

## PREPARATION AND SOME BASIC PHYSICAL PROPERTIES OF THE AMORPHOUS ELECTRODEPOSITED NiCoP FILMS

MICHAL KONČ\*, JURAJ DANIEL-SZABÓ\*, ADAM KOŠTURIÁK\*, BARNABÁŠ ZAGYI\*\*,  
OTO DUŠA\*\*, Košice

Amorphous ferromagnetic thin films and foils on the basis of NiCoP with a high content of phosphorus (20—24 at. % P) were prepared by the usual method of electrodeposition. The transition of these films from the amorphous to the crystalline state was investigated from the dependence of the change of the electrical resistivity upon temperature, using x-ray and electron diffraction methods.

### НЕКОТОРЫЕ ОСНОВНЫЕ ФИЗИЧЕСКИЕ СВОЙСТВА АМОРФНЫХ ПЛЁНОК НА БАЗЕ NiCoP, НАНОСИМЫХ ЭЛЕКТРОЛИТИЧЕСКИМ СПОСОБОМ

Применяя обычный способ электролитического покрытия, получены аморфные ферромагнитные тонкие плёнки на основе NiCoP с высоким содержанием фосфора (20—24 % фосфора). На этих плёнках исследован переход аморфного состояния в кристаллическое на основе измерения зависимости электрического сопротивления от температуры с помощью метода дифракции рентгеновских лучей и электронов.

### I. INTRODUCTION

At present much attention is given to the preparation and the study of the physical properties of amorphous materials. Many materials, crystalline under normal conditions, can be prepared in the non-crystalline form by one of the following methods: 1) extremely rapid cooling of the melt, [1], [2], and [3]; 2) condensation of vapours onto substrates cooled with liquid helium etc. [4], [5], resp. sputtering in vacuum; 3) chemical deposition [6]; 4) electrolytic deposition [7—9]; 5) explosion of thin wires and ribbons in vacuum. Particular attention is paid to the amorphous films of the transition metals and their alloys with some other elements, above all with the rare earth elements, which may provide valuable

\* Department of Experimental Physics, Faculty of Natural Sciences, P. J. Šafárik University, nám. Febr. víťazstva 9, CS-041 54 Košice

\*\* Department of Physics, Technical University, Park Komenského 2, CS-040 01 Košice.

information about the influence of the structure on various physical properties and which may also have a wide practical application.

The authors of papers [8—10] have studied amorphous NiP and CoP samples prepared electrolytically, above all their local atomic ordering by means of the radial distribution function on the basis of the roentgen diffraction, the temperature dependence of magnetization in saturation and the Curie temperature.

Electrolysis is a relatively simple method for the production of amorphous films and it enables to produce films in a wide range of thicknesses and compositions with varying physical properties according to the conditions of the preparation. There are data about the preparation of amorphous CoP and NiP films in [7—10], but we do not have any detailed information about the technology of the preparation of the amorphous films of the ternary alloy NiCoP and about their structure, only Cargill et al. [11] mention briefly the NiCoP film (24 at. % P and 26 at. % Ni). Neither are accessible data about the temperature dependence of the electrical resistivity of the films of the binary and ternary alloys of the transition metals Ni resp. Co with phosphorus, produced electrolytically.

Our work was devoted to the working-out of the technology of the preparation of NiCoP films with various chemical compositions by the electrolytic method and we have studied the structure and the electrical properties of the CoP and NiCoP films, mainly in the transition phase from the amorphous to the metastable crystalline state.

