in magnetic recording and reading. In order to achieve a higher density of information packing, what is followed by smaller size of indicators, multilayers' borders contribute in the whole volume of the multilayer system. Therefore, the physical state of an interface has a significant effect on electric, magnetic and structural properties of the whole system. The multilayer systems of transition metals may be used as magneto-resistential or hallotronic indicators of magnetic field [1].

The aim of this paper was to compare properties of Ni/Cu multilayer systems heated in the 250–350 ºC temperature range, concerning the change of interplanar $d_{111}$ and $d_{200}$ distances for various thicknesses of the systems of monolayers heated at various temperatures.

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The results are a part of investigations of Ni/Cu systems in terms of their structural, magnetic and emissive properties. With regard to magnetic properties, the multilayers were heated in the passed higher range of temperatures ( heating up of these systems probably will change coupling from antyferromagnetically in ferromagnetically [2]).

## 2. Experimental

Single-crystalline n-type silicon (100) oriented wafers (Sb doped, $\rho$ = 0.017 Ω·m) were used as substrates for deposition. The thickness of the Si substrate was 280 ± 25 μm. Before the main process, it was suitably treated, rinsed in detergent and acetone and activated in 10% HF.

A mixture of 1.5 mol $Ni(SO_3NH_2)_2$, 0.01 mol $CuSO_4$ and 0.5 mol $H_3BO_3$, at 20 °C and pH equal to 3.5 was used to deposit Ni/Cu multilayers. The deposition potential for Cu layers was equal to –500 mV and for Ni layers –900 mV. The systems consisted of 100 double layers deposited in the form of circles of ca. 1 cm in diameter; Ni layers were 20 Å thick and the thicknesses of Cu layers were 8, 9, 18 or 19 Å. The thickness of a layer was estimated using the charge flow during electrochemical deposition. All electrochemical experiments and deposition processes were carried out in a standard three-electrode electrochemical cell equipped with a platinum net as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. More details relating to the electrochemical method of deposition have been described elsewhere [3–5]. Based on the literature [4–6], it was assumed that the layers of the Ni/Cu systems are continuous ones.

The multilayer systems were investigated after deposition and after heating for 1 h under the $10^{-6}$ Pa vacuum at 250, 300 and 350 °C. After heating, the multilayers and the furnace were cooled simultaneously. Structural changes which appeared during heating were studied by the X-ray diffraction method performed on a Seifert 3003TT diffractometer with the use of filtered $CoK_\alpha$ radiation in the 45–64° angle range. All X-ray measurements were made under the same, allowing direct comparison of diffractograms.

## 3. Results and discussion

The X-ray analysis revealed that inside the applied angle range the (111) and (200) reflexes arising from Cu and Ni, respectively, were present. The proximity of diffraction peaks ((111) for Cu and Ni, and (200) for Cu and Ni) did not allow one to separate these peaks under measurement conditions.

An insignificant broadening and increase of peak intensities was observed. The recorded peaks were characterized by small half-widths, high maximum intensities and precise symmetries in relation to the axis determining the angular position of the analyzed maximum (Fig. 1); no attempts were made to separate them.

