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INVESTIGATION OF CHEMICALLY DEPOSITED AND ELECTRODEPOSITED AMORPHOUS Ni-P ALLOYS

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**CENTRAL
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BUDAPEST

INVESTIGATION OF CHEMICALLY DEPOSITED AND ELECTRODEPOSITED AMORPHOUS Ni-P ALLOYS

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ABSTRACT

The structural and electronic properties of amorphous Ni-P systems pre-
pared by different techniques (by chemical deposition from aqueous solutions
containing either hydrocloric or sulphuric acid, by electrodeposition and by
rapid quenching) were studied by TEM and DSC methods, by measuring electrical
transport properties and by ^{31}P NMR spectroscopy. The samples chemically re-
duced from hydrocloric bath seemed to be very inhomogeneous both as regards
the amorphous state and the amorphous-to-crystalline transformation. The
samples prepared by the other methods showed a more homogeneous, common be-
haviour, including a systematic dependence on P content of the DSC quantities
and the transport properties.

АННОТАЦИЯ

Методами ТЕМ /трансмиссионная электронмикроскопия/ и DSC /дифференциаль-
ная сканирующая калориметрия/, измерением транспортных свойств и ЯМР-спектров
31Р изучались свойства аморфных сплавов Ni-P, полученных различными методами
/химическим восстановлением из хлоридных или сульфатных растворов, электро-
литическим разложением, быстрым охлаждением/. Образцы, полученные химическим
восстановлением из хлоридного раствора, были неоднородными как с точки зрения
аморфного состояния, так и процесса аморфно - кристаллического перехода.
Остальные образцы показали более гомогенное поведение, включая и системати-
ческую зависимость от состава DSC и транспортных величин.

KIVONAT

Különbözö módon (kémiai redukcióval kloridos vagy szulfátos oldatból,
elektrolitikus leválasztással, gyorshütéssel) elöállitott Ni-P amorf ötvöze-
tek tulajdonságait vizsgáltuk TEM és DSC módszerrel, elektromos transzport
tulajdonságok mérésével és ^{31}P NMR spektroszkópiával. A kloridos oldatból
kémiailag redukált minták nagyon inhomogének voltak mind az amorf állapotot,
mind az amorf-kristályos átalakulás folyamatát illetöen. A többi minta egysé-
gesen homogénebb viselkedést mutatott, beleértve a DSC és transzport mennyi-
ségek szisztematikus összetételfüggését is.

INTRODUCTION

The Ni-P deposits belong to the amorphous alloys which have been investigated for the longest time [1] and although they have been the subject of several studies in the last decade, we still don't possess a generally accepted, uniform picture about their physical properties. Contradictions can be found in the literature as regards both the calorimetric measurements and the description of the crystalline structure of phases occuring after crystallization [2-7]. The discrepancy in the results on amorphous Ni-P deposits have been attributed by many authors to concentration inhomogeneities being present in the amorphous samples and it was pointed out in some cases that the degree and distribution of inhomogeneities depends on the way of preparation. In chemically reduced Ni-P layers, for instance, a difference in the concentration inhomogeneity was observed between layers deposited from solution containing either nickel chloride or nickel sulphate [8]. The aim of the present study was with the help of different experimental methods, a comparison of the properties of amorphous Ni-P alloys prepared by different techniques.

SAMPLE PREPARATION

The samples used in the present work were obtained by chemical reduction from two different solutions and by electrodeposition. Measurements were also done on rapidly quenched samples of two different compositions, the detailed results of their study, however, will be published elsewhere. The conditions for electrolytic deposition are described in details in Ref. [9].

The chemically reduced samples were obtained from acidic baths and the chemical reduction was achieved by sodium hypophosphite. An exact knowledge of chemical nickel plating would be of

great theoretical and practical importance. However, at present no theory is available to explain every details of the reduction process in a consistent manner. The description of the generally accepted steps of the reduction process can be found in the literature [10]. The reduction can be started only by catalysis; Ni, Pd or Rh can act as a catalytic agent.

The two solutions used for chemical reduction differed from each other only in type of the nickel salt dissolved: bath C contained 15-30 mg/cm^3 $NiCl_2 \cdot 6H_2O$ and bath S contained 15-25 mg/cm^3 $NiSO_4 \cdot 7H_2O$. The rest of the ingredients was the same in both cases: 10-20 mg/cm^3 $NaH_2PO_2 \cdot H_2O$, 50 mg/cm^3 $CH_3COONa \cdot 3H_2O$, 0.005 mg/cm^3 stabilizer. The pH-value was 4-5 and the bath temperature was kept constant at 91 ^{O}C. The same substrate material, substrate degreasing technique, as well as method of activation of substrate surface by $SnCl_2$ and $PdCl_2$ solution, the same surface - to - volume ratio and mixing rate were applied in every cases.