## II. EXPERIMENTAL DETAILS

### A. Preparation of samples and their chemical composition

The various amorphous ferromagnetic NiCoP samples were prepared by electrodeposition from solutions similar to those which were first described by Brenner et al. [7] and then used with modifications by Cargill et al. in their works [8], [9]. The samples were electrodeposited onto glass substrates with dimensions  $5 \times 5$  cm, covered in vacuum of about  $2 \times 10^{-5}$  torr by a copper film approximately  $0.3 \mu\text{m}$  thick. The film was deposited onto an area of  $15 \text{ cm}^2$ . This procedure enabled a simple separation of the deposited film without damaging it. The separation was done by chemical etching in the solution of  $500 \text{ g CrO}_3$  and  $50 \text{ g H}_2\text{SO}_4$ , to which distilled water was added up to 1 l; the etching temperatures were up to  $70^\circ\text{C}$ , which was sufficient under the temperature of crystallization. The thickness of films was controlled by varying the temperature of crystallization. The thickness of films was controlled by varying the time of deposition and later was determined by other suitable methods. All films were deposited in the magnetic field produced by Helmholtz coils and the intensity of this field was about  $2.5 \times 10^4 \text{ Am}^{-1}$ , higher by almost two orders than the later determined coercive force. The composition of solutions for electrolytic deposition is given in Table 1.

Table 1  
Composition of the electrolytic solutions  
All values in Table 1 are in g/l.

Type of solution	1	2	3	4	5
H <sub>3</sub> PO <sub>3</sub>	44.3	34.0	46.3	44.2	75.0
H <sub>3</sub> PO <sub>4</sub>	50	50	50	50	50
NiCO <sub>3</sub>	5.4	8.0	22.5	25.0	—
NiCl <sub>2</sub> ·6H <sub>2</sub> O	17.0	25.5	110.7	123.0	—
CoCO <sub>3</sub>	26.3	19.7	9.9	6.6	50
CoCl <sub>2</sub> ·6H <sub>2</sub> O	120.7	90.5	45.3	30.2	170

Optimum working conditions were as follows: pH ~ 0.5 ÷ 1, cathodic current density  $i_k = 10 \text{ A/dm}^2$ , temperature of the electrolyte was maintained at  $75 \pm 2^\circ\text{C}$  by means of a contact thermometer and a transistorized relay RPX 101 B regulating the input power of the heating unit. The anode was made of the rolled Co, resp. Ni sheet and had the same dimensions as the deposited film. The rate of deposition was on the average  $0.016 \mu\text{m/s}$  for all films prepared by us on copper substrates.

The prepared electrolytic films were analysed polarographically and spectrophotometrically. The results of these analyses are summarized in Tab. 2. Polarographic determination was realized using the polarograph LP 7 with the recorder EZ 7 and for spectrometric measurements the spectrophotometer Perkin-Elmer type 402 working in a wavelength range of 300 to 450 nm was used. The accuracy of the determination was in both cases better than  $\pm 1.0\%$  at. The values in Tab. 2 are average values obtained on various films of the same set, resp. taking into account the dispersion in the middle and on the border of the sample. This dispersion was less than 2.5 at. % for the content of phosphorus.

Table 2

Results of the chemical analysis of the films prepared according to Table 1.

The values in Table 2 are average values obtained on various films of the same set, resp. taking into account the dispersion in the middle and on the border of the sample. This dispersion was less than 2.5 at. % for the content of phosphorus.

Number of electrolyte	Values in at. %		
	Ni	Co	P
1	16.4	64.5	19.1
2	19.1	59.3	21.6
3	31.5	44.4	24.1
4	43.1	32.6	24.3
5	0	76.3	23.7

## B. Experimental results

The amorphous state of the prepared films resp. bulk foils was investigated by roentgen and electron diffraction methods, using the transmission electron microscope JEM — 7. Roentgenograms of the prepared films in the initial state show the characteristic blurred (diffusion) diffraction rings evidencing the amorphous state of our samples; this is in consistence with papers [6—7], [12—15]. No changes in diffraction patterns were observed after heat treatment (lasting 30 min.) up to a temperature of about 260 °C. When the temperature of annealing exceeds the above mentioned value, a pronounced change in diffraction patterns is observed, and this change is manifested by the increase of the number of diffraction rings, which indicates the process of gradual crystallization. Similar changes were observed also by means of electron diffraction. Since all samples prepared from various electrolytes showed the same behaviour, only the results from a few samples are presented in the following. Figs. 1a and 1b show roentgen diffractograms in the initial (amorphous) state and after annealing at the temperature of 310 °C, obtained on the film NiCoP prepared from solution No. 2. The following figures show electron micrographs made by a transmission electron microscope both in the as-grown state of the samples and after their annealing (30 min.) at 330 °C. Figs. 2a and 2b show electron micrographs of the CoP sample prepared from the electrolyte No. 5. The following Figs. 3a and 3b are the electron micrographs of the amorphous NiCoP alloy prepared from solution No. 1; (a) is in the as-grown state, (b) is after annealing at 330 °C. These results give clear evidence of the structural changes, which took place in the samples after their heat treatment.