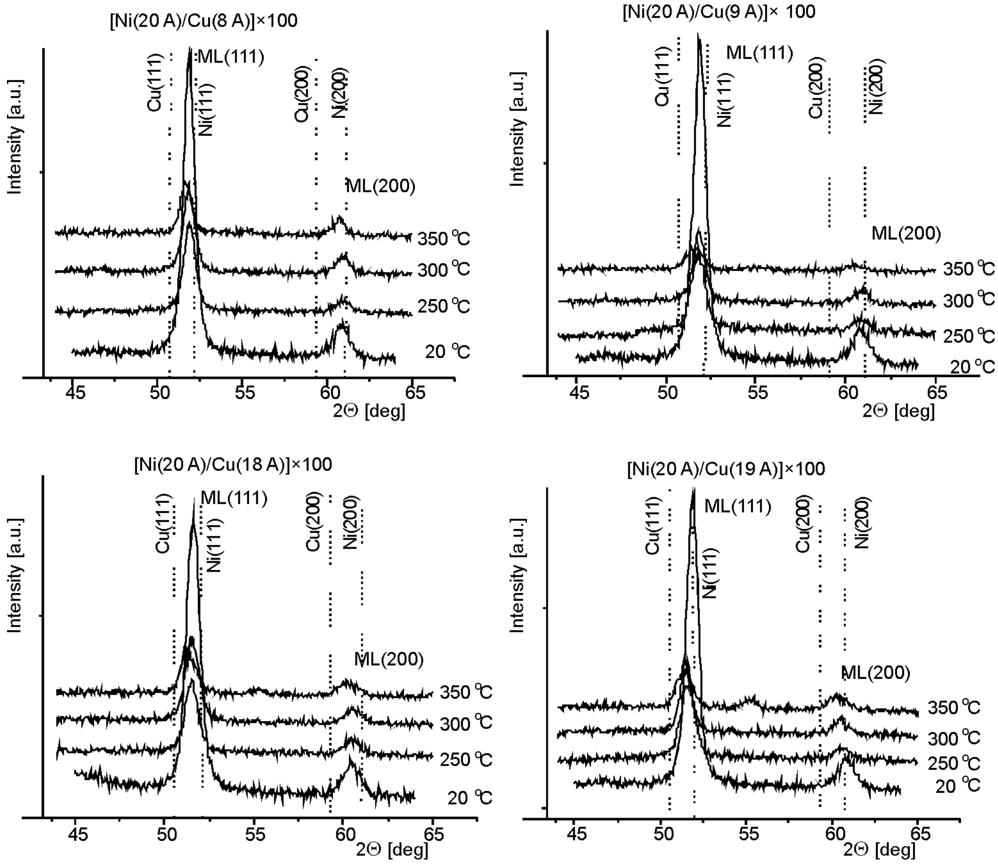


Fig. 1. Diffractograms of Ni/Cu multilayers ($d_{Ni}$ = 20 Å, $d_{Cu}$ = 8, 9, 18 and 19 Å) before and after heating

From the comparison of (111) reflexes for multilayers with Cu thicknesses equal to 8 Å and 1.8 Å, it was confirmed that the applied proportions of the thicknesses of multilayers did not cause any changes in the integral intensity of the reflex, resulting, however, in its shift. In the $Ni_2Cu_{0.8}$ multilayer with an excess of Ni, the maximum of the reflex is shifted towards the position characteristic of pure Ni with respect to the same reflex measured in the $Ni_2Cu_{1.8}$ containing approximately equal proportions of both elements (cf. Fig. 2). It was found that relative intensity of reflex (111) strongly decreases upon increasing temperature of heated multilayers. In as-obtained multilayers, the relative intensity of the (200) reflex is very low, and only in multilayers heated at 350 °C it approaches standard intensities of Cu and Ni ($I_{(111)}$100% : $I_{(200)}$46/42%).

Using the Bragg equation, the values of interplanar distances have been calculated. The results of investigation have been compared with those obtained for multilayers which were not heated (Figs. 3 and 4).

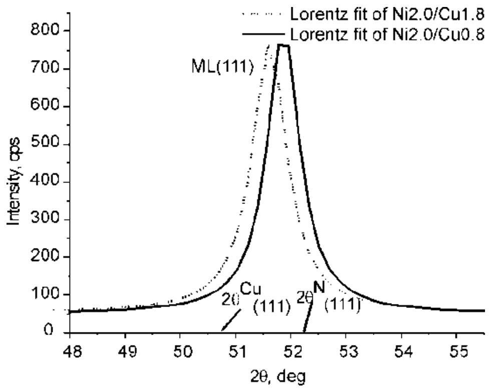


Fig. 2. Lorentz fit for diffractograms of Ni/Cu multilayers ($d_{Ni}$ = 20 Å, $d_{Cu}$ = 8 and 18 Å) for the peak (111)

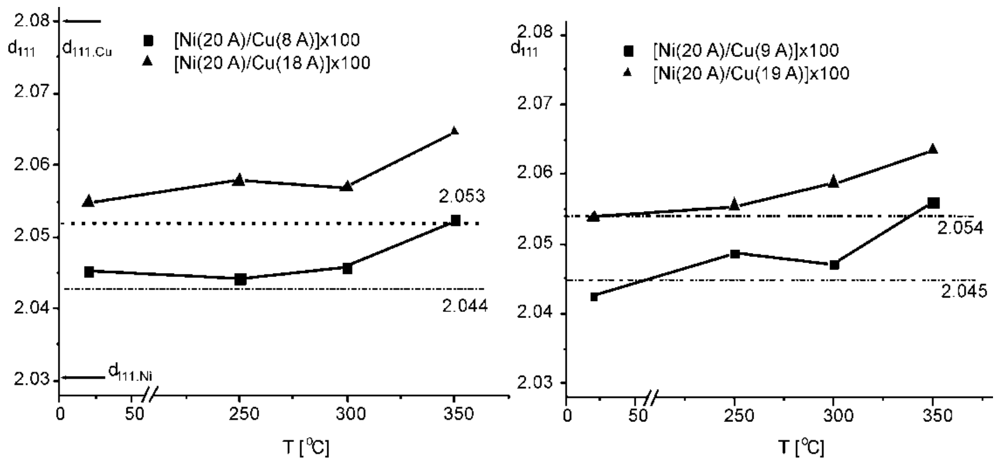


Fig. 3. Experimental $d_{111}$ values for Ni/Cu multilayers (dotted lines show average $d_{111(Cu+Ni)}$ calculated for a given thickness of sublayers)

