

phys. stat. sol. (b) **176**, K63 (1993)

Subject classification: 61.30 and 72.15; S1.62

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Microstructure of Ni–P Alloys and Its Effect on the Resistivity

By

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Introduction Recently there has been increasing attention to glassy metallic materials. Their study reveals many interesting phenomena which are not present in the crystalline metals.

It is well known that the amorphous alloys can be classified into two large groups. The first group is characterized by the “metallic” temperature dependence of the electrical resistivity, i.e. by a positive temperature coefficient, while the second one is characterized by a negative temperature coefficient. It was shown [1, 2] that these groups differ in the value of the residual resistivity, too, since for the alloys of the first group $\rho < 150 \mu\Omega \text{ cm}$, for the second group $\rho > 150 \mu\Omega \text{ cm}$.

We have calculated the specific resistivity of some Ni–P alloys, [3], finding that $\text{Ni}_{85}\text{P}_{15}$ belongs to the first group with $\rho_0 = 104 \mu\Omega \text{ cm}$, and $\text{Ni}_{75}\text{P}_{25}$ to the second with $\rho_0 = 175 \mu\Omega \text{ cm}$. These data are in fair agreement with the experiments, and substantiate Mooij’s correlation concept [1]. The alloys have resistivity–temperature coefficients corresponding to their grouping.

The object of our present note is to investigate the microstructure of the above two alloys with molecular dynamics (MD) calculations, and to search for differences which may be regarded as the fundamental cause of the above behaviour.

Results In the molecular dynamics calculation (for details, see elsewhere [4, 5]) we work in a micro-canonic assembly (constant volume, energy, and number of particles in the system), containing 256 particles. This system was heated first to 2000 K, then cooled to 1600 and 300 K. The radial partial distribution function and the polyhedral arrangement for every atom were calculated for both temperatures after 10000 steps each. For the polyhedral environment we assumed every atom to be central, and the radii connecting this atom with its nearest neighbours were bisected with planes. These planes form the so-called Voronoi polyhedra, [6]. The designation of the polyhedra is the customary one, i.e. $n_3n_4n_5n_6 \dots$, where n_k denotes the number of polygons (which are the faces of the given polyhedra), having actually k vertexes. In general the denotation by k is not used, and only the position of the number in a row indicates the given polygon. (For example, the denotation 0608 means that the given polyhedron actually has 0 triangle, 6 quadrangles,

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0 pentagon, and 8 hexagons. This is actually the well-known b.c.c. unit cell (Wigner-Seitz cell).)

The electrical resistivity in the coherent scattering picture (perfect long-range order (LRO)) is well phonon-dependent [7], but in the incoherent scattering limit it is determined by the phase shifts at the Fermi surface [8] and in the amorphous case (short-range order (SRO) dominance) it depends on the partial structure factors $S(q)$ [9]. Mostly $S(q)$ is determined by the Percus-Yevick equation for the hard-sphere model [10] and the temperature dependence is considered only as a change in the packing coefficient, neglecting the temperature dependence of the hard-sphere radii [11]. Based on these assumptions the temperature dependence of the temperature coefficient of resistivity (TCR) had been calculated [11], and the sign change at a definite composition in the Ni-P system is correctly obtained. This calculation was done by the extended Ziman theory for liquid transition metals [12] which seems to be successful to describe the electron transport in amorphous alloys as well.

Discussion Our present study focuses on the microscopic behaviour of the structure observing remarkable differences between the compositions having opposite sign of TCR.

The first inspection of the result obtained by the Voronoi analysis (Table 1) shows that the number of icosahedral and Archimedean antiprism polyhedra is roughly the same in both alloys. B.c.c. type polyhedra (0608) are almost entirely lacking. The difference in the two compositions is most manifest in the number of the destroyed b.c.c. type (036X) and (044X) polyhedra (where X is the number of the hexagons in the given polyhedron), and this can be different, slightly distorting the regular b.c.c. (0608) and/or f.c.c. (00120) Wigner-Seitz cell. (Some examples of different polyhedra are shown in Fig. 1.)

The characteristic difference between the Voronoi analysis of the two investigated compounds is obvious from Table 2: the number of the b.c.c.-like polyhedra is approximately doubled in the smaller phosphorus concentration alloy. The 'normal' temperature dependence of resistivity (growing resistivity with increasing temperature) is observed in the material which realizes much more LRO arrangements than its 'non-normal' counterpart.

