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INVESTIGATION OF CHEMICALLY DEPOSITED AND ELECTRODEPOSITED AMORPHOUS Ni-P ALLOYS

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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 occurring after crystallization [2-8]. The discrepancy in the results on amorphous Ni-P deposits have been attributed by many authors to concentration inhomogeneities 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. 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. The description of the generally accepted steps of the reduction process can be found in the literature [10]. The two solutions used for chemical reduction differed only in type of the nickel salt dissolved: bath C contained 15-30 mg/cm³ NiCl₂·6H₂O and bath S contained 15-25 mg/cm³ NiSO₄·7H₂O. The rest of the ingredients was the same in both cases: 10-20 mg/cm³ NaH₂PO₂·H₂O, 50 mg/cm³ CH₃COONa·3H₂O, 0.005 mg/cm³ stabilizer. The pH value was 4-5 and the bath temperature was kept constant at 91°C. The same substrate material, sub-

strate degreasing technique, as well as method of activation of substrate surface by SnCl₂ and PdCl₂ solution, the same surface - to - volume ratio and mixing rate were applied in every cases.

Experimental methods. The amorphous state and the amorphous-to-crystalline transformation of the Ni-P layers prepared by different techniques were investigated by transmission electron microscopy (TEM) by a JEOL 100-CX electron microscope, by nuclear magnetic resonance (NMR) using a home-built continuous wave spectrometer, by measurements of electronic transport properties (electrical resistivity by the four-point DC method, and thermopower by the differential method [11]), and by differential scanning calorimetry (DSC) using a Perkin-Elmer calorimeter.

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. 1b. 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 occurring line 220 of the Ni₅P₂ compound (see Fig. 1c). A detailed ³¹P NMR study on these amorphous Ni-P alloys is reported elsewhere [9]. Here we discuss only the relation between the Knight shift K and the parameter k₁ characterizing the width of the Knight shift distribution. Assuming that the basic contribution to K is the contact shift $K_s = \frac{8\pi}{3} \chi_P \langle |\psi_s(0)|^2 \rangle_{FS}$ 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

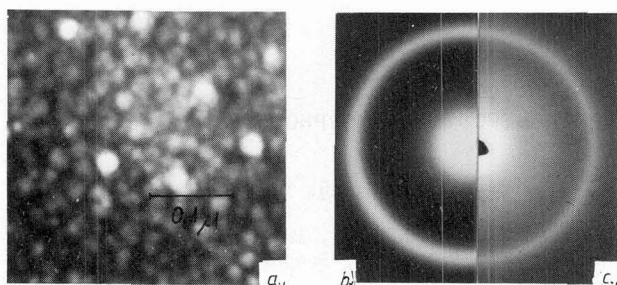


Fig. 1. Amorphous state of Ni-P alloys as shown by TEM: (a) electron micrograph; (b) selected area diffraction pattern; (c) internal diffuse diffraction ring appearing in some samples.

average over the Fermi surface, the k_1 vs K 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 degree 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. 6). It was found by DSC on C-type samples ground to half thickness that the solution side and the substrate side exhibited markedly different crystallization processes. This difference can be assumed to be a consequence of inhomogeneities already being present in the amorphous state. A common characteristic of the C-type samples is the onset of the crystallization process at unusually low temperatures (at 200°C). According to the TEM diffraction studies this first crystallization process is always accompanied by the occurrence of Ni precipitates (see Fig. 4). 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. 5.