Electrical resistivity is a significant indicator of the transition from the amorphous to the crystalline state. The electrical resistivity of the investigated samples was measured by means of the Wheatstone bridge on ribbons of  $25 \times 2$  mm,  $2 \pm 10$   $\mu$ m thick, in the temperature range from 20 °C to 350 °C. The measured ribbon was clamped in spring brass contacts. The whole arrangement was submerged into a bath (silicon vacuum oil) of the ultrathermostat UT 1. The oil bath was continuously agitated, so that it was possible to control the temperature and read the thermometer with an accuracy better than  $\pm 1$  °C. Since the temperature dependences on CoP and NiCoP samples of various compositions and thicknesses are similar, only some results are presented. Figs. 4a, b show such dependences for two samples. Fig. 4a shows the dependence for the NiCoP sample 1 from Tab. 2, and Fig. 4b for the CoP sample with a high content of phosphorus. It follows from these dependences that up to a temperature of about 260 °C the resistivity of all measured samples monotonously increases and then a slight decrease takes place after which a sharp decrease of the electrical resistivity is observed, corresponding to the gradual growth of the crystalline phase. In the last phase of the transition,

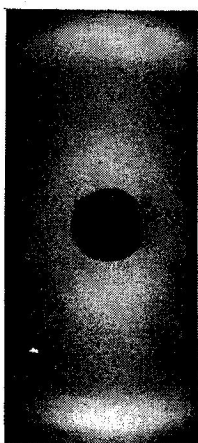


Fig. 1a: Roentgen diffraction patterns of the amorphous NiCoP film in the initial (amorphous) state.

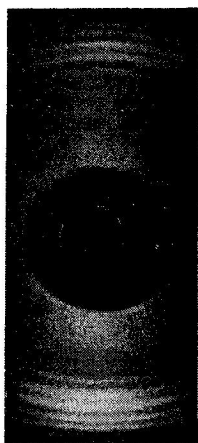


Fig. 1b: Roentgen diffraction patterns of the amorphous NiCoP film after 30 min. of heat treatment at 310 °C.

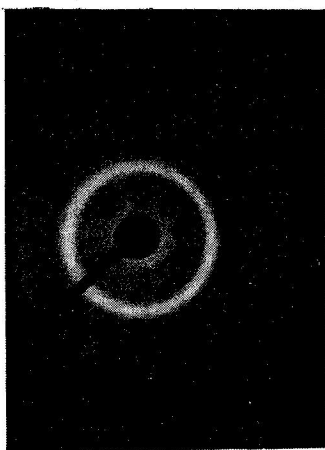


Fig. 2a: Electron micrographs obtained on the amorphous CoP film in the initial (amorphous) state.

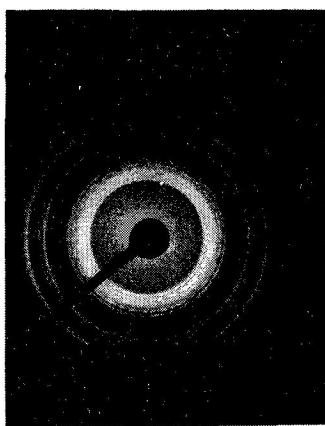


Fig. 2b: Electron micrographs obtained on the amorphous CoP film after heat treatment at 330 °C.

