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АННОТАЦИЯ

Изучался процесс кристаллизации в аморфных сплавах Ni-B и Ni-P, полученных химическим разделением методом дифференциальной калориметрии /DSC/, трансмиссионным электронмикроскопом /TEM/, измерением электросопротивления и измерением микротвердости нескольких быстроохлажденных с различных значений температур образцов. Слои были получены из водных растворов, содержащих или хлорид никеля /образец типа "Cl"/ или сульфат никеля /образец типа "S"/. Аморфная структура и процесс кристаллизации различны в образцах, полученных различными методами. Процесс кристаллизации слоев NiP типа "S" происходит в три стадии, а процесс кристаллизации слоев типа "Cl" более сложный, по всей вероятности из-за химических неоднородностей. Определена последовательность кристаллизации, образовавшиеся фазы были идентифицированы методом электронной дифракции.

KIVONAT

Kémiai leválasztással elõállitott Ni-B és Ni-P amorf ötvözetek kristályosodási folyamatait tanulmányoztuk differenciál scanning kaloriméterrel (DSC), transzmissziós elektronmikroszkóppal (TEM), elektromos ellenállás mérésével és néhány, különböző hõmérsékletrõl kvencselt minta mikrokeménységének mérésével. A Ni-P rétegek elõállitása vagy nikkel-kloridot - "Cl"-tipusu minták - vagy nikkel-szulfátot - "S"-tipusu minták - tartalmazó vizes oldatból történt. A különböző módszerrel elõállitott minták amorf szerkezete és kristályosodási folyamata különböző. Az "S"-tipusu Ni-P rétegek kristályosodása általában három-lépcsõs folyamat, ugyanakkor a "Cl"-tipusu rétegek kristályosodása bonyolultabb, valószinüleg a kémiai inhomogenitások következtében. Meghatároztuk a kristályosodási szekvenciát és a kialakult fázisokat elektrondiffrakciós módszerrel azonositottuk.

ABSTRACT

Crystallization processes of Ni-B and Ni-P electroless amorphous alloys have been studied by differential scanning calorimetry (DSC), transmission electron microscopy (TEM), electrical resistance measurements and by measuring microhardness on some samples quenched from different temperatures. The investigated Ni-P layers were prepared from aqueous solutions containing either nickel chloride - "Cl" - type samples - or nickel sulphate - "S" - type samples. Differences of the amorphous structures and of the crystallization processes were detected between the "Cl"- and "S"-type samples. Three well separated processes were found during the crystallization of the "S"-type Ni-P layers, whereas the crystallization processes of the "Cl"-type samples are more complicated, probably due to some chemical inhomogenities. The sequence of crystallization has been established and the nucleated phases were identified by electron diffraction measurements.

INTRODUCTION

It is well known that the amorphous layers produced by any type of deposition technique have a somewhat different structure than that of the rapidly quenched materials. It was shown by high resolution electron microscopy [1] that the deposited layers contain voids of some ~10 Å size, their formation may be connected with the deposition process. Besides that the degree of chemical heterogeneity is significantly higher in deposited layers than in splat-cooled alloys. These effects influence the structure and crystallization of amorphous layers as it is shown in the present paper reporting our work on chemically deposited Ni-B and Ni-P samples.

SAMPLE PREPARATION AND EXPERIMENTAL METHODS

The parameters of the chemical reduction of the Ni-B and Ni-P amorphous alloys are given in Table 1.

Sample	Ni-B	"Cl"-Ni-P	"S"-Ni-P
Nickel salt	$NiSO_4.7H_2O$ 40 mg/cm^3	$NiCl_2.6H_2O$ 15-30 mg/cm^3	$NiSO_4.7H_2O$ 20-40 mg/cm^3
Reduction with	$NaBH_4$ 0.5-1 mg/cm^3	$NaH_2PO_2.H_2O$ 15-25 mg/cm^3	$NaH_2PO_2.H_2O$ 20-30 mg/cm^3
Complex forming with	Sodium citrate 60 mg/cm^3	Sodium acetate 100 mg/cm^3	Sodium acetate 100 mg/cm^3
Stabilizator	100 g/m^3	2-4 g/m^3	2-5 g/m^3
Value of pH	11-12 with NaOH	4-5 with HCl	4-6 with H_2SO_4
Temperature	85 ^oC	91 ^oC	91 ^oC
B/P content	20-30 at%	10-15 at%	15-22 at%

The crystallization processes have been studied by a Perkin-Elmer DSC-2 differential scanning calorimeter, a JEOL 100-CX electronmicroscope and a calculator controlled four-probe resistance measuring system. The temperature scale of the "in-situ" TEM investigations was taken from DSC measurements.