On the contrary, the S-type chemically reduced samples show a much more systematic behaviour. According to the DSC thermograms and the resistivity

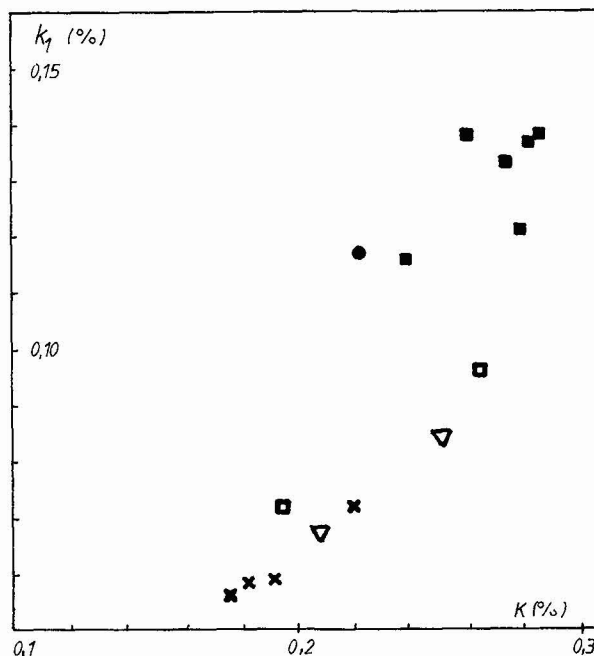


Fig. 2. Parameter k_1 describing the strength of the field dependence of ^{31}P NMR linewidth vs. Knight shift in amorphous Ni-P alloys prepared by chemical reduction from bath C (■), chemical reduction from bath S (□), electrodeposition (x), rapid quenching (▽). The point labelled ● was taken from Ref. [12] (chemical reduction without specification of bath).

vs. temperature plots displayed on Fig. 6 one can conclude a three-stage crystallization process. In these amorphous alloys the strength of the first step decreases with increasing phosphorous content and the situation is reversed for the third step. After the first stage TEM did not reveal the appearance of any crystalline phases in spite of the fact that according to the DSC measurements an exothermic

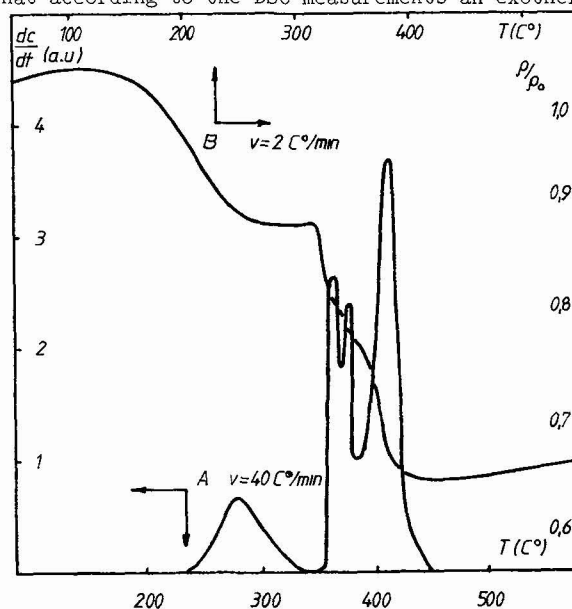


Fig. 3. DSC thermogram (A) and resistivity vs. temperature plot (B) of an amorphous Ni-P alloy (11.5 at.%P) obtained by chemical reduction from bath C

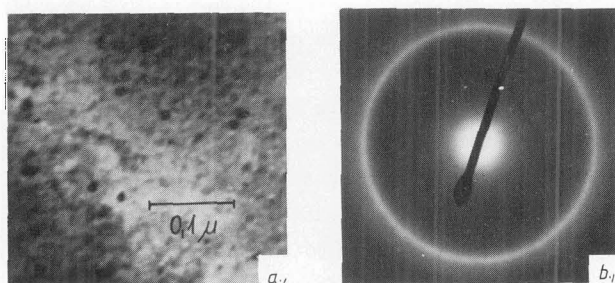


Fig. 4. In alloys chemically deposited from bath C the structure Ni+ amorphous can be observed by TEM after the first crystallization process.

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. 7 shows TEM 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. 8 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 electro-deposited and rapidly quenched samples, too).

