COMPLEX INVESTIGATION OF EN Ni—P METALLIC GLASSES HAVING ANOMALOUS BEHAVIOR DURING LONG TIME ISOTHERMAL HEAT-TREATMENT**

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Abstract

An EN Ni—P layer consisting of two metallic glass components were examined after a short-time pre-heat treatment at 200°C, followed by a 5000-hour heat treatment at 160°C, then a 5-year relaxation at room temperature. X-ray diffraction, DSC, AES, and micro-hardness measurements were used in the study.

Our only surprising experience was that the metallic glass recrystallized fully only during the room-temperature relaxation.

1. Introduction

Ni—P (since 1985: EN nickel) coating, produced through chemical reduction from aqueous solutions (electroless) can be made from about 100 solutions of different compositions. Only 10 to 15% of solutions give an amorphous coating. One of these is the Kanigen^R procedure, which has been applied on an industrial scale since the 1960's. In 1980, out of 2000 EN nickel manufacturing companies in the United States, 1600 applied the Kanigen^R procedure, which yields an amorphous coating. Typical of industrial application are (according to 1979 data) [1]:

U. S. total industrial use of galvanic industrial Ni:	$ 495,000,000
use of EN—Ni:	$ 55,000,000

In Hungary the Kanigen^R procedure has been applied by Ganz MÁVAG since 1975 in the coating of diesel locomotives and of various machine parts to be exported to the West. The EN—Ni application began to develop in the period 1980—1988, which is shown by the increase in chemicals used for this procedure (without Ni), see Fig. 1 [2]. The share of individual industries in EN use is demonstrated in Table 1 [2].

Around 1985 three new areas of application began to develop rapidly: the manufacturing of laser-burnt memory disks needs a special EN nickel

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** Dedicated to Prof. J. Giber on the occasion of his 60th birthday.

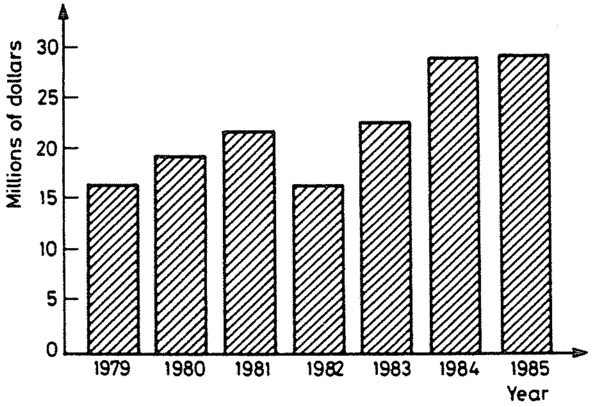

Fig. 1. Value of chemicals used to produce EN nickel [2]

Table 1

Percentage Use of EN by Industry [2]

Industry	1981	1983	1985
Aerospace	9%	9%	9%
Automotive	5	9	9
Electronics/computers	12	20	15
Food	5	4	5
Hydraulics	2	2	2
Machinery	10	8	8
Nuclear	5	5	5
Oil and gas production	9	3	4
Chemical production	2	2	3
Plastics	9	4	4
Power transmission	3	3	3
Printing	2	3	3
Pumps	4	4	4
Textile	2	5	5
Valves	6	134	15
Other miscellaneous	15	6	6
Total	Approximately 100%		

coating; another area is high-frequency shielding; finally, amorphous Ni—B coating can replace the gilding of disconnectable contacts in microelectronics.

Since 1980, Ni—P and Ni—B coatings have been handled together in literature and in statistics. Ni—B is in use mainly in Europe.

