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Comparison between the amorphous and microcrystallised structures

by

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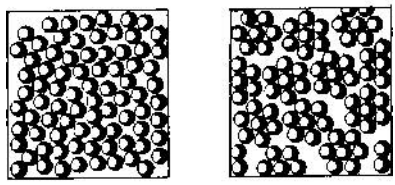
A substance is called crystallised if its Debye-Scherrer X-Ray diagram is constituted by a series of numerous sharp lines defining a set of well defined Bragg angles. It is "not crystallised" when the diffraction diagram is formed by a small number of more or less broad rings. From this criterion, it is then generally said to be "amorphous".

But a diffraction pattern corresponding to the above definition may be given by two different models of structure. One of them, of course, is the structure of a glass or an amorphous body, in the strict sense. But there is another possibility. Let us consider a powder of crystallites irregularly oriented and arranged; Fig.1 is a two dimensional scheme of a homogeneous amorphous structure (Fig.1a) and a set of microcrystallites (Fig.1b). If the size of the individual



a b

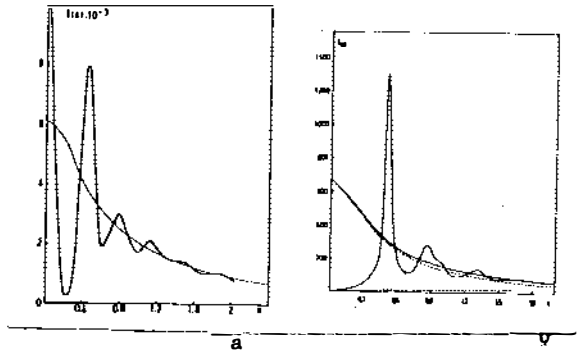
Fig.1 : Two dimensional scheme of a homogeneous amorphous structure.

crystallites is progressively decreased, their internal structure remaining unchanged, the lines of the D.S. pattern broaden progressively, their width being inversely proportional to the average crystallite size. And when the crystallites are so small that they contain only a small number of cells, the D.S. lines are replaced by broad rings. The few first of them (low indices lines) are separated from each other, but for higher indices, the diffraction lines are closer so that they overlap when they

are broadened and the diffracted intensity tends towards a monotonous curve without marked oscillations. Thus, we see that this model of microcrystallised substance corresponds to a diffraction pattern which is qualitatively very similar to that of a glass or true amorphous body.

Fig. 2 shows an example of two diffraction patterns which look very similar and, nevertheless, we shall show that a careful analysis of the two intensity curves allows to distinguish them: one specimen, Pt-C, must be considered as microcrystallised whereas the second, Ni-P, has a truly amorphous structure. For clarity sake, we shall here consider only two typical cases which may be classified without doubt,

Fig.2 : $I(s).10^{-3}$ for :
a. Pt-C alloy
b. Ni-P alloy



but it is true that there may be intermediate cases for which a clear cut definition of thestructures is less justified. Nevertheless, one must try to avoid any confusion whenever it is possible, even at the prize of a somewhat exaggerated schematisation.

It is important to point out that the condition for drawing legitimate conclusions from the diffraction diagrams is a good accuracy of the intensity curves. Not only the incertitude on the measurements must be reduced as far as possible which is now within the possibilities of a modern apparatus, but also every corrections should be made very carefully because the causes of systematic errors are numerous and often subtile. It is usual to calculate Fourier transforms: one must then suppress the parasitic effects which may profoundly viciate the result (such as termination errors, error on the scaling factor..).

An example of a microcrystallised body, Pt-C .

Electron-microscopists use commonly carbon replicas obtained by evaporation. To enhance the contrasts, Platinum is coevaporated

with carbon to increase the absorption, hence the sensitivity, of the replica.

This mixture of Pt and C atoms has been considered as "amorphous", the Pt atoms being described as dispersed at random into the carbon. But this simple scheme has been suggested without definite proof.

We have studied the structure of a mixture of 20at.% Pt and 80 at.% C. by X-Ray diffraction and electron microscopy. The scattering factor of the carbon is so low in comparison to that of the Platinum that it is a good approximation to consider the Pt atoms alone and to completely neglect the contribution of C to the diffraction.