Table 1

Calculated distribution of Voronoi polyhedra in the investigated compounds ($T = 300$ K)

compound		dodecahedral 00120	Archimedean antiprism 028X *)	distorted b.c.c. like		b.c.c. 0608
				036X *)	044X *)	
in Ni ₈₅ P ₁₅	Ni	22	23	19	10	1
	P	13	37	24	5	0
	in average	21	25	20	9	1
in Ni ₇₅ P ₂₅	Ni	29	23	10	2	0
	P	9	33	14	2	0
	in average	24	26	11	2	0

*) $0 \leq X \leq 8$.

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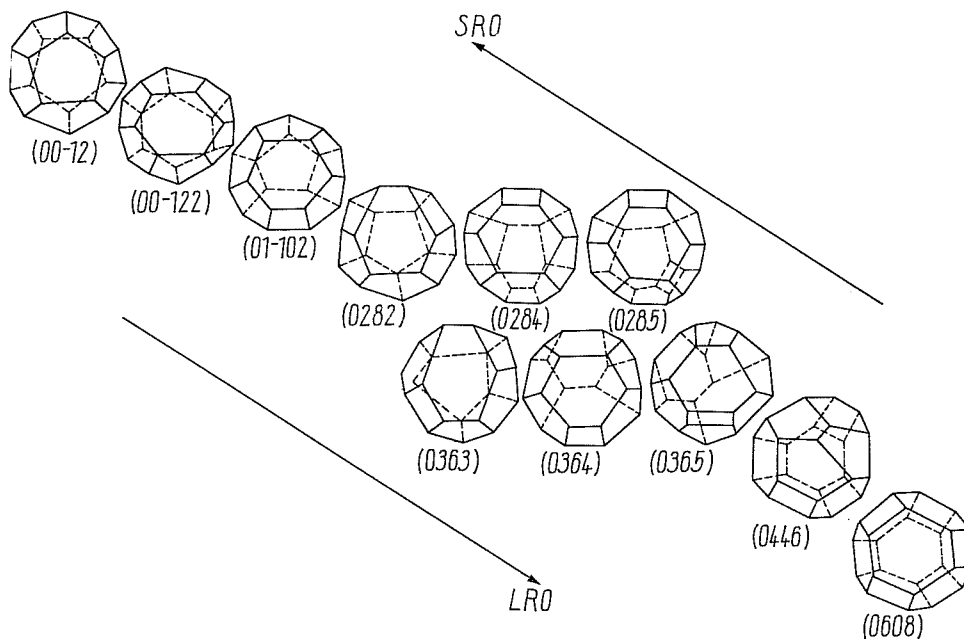


Fig. 1. Examples of Voronoi polyhedra. The enhancement of the long-range order (LRO) and oppositely the gain of short-range order (SRO) is indicated by arrows

The mechanism of the growing electric resistivity with temperature in a crystalline alloy is obvious, so the composition having a mass of the polyhedra characteristic of long-range order can be regarded as a modification of the standard crystalline case, so the normal (positive) TCR has to be expected and obtained. Our conjecture is that if the proportion of such crystalline-type environments is large enough, the TCR behaviour of the alloy becomes standard metallic. However, if the microarrangements are dominantly not

Table 2

The Voronoi statistics in the investigated compounds. The short-range order (SRO) preference means the dodecahedral and Archimedean antiprism arrangements (emphasized five-fold symmetry), while the LRO preference is collecting the b.c.c.- and f.c.c.-like clusters

compound	SRO preference		LRO preference	
	number	percentage (%)	number	percentage (%)
in Ni ₈₅ P ₁₅ around	Ni	45	30	40.0
	P	50	29	36.7
	in average	46	30	39.5
in Ni ₇₅ P ₂₅ around	Ni	52	12	18.8
	P	42	16	27.6
	in average	50	13	20.6

corresponding to crystalline environments (dominating dodecahedral and Archimedean antiprism polyhedra) the increasing temperature is lowering the electric resistivity (negative TCR) supporting the slight rearrangements to more and more crystalline (space filling) microstructures improving the electrical transport in the system.

Conclusions Characteristic microclustering has been observed in the given amorphous Ni-P systems. It was learned that the clusters corresponding to the crystalline long-range order are more massively presented in the alloy having normal TCR, while the alloy with negative TCR mostly consists of clusters that are far from the arrangements required by the long-range order. The materials with negative TCR can be characterized well by the short-range order.

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(Received September 3, 1992; in revised form November 27, 1992)