RESULTS

In agreement with the literature [1] our electronmicroscopic investigations have shown (*Fig. 1*), that the deposited layers have a special structure containing voids. The formation of the voids is connected probably with the process of deposition from the solution. In *Fig. 2* we can see a model of the growth of the deposited layers proposed by Standinger and Nakahara [1].

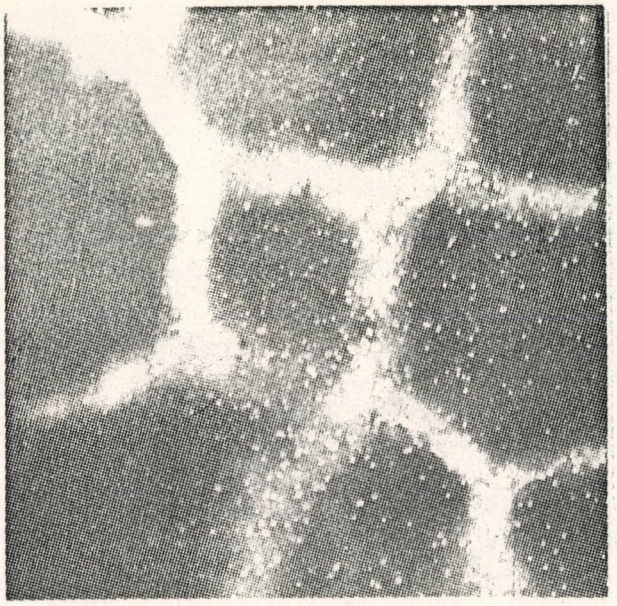


Fig. 1. Characteristic electron micrograph of an amorphous layer (16.4 at.% P). Voids are shown by arrows.

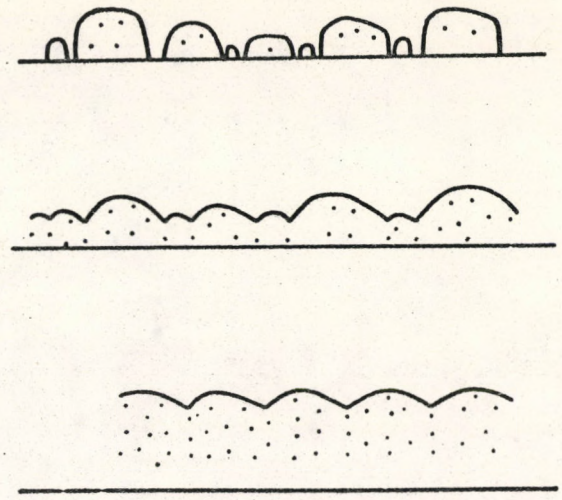


Fig. 2. The growth of the layers starts at different places simultaneously in an isotropic way. The contacting points of the half-spheres form loosely packed places, voids, marked by black points.

Ni-B system: The amorphous-to-crystalline transformation is a two-step process as it can be seen on the DSC thermograms *(Fig. 3)*. The structure of the amorphous state can be characterized by its selected area diffraction pattern which shows a diffuse ring at the position of the strongest line (111) of Ni as shown in *Fig. 4a*. After the first crystallization step Ni_3B+Ni phases were detected by TEM *(Fig. 4b)*, and after the second crystallization step the average diameter of the subcrystallites became larger and the diffraction patterns show *(Fig. 4c)* Ni_3B+Ni and NiB+Ni phases.

Ni-P system: The "Cl"-type samples have a very complicated multistage crystallization process as one can see on the DSC thermograms and the resistivity vs. temperature diagram as shown in *Fig. 5*. It is suggested that this behaviour of