To express the results of the X-Ray diffraction measurements, we shall make use, as it is usual, of a reduced diffracted intensity

$$i(s) = \left(\frac{I(s)}{Nf^2} - 1 \right) s.$$

I(s) is the intensity diffracted by N atoms of scattering factor f, and $s = \frac{2\sin\theta}{\lambda}$. If the N atoms were scattering independently, i(s) would be nil: thus i(s) is a measure of the interference effects. i(s) has a Fourier transform, p(r), which is related to the repartition function of the atoms by the formula

$$p(r) = r\,(P(r) - 1)$$

If the Fourier transformation does not introduce errors, p(r) and i(s) are equivalent in the sense that they contain under two different forms the same information.

We first remark on the experimental intensity curve (Fig.2a) that there is a strong small angle scattering which is the proof of the heterogeneity of the repartition of Pt atoms in the carbon: A Guinier plot (Ln I, s^2) gives 8 Å for the radius of the clusters. That is confirmed by the electronmicrograph (Fig.3a) which shows a granulation at a scale of about 10 Å, i.e. at the limit of the resolving power.

These observations lead us to try a model of small clusters of Pt dispersed in the carbon, and the simpler assumption is to suppose that the clusters are crystallites in which the Platinum atoms have a regular structure. A powder of identical crystallites of a given number of atoms produces a diffraction pattern which is easy to calculate.

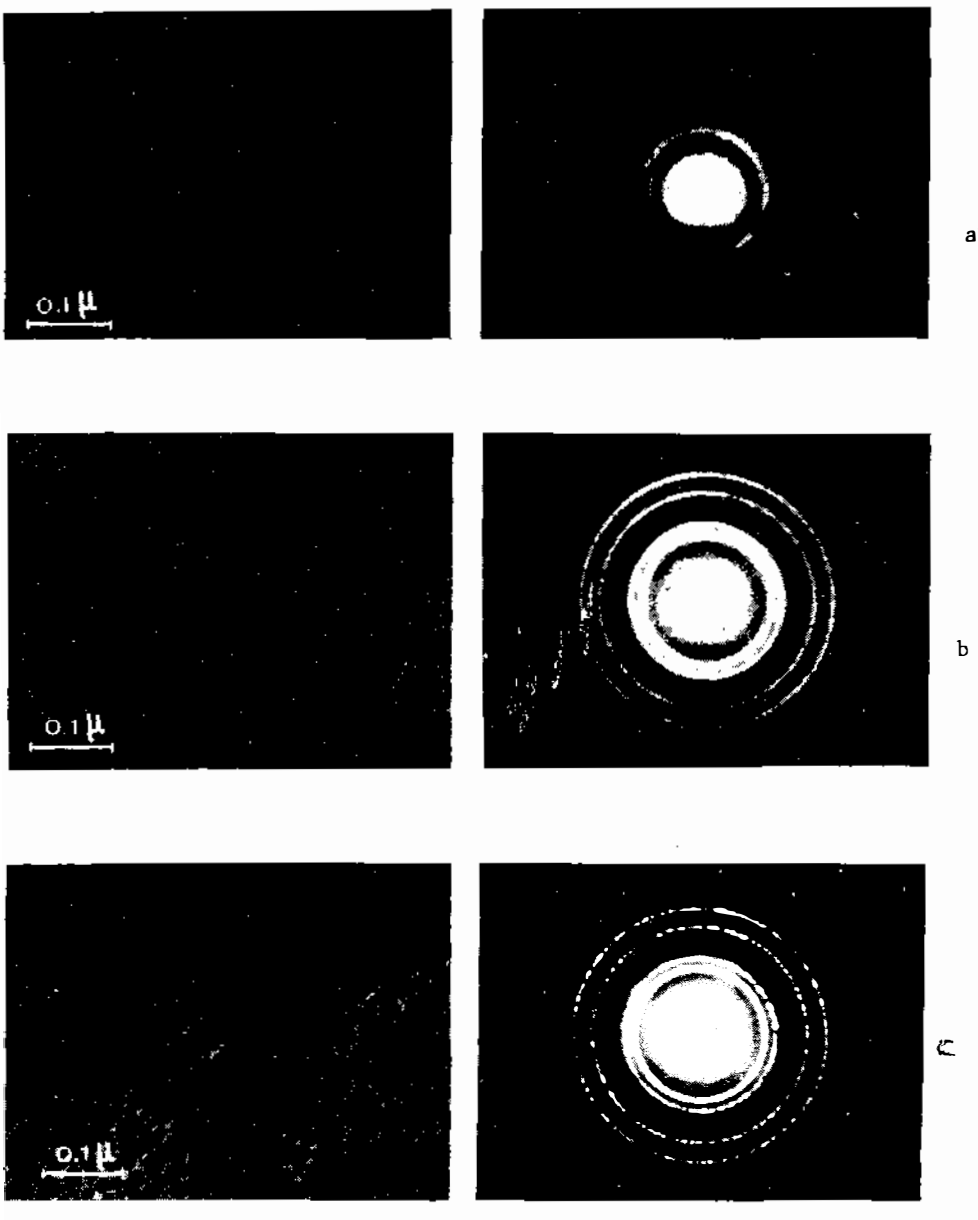


Fig. 3

Electronmicrographs and microdiffractions of:

a - Amorphous Pt-C

b - Pt-C annealed one hour at 200°C.

c - Pt-C annealed one hour at 300°C.