The effect of phosphorous concentration was found to be systematic (except the C-type chemically deposited alloys) as regards both the amorphous-to-crystalline transformation (see Fig. 6) and the

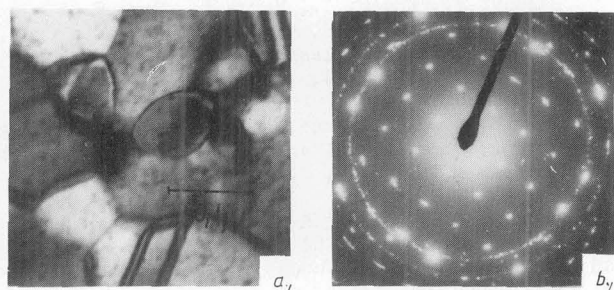


Fig. 5. In samples chemically deposited from bath C the final phases after crystallization are Ni_3P (tetragonal) and Ni (random) as shown by TEM.

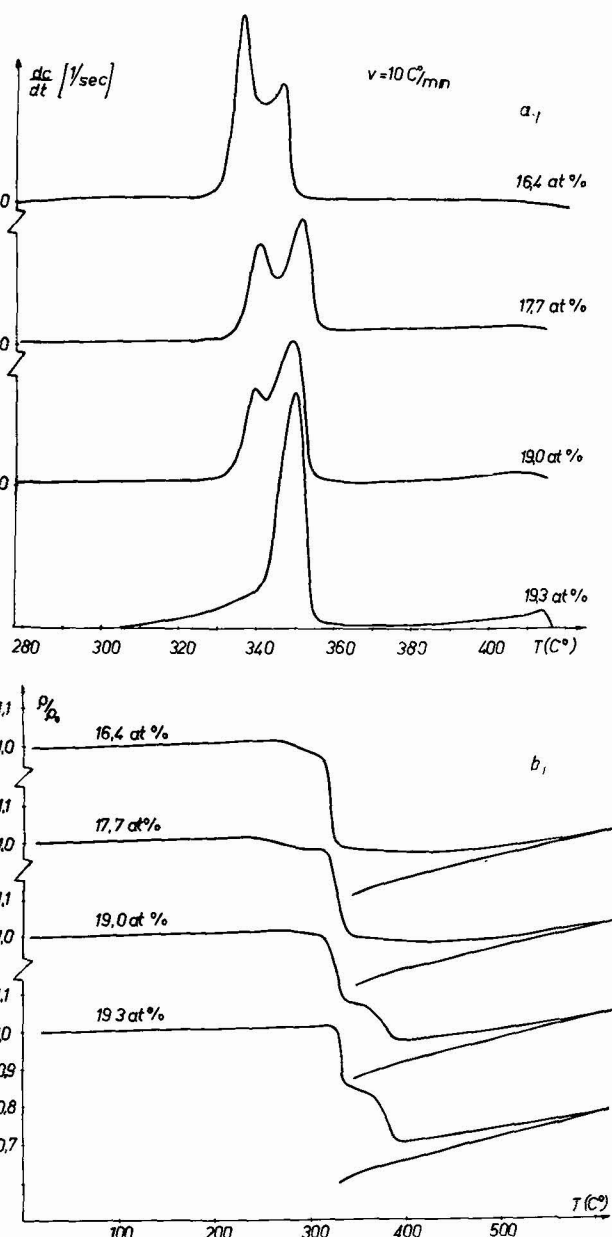


Fig. 6. DSC thermograms (a) and resistivity vs. temperature plots (b) of amorphous Ni-P alloys chemically deposited from bath S.

amorphous state as it is depicted by Fig. 9 summarizing the main results and including literature data. 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 by 10 to 30 % in our case. A detailed study of these results together with the temperature dependences and the interpretations based on the extended Ziman theory will be discussed elsewhere. The transforma-

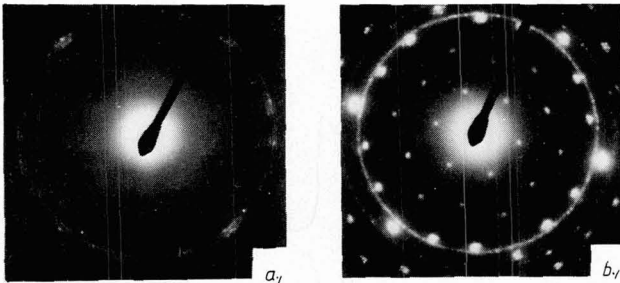


Fig. 7. In amorphous Ni-P alloys chemically deposited from bath S the following structures can be detected after the second crystallization step: (a) Ni_7P_3+Ni ; (b) Ni_5P_2+Ni .