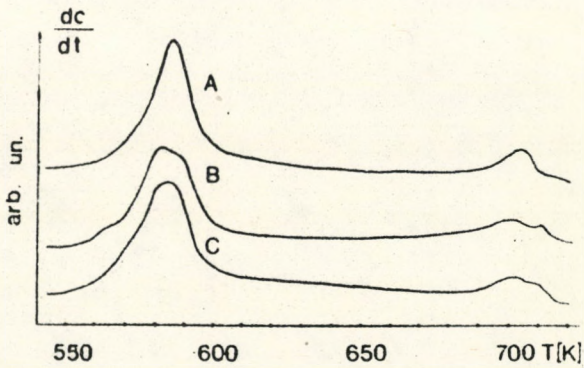
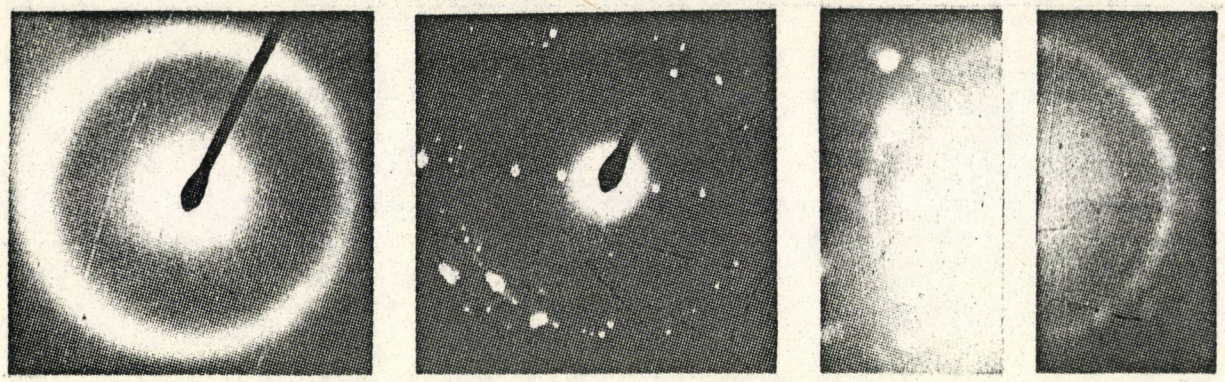


Fig. 3. DSC thermograms of three different Ni-B layers



a b c d

Fig. 4. Crystallization sequence of Ni-B alloys. Electron diffraction patterns of: a) amorphous stage, b) Ni_3B + Ni after the first step and c) Ni_3B + Ni, d) NiB + Ni after the second step of the transformation.

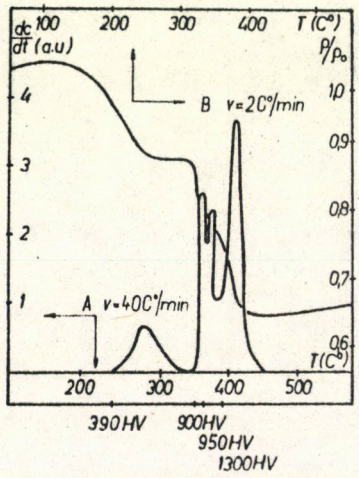


Fig. 5. DSC thermograms (A) and resistivity vs. temperature plots (B) of an amorphous Ni-P alloy (11.5 at%) obtained by chemical reduction from bath "Cl". Below we can see the HV values measured on the samples quenched down from the given temperatures.

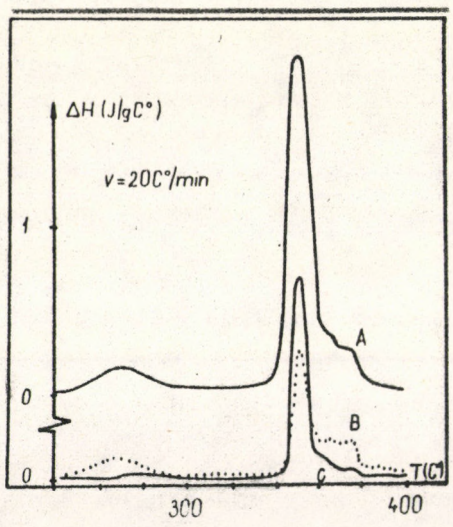
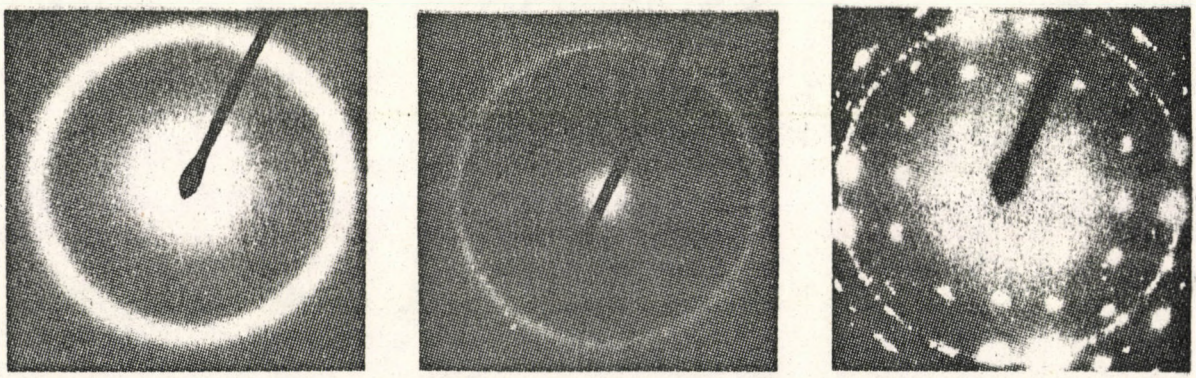