According to the Debye formula, the scattered intensity is given by :

$$\frac{I(s)}{Nf^2} - 1 = \frac{1}{N} \sum_m \frac{\sin 2\pi r_m s}{2\pi s r_m}$$

Where r_m is the distance of pairs of atoms and the summation is extended to all the pairs in the crystallite. When N is very large, this Debye formula corresponds simply to the Debye-Scherrer pattern, the lines of which become sharper and sharper when N increases.

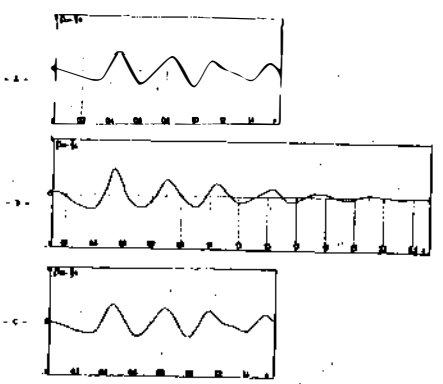
For small N (less than 1000), the intensity curve is of the "amorphous" type as it was previously shown in a qualitative way. Only the first peaks are well separated from each other : in particular the first one (at the smallest angle) is the more intense and its width is roughly inversely proportional to N. A series of curves have been calculated for different N and different crystalline structures (h.c.p. and f.c.c.). The comparison of the observed first peak with the peaks in this series indicates the value of N which must be chosen to account for this first peak and thus gives the size of the crystallites if the structure is really microcrystallised. This method gives the same result as the data of small-angle scattering: the more convenient model is an ensemble of 13 atoms (one atom and the 12 of the first shell of neighbours). Fig.4 shows the comparison of the observed i(s) and the calculated for 13 atoms in h.c.p. or f.c.c. arrangement. The agreement with the h.c.p.

<u>Fig.4</u> : Reduced interference functions (I(s)-1)s.

a - calculated for 13 atoms in f.c.c. arrangement

b - measured for amorphous Pt-C.

c - calculated for 13 atoms in h.c.p. arrangement.



crystallites is the better.

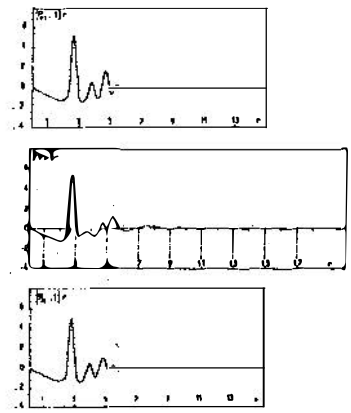
Another comparison may be made between the repartition functions calculated by Fourier transformation from the observed and the calculated curves i(s), (Fig.5). A characteristic of the observed p(r) is that the oscillations are practically completely damped

Fig.5 : Reduced radial distribution functions.

a - calculated for 13 atoms in f.c.c. arrangement.

b'- calculated from the measured interference function for amorphous Pt-C.

c - calculated for 13 atoms in h.c.p. arrangement.



at distance greater than 8 Å, that is approximately the diameter of the microcrystal of the adopted model. Inside the crystallite, the degree of order is good, and at the limit of the crystallite, the order disappears abruptly. The h.c.p. model here again is the better. Of course, the agreement is not perfect and that is not surprising, being given the simplicity of our hypothesis.

The important point is that the size effect alone of a crystallite of 13 atoms is sufficient to account for the mean features of the observed diffraction diagram. In a good first approximation, no atomic disorder is necessary inside the structure. Thus we can say that the Pt-C sample is microcrystallised. The case is a particularly simple one, because the crystallites of Pt are separated by carbon layers. If there

were no other phase, the crystallites would be in contact and some atoms along the intercrystallite boundaries would be displaced from their normal sites in the adjacent lattices.