The literature on the examination of the peculiarities of amorphous Ni—P alloys separated by chemical reduction is fairly extensive. Suffice it to

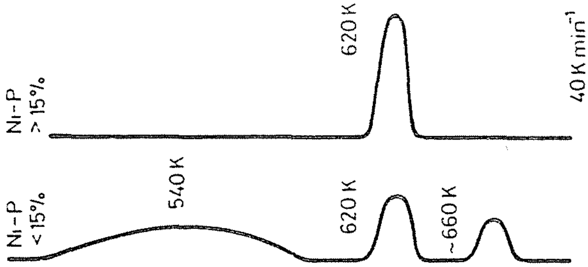

Fig. 2. Schemes of different DSC curves of Ni—P layers [3]

refer to a characteristic finding, already published in 1970 [3], saying that two amorphous types, which behave in different ways, can be separated by DSC (differential scanning calorimetry) measurements. Leaving out of consideration the flat maximum at low temperature, which is due to the Ni—P of low phosphorus content, some authors [4, 5, 6] describe only one crystallization maximum on the DSC curves, whereas others [3] suggest two crystallization maxima. E.g. Clements et al. [3] give the DSC curve shown in Fig. 2 for Ni—P $P<15$ at% and Ni—P $P>15$ at%. The authors have not found any relationship between the characteristics of the anions (chloride or sulphate) of the solution and the characteristics of the curves. The two maxima are explained by the formation of Ni—P solid solution and of Ni + precipitates. On the other hand, Cziráki et al. [6] have obviously found two maxima in

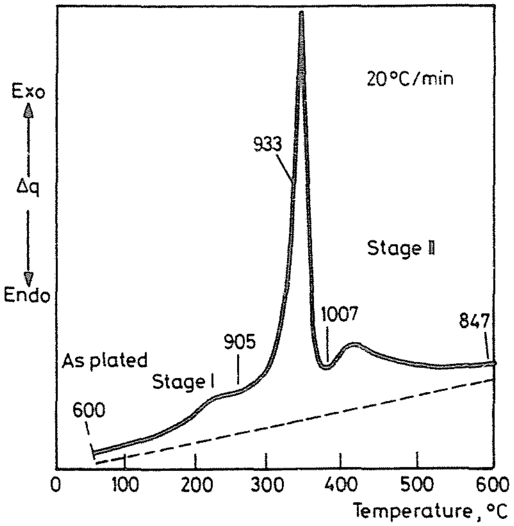

Fig. 3. Hardness data measured at different points of DSC curves [5]

the case of a layer deposited from the sulphate solution, and at the same time, electric transport changes have been found in the two maximum temperature range. Greval et al. [5] have measured HV hardness at various points of the DSC curve. As seen in Fig. 3, according to other authors, HV is 933—1097 at the solid solution crystallization point (Stage A); this value is in conformity with the hardness of the decomposition of the solid solution into $Ni + Ni_3P$. Cziráki et al. [6] have found a Ni_5P_2 transitional metastable phase at the decomposition of the solid solution, before the appearance of Ni_3P. Our electron diffraction investigations for layers deposited from chloride-containing solutions [7] have indicated the presence of two amorphous phases. The two amorphous phases of Ni—P amorphous alloys have also been found in the P = 10—25 at% range by Lahsmohre et al. [8]; they call this phenomenon polymorphism, which has also been proved with electric transport measurements made by Cote [9, 10] and Carini et al. [11].

2. Results

The present paper reveals our results for the Ni—P layers deposited from type 3 solutions (Table 2). The type 3 solution, often referred to in Hungarian literature as chloride-containing solution, is not a stabilized solution, only contains a complex forming agent. We have examined in situ the crystallization kinetics of type 3 Ni—P layers, using in situ TEM equipment (Fig. 4). First the metallic glass in conjunction with the external, weaker (dimmer) ring, seen in this figure, began to crystallize, and it is only following this, when this process is complete, that the crystallization of the metallic glass, forming the internal ring, of considerably higher intensity, begins. That is, two amorphous phases, consisting of metallic glass, are forming already in the process of the deposition of the layer. This direct observation of ours

Table 2

Composition and features of the type 3 solution

$NiCl_2 \cdot 6H_2O$	20g/l
$NaH_2PO_2 \cdot H_2O$	20g/l
Na acetate $\cdot 3H_2O$	50g/l
NaOH	to set pH
HCl	to set pH
optimum pH	4.5 – 5.0
T °C	90

