
MODELING OF THE SHORT-RANGE STRUCTURE IN Ni—P ALLOYS

O.S. BASKEVICH, O.M. GULIVETS, V.O. ZABLUDOVSKY

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Lazaryan National Dniepropetrovsk University of Railway Transport
(2, Academician Lazaryan Str., Dniepropetrovsk 49010, Ukraine)

The local atomic structure of amorphous and nanocrystalline Ni—P alloys obtained by the pulsed electrodeposition method has been studied. The model describing the structure of alloys of such kinds is proposed, as a result of the combined analysis of the atomic radial distribution function (ARDF) and the simulated diffraction peak profiles of structural factors.

Introduction

Amorphous and nanocrystalline films display unique physico-chemical properties due to peculiar features of their short-range structure. For this reason, the interest in studying these kinds of materials has continued to grow [1–4]. The structural investigation of the transition metal — metalloid amorphous alloys, mainly aimed at understanding of the features of the short range order formation, can be efficiently carried out by means of the simulation of the structure of a modified ARDF and the examination of the experimental structural factor [5–8]. The comprehension of a local structure makes it possible to establish a relation between the structural features of amorphous alloys and their physical properties. The investigation of the structure of amorphous and nanocrystalline alloys, however, is a rather complicated task. Thus, the known methods of processing the data of X-ray studies need to be improved. To date, the features of a short range arrangement in Ni—P amorphous alloys have been investigated very poorly. In this work, the results of the studies of a local atomic arrangement in the Ni—P amorphous alloys are presented, which are based on the results of X-ray diffraction measurements.

Experiment

Ni—P alloys were prepared by means of the electrodeposition method from a sulfuric nickel solution admixed with sodium hypophosphate. X-ray diffraction measurements, whose results were subsequently used for both the phase composition determination and the short-range structure simulation, were made on a

DRON-3.0-IBM automated experimental complex in monochromatic $\text{CuK}\alpha$ and $\text{MoK}\alpha$ radiations (a Li convex monochromator) in the step-scan mode with a step of 0.1° and the counting time of no less than 100 s per data point. To accumulate the data for statistical processing, no less than five diffractograms were taken for each sample with the following averaging of the scattering intensity curves. The elemental composition was determined on VRA 20 and VRA 30 X-ray spectrometers by means of the measurements of the intensity of analytical $K\alpha$ lines for nickel (35 kV, W—anode) and phosphorus (35 kV, Rh—anode).

Results and Discussion

The studies performed have shown that the structure of Ni—P amorphous alloys depends on the deposition regimes, composition of electrolyte solutions, and conditions of the migration of constituent ions in the process of deposition. The formation of the regions of ordered arrangement of atoms (ROAA) or clusters depends on a number of factors predetermining the conditions of the chemical bond formation. The extremely high cathode voltage during the pulse current deposition process gives rise to an increase in the velocity of deposited atoms. This makes the atoms be located in the places which not necessarily correspond to equilibrium positions. As a result, the changes in the energy of the interatomic interaction occur, which leads to the formation of a structure that is far from the ideal crystalline one.

To comprehend the structure of Ni—P amorphous alloys, it is necessary to understand a manner of the ROAA mutual allocation as well as a character of the atomic arrangement within the clusters and on their boundaries. The only way to achieve the sufficient degree of accuracy in the ripton of the structure of amorphous alloys is the combined analysis of the modified ARDF and the structural factor.

A profile of a diffraction maximum is determined from the relation [8]

$$I(s_0) = \frac{Q_2 Q_3}{d_{hkl}} g(L) \exp\left(-\frac{\delta^2 s_0^2}{2}\right) \int_{-\infty}^{\infty} V(t) \cos(s_0 t) dt, \quad (1)$$

where Q_2 and Q_3 are the coefficients accounting for the influence of three-dimensional oscillations of atoms on the diffraction patterns (for the FCC structure, Q_2 and Q_3 equal 0.9544 and 0.9654, respectively) [7], $g(L)$ is a function of the ROAA distribution in size, and δ is the coefficient that accounts for the static and dynamic root-mean-square (rms) deviations of atoms from the equilibrium positions [8].

The normalization of the scattering intensity was carried out according to the procedure described in [9]. After this, the modified ARDFs were calculated from the structural factors of $\text{Ni}_{85.5}\text{P}_{14.5}$, $\text{Ni}_{88}\text{P}_{12}$, and $\text{Ni}_{89.5}\text{P}_{10.5}$ amorphous alloys.