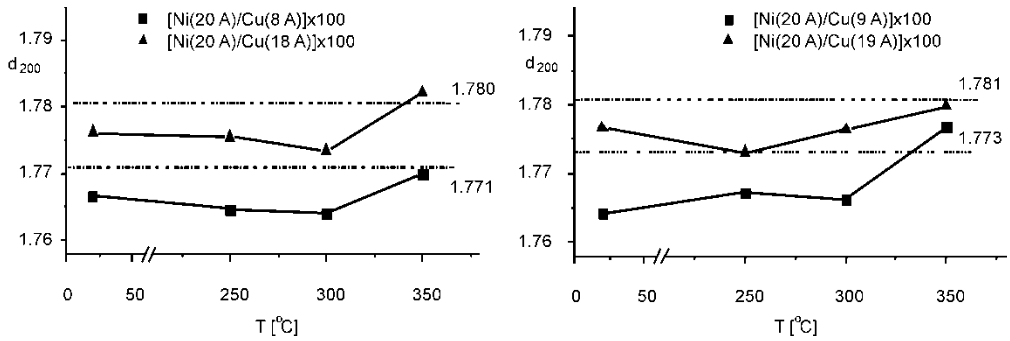


Fig. 4. Experimental $d_{200}$ values for Ni/Cu multilayers (dotted lines show average $d_{111(Cu+Ni)}$ calculated for a given thickness of sublayers)

The trends of changes of interplanar distances in multilayers, independent of Cu and Ni contributions have been observed. In Figures 2 and 3, the interplanar distances are given for the alloy obtained by the traditional method; it forms a solid solution in which the mass contribution of components corresponds to that in multilayers (dotted line). The calculated interplanar distances for diffractions arising from (111) and (200) planes of these systems are also shown. They are presented taking into account changes of a nonmagnetic spacer. The mass contribution of components was calculated based on the layer thicknesses determined from measurements of the charge during electrochemical deposition.

Comparison of interplanar distances determined by diffractometric measurements with those calculated for a theoretical continuous solid solution shows that experimental $d_{111}$ values for multilayers are higher, while the experimental $d_{200}$ values are lower than the theoretical ones.

The observed changes of interplanar distances and of relative intensities of observed diffractions, and their broadening may result from:

- formation of solid solutions, especially in border regions of sublayers (interfaces),
- kind, structure and thickness of interfaces,
- presence of stresses in multilayer planes, especially in the border regions.

Moreover, as is shown in Fig. 3, the interplanar distances connected with (111) reflexes increase upon increasing temperature. For initial, unheated system ($d_{Cu}$ = 8 and 18 Å), the $d_{111}$ distances were 2.045 Å and 2.055 Å, respectively. After heating at 350 °C, the $d_{111}$ values for these multilayers increase to 2.052 Å and 2.065 Å, respectively. A similar trend was observed in multilayers with $d_{Cu}$ = 9 and 1.9 Å.

The analysis of the interplanar distances connected with the (200) reflexes does not indicate their distinct increase with temperature. Up to 300 °C, the $d_{200}$ values decrease, and only after heating at 350 °C they increase up to the theoretical value (Fig. 4). For all multilayers, the intervals between points representing $d$ values for 250 and 350 °C have a nearly identical slope. A deviation from linearity occurs for 300 °C, when first cracks in the multilayers were observed [7]. This may suggest that the similarity of structures explains the facility of formation of solid solutions. A factor limiting formation of solid solution is rather the number of atoms replaced by atoms of the other metal, and not their weights. The most probable is the formation of a substitutional solid solution in which replacement of atoms by other ones occurs [8]. After Goldschmidt [9], the substitutional solutions may by present only in the case when the radii of one kind of atoms do not differ from the radii of the other ones more than 15%; in the case of the investigated multilayer $\Delta r \approx 3\%$. Since the system analyzed in this work consists of multilayers of nanometric dimensions, one cannot rule out that some atoms may occupy interstitial positions, or statistically disordered or nonstoichiometric systems may be present in border regions. The additional diffraction maximum obtained for various thicknesses of Cu heated only at 350 ° C (Fig. 5) confirms probability of formation of solid solution.

The intensity of additional maxima increases with the thickness of the nonmagnetic spacer (Fig. 5). It is possible that in solid solutions stable over wide range of compositions (during homogenization), some superstructures may be present. Their formation involves creation of a certain state of atom ordering in a statistically disordered solid solution; in the ordered state, both Cu and Ni atoms occupy given lattice sites in the crystal lattice. It is known that such superstructures cause the appearance of new interferences in the diffraction pattern arising from lattice planes for which at a statistically disordered distribution of atoms the structure factor was equal to zero.