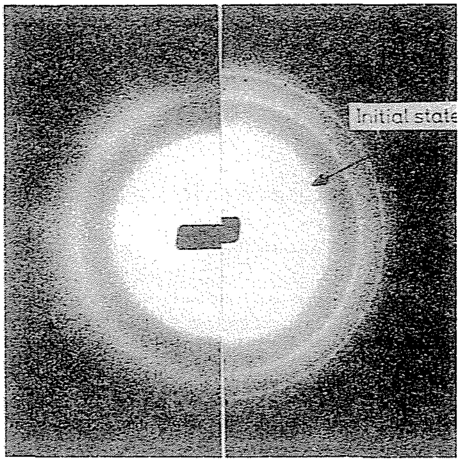

Fig. 4. In-situ electron diffraction pattern of the solution-side surface of a Ni—P amorphous layer (after deposition for hours). Taken by a Tesla BS 540 equipment

is in good agreement with the results of Cziráki et al. [6]. We also examined heat-treatment kinetics in the system consisting of two amorphous phases. As seen in Fig. 5, during the heating the crystallization starts in the external amorphous ring, this metallic glass being less stable than the other, and a microcrystalline structure develops. The grain growth phase is shown in Fig. 6, Fig. 7 indicates the decomposition of the solid solution.

The DSC measurements (Fig. 8) seem to confirm that the Ni—P metallic glass sample deposited from the type 3 solution was in a state of decomposition

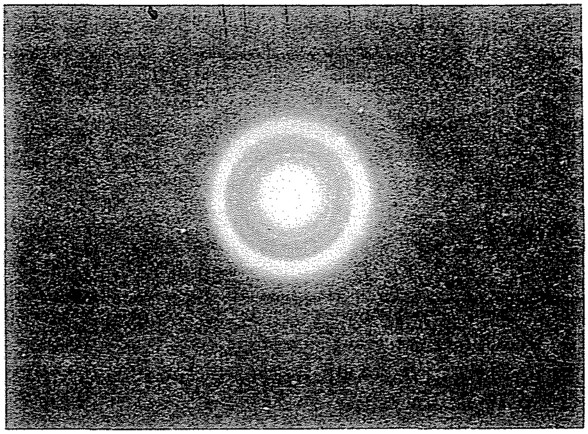

Fig. 5. Electron diffraction pattern of a sample exposed to a 40-min. heat-treatment at a temperature of 673 K. Phase 1: Fine grain structure in statistical distribution.
Phase 2: Amorphous

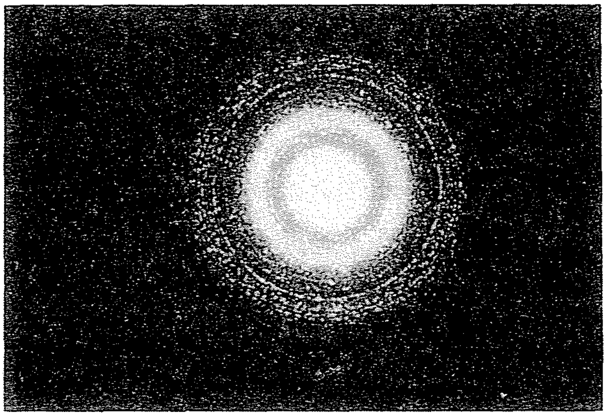

Fig. 6. Electron diffraction pattern taken after a 20-min. heat-treatment at 773 K