As is seen from Fig. 1, the films studied have different degree of amorphousness, and this is reflected in a growth of the height of the first peak and the appearance of a fine structure on the following ones.

ARDFs were calculated according to the formula

$$G(r) = 4\pi\rho_0 r + \frac{2}{\pi} \int_0^{s_{\max}} [i(s) - 1] s e^{-\alpha s^2} \sin(s_0 r) dr, \quad (2)$$

where ρ_0 is the average atomic density, s is a current value of the reciprocal lattice vector, $i(s)$ is the current value of the structural factor, α is the correction factor determined according to [9], and σ_m is the rms relative displacement of atoms of the m -th coordination sphere from the equilibrium positions [9].

The symmetric properties of the ARDF peaks attract a considerable attention, and there have been a number of specific investigations considering various methods of separation of the first ARDF peaks. If we reject the assumption that atoms of the second coordination sphere can penetrate into the first one not deeper than a position of the first peak maximum, we should also refuse those methods of the ARDF decomposition, which are grounded on the utilization of visual data obtained upon the ARDF investigation. In fact, the ARDF correlation peaks have a finite width which is determined by the temperature dependent rms relative displacements of atoms.

In this work, a fitting of the ARDF curves was performed according to the procedure described in [10–

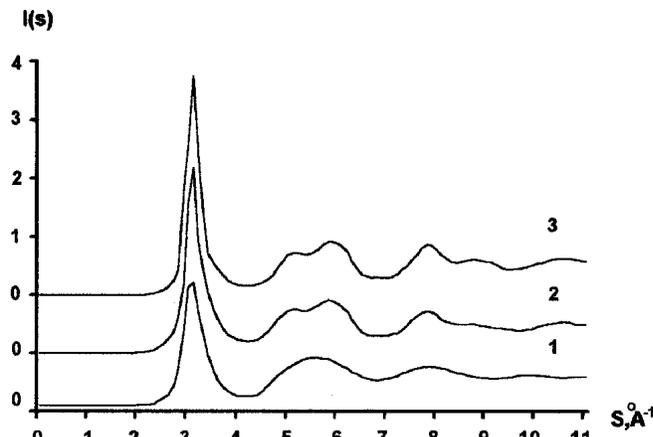


Fig. 1. Structural factors for $\text{Ni}_{85.5}\text{P}_{14.5}$ (1), $\text{Ni}_{88}\text{P}_{12}$ (2), and $\text{Ni}_{89.5}\text{P}_{10.5}$ (3) alloys

[13], i.e. by means of the approximation of a curve with the set of peaks and the introduction of a second exponential term in order to fulfill the following conditions for the ARDF: $G(r) = G(-r)$, $G(0) = 0$. Under such conditions,

$$G(r) = \sum_m \frac{Z_m (r + 2r_m \alpha / \sigma_m^2)}{\sqrt{2\pi\sigma_m (1 + 2\alpha/\sigma_m^2)^{3/2} (r_m^2 + \sigma_m^2)}} \times \left[\exp\left(-\frac{(r - r_m)^2}{2\sigma_m^2 + 4\alpha}\right) - \exp\left(-\frac{(r + r_m)^2}{2\sigma_m^2 + 4\alpha}\right) \right], \quad (3)$$

where r_m is the most likely radius of the m -th coordination sphere, Z_m is the coordination number of this sphere, σ_m is the rms relative displacement of atoms from the equilibrium positions, and α is the correction factor.

It is known that a shape of the ARDF peaks depends on a value of the decay coefficient chosen. That's why the correction factor was picked out as carefully as possible to allow the more accurate fitting of a short-range structure. The following values of the correction factor were used: $\alpha = 0.01, 0.02, 0.03, 0.05$.

Table 1 presents the results obtained upon the fitting of the curves depicted in Fig. 2. It is noteworthy that the radii of the coordination spheres with numbers 1–9 are close to those corresponding to the FCC structure [10], and this correlates with the arrangement of atoms in the crystalline nickel. Intermediate coordination spheres reflect the distribution of inhomogeneities in the Ni–P alloys and that of the separate atoms of nickel and phosphorus on the ROAA interfaces.

