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POSITIONAL (DIS)ORDER AND COMPOSITIONAL (NON-)HOMOGENEITY IN METALLIC GLASSES

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Résumé - Dans les modèles de structure des verres métalliques qui reposent sur un empilement corrélé d'unités structurales, il est assez facile d'explorer les liens qui existent entre l'ordre de position et la concentration. Cet article s'intéresse à ce problème et attire l'attention sur d'éventuelles sources de désordre qui proviendraient ou entraîneraient des fluctuations de concentration locale. On examine brièvement leur relation avec la formation et la stabilité des verres.

Abstract - In models for the structure of metallic glasses based on a correlated packing of structural units, it is relatively easy to explore the coupling between positional order and composition. This paper deals with this problem and focuses on some (possible) sources of disorder arising from or involving local concentration fluctuations. Their relevance to glass formation and stability is briefly examined.

I - INTRODUCTION

The notion that positional order - the spatial (static) distribution of the centres of gravity of the particles - and chemical order - the occupancy distribution of these points by the different species - are usually not independent quantities in amorphous alloys can be raised experimentally by inspection of Bhatia-Thornton partial pair functions. An equivalent point of view can of course be given by the same functions calculated for a list of atomic coordinates in a structural model but detailed knowledge about the coupling between positional and chemical orders is inherently much more difficult to achieve without any a priori information on the packing algorithm of the model.

In dense random packing models of individual atoms, no such ab-initio information is available but may be contained in the final list of coordinates as a result of the subsequent energy minimization procedure under suitable interatomic potentials. At contrast, this coupling is an in-built ingredient of non-crystallographic curved space models or of models based on the local structure of crystalline compounds. In non-crystallographic "vitrons", like those presented by Gaskell in a recent paper [2], a coupling between atomic positions and local concentration is induced via the linkage of structural units by regular polyhedra and imposes the curvature of the elliptic space. In models with icosahedral short range order, a similar coupling should also be considered if e.g. the interaction between unlike species is large and leads to a strong chemical order, i.e. to the existence of identifiable cells of one element surrounding another (as in Frank-Kasper phases).

II - STRUCTURAL UNIT AND POSITIOnAL (DIS)ORDER

The relationship between geometrical and chemical disorders is easier to assess if any suitable structural unit may be defined around one of the species. In a large number of transition metal-metalloid crystalline compounds (but also in...
many rare earth-transition metal or early-late transition metal crystals), such a unit is readily identifiable. It is a triangular prism of six large atoms M (e.g. transition metal atoms) centred by a small atom X (e.g. a metalloid). This unit is common to a wealth of different compounds with compositions ranging from MgX (or even poorer in X species) to MX$_2$ and what differentiates the diverse structural types is the way the units are interconnected or, in other words, the underlying structural operation which couples position and local concentration.

It turns out that in metallic glasses of similar nature, some convincing experimental evidence that this type of local unit exists is now available [3]. Furthermore, some results indicate that structural organization may extend up to several atomic diameters. There is, however, no direct proof that the medium range order in an amorphous material is of the same nature (nor is intrinsically different) than in its crystalline counterpart on the one hand and is compatible or not with translational symmetry on the other hand. The claim [4] that the atomic coordinates in an amorphous structure model may be accounted for by a set of rules defined with respect (but not necessarily identical) to the rules which apply in the crystalline state is thus supported by nothing else but the assumption of the existence of local arrangements able to break the translational symmetry of the crystal while being compatible with the global homogeneity of the structure imposed by the interatomic potentials.

The very important point here is that the number of different connections which a - fulfill the above space filling requirements and b - account for the stoichiometry is in fact small. To illustrate this point, consider a M$_{1-x}$X$_x$ network with fixed stoichiometry $x = 0.25$ and assume that each X atom lies in the centre of a prism. As a consequence of the mean composition, the M atoms belong to I = 2 prisms on an average and accordingly, there are several connections between units able to achieve this mean value. However, suitable connections are restricted to packing configurations which do not involve i - highly constrained bonds or ii - large empty interstices. Adequate solutions can be found by trial and error and the most adequate - characteristic of the Fe$_3$B, Fe$_3$C and Ti$_3$P crystal types - are depicted in figure 1. Because of the composition, each prism vertex is also a capping atom for another prism and therefore, the triangular prisms will fit together with only little degrees of freedom in the choice of their respective arrangements. For the configurations C = -1 and C = +1 shown in figure 1, the prisms will be found on top of each other. Depending on the $r_X/r_M$ ratio or/and the strength of the X-M interaction, they will occur in Fe$_3$C isotypes (C = +1) or in Ti$_3$P isotypes (C = -1) with the possibility of polymorphism (e.g. Fe$_3$B) for couples of elements in between.