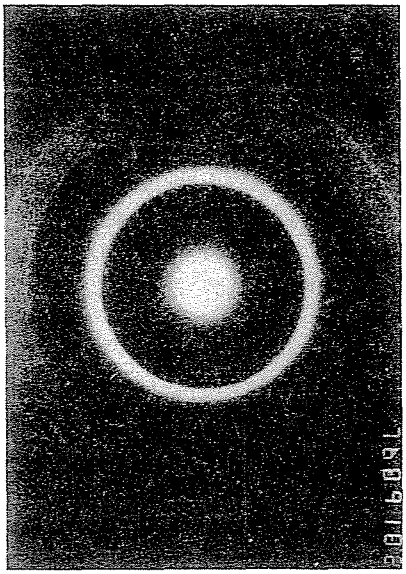

Fig. 7. Electron diffraction pattern of the microcrystallization of amorphous Ni—P. (Taken in a Jeol 100CX equipment.)

into two amorphous phases. As seen in this figure, the first maxima of the DSC curve are of the type which is typical of the deposition of the two amorphous phases, together with the two little maxima which occurred at 650 K and 670 K. It is to be noted that the deposition of the layer from the type 3 solution has a poor reproducibility. We show on Figure 9 DSC curves of a sample-series, all of the amorphous-state samples were deposited from chloride-containing solutions. The result that the metallic glass with the higher

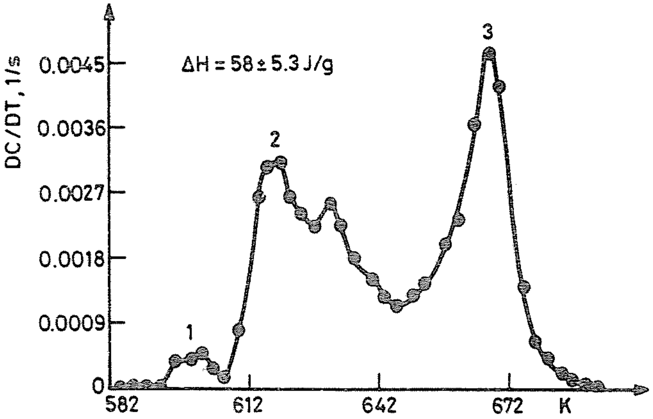

Fig. 8. DSC image of a Ni—P layer
1: solid solution; 2: two amorphous phases; 3: crystallization and decomposition. Taken in a Perkin differential scanning colorimeter

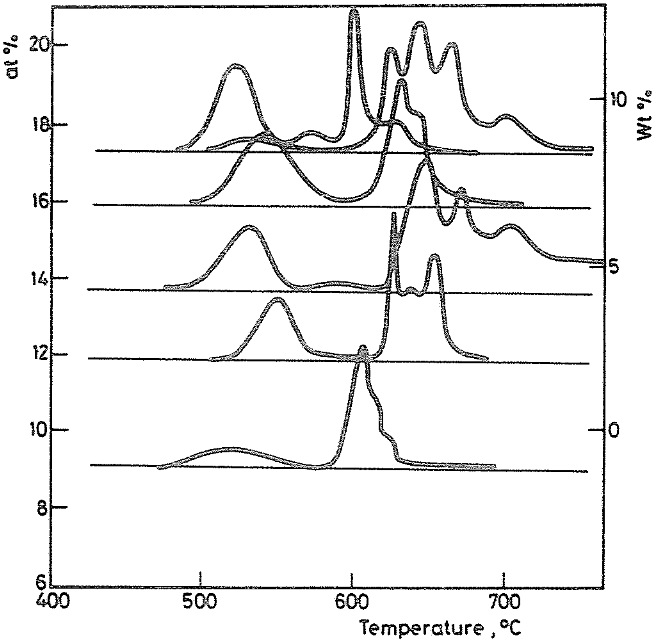

Fig. 9. Calorimetric curves of Ni—P layers deposited from a chloride-containing solution [10]

T_x value will transform first and the amorphous alloy with the lower T_x value is more stable, is difficult to explain. According to our general knowledge of amorphous alloys [12, 13], the opposite would be expected. The answer was indicated by a DSC curve taken on a layer where the Ni—P alloy was deposited from the type 3 solution during the bubbling process. The bubbling process caused the T_x value to drop from 359°C to 328°C (at a 5 K/min. heating rate), the original maximum, around 340°, of the curve to disappear, the area under the curve to largely decrease and the second maximum to disappear.