Fig. 6. DSC thermograms of an amorphous Ni-P alloy (10 at% P) chemically reduced from bath "Cl" for as prepared sample (A), for sample with solution side removed (B), for sample with substrate side removed (C).

the "Cl"-type samples is a consequence of an inhomogeneity between the sides toward the substrate and the solution. In order to make a decision in this respect, one side of a "Cl"-type sample and the other side of a second layer with the same nominal composition were ground and these samples were studied by DSC as shown in *Fig. 6*. It can be established, that in the case of "Cl"-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. There are however some common characteristics of the "Cl"-type samples: the selected area electron diffraction patterns of the amorphous state show a diffuse ring at the position of the strongest line (111) of Ni *(Fig. 7a)*. The onset of the crystallization process is at an unusually low temperature, near 200 ^{o}C, the first step of the crystallization is always accompanied by the occurence of Ni crystallites *(Fig. 7b)* and the final phases are Ni_3P + Ni *(Fig. 7c)*. The microhardness of the samples increases very much during the crystallization as it is shown in connection with Fig. 5. It is remarkable, that the increase starts already in the amorphous state.



a *b* *c*

Fig. 7. The common characteristics of transformation of the Ni-P alloys obtained by chemical reduction from bath "Cl" are: a) selected area diffraction pattern has only one diffuse ring, b) the diffraction pattern of Ni + amorphous can be observed by TEM after the first crystallization process, c) the diffraction pattern of Ni_3P + Ni are detected as final phases in every case.

The amorphous-to-crystalline transformation of the "S"-type samples is a three-step process according to their DSC thermograms and their resistivity vs. temperature plots as shown in *Fig. 8*. There are apparent correlations between the relative in-

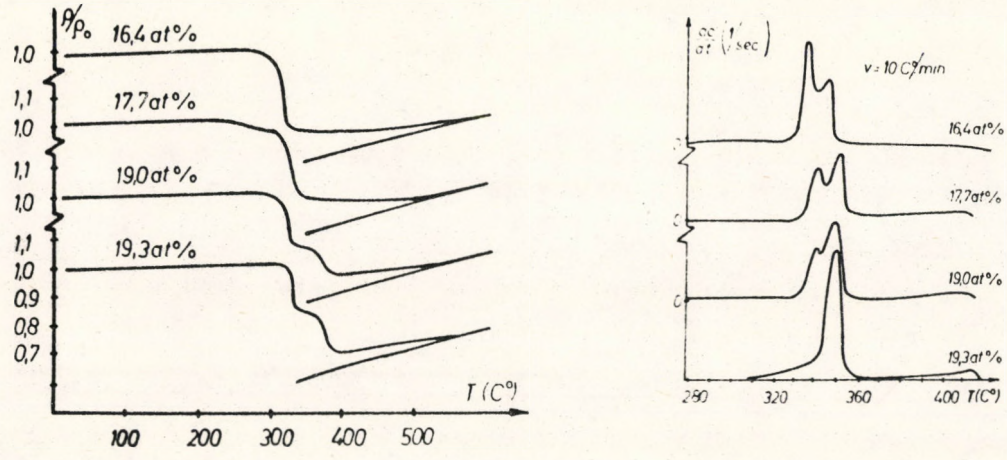
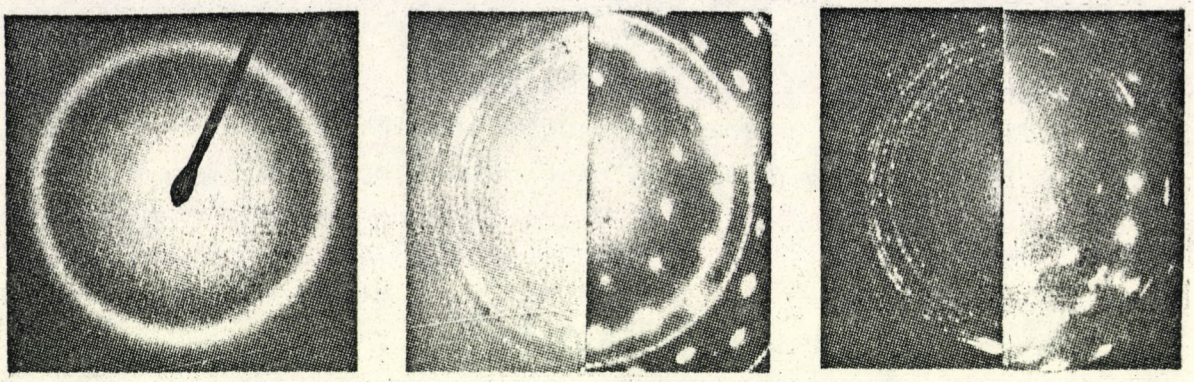