The microcrystallites are not in an equilibrium state : thus the structure changes when the sample is annealed. This evolution is a confirmation of its initial microcrystalline structure. The diffraction patterns as well the electron micrographs (Fig.3b,c) show the progressive growth of the crystallites. After an anneal of 1 hour at 300°C, the grains are clearly visible on the micrograph (> 100 Å) and the diffraction pattern becomes a normal crystalline pattern with well defined lines. After annealing at a lower temperature (170°C), the diagram is still made of broad rings; the width of the first peak (Fig.6b) indicates that the elementary crystallite should contain about 100 atoms. But the calculated intensity curve for a model of 110 atoms in f.c.c. arrangement is quite different from the observed one (Fig.6a) the agreement is slightly better with a h.c.p. structure (model of 106 atoms (Fig.6c) but the discrepancies exceed the experimental errors. But such small crystallites may likely contain many stacking faults. Thus one can expect to improve the model by introducting some faults in the h.c.p. stacking. In fact, with a model comprising 3 stacking faults the experimental curve is rather well reproduced (Fig.7). On the other

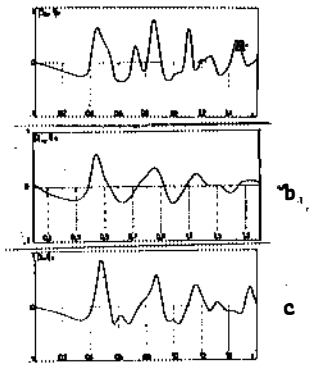


Fig.6: (I(s)-1)s. for:
a - 110 atoms in f.c.c. arrangement.
b - measured for Pt-C annealed at 170°C.
c - 106 atoms in h.c.p. arrangement.

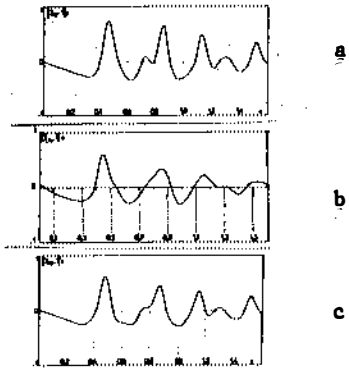


Fig.7: (I(s)-1)s. for:
a - 110 atoms with 2 stacking faults.
b - measured for Pt-C annealed at 170°C.
c - 106 atoms with 3 stacking faults.

hand, the existence of these stacking faults is necessary to explain the change from h.c.p. structure of the first small crystallites to the normal f.c.c. structure of platinum, when the grains are large (> 300 Å).

An example of an amorphous structure : Ni-P.

We shall take as a second example the "amorphous" Ni-P obtained by electroless deposition, because its structure is typical of many amorphous alloys obtained by splat cooling (for instance Pd-Si or Au-Si).

The particular alloy Ni-P we are considering contains 17 at.% P, and is a single phase. The P atoms may be neglected in the interpretation of the X-Ray diffraction pattern, because their contribution on account of their number and their weak scattering factor is negligible compared to the influence of the Ni atoms. The diffraction curve is given by Fig.2b. By comparing it to the qualitatively similar curve for Pt-C two facts are apparent :

1/ There is no small angle scattering; on the contrary, the diffracted intensity reaches a very small value for small angle of diffraction. Thus the electronic density in this sample has no large scale fluctuations: there is no indication of clusters of Nickel, but that fact by itself does not eliminate the possibility of a microcrystallised structure, because the different crystallites may be in close contact, as in a coarse grained material.

2/ Let us now consider apart the first peak of the intensity curve: its width corresponds by the Scherrer formula to a crystallite size of 17 Å. It is only slightly larger than the crystallites used as model in the Fig.6, but the curve given by Ni-P is definitely distinct from the curves corresponding to crystallites. For the f.c.c. structure, when the first peak is as

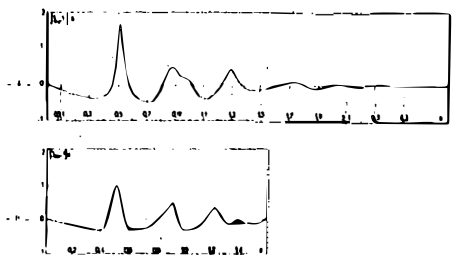


Fig.8: (I(s)-1)s.
a - measured for amorphous Ni-P.
b - calculated interference function for 106 atoms of Ni in h.c.p. arrangement.