The phosphorous content of the deposits was obtained by spectrophotometric methods, while other constituents were determined by atomic absorption technique, by Balzers EA-2 gas analyser and LECO carbon alayser. It was obtained that besides Ni and P the samples contained 1 wt.%C, 0.1-0.2 wt.% Cu, Fe, and Co, the amount of H_2 and O_2 was found to be of the order of 100 ppm. All the samples used for the measurements were found to be amorphous by X-ray diffraction.

EXPERIMENTAL METHODS

The amorphous state and the amorphous - to - crystalline transformation of the Ni-P layers prepared by different techniques were investigated by transmission electronmicroscope (TEM), by nuclear magnetic resonance (NMR), by measurements of electronic transport properties (electrical resistivity and thermopower), and by differential scanning calorimetry (DSC).

The structural studies were performed on a JEOL 100-CX electronmicroscope by applying "in-situ" electron beam heating. These measurements were in every cases complemented by TEM

measurements on samples quenched from a certain temperature the
purpose of what was, first, to avoid possible thin film effects,
and second, to obtain a temperature scale for the "in-situ"
measurements. Etching of the samples was performed by electro-
lytic method at -40 $^\circ$C temperature using a mixture of methane
alcohol and nitric acid with a ratio of 3:1.

The NMR studies were performed on a home-built continuous
wave spectrometer with the usual field modulation technique. The
^{31}P NMR absorption derivative signal was studied at room tempera-
ture at 0.23, 0.43 and 0.66 T external magnetic fields and the
peak-to-peak linewidth and the shift of the zero crossing point
(Knight shift) with respect to solid red phosphorous were
measured.

The electronic transport properties were measured from room
temperature up to crystallization in probes developed especially
for thin amorphous alloy samples. Keithley nanovolt amplifiers,
and a Solartron data logger system were applied and a HP-97-S
desk computer was used for direct data processing and measure-
ment control. The electrical resistivity measurements were per-
formed by the classical four-point DC method and the thermopower
was measured by the well known differential method [11]. For the
thermopower measurements pure Al was used as reference material
and its literature data were checked by measurements with respect
to Pt and Ag-normal. Due to uncertainties in sample geometry
specific resistivity could be measured only with low accuracy.
Measurements of specific gravity and sample mass in order to im-
prove to some extent the accuracy of specific resistivity data
were not performed.

The DSC studies were made by using a Perkin-Elmer differen-
tial scanning calorimeter which was supplied by a digitizer
enabling the data to be punched on tape for computer evaluation.
On the plots demonstrating transformation processes, the enthalpy
change normalized by the total enthalpy change is displayed since
this is the quantity which is characteristic for the kinetics of
the process.

RESULTS

It is always helpful to perform the first studies by DSC to obtain some orienting results. First, this qualifies the sample, and second, a temperature scale is defined in this manner for the material under study. Even these measurements indicated a difference in behaviour between samples prepared by chemical reduction and electrodeposition or rapid quenching and also between chemically reduced samples obtained from bath C and bath S. Differences occur in the amorphous state, in the amorphous-to-crystalline transformation and in the final crystalline phases and a systematic change of physical properties with phosphorous concentration can be observed for samples obtained by rapid quenching and by chemical reduction from bath S.

The structure of the amorphous state in both chemically and electrolytically deposited samples can be characterized' by a selected area electron-diffraction pattern which, in accordance with the literature data, shows a diffuse ring at the position of the strongest line 111 of Ni (2.03 Å) as shown in *Fig. 1a*. In the case of electrodeposited and some of the S-type chemically reduced samples, however, another diffuse ring occurs at a position corresponding to 3.3 Å. It is worth to note that this ring can correspond to a second neighbour distance (higher harmonics) as well but in any case, it is remarkable that its position coincides with the first occuring line 220 of the Ni_5P_2 compound (see *Fig. 1b*).
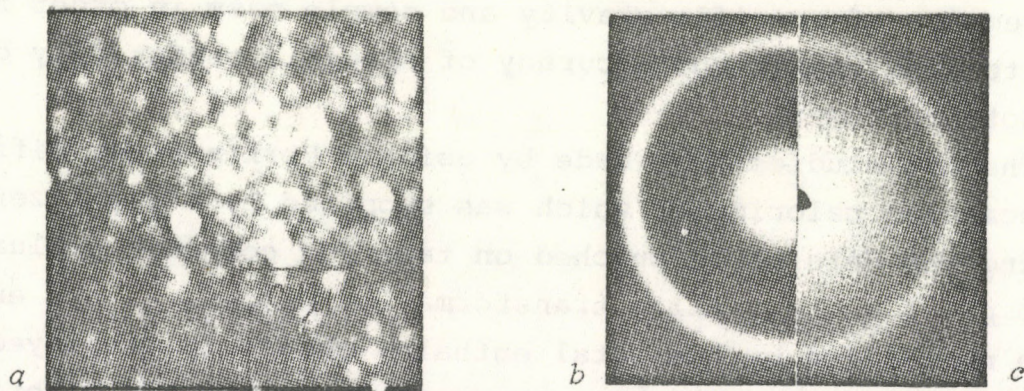