which is reached for the majority of samples at a temperature of about 290 °C, again the slow decrease of the resistivity is observed. After passing a minimum, which is observed in a interval of various widths for various samples, the resistivity increases again with temperature. During cooling the resistivity decreases linearly with the decrease of temperature (Fig. 4a, b), as usual in normal crystalline metals. During repeated heating the resistivity again linearly increases, following approximately the same dependence as during the cooling. The observed dependences are analogous to those measured on other types of amorphous alloys by Meitrepierre [3], Felsch [4]. All our results connected with the transition from the amorphous to the crystalline state are consistent with the results obtained by the roentgen and electron diffraction. In addition to measurements of electrical resistivity also specific masses were determined, using the method of double weighing in the air and in the bromophorm ( $\rho = 2.889 \times 10^3$  kg m<sup>-3</sup>). The accuracy of this method was verified on a number of materials of known specific masses and was better than 1 %. Results of measurements of electrical resistivity and of the specific mass are presented in Table 3.

Table 3

Some physical characteristics of the samples

according to Table 2.

$\alpha_a(\alpha_c)$  is the temperature coefficient of resistivity in the amorphous (crystalline) state,  $T_k$  — temperature of the onset of crystallization, determined from the temperature dependence of the resistivity,  $T_{inf}$  — temperature corresponding with the intense growth of the crystalline phase.

Sample number	Density at 20 °C [kg/m <sup>3</sup> ] × 10 <sup>-3</sup>	Specific resistivity $\rho_{20}$ [ $\mu\Omega$ cm]	$\alpha_a$ [1/°C] × 10 <sup>4</sup>	$\alpha_c$ [1/°C] × 10 <sup>4</sup>	$T_k$ [°C]	$T_{inf}$ [°C]
1	7.97	140.5	1.49	4.04	260	283
2	7.99	157.7	1.18	4.54	265	310
3	7.89	164.4	0.118	0.125	280	290
4	7.55	167.0	1.36	2.11	255	296
5	7.94	137.2	0.99	5.73	265	206

have also shown that the most intense growth of the crystalline phase takes place at about 290 °C. The temperature coefficient of resistivity in the crystalline state is a number of times higher than that in the amorphous state, which indicates a higher degree of ordering in the crystalline system. The small value of the temperature coefficient of resistivity in the amorphous state indicates that the contribution from the phonon scattering is small. The decisive contribution to resistivity is connected with the nonordering of the structure. The slight decrease of the resistivity at about 260 °C followed by the sharp decrease corresponding with the rapid growth of the crystalline phase indicates that the dynamics of the crystalline process is very complex. The process of crystallization needs a more detailed study by the electron microscope. Results of these investigations will be published later.

#### IV. CONCLUSION

NiCoP thin films and foils of various compositions show an amorphous structure up to transition temperature, which is about 260 °C according to our present measurements. In the amorphous electrodeposited films of the given composition a strong irreversible change (decrease) of electrical resistivity at the transition from the amorphous to the metastable crystalline state is observed. The temperature coefficient of resistivity is in general lower than that for the crystalline state. Roentgen diffraction patterns show no qualitative change when the samples are heat treated up to the temperature of 260 °C, at which the gradual transition from the amorphous to the crystalline state begins.

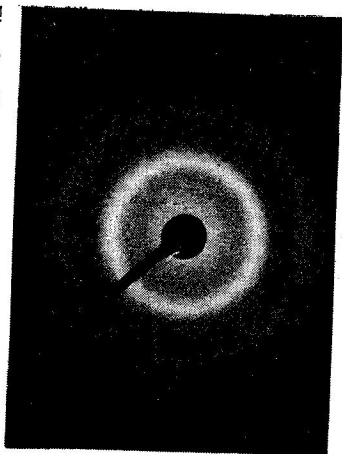


Fig. 3a. Electron micrographs obtained on the NiCoP amorphous alloy in the initial state.

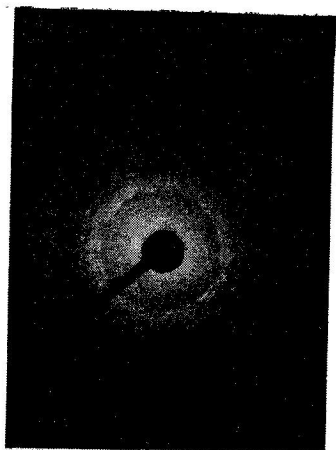


Fig. 3b. Electron micrographs obtained on the NiCoP amorphous alloy after annealing at 330 °C.