Figure 1 : Edge connection can be achieved in two different ways so that rotation around this edge superimposes the reference frames of the prisms (C=+1) or transforms a right oriented frame into a left oriented one (C=-1). A third configuration - face sharing - is obtained by translation (noted C=0). For the sake of clarity, only the specificity of each connection is drawn and the number of prisms to which each M atom belongs to is indicated by small number

III - AMORPHOUS STRUCTURE AND STRUCTURAL OPERATIONS

More systematically, each type of connection is expressed in terms of a structural operation [5] which may be viewed as a specific one to one correspondence from an ideal stress - relieved close packed array (of two or more components) towards the euclidian 3D space. This correspondence involves an anisotropy of the real space and is characterized by a set of a few rules describing all the possible relationships from one unit to another which are equivalent to the local configurations actually found in the crystalline state. (For a typical example, see [6]).
As far as short range pair potentials are concerned, this defines atomic environments either identical to (crystallographic) or very similar (though non-crystallographic) to the crystalline ones. Occurrence of such non-crystallographic configurations is therefore energetically tolerable and is able to change the direction of application of the structural operation. This breaks the crystalline sequence but not the overall homogeneity of the material in the sense that the structural operation still assigns the connections between every two units.

A model was built for the Ni80B20 glass according to the above principle [6]. It is an example of an amorphous structure generated by a single structural operation into which disorder arises from direction changes. They are however other ways to disorder such networks either by mixing different structural operations or by mixing different periodicities of a structural operation. In fact, a lot of similar or even more sophisticated examples is known in the crystalline state [7] which are worth considering to understand the amorphous structure. Therefore, the purpose of the next section is just to illustrate—among all other possibilities—how disorder may arise from the application of i - one single structural operation, ii - a mixture of two structural operations and iii - a change in the periodicity of the operation.

IV - POSITIONAL DISORDER AND COMPOSITIONAL NON-HOMOGENEITY

Figure 2a presents a schematic illustration of several prisms arranged in an (ideally perfect) array generated by a structural operation corresponding to the stoichiometry MgOx20. By virtue of this operation, such a long range ordered network yields M atoms belonging to \( L = 2 \) prisms and to \( L = 0 \) prism (for more details, see [6]). It is possible to induce disorder by stopping the crystal growth at the level of the shaded triangular faces and continuing the network with prisms arranged as in b. These new units are connected to the previous ones according to a few simple rules characteristic of the former operation (as acting in a) and are themselves correlated by the same structural operation. However, some of the atoms which ought to belong to \( L = 0 \) or \( L = 2 \) prisms, now belong to one unit. The number of units found in the vicinity of a given M atom is thus not (always) retained with respect to the same number defined by a single direction of the structural operation.

Another such example is depicted in the centre of figure 3. In this structure, prismatic units (projected as triangles onto the plane of the figure) are generated by a structural operation called Simple Chemical Twinning (S.C.T.) [5] with a periodicity \( 13,1,3,1,1... \). They form planar networks of prisms connected either by sharing a rectangular face or an edge (or a vertex) of a triangular face, as in figure 1 (\( C = +1 \)). (Prisms with this latter connection are not drawn to simplify
There are several possibilities to change the propagation direction of the structural operation but the most obvious is to place another set of prisms in a position enantiomorphous to the former one with units in contact sharing a rectangular face as shown in the upper part of the figure. The crystalline sequence is broken accordingly but not the characteristic connection between any two units.