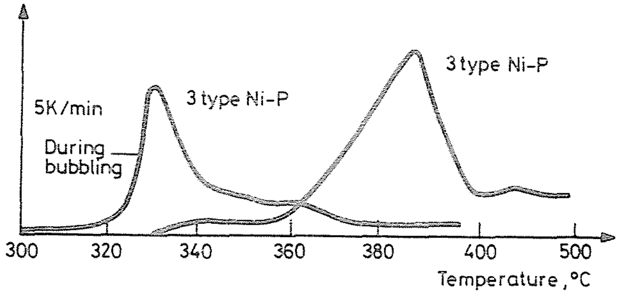

Fig. 10. DSC curves of a Ni—P layer deposited from a chloride-containing solution during bubbling

So the evaluation of our results of the DSC measurements indicates that two amorphous phase-containing Ni—P layers deposit from the type 3 solution.

A series of microhardness measurements was also performed, both on the initial sample and after the multi-stage heat-treatment and storage for a long time. The results of microhardness measurements are shown in Table 3 and Fig. 11.

Table 3

Results of microhardness tests

Sample	State of sample		HV 1983	HV 1988	HV%
3	original (3/1)		485	565	+16.9
	473K for 2 hrs		605	674	+11.4
	original 433K for	500 hrs	420	845	+101.1
		1000 hrs	460	550	+19.5
		2500 hrs (3/2)	465	823	+76.9
	473K+433K	500 hrs	702	1220	+73.7
		1000 hrs	565	1074	+90.0
		2500 hrs	573	1334	+132.8
		5000 hrs (3/3)	550	1285	+133.6
	Bubbling: original		353		
	Bubbling: original for	5000 hrs	494	449	−9.1
	Bubbling: +473K		362		
	Bubbling: +473K for	5000hrs	456	493	+8.1

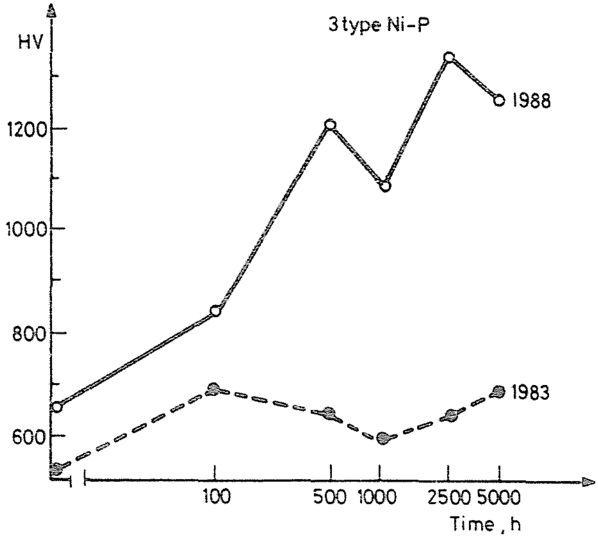

Fig. 11. Change in micro hardness in case of different heat-treatment of Ni—P layers at room temperature between 1983—1988

According to the literature, the value of HV = 600 characterises the crystallization of a solid solution, while HV = 1000 indicates decomposition [5]. Our results confirm these observations. According to the tabulated data in Fig. 11, after a two-stage heat-treatment (for 5000 hours at 160°C), the X-ray diffraction pattern of the metallic glass indicates a micro-crystalline