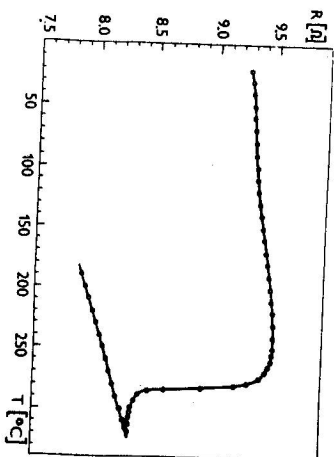
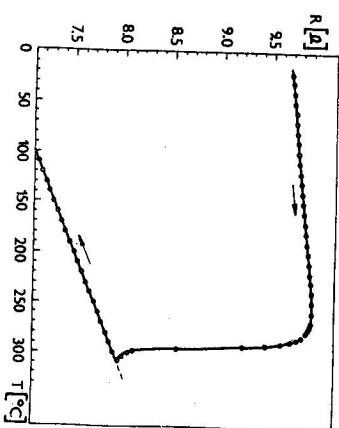


Fig. 4a, b. The temperature dependence of the electrical resistivity of amorphous films: a) NiCoP No. 1,



b) CoP No. 5.

Results summarized in Table 3 are comparable with results published in [3], [7], [9] and obtained for similar types of amorphous alloys.

#### III. DISCUSSION

Electron and roentgen diffraction confirmed unambiguously that NiCoP samples prepared by electrodeposition are amorphous. Roentgen diffraction showed that the process of crystallization begins at about 270 °C. This result is consistent with the measurements of the electrical resistivity, which showed that the temperature of the onset of crystallization is in the range from 255 to 280 °C. Amorphous NiCoP films have a high value of specific resistivity (Table 3) as compared with the pure crystalline Ni and Co, which have specific resistivity of 7.2 and 9.7  $\mu\Omega$ cm. This property is typical for amorphous materials. Measurements of electrical resistivity

## REFERENCES

- [1] Hasegawa, R.: *Phys. Rev. B* 3 (1971), 1631.
- [2] Tsuei, C. C., Longworth, G., Lin, S. C. H.: *Phys. Rev.* 170 (1968), 603.
- [3] Maittepiette, P.: *J. appl. Phys.* 41 (1970), 498.
- [4] Felsch, P.: *Z. angew. Phys.* 30 (1970), 275.
- [5] Bennet, M. R., Wright, J. G.: *Phys. Stat. Sol. (a)* 13 (1972), 135.
- [6] Simpson, A. W., Brambley, D. R.: *Phys. Stat. Sol. (b)* 43 (1971), 291.
- [7] Brenner, A., Couch, D. E., Williams, E. K.: *J. Res. natn. Bur. Stand.* 44 (1950), 44; Brenner, A.: *Electrodeposition of Alloys*, Vol I, II. Academic Press, New York 1963.
- [8] Cargill, G. S. III.: *J. appl. Phys.* 41 (1970), 12.
- [9] Cargill, G. S. III.: Corchane, R. W.: *Amorph. Magnetism*; Eds. Hooper H. O., deGraaf, A. M., New York 1973.
- [10] Pan, D., Turnbull, D.: *J. appl. Phys.* 45 (1974), 1406.
- [11] Cargill, G. S. III., Gambino, R. J., Cuomo, J. J.: *IEEE Trans. Magn. MAG-10* (1974), 803.
- [12] Wiesner, H., Schneider, J.: *Phys. Stat. Sol. (a)* 26 (1974), 71.
- [13] Bagley, B. G., Turnbull, D.: *Acta metalurg.* 18 (1970), 857.
- [14] Ichikawa, T.: *Phys. Stat. Sol. (a)* 19 (1973), 707.
- [15] Bondar, V. V., Gorbunova, K. M., Polukarov, J. M.: *RMM* 26 (1968), 568.

Received May 17<sup>th</sup>, 1977