Fig. 8. DSC thermograms (A) and resistivity vs. temperature plots (B) of amorphous Ni-P chemically deposited from bath "S".

tensities of the three stages and the phosphorous content. In the amorphous state the diffraction patterns of the "S"-type samples are similar to those of the Ni-B and "Cl"-type systems, but in the case of some samples with larger phosphorus content another diffuse ring occurs at a position corresponding to 3.3 Å. It may be either a second neighbour distance, or the position connected with the first occuring line (220) of the Ni_5P_2 compound *(Fig. 9a)*. After the first stage TEM did not reveal the appearance of any crystalline phases, whereas there is an exotherm reaction with rather high heat evolution, a small change in the resistivity, and the samples became magnetic. These facts suggest that the first stage of crystallization can be considered as a development of Ni-rich clusters. The strength of the first stage decreases with increasing phosphorous content. After the second crystallization step Ni_7P_3 + Ni were detected and in the samples with higher phosphorous content Ni_5P_2 structure was also found *(Fig. 9b)*. After the third crystallization stage Ni_7P_3 + Ni and Ni_3P + Ni phases were identified *(Fig. 9c)* in agreement with the

literature [2], where the Ni_5P_2 + Ni ⟶ Ni_3P + Ni transformation was also observed. It is remarkable that the third transformation stage has not been observed in the samples where diffraction measurements do not detect the Ni_5P_2 structure.



a b c

Fig. 9. Selected area diffraction patterns of the phases observed during the transformation of the sample chemically deposited from bath "S": a) in amorphous state it has two diffuse rings, b) after the second crystallization step Ni_7P_3 + Ni and Ni_5P_2 + Ni phases can be detected, c) after the third crystallization step Ni_7P_3 + Ni and Ni_3P + Ni phases can be detected.

CONCLUSIONS

- The chemically deposited Ni-based amorphous layers have a characteristic microstructure containing a large number of voids which is probably a consequence of the deposition technique.

- The crystallization sequence of the Ni-B samples is the following: "a" Ni-B → Ni + Ni_3B → Ni + Ni_3B + NiB.

- The Ni-P samples deposited from bath "Cl" are characterized with a high chemical inhomogeneity, the gradient is perpendicular to the plane of the layer. Their thermal stability is very low, the complicated multistage crystallization starts near to 200 °C. The characteristic processes are the following: "a" $Ni\text{-}P_{"Cl"}$ → Ni + amorphous → intermediate stages → Ni+Ni_3P.

- The crystallization of Ni-P samples deposited from bath "S" is generally a three-stage process: "a" $NiP_{"S"}$ → "modified" → Ni + + Ni_7P_3 + Ni_5P_2 → Ni + Ni_7P_3 + Ni_3P.
  The main characteristics of the transformation from the "as-received" to the "modified" state are the following:
  a) significant heat evolution,
  b) the appearance of ferromagnetism,
  c) small, but well resolved changes in electrical resistivity,
  d) no crystalline phases can be detected by TEM.
  It is suggested that Ni rich clusters form in this stage.

At low P concentrations the Ni_5P_2 structure does not appear, and as a consequence no third transformation stage is detected.

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