Fig. 1. Amorphous state of Ni-P alloys as shown by TEM:
    (a) electron micrograph
    (b) selected area diffraction pattern
    (c) internal diffuse diffraction ring appearing
       in some samples

A detailed ^{31}P NMR study was performed on amorphous Ni-P alloys in order to see the dependence of NMR parameters on concentration and preparation technique. The results of this investigation were published in details elsewhere [9]. In the present paper our aim is to discuss only those from the atomic and/or electronic structure sensitive NMR parameters which show a dependence on preparation technique. Among the measured ^{31}P NMR parameters the Knight shift K and the quantity k_1 describing the strength of the field-depencence of the linewidth shows a considerable dependence on both phosphorous content and method of preparation. The dependence on preparation technique can be best demonstrated by a k_1 vs. K plot (*Fig. 2*) where the concentration
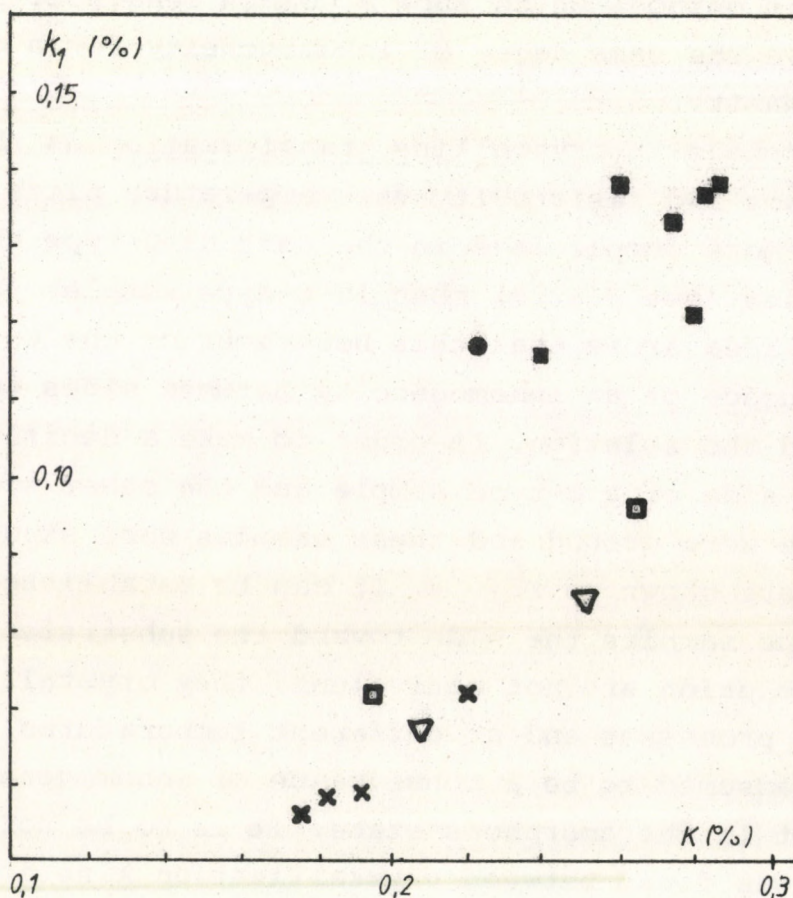
Fig. 2. Parameter k_1 describing the strength of the field dependence of ^{31}P NMR linewidth vs. Knight shift in amorphous Ni-P alloys prepared by chemical reduction from bath C (■), chemical reduction from bath S (□), electrodeposition (x), rapid quenching (∇). The point labelled ● was taken from Ref.[12] (chemical reduction without specification of bath)

enters only as an implicit parameter. The contact part of the Knight shift for the conductions electrons can be written in the form $K_s = \frac{8\pi}{3} \chi_p < |\Psi_s(0)|^2 >_{FS}$ where χ_p is the Pauli susceptibility, $\Psi_s(0)$ is the wave function of the s electrons at the nucleus site, and FS denotes an average over the Fermi surface. Assuming that the main contribution to K originates from hyperfine interactions in the form of K_s the plot of Fig. 2 displays the dependence of the electronic density fluctuation at the Fermi level on the average electronic density at the Fermi level. A fluctuation in the electronic density can be considered as a consequence of the diversity of phosphorous sites. It can clearly be seen from Fig. 2 that the samples prepared by chemical reduction from bath C exhibit a much higher degree of inhomogeneity than the samples prepared by other methods which show a common behaviour in the sense that they have the same degre of inhomogeneity for a given average electronic density.

