Fractal Behaviour of Amorphous $Ni_{32}Pd_{52}P_{16}$ Studied by SANS

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Small angle neutron scattering (SANS) was done with meltspun amorphous $Ni_{32}Pd_{52}P_{16}$ in the as-quenched state as well as after annealing at 533 K, 570 K, and 607 K, 20 h each. The double logarithmic plot of the structure factor versus the momentum transfer shows linear behaviour with noninteger Porod-slopes. The results are interpreted with the scattering from fractally rough inner surfaces.

The as-quenched state contains fluctuations of the scattering length density associated with smooth boundary interfaces. Annealing yields rough boundary interfaces, the roughness being largest after the 570 K annealing. Annealing at the higher temperature of 607 K yields less rough boundary interfaces.

1. Introduction

The log-log plot of the SANS-intensity versus the momentum transfer for binary amorphous alloys such as $Ni_{81}B_{19}$ [1], $Ni_{80}P_{20}$ [2], and $Ni_{63}Nb_{37}$ [3] yielded straight lines with noninteger slopes. The same is observed with the ternary alloy $Ni_{32}Pd_{52}P_{16}$ which was thoroughly investigated using neutron wide angle scattering concerning its relaxation behaviour [4]. We refer to recent papers [5–8] in which the result of small angle scattering methods in substances such as gels, aerosols, polymers, coals, soot etc. was interpreted in terms of fractal dimensions, and we will apply this concept to the amorphous alloy $Ni_{32}Pd_{52}P_{16}$.

2. Theoretical Fundamentals

Since disordered materials show neither translational nor rotational symmetry, crystallographic classifications are insignificant. However, certain structural features of such materials often show a dilation symmetry which means that they are geometrically self-similar during change of scale. Within certain limits the essential geometrical properties of a fractal object are independent from the gauge. Such self-similar structures can be characterized by the so called mass fractal dimension D which is defined as the exponent which yields the relationship between the mass m of an object and its radius R:

$$m \sim R^{D}. \tag{1}$$

Besides the thus defined mass fractal also a surface fractal dimension D_S is defined which yields the relationship between the surface s of an object and its radius R:

$$s \sim R^{D_S}. \tag{2}$$

D can assume values $\leqq 3$, D_S lies between 2 for smooth and 3 for extremely rough surfaces and thus represents a quantitative measure of the roughness of an object.

According to [5] the structure factor $S(Q)$ of a fractal object is related to the momentum transfer Q within the small angle scattering region, i.e. $Q \leqq 0.1$ Å^{-1}, and the fractal dimensions by the power law

$$S(Q) \sim Q^{-2D+D_S} = Q^{P} \tag{3}$$

with $$Q = 4\pi(\sin\theta)/\lambda = \frac{2\pi}{l}, \tag{4}$$

2θ = scattering angle, P = Porod slope,
λ = wavelength, l = characteristic length.

In the present paper we use the Ashcroft Langreth [9] structure factor, which is obtained from the coherently scattered intensity I_{coh}:

$$S(Q) = \frac{I_{coh}}{\langle b^2 \rangle} \tag{5}$$

with $$\langle b^2 \rangle = c_1 b_1^2 + c_2 b_2^2 + c_3 b_3^2, \tag{6}$$

c_i = atomic fraction of component i,
b_i = scattering length of component i.

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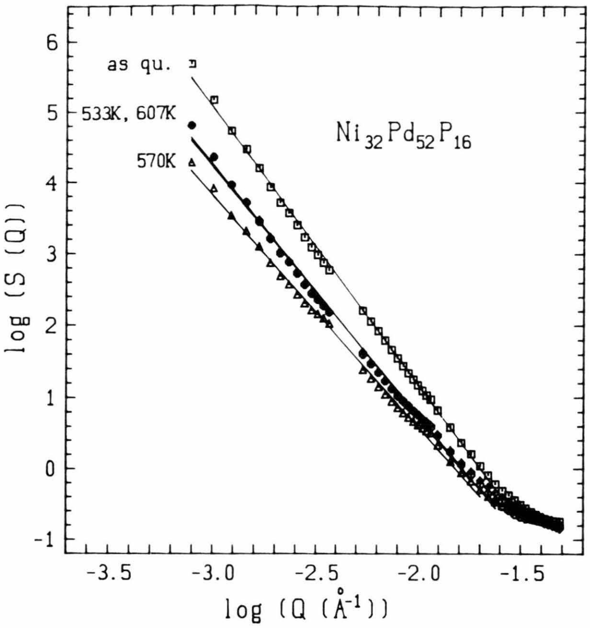

Fig. 1. Amorphous $Ni_{32}Pd_{52}P_{16}$; neutron diffraction ($\lambda = 10$ Å); log $S(Q)$ vs. log Q; annealing time 20 h.

Table 1. Porods-slopes from Fig. 1 and their interpretation.

Heat treatment	Porod-slope P	Surface fractal dimension D_S	Interpretation
as-quenched	−3.85	2.15	almost Porod-law
533 K, 20 h	−3.44	2.56	objects with rough surfaces
570 K, 20 h	−3.23	2.77	objects with very rough surfaces
607 K, 20 h	−3.44	2.56	with rough surfaces

3. Experiments and Results

Ternary amorphous $Ni_{32}Pd_{52}P_{16}$-alloys were produced using the melt-spin technique and heat treated at 533 K, 570 K, and 607 K for 20 hours. SANS-experiments were done with the annealed specimens and with an as-quenched specimen using the instrument D11 at ILL, Grenoble [10]. For the experimental details and the data reduction we refer to [11].