The symmetric decomposition of the ARDF peaks shows that the structure of the ordered regions is sufficiently close to the FCC crystal structure of the

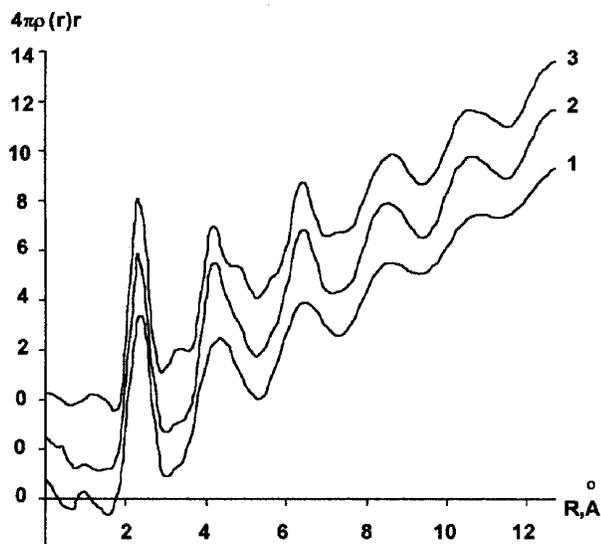


Fig. 2. Modified ARDFs for Ni—P alloys. Designations are the same as in Fig. 1

parent metal, although there exists a considerable deviation of some coordination numbers from those of the ideal FCC crystal. This fact may be interpreted as originating from the gaps which, being located between ROAA are chaotically filled up with nickel and phosphorus atoms and don't form any ordered structure [14]. A probability that they can form an ordered structure is less for the atoms filling the gaps than for those which belong to the ROAA [15]. The effect which is observed on a reduction of the phosphorus content can serve as a confirmation of this assumption. In this case, the ROAA dimensions are expected to increase, and the gaps between them should decrease, as a result of the formation of phosphide compounds from nickel and phosphorus atoms. As follows from the diffractograms of the Ni—P alloy (Fig. 3), it is this effect that occurs in the course of isothermal annealing. It is seen from the figure that the diffraction

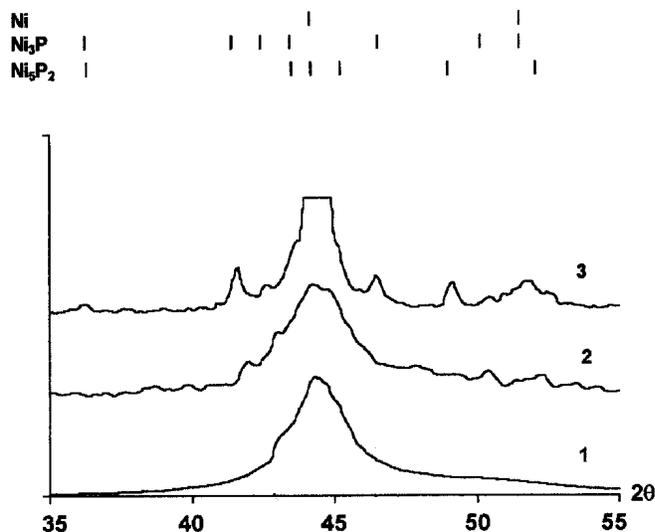


Fig. 3. X-ray diffractograms ($\text{CuK}\alpha$ radiation) for Ni—P alloy annealed at temperatures 573 K (1), 673 (2), and 773 (3)

maxima, which are observed upon the increase of temperature up to 773 K, correspond to the structures of Ni, Ni_3P , and Ni_5P_2 . The positions of the diffraction peaks for the Ni, Ni_3P , and Ni_5P_2 reference samples, which have the cubic, tetragonal, and hexagonal crystal lattices, respectively, are shown in the upper part of the figure.

These results form a firm foundation allowing us to suggest the most prevalent ROAA shapes, which make it possible to describe a short-range structure similar to FCC [7, 9]. Basing on the assumptions made, it was established that the profile of a diffraction peak is determined by a number of factors, namely, by a shape and dimensions of the ordered regions, ROAA distribution in size, degree of cluster \rightarrow ordering, orientation of the regions of short-range ordering relative to the crystal lattice, and rms displacements of atoms from the equilibrium positions.