The amorphous-to-crystalline transformation as shown by the DSC thermograms and resistivity vs. temperature plots seems to be considerably more complicated in the case of C-type chemically reduced samples (see *Fig. 3*) than in S-type samples (see later *Fig. 7*). The idea arose that this behaviour of the C-type samples was a consequence of an inhomogeneity between sides toward the substrate and the solution. In order to make a decision in this respect, one side of a C-type sample and the other side of a second C-type sample were ground and these samples were studied by DSC. The results are shown on *Fig. 4*. It can be established that in the case of C-type samples the side toward the substrate and that toward the solution are not equivalent: they crystallize according to different processes and at different temperatures. This difference can be assumed to be a consequence of inhomogeneities already being present in the amorphous state. It is to be noted that no correlation was found between crystallization kinetics and phosphorous content for C-type samples and, therefore, further detailed investigations were conducted only for the S-type alloys. A common characteristic of the C-type samples is, however, the onset of the crystallization process at unusually low temperatures (at 200 ^{O}C). According to the TEM diffraction studies this first crystallization process is always accompanied by the occurence of Ni precipi-
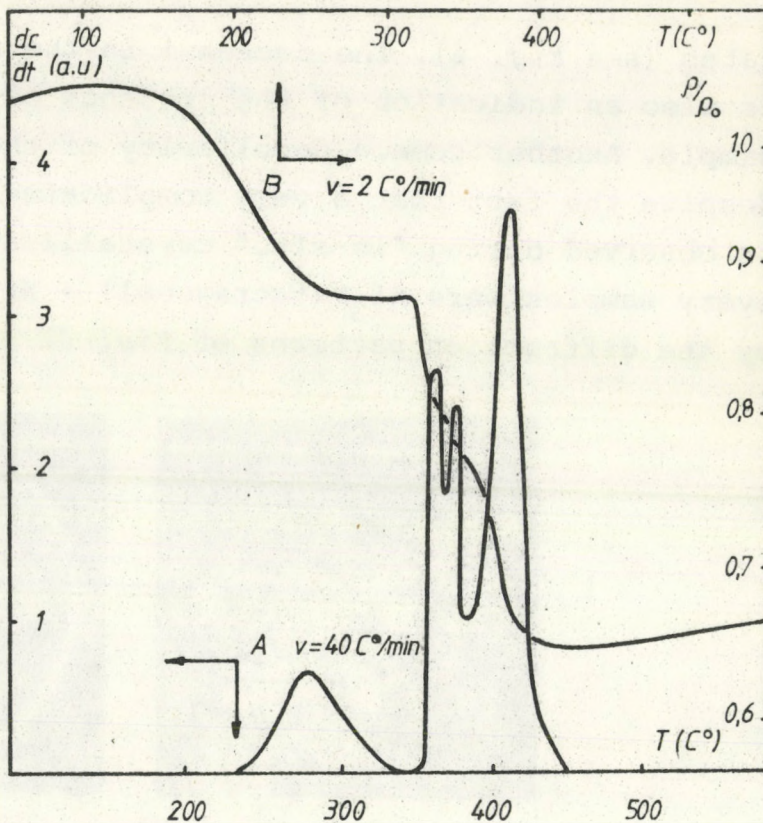
Fig. 3. DSC thermogram (A) and resistivity vs. temperature plot (B) of an amorphous Ni-P alloy (11.5 at.%P) obtained by chemical reduction from bath C
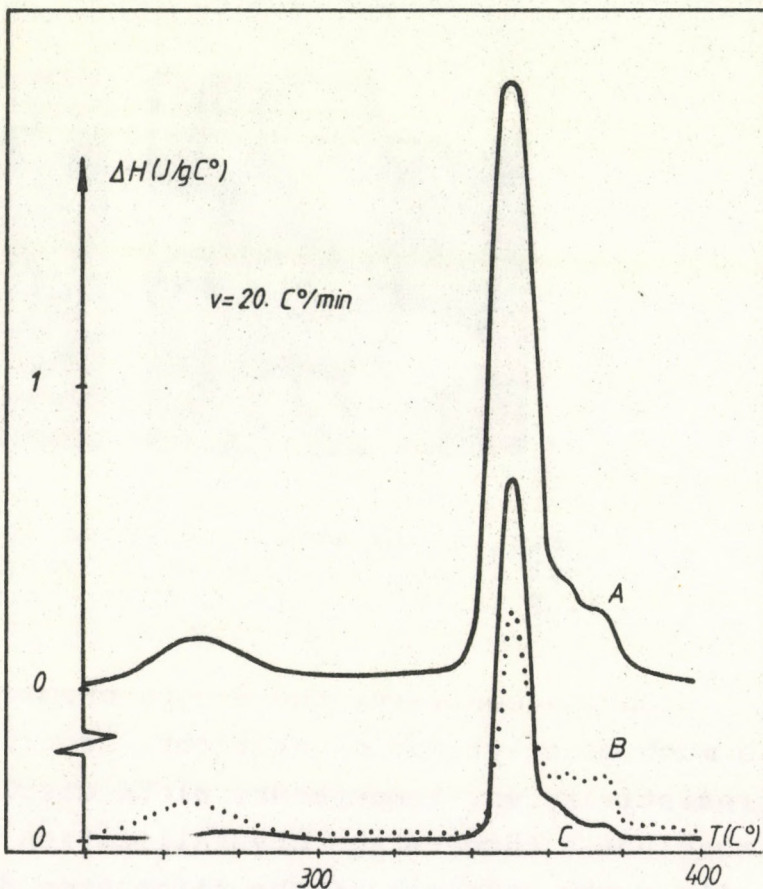