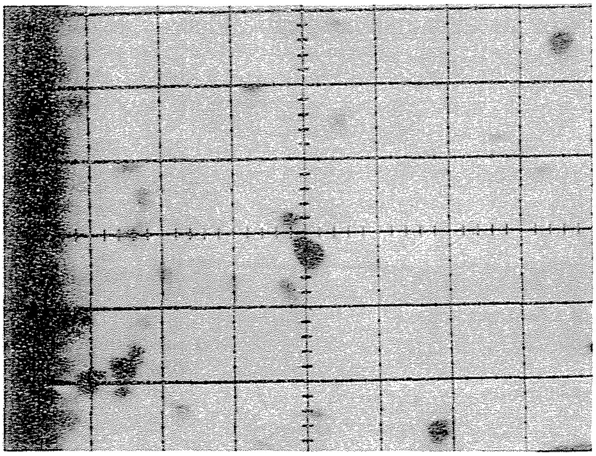

Fig. 12. Absorbed current pictures (ABS) made of the surface of an amorphous Ni—P alloy sample (enlarged 40 ×). Measurements have been carried out in a PHI 545A instrument. (primary electron beam energy: 5 keV, current: 1 μA, angle of incidence: 30° to the surface normal, mean diameter of the beam on the surface: 15 μm)

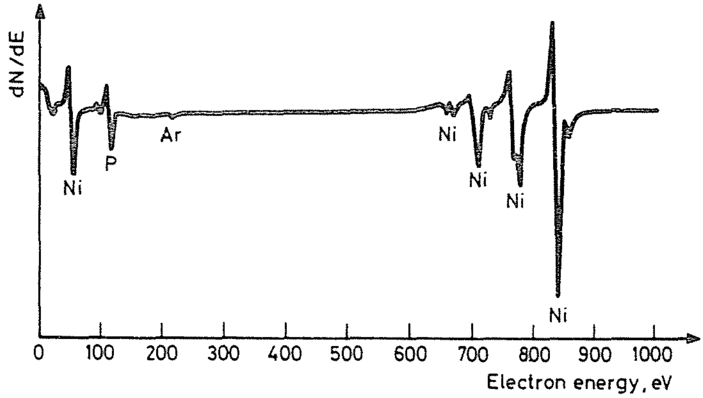

Fig. 13. Auger spectrum of an amorphous Ni—P alloy sample (homogeneous area)

condition, instead of an amorphous one. It is likely that after a 2-hour heat-treatment at 200°C such changes begin (atomic shifts), which continue at room temperature, during the storage for a long time, and lead to the transformation of the solid solution.

On the picture (Fig. 12) of the AES (absorbed current pictures) demonstrating the topography of the surface of the initial-state Ni—P sample (denoted 3/1) deposited from the type 3 solution, 10—100 μm size surface inhomogeneities (darker and lighter spots) appear. The AES spectra of a homogeneous surface area is shown in Fig. 13, and the AES spectrum of a 100 μm inhomogeneity is shown in Fig. 14. The Ni content of the inhomogeneity is only 51 at%, while that of the homogeneous surface is over 80 at%. During the grain growth of metallic glasses, great differences can be produced in the

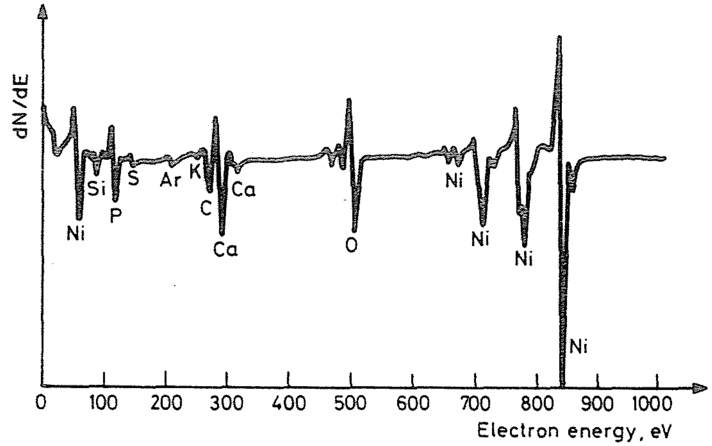

Fig. 14. Auger spectrum of an amorphous Ni—P alloy sample (inhomogeneity)

Table 4

Elemental surface composition of amorphous Ni–P samples determined from AES spectra