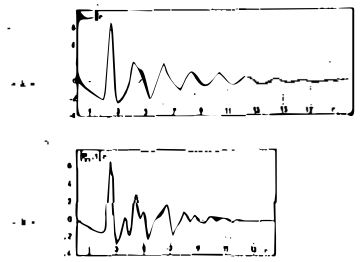


Fig.9: (P(r)-1)r.
a - calculated from measured (I(s)-1)s.
b - calculated for 106 atoms of Ni in h.c.p. arrangement.

sharp as the Ni-P peak, the 200 line is already visible forming a hum on the right of the first peak which is absent in Ni-P. For the h.c.p. structure of the same size, the peak (102) is clearly distinct from the first (Fig.8). In both cases the series of peak at large angles is more intense in comparison to the first and sharper than it is observed in Ni-P. So when the crystalline model is adjusted to fit the first peak the rest of the curve is not accounted for, or vice versa that is the reason why one cannot find any cristallite size which agrees with the observed curve. Thus we can say that the substance is amorphous.

The same contradiction appears in the comparison of the repartition functions p(r) (Fig.9) for Ni-P thus function oscillates until a large value of r and the damping is progressive, whereas for a crystalline model giving nearly the same first peak, the following peaks remain sharper then vanish above the maximum diameter of the crystallite. The amorphous structure is characterized by the fact that the immediate surrounding of an atom is not precisely determined, there are fluctuations into the distances and the directions of the bonds to the first neighbours. This is the essential difference with the crystallised structure. Of course, these fluctuations become more important for the 2nd, 3rd... shell of neighbours and any order disappears above distances greater than 10 - 15Å as in the case of crystallites with a diameter smaller than 10 - 15 Å . These differences of structure have a sufficient influence on the diffraction curves to be detected without difficulty by experiments of good accuracy.

The evolution of Ni-P towards the equilibrium structure during annealing is quite different from that of a microcrystallised body. The amorphous phase decomposes into a mixture of two crystalline phase Ni and Ni_3P : crystalline nuclei appear and grow progressively at the expence of the amorphous phase, the volume of which decreases. The diffraction lines of Ni at first, then of Ni_3P become visible and the diffraction diagram of the amorphous phase becomes less intense but is not changed: the structure of the remnant amorphous phase is thus unmodified. This is in sharp contrast with the evolution of the diagram of a microcrystalline body, which changes continuously from the pattern with broad rings into a pattern with sharp lines.

To sum up, a detailed analysis of the diffraction pattern shows that a substance giving an apparently amorphous diffraction pattern may have either a microcrystallised structure or a true amorphous structure.

One may wonder why one or the other of these structures is formed. We suggest that an important factor is the nature of the bonding of the atoms. When the substance has a true amorphous structure, there are covalent bonds but when the bonds are metallic or ionic, the structure is microcrystallised.

In the usual glasses, the bonds are generally strongly covalent; there are no purely ionic glasses. The non crystallised alloys obtained by splat cooling, always contain one element which is not a true metal (B, P, Si ...). Conversely the result of the quench is always crystallised (with even sometimes large grains) if all the elements of the alloy are "good" metals. It is very likely that the "amorphous" metals obtained by vapor quenching are microcrystallised.

When atoms are packed together by metallic cohesion or Coulomb forces, there is not much freedom left and they take their regular crystalline structure without not many faults. But the growth of the crystallites may be limited, by the diffusion rate of the atoms to the surface of the nucleus (that is the case of Pt-C), or by the great number of nuclei growing simultaneously (as in an evaporated layer). On the other hand covalent bonds are more flexible and the arrangement of one atom and its neighbours may differ from the ideal scheme, if the presence of impurities, stoechiometric defects or a too large viscosity of the solidifying liquid prevents the formation of the regular structures. The metastable amorphous structure is derived from a crystal in which every cell is more or less distorted. This is called a paracrystal. Molecules bound by Van der Waals forces might give rise also to these irregular structures that is observed, for example, in high-polymers. However, in that case, the degree of irregularity may be smaller. Many intermediate steps are found from the "good" crystal to the poorly crystallised and the amorphous substances. There is no sharp distinction between these later types of structures.

Thus, microcrystallised and amorphous structures are well differentiated as well in their origins as in their properties. But to distinguish them, a quantitative analysis of the diffraction pattern is required. One cannot draw valuable conclusions from the qualitative aspect of the pattern. This is very often the case of electron diffraction diagrams which do not permit diffracted intensity measurements of sufficient accuracy; it may happen that only electron diffraction is possible (e.g. for thin films).

But when good X-Ray measurements are possible, they are very interesting because they lead to a better understanding of the atomic structure.

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