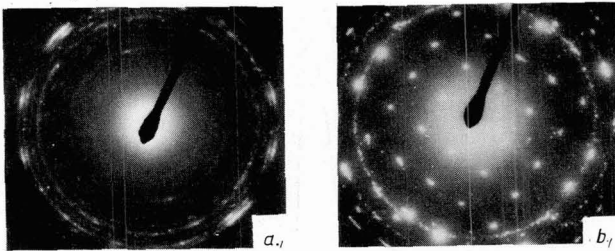


Fig. 8. The same as in Fig. 7 but after the third crystallization step: (a) Ni_7P_3+Ni ; (b) Ni_3P+Ni .

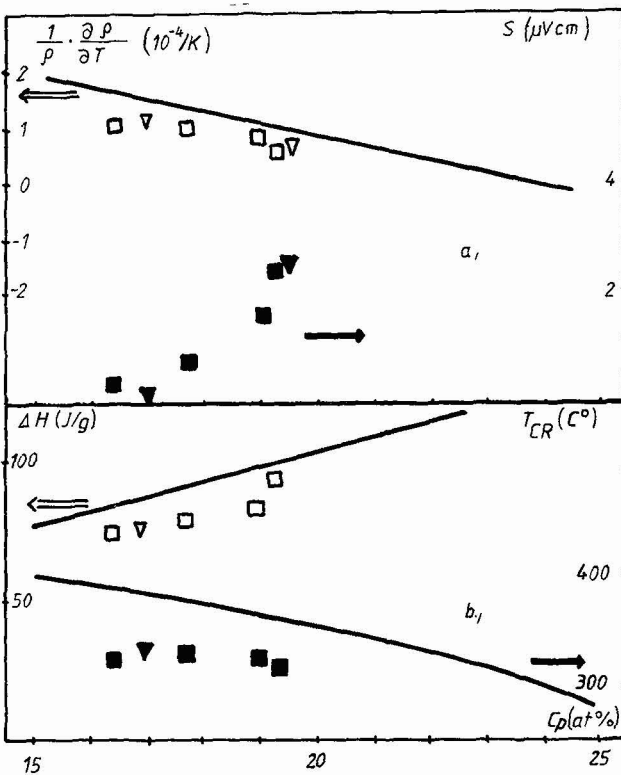


Fig. 9. Physical properties of amorphous Ni-P alloys prepared by different methods: (a) temperature coefficient of resistivity (light symbols) and thermo-power (solid symbols), both at 0 C°; (b) heat released during amorphous-to-crystalline transformation (light symbols) and transformation temperature (solid symbols). The solid lines represent data on electrodeposited alloys taken from Ref. [14] and the symbol • from Ref. [15]. Present results: chemical reduction from bath S (■ and □), rapid quenching (▽, ▽). tion 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 composition range studied.

Conclusions. Ni-P amorphous layers chemically deposited from chloride bath are very inhomogeneous and this masks any composition dependence. These alloys exhibit a complicated, multistage crystallization process, and the both sides of the layers are inequivalent. The thermal stability of the substrate side is very weak, the precipitation of Ni phases starts below 200°C. The crystallized sample consisted in every case from Ni_3P and Ni phases. Chemical reduction from sulphuric bath results in more homogeneous Ni-P layers which 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 exothermic reaction with high heat evolution takes place during this step and that the sample becomes magnetic. In the second state Ni_7P_5 , Ni and sometimes Ni_5P_2 phases develop in the sample. After the third process Ni_3P can be detected.

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