Fig. 4. DSC thermograms of an amorphous Ni-P alloy (7.2 at%P) chemically reduced from bath C for as-prepared sample (A), for sample with solution side removed (B), for sample with substrate side removed (C)

tates (see *Fig. 5*). The decrease in the resistivity shown in Fig.3 is also an indication of the presence of Ni-grains shunting the sample. Another common peculiarity of the C-type samples is that despite the fact that a very complicated, multistage process can be observed during "in-situ" crystallization the final phases in every samples were Ni_3P(tetragonal) + Ni(random) as it is indicated by the diffraction patterns of *Fig. 6*.
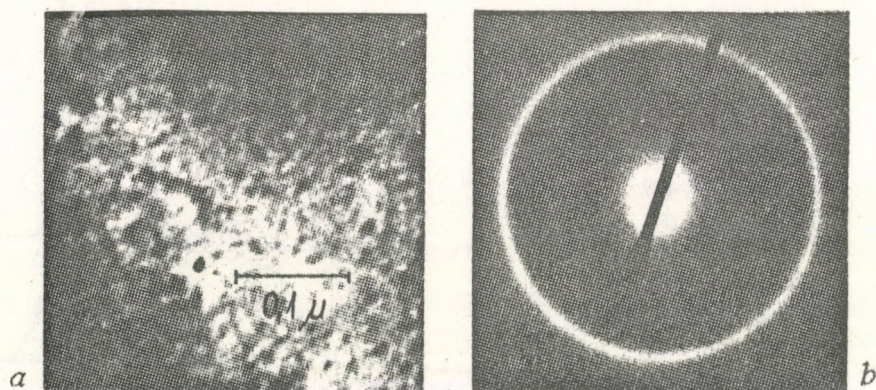

Fig. 5. In alloys chemically deposited from bath C the structure Ni+ amorphous can be observed by TEM after the first crystallization process
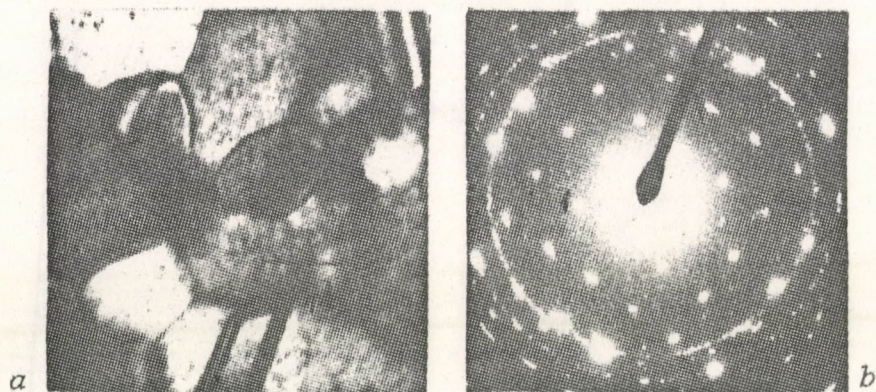
Fig. 6. In samples chemically deposited from bath C the final phases after crystallization are Ni_3P (tetragonal) and Ni (random) as shown by TEM