Table 1. Structure refinement data for Ni—P alloys derived from the ARDF analysis

No.	FCC		$\text{Ni}_{89.5}\text{P}_{10.5}$			$\text{Ni}_{88}\text{P}_{12}$			$\text{Ni}_{85.5}\text{P}_{14.5}$		
	(r_n/r_0)	N	r_n	(r_n/r_0)	N	r_n	(r_n/r_0)	N	r_n	(r_n/r_0)	N
1	1.000	12	2.4605	1.000	11.735	2.4562	1.000	11.711	2.4381	1.000	10.4253
2	1.414	6	3.4134	1.387	2.4558	3.4135	1.398	2.8442	3.4412	1.411	5.7822
3	1.732	24	4.2560	1.729	22.721	4.2484	1.731	22.113	4.2483	1.742	17.6178
4	2.000	12	4.9062	1.994	15.449	4.9309	2.009	17.175	4.8762	2.000	15.2246
5	2.236	24	5.5806	2.268	14.265	5.5419	2.258	9.9868	5.5164	2.262	17.9125
6	2.449	8	5.9838	2.431	6.9410	5.5112	2.408	7.147	6.0010	2.461	1.3202
7	2.646	48	6.4791	2.633	46.920	6.4594	2.632	47.134	6.4365	2.639	47.9443
8	2.828	6	6.9038	2.806	5.937	7.0000	2.852	3.2628	6.6577	2.730	4.8893
9	3.000	36	7.3659	2.993	35.051	2.9967	2.996	35.603	7.3511	3.015	36.022
10	3.162	24	—	—	—	—	—	—	7.0002	2.461	0.9992

Table 2. Dependence of the short-range order parameters of Ni—P alloys on the phosphorus content

Alloy	ROAA shape	a , nm	Δa , nm	δ^2 , nm ⁻²	Z , nm	L , nm	ΔL , nm	$\langle N \rangle$	E , %
Ni _{85.5} P _{14.5}	octahedron	0.3458	0.0312	0.0110	0.1268	1.878	0.121	90	7.825
Ni ₈₈ P ₁₂	octahedron	0.3486	0.0332	0.0115	0.1075	2.326	0.132	140	5.654
Ni _{89.5} P _{10.5}	octahedron	0.3519	0.0385	0.0119	0.9248	4.505	0.135	256	3.856

Designations: a and Δa are the lattice parameter of the elementary cell and the absolute error of its determination, respectively, Z — mean value of the gap between ROAA, δ^2 — rms displacements of atoms from the equilibrium positions, L and ΔL — mean size of ROAA and the error of its determination, respectively, N — number of atoms in ROAA, E — measure of the inaccuracy of the approximation of the diffraction peak profile.

In this work, for a reliable description of both the atomic structure and ROAA shape, we concentrate on the analysis of two maxima of the structural factor of the amorphous matter, using expression (1). For the structures close to FCC, the reflections from (111) and (200) crystallographic planes were used to calculate the profiles of the corresponding patterns for various shapes of ROAA.

Table 2 presents the structure refinement parameters for Ni—P alloys, with the phosphorus content being a parameter.

ARDF data show that the films contain the stable and isolated octahedral ROAA, whose atomic crystal ordering and density are close to those of the crystalline nickel. As the phosphorus content decreases, the ROAA size grows, interatomic distances decrease, and this results in a decrease of the gaps between clusters.

Conclusions

1. The analysis of ARDF as well as the simulation of the profiles of the diffraction peaks of structural factors, both performed simultaneously, allow making a conclusion that the short-range order in the Ni—P amorphous alloys is of the cluster type. Nickel atoms form octahedral-shaped ROAA with a structure close to FCC, with the gaps between the ROAA being filled with the disordered atoms of nickel and phosphorus.

2. It is shown that the procedure proposed is suitable for the analysis of the features of the short-range atomic arrangement in other two-component amorphous alloys.

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МОДЕЛЮВАННЯ СТРУКТУРИ БЛИЗЬКОГО ПОРЯДКУ В СПЛАВАХ Ni—P

О.С. Баскевич, О.М. Гулівець, В.О. Заблудовський

Резюме

Досліджено локальну атомну структуру аморфних та нанокристалічних сплавів Ni—P, отриманих методом імпульсного електроосадження. За результатами спільного аналізу радіальної функції розподілу атомів і моделювання профілів дифракційних піків структурних факторів запропоновано модель будови аморфних та нанокристалічних сплавів Ni—P.