Sample	Sputtering depth (nm)		Elemental composition (at%)						
			Ni	P	C	O	S	K	Ca
3/1	25	homog. surf.	88.2	11.8	—	—	—	—	—
		inhomogeneity	51.8	6.3	12.6	13.0	0.7	—	11.8
3/2	25	homog. area	88.3	7.4	2.7	1.5	—	—	—
		inhomogeneity	49.0	4.5	27.0	5.4	1.9	1.0	10.6
	50	homogenous area	88.7	9.1	—	2.2	—	—	—
3/3	25	homog. area	85.0	4.9	5.5	4.3	—	—	—
		inhomogeneity	58.0	3.8	33.0	5.1	—	—	—
	50	homogenous area	91.0	7.1	—	1.9	—	—	—

concentration of the solution, which may be responsible for the detected variations in the local Ni concentration. Table 4 contains the result of AES investigations of different heat-treatments and after storage for a long time. As seen in this table, the contamination content of layers close to the surface will increase with heat-treatment, including that of the homogeneous areas, which is a direct result of the diffusion toward the surface, described by several authors. The heat-treatment causes, on the one hand, a surface-directed diffusion and, on the other hand, an oxidation process. The value of the P/Ni ratio also changes, it will decrease from 0.13 to 0.06, in a sequence of $3/1 > 3/2 > 3/3$; that is, the phosphorus content of layers close to the surface decreases. Very important is the result that the amount and size of the inhomogeneities on the surface of samples also change. The amount and size of the inhomogeneities decrease in a sequence of $3/1 > 3/2 > 3/3$. In the rest of inhomogeneities the degree of Ni impoverishment does not change substantially. The decrease in the amount and size of inhomogeneities indicates that the distribution of the Ni and P concentrations becomes more even.

3. Discussion

The overall results of the amorphous Ni—P layer consisting of two amorphous phases and deposited from non-stabilized solutions can be summarized as follows.

The simultaneous presence of the two amorphous phases has been indicated both by the electron diffraction patterns and the DSC measurements.

The in-situ electron diffraction has clearly shown the different crystallization of the two amorphous phases.

According to the X-ray diffraction patterns, the structure of the amorphous metallic glasses becomes microcrystalline — after a heat-treatment at 200°C, usually applied in manufacturing [4] and after a 5000 hour heat-treatment following the original state. The microcrystalline texture is a Ni—P solid solution.

After a natural ageing at room temperature for 5 years, a great difference in the HV% was found between the samples exposed to a 2-hour preliminary heat-treatment done at 200°C and those samples not exposed to such a treatment. While the HV increase of the original samples and that of the samples exposed to a 2-hour preliminary heat-treatment at 200°C was less than 20%, the HV hardness of samples exposed to heat treatment for different times at 160°C or those naturally aged for 5 years showed a minor increase, and the HV hardness of samples exposed to a 200°C preliminary heat-treatment or a 160°C heat-treatment for a long time showed a major increase during the natural ageing process. In the case of the last group, an HV increase of +70—+130% has been found, which indicates the decomposition of the solid solution into $Ni+Ni_3P$.

According to AES investigations the low-temperature long-time heat-treatment caused the external surface layer of EN nickel to reduce in P, which is in contradiction with Lubovsky [15], who reported a strong surface P enrichment at 110°.

Impurities will also increase in the surface layer, in agreement with the results of Suzuki et al. [16] of AES investigations carried out after a short-time exposure to electron beams at 133°C.

The AES measurements also demonstrated the oxidation of the surface, which also applies to the impurities.

The development of the microcrystalline state as well as the decomposition of the solid solution goes with homogenization, which is supported by AES tests (i.e., a decrease in the amount and size of inhomogeneities), which confirms our suggestion as to the cause of the HV change.

Acknowledgement

The authors are deeply indebted to Prof. Dr. J. Giber who did firstly Auger spectroscopy investigation on EN Ni—P amorphous layers and emphasized the importance of information obtained in this way.

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