On the contrary, the S-type chemically reduced samples show a much more sytematic behaviour. According to the termograms and resistivity vs. temperature plots displayed on *Fig. 7* one can conclude a three-stage crystallization process. In these amorphous alloys the strength of the first step decreases with increasing
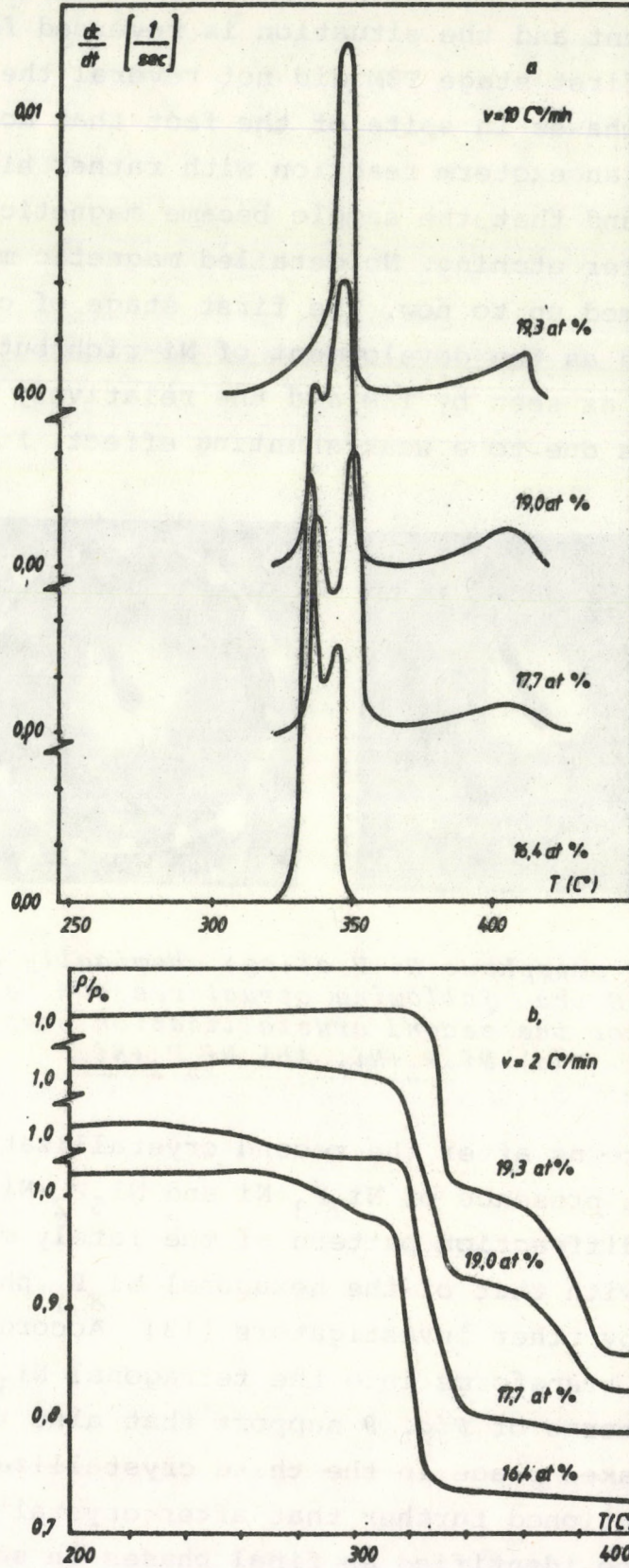
Fig. 7. DSC thermograms (a) and resistivity vs.
temperature plots (b) of amorphous Ni-P alloys
chemically deposited from bath S

phosphorous content and the situation is reversed for the third step. After the first stage TEM did not reveral the appearance of any crystalline phases in spite of the fact that according to the DSC measurements an exoterm reaction with rather high heat evolution took place and that the sample became magnetic and remained magnetic even after etching. No detailed magnetic measurements have been performed up to now. The first stage of crystallization can be considered as the development of Ni-rich but still amorphous regions at least as seen by TEM and the relatively small decrease in resistivity is due to a weak shunting effect. *Fig. 8* shows TEM
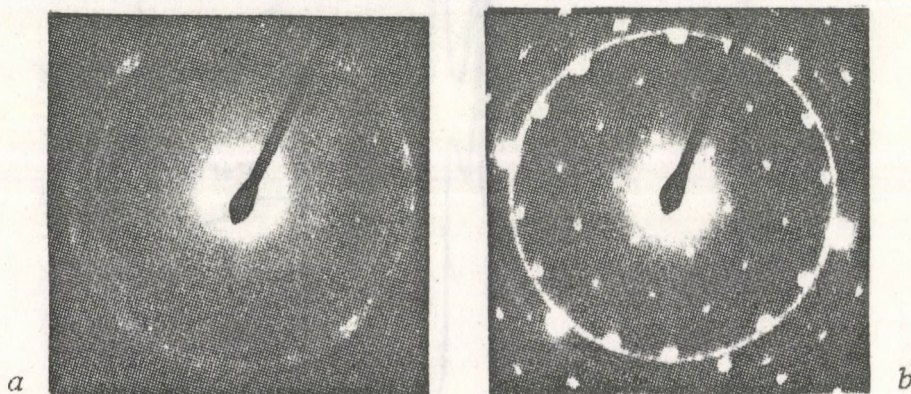