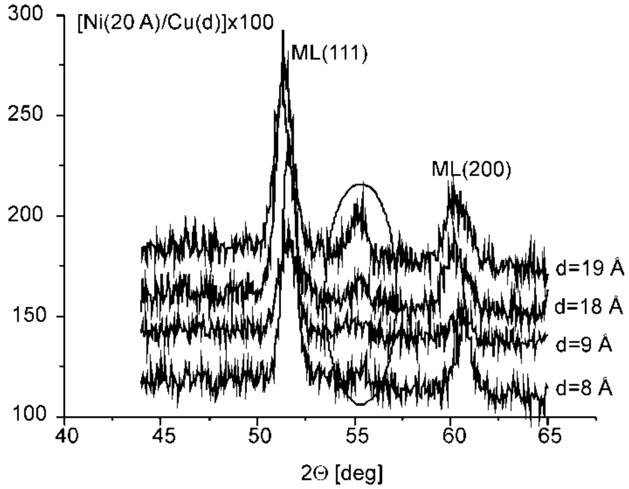


Fig. 5. Diffraction patterns for Ni/Cu systems ($d_{Cu}$ =8, 9, 18 and 19 Å), heated at 350 ºC

The analysis of changes of $d$ values in function of heating temperature (Fig. 5) allows one to suggest that the resultant tensile stresses in (111) planes increase during heating, whereas in (200) planes they are compressive transforming into tensile ones above 300º C. One cannot also exclude the fact that the lowering of $d_{200}$ value results from the formation of a solid solution based on nickel. Therefore, it may be assumed that increase of stresses resulting from the thermal expansion of multilayers most strongly influences the increase of interplanar distances and that the deviations from the linearity at 300 ºC arise from a relaxation of stresses as a result of cracks [7]. A simultaneous formation of solid solution is confirmed by changes of relative intensities of reflexes.

## 4. Conclusions

The Ni/Cu multilayers of the Ni layer thickness 20 Å and the Cu layer thickness 8, 9, 18 and 19 Å deposited by electrochemical method on Si(100) substrate are thermally stable up to 250 ºC [2]. At 350 ºC the multilayers undergo a total deformation and exfoliation from the substrate. The interplanar distances of multilayers differ from interplanar distances in conventional alloys of identical compositions; $d_{111}$ distances are higher and $d_{200}$ are lower than in the alloy.

Heating of multilayers between 250 ºC and 300 ºC results in an increase of tensile stresses in external layers and increase of compressive stresses in layers adjacent to the substrate. The cracks of a multilayer at 300 ºC cause decrease of stresses, while upon heating at 350 ºC, only tensile stresses occur as a result of the loss of adhesion to the silicon substrate; due to these tensile stresses the coating undergoes a deformation. As a result of heating of multilayers in the 250–350 °C range, Ni/Cu solid solutions are formed causing a favoured (111) orientation.

## References

[1] BARSHILIA C.H., RAJAM K.S., Surface Coating Techn., 155 (2002) 195.
[2] JIMBO M., KARIYA T., IMADA R., FUJIWARA Y., TSUNASHIMA S., J. Magn. Magn. Mater., 165 (1997) 304.
[3] TOKARZ A., NITKIEWICZ Z., WOLKENBERG A., Electr. Techn. Int. J., 35 (2003), 1.
[4] TOKARZ A., Polish J. Appl. Chem., 49 (2005), 283.
[5] TOKARZ A., FRĄCZEK T., BAŁAGA Z., NITKIEWICZ Z., Rev. Adv. Mater. Sci., 15 (2007), 247.
[6] TOKARZ A., STOKŁOSA H., *Application of the SEM Technique In Examination of Cross-Sections of Cu/Ni, Cu/Co and NiFe/Cu Multilayers Deposited Electrolytically* (in Polish), Wyd. Politechniki Częstochowskiej WIPMiFS, ser. Metalurgia, Częstochowa 2006, pp. 551–554.
[7] GĄGOROWSKA B., DUŚ-SITEK M., KUCHARSKA B., TOKARZ A., *Effect of Annealing on the Stability of CuNi Multilayers* (in Polish), Wyd. Politechniki Częstochowskiej WIPMiFS, seria Metalurgia, Częstochowa 2007 (in press).
[8] KANAK J., STOBIECKI T., WIŚNIOWSKI P., GŁADYSZEWSKI G., MAASS W., SZYMAŃSKI B., J. Magn. Magn. Mater., 239 (2002), 329.
[9] AZAROFF L.V., *Struktura i właściwości ciał stałych*, PWN, Warszawa, 1960, pp. 97–428 (In Polish).

*Received 28 April 2007*
*Revised 16 February 2008*