Figure 1 shows the results. The run of log $S(Q)$ versus log Q is linear within the region $-3.1 \leqq \log Q \leqq -1.6$ corresponding to $8 \cdot 10^{-4}$ Å $\leqq Q \leqq 0.025$ Å^{-1}. According to (4) this corresponds to characteristic lengths l between 8000 Å and 250 Å. Above $Q = 0.025$ Å^{-1} the run of log $S(Q)$ vs. log Q is not linear. Also a Guinier plot [12], i.e. the presentation of ln $S(Q)$ vs. Q^2 is not linear, which means that the $Ni_{32}Pd_{52}P_{16}$-alloys do not contain regions with uniform radii of gyration.

In Table 1 the slopes P of the straight lines in Fig. 1, the so called Porod-slopes are compiled.

All slopes P are noninteger. For the as-quenched specimen, however, the slope P is close to the value -4, i.e. the Porod law is almost fulfilled. In the three other cases the slopes P in the range, $3 < P < 4$ suggest the scattering to originate from fractally rough inner surfaces [13]. Remembering that the small angle scattering from metal-metalloid glasses mainly is caused by concentration fluctuations rather than by density fluctuations [1, 2, 14], we state that the inner surfaces must be characterized by a non uniform composition of the amorphous system. Consequently, the fractal dimensions D and D_S in (1)–(3), for the case of metallic glasses, are attributed to the inhomogeneous distribution of the different atomic species (concentration fractals).

In the following two different models for this behaviour will be discussed.

i) *Phase separation.* The alloy is separated into two amorphous phases with different composition where the regions of one phase are separated from the other phase by the inner surfaces. If we assume the composition of the regions to be independend of their radius R, the mass of A-type atoms m_A within the regions scales with R according to

$$m_A \sim R^3 \,. \tag{7}$$

Then the mass fractal dimension in (1) and (3) is $D = 3$, and (3) yields

$$D_S = 6 + P \,. \tag{8}$$

Within the picture of decomposition, the experimentally observed self-similarity of the scattering with characteristic lengths up to at least 8000 Å would imply the formation of very large phase-separated regions during the rapid solidification.

An alternative model can be imagined where such large regions are not necessary in order to explain the scattering behaviour:

ii) *Decorated domain walls.* In [15] a model has been proposed where the amorphous system consists of domains which are separated by an irregular network of domain walls. Although the nature of these domains is not specified one might imagine that they are caused by inhomogeneous inner stresses built up during the rapid solidification. In the model the walls are decorated by concentration profiles in such a way that during their formation they act as sites for the enrichment or depletion of certain atomic species. In [15] impurities in amorphous Cu–Tb were considered, but also the constituents of the amorphous alloy itself may be involved in the process. Although the domain walls must be very extended, up to at least 10^4 Å, in order to cause small angle scattering with the large observed correlation lengths, the decay of the concentration profiles perpendicular to the walls to the constant level inside the domains may take place within only some ten Å, Thus, this model does not require large long distance variations of the concentration during the rapid solidification. Because the domains are supposed to have the same average composition, regardless of their size, (7) and (8) again apply.

Enrichment of metalloid atoms at the fracture surfaces after annealing has been found, e.g. with $Ni_{40}Fe_{40}P_{14}B_6$ [16] and $Fe_{40}Ni_{40}B_{20}$ [17]. The concentration profiles at these extended surfaces showed depths in the order of some ten Angstroms. This observation is in support of the second model, where compositionally decorated interfaces are considerd in the amorphous material, and which seems to be the more appropriate model compared to model i), which demands concentration fluctuations with correlation lengths in the order up to about 8000 Å, which is rather unlikely.

In conclusion of this discussion we state that in any case the small angle scattering gives evidence for the existence of some kind of regions which are separated by interfaces. From the Porod slopes obtained with the $Ni_{32}Pd_{52}P_{16}$ specimen, the surface fractal dimensions D_S were calculated according to (8) and compiled in Table 1. D_S lies in the region $2 \leqq D_S \leqq 3$. For smooth surface of the region ($D_S = 2$) follows $P = 4$, i.e. the so called Porod law [18] for small angle scattering from such objects.

Since large D_S means large roughness of the scattering objects, we recognize from Table 1 that the roughness observed is largest at the annealing temperature of 570 K. At 607 K we observe a smaller D_S-value corresponding to that obtained at 533 K.

Finally the important fact should be stressed that already the as-quenched state shows the strongest SANS-signal. This means that already the as-quenched state contains inhomogeneities which differ in their scattering length density from the surrounding. The SANS signal after annealing at 570 K is smaller than that obtained with the as-quenched specimen. Thus from the present SANS-experiments we cannot derive that relaxation involves phase separation as has been concluded from DSC measurements in [19]. With respect to this question we refer to a small angle X-ray study with amorphous $Ni_{36}Pd_{46}P_{18}$ where no evidence for phase separation during heating prior to crystallization has been found [20].

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