Fig. 8. In amorphous Ni-P alloys chemically deposited from bath S the following structures can be detected after the second crystallization step:
(a) Ni_7P_3+Ni, (b) Ni_5P_2+Ni

diffraction patterns after the second crystallization step and demonstrates the presence of Ni_7P_3+Ni and Ni_5P_2+Ni phases. We think that the diffraction pattern of the lately mentioned phase (Ni_5P_2) agrees with that of the hexagonal Ni_xP_y phase identified as a new phase by other investigators [13]. According to their observations it transforms into the tetragonal Ni_3P phase. The diffraction patterns of *Fig. 9* support that also in our case this same reaction takes place in the third crystallization process. It should be mentioned further that after crystallization only Ni_7P_3+Ni could be identified as final phases in samples in which the third crystallization step was absent (this was found besides the S-type chemically reduced samples with low P-content in both electrodeposited and rapidly quenched samples, too).
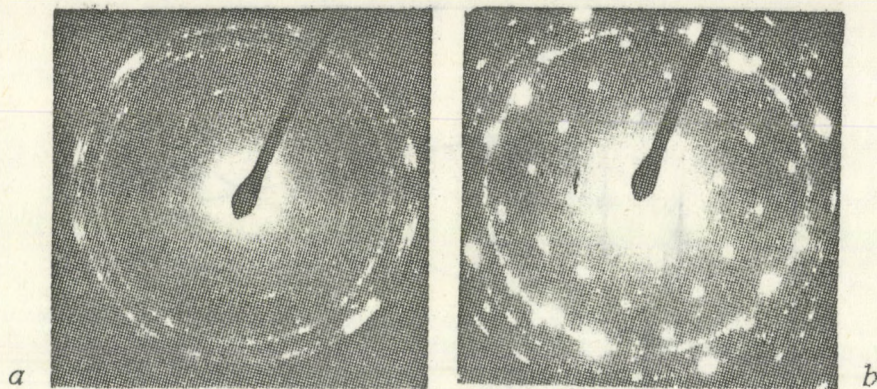
*Fig. 9. The same as in Fig. 8 but after the
third crystallization step:
(a) Ni_7P_3+Ni, (b) Ni_3P+Ni*

The effect of phosphorous concentration was found to be
systematic (with the exception of the C-type chemically deposited
alloys) as regards both the amorphous state and the amorphous-to-
crystalline transformation as it is depicted by *Fig. 10* summariz-
ing the main results and including literature data as well for the
sake of comparison. Our room temperature results on the electrical
resistivity, the temperature coefficient of resistivity, and the
thermopower are in agreement with the measurements of Cote et al.
[14,15] although the specific resistivity which can be measured
only with great uncertainty seems to be systematically higher in
our case. A detailed study of these results together with the
temperature dependences and the interpretations based on the ex-
tended Ziman theory [16] will be discussed elsewhere. The trans-
formation heat values agree well with the literature data [4,14]
whereas the transformation temperatures only to a less extent, in
our samples they showed almost no change in the concentration
region investigated. Returning to Fig. 7 it can clearly be seen
that by increasing the P content in S-type samples the first
crystallization step diminishes on one hand, that is, less amount
of Ni-rich regions develops, and, on the other hand, the third
stage gets stronger, that is, the amount of Ni_5P_2 phases and that
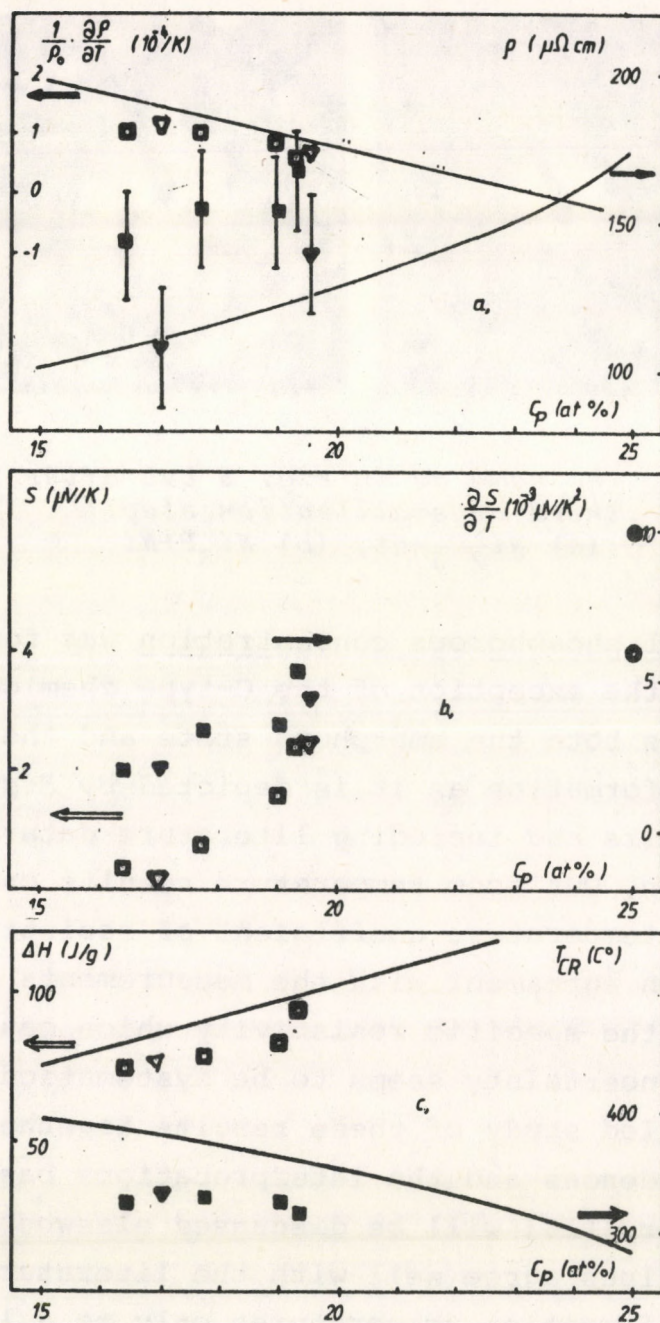of Ni_3P phases developing from the former phase increases.

Fig. 10. *Electronic transport properties of amorphous Ni-P alloys prepared by different techniques:*

(a) *specific resistivity (solid symbols) and temperature coefficient of resistivity (light symbols), both at 0 °C;*
(b) *thermopower (light symbols) and slope of thermopower vs. temperature plot (solid symbols), both at 0 °C;*
(c) *heat released during amorphous-to-crystalline transformation (light symbols) and transformation temperature (solid symbols)*

The solid lines represent data on electrodeposited alloys taken from Ref. [14] and the symbols ● and ○ from Ref. [15]. Present results: chemical reduction from bath S (■ and □), rapid quenching (▼,▽)

CONCLUSIONS

Ni-P amorphous layers chemically deposited from bath containing nickel chloride are very inhomogeneous. In these alloys the amorphous-to-crystalline transformation is very complicated and takes place in several stages and the sides of the samples toward substrate and bath are inequivalent. The thermal stability of the substrate side is very weak, the precipitation of Ni phases starts below 200 $^{\circ}$C. In spite of the complicated crystallization process the crystallized sample consisted in every case from Ni_3P and Ni phases.

The chemically reduced amorphous Ni-P alloys deposited from solution containing nickel sulphate seem to be more homogeneous and they exhibit a three-stage crystallization process. After the first step no microcrystallites can be detected by TEM diffraction in spite of the fact that an exoterm reaction with high heat evolution takes place during this step and that the sample becomes magnetic. In the second stage Ni_7P_5, Ni and sometimes Ni_5P_2 phases develop in the sample. After the third process Ni_3P can be detected.

In the case of C-type samples (chemically deposited from bath containing nickel chloride) the dependence of physical properties upon phosphorous content is masked by inhomogeneities. In the rest of the preparation techniques (chemical reduction from bath containing nickel sulphate, electrodeposition, and rapid quenching) the samples investigated exhibited a systematic dependence on P concentration as regards the structural, thermal and electronic properties in agreement with the existing literature data. The different behaviour of chemically reduced samples obtained from solutions containing either chloride or sulphate may be in connection with the different mechanisms of layer deposition which are not known sufficiently yet.

ACKNOWLEDGEMENTS

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