Clusters of four face-sharing units appear then and are linked together by capping atoms or by edge and vertex connections (not visible in the figure) as elsewhere in the network between the other prisms. This results also in an increase of the local number density of X atoms which truly represents a concentration fluctuation with respect to the average stoichiometry of the structural operation. To balance this effect, an increase of the operation periodicity may be introduced elsewhere in such a way that an average over the whole network brings the composition back to M₂X. The most natural change is to transform the structural operation from \{3,1,3,1,...\} to \{3,3,...\} as schematised in the right hand side part of figure 3. A typical arrangement of these units is that in figure 1 with C = +1 which has again the same edge and vertex connections as in the central part of figure 3 (with prism vertices as capping atoms of neighbouring prisms as well). In this region, the composition is M₃X. It turns out that the Y₂Ni glass has no crystalline counterpart of identical composition but leads to the formation of the Y₃Ni and Y₃Ni₂ compounds \[8\]. The cementite-type Y₃Ni compound is generated by \{3,3,...\} SCT. The Y₃Ni₂ crystal has a more complicated structure built up by 4-prisms clusters identical to those in figure 3 (but alternatingly rotated by π/2 from one layer to another). Note that the sole structural operation with the \{3,1,3,1\} periodicity already entails the most salient features exhibited by the experimental pair correlation functions published by MARET et al \[8\]: a close contact Ni-Ni distance (through face sharing) and a well defined first peak of the Ni-Y function followed by two subpeaks which correspond in this model to distances from Ni to the prism vertices and to the two different types of capping atoms. A suitable guide to the modelling of the Y₂Ni glass may thus be found in figure 3 and corresponding work is in progress.

More generally than in the previous example, the number density of X atoms can be changed almost continuously along a given direction by varying the periodicity of the structural operation. Figure 4 is an illustration (among many other possibilities) for the case of SCT of a hcp lattice. The numbers given in this figure represent the composition of a large lattice generated by the corresponding sequence but repeated "ad infinitum".

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**Figure 3:**

Prisms (projected as triangles) arranged according to SCT with \{3,1,3,1\} (bottom left corner) or \{3,3,...\} (bottom right corner) periodicities. Rotation by π of the direction of the structural operation produces the upper part of the figure (black circles are shifted with respect to white circles by half a prism length normally to the plane of the figure).
Mixing structural operations is an attractive possibility either in binary systems which may exhibit polymorphism as mentioned in section 2 (e.g. Fe-B) or in multi-component systems (e.g. ternary Fe-B-C) in which each solute species may be associated with one type of structural operation. However, under usual preparation conditions, these glasses behave as homogeneous media, suggesting either that the correlations operate in too small volumes to be distinguished or that B and C belong to the same structural operation. Figure 5 is a speculative description of a single structural operation related to SCT but mixing the connections with C = -1 (i.e. Fe3B) and C = +1 (i.e. Fe3C). Periodic intermixing of C = 0 and C = -1 connections is known to operate in crystalline compounds [9] but in this example, no periodic repetition is considered. Here, prisms form swinging chains arranged in planar layers and, if occupied by a small X atom, may continue the network with a C = +1 connection or, if X is larger, with a C = -1 connection. Again, this example emphasizes a coupling between positional disorder and composition non-homogeneity. Moreover, the linkage deficit in the C = -1 connection (ℓ = 1 instead of ℓ = 2 or 3 as in figure 1) also leads to a variation in the X-number density which, conversely, is able to accommodate local fluctuations.

Finally, it is worth considering a M1-xXx amorphous structure in the low-x limit as then, part of the M atoms will not contribute to any unit either as prism vertex or as capping atom, i.e. will not interact directly with X atoms. In order to accommodate such atoms, the system has the possibility to "break" the generative symmetry of the structural operation in such a way that the structure is divided in two components : regions A X where a structural operation applies and of average composition M1-xX XxX and regions AM of pure M element where no more correlation operates.

A pictorial description of the structural changes occurring when the concentration decreases below x in 4 has already been published in [4]. This model seems to be helpful in the interpretation of the physical properties -concentration relationships of Fe-B and derived ternary glasses and has received attention in several papers.
The question to know what actually is the structure of the -presumably mono-atomic- \( \text{AM} \) regions is open as there are several candidate models for this purpose: disordered micro-crystals, dense random packed or icosahedral bond oriented clusters.

V - WHAT ABOUT REAL GLASSES?

A striking duality of these metallic glasses is related to their (usually) broad composition range: at the macroscopic level, they behave as continuous solid solutions while, at the microscopic level, their similarity with crystalline compounds with narrow stoichiometry ranges seems to be in contradiction with their macroscopic homogeneity. The chief merit of the model developed in the previous sections appears thus to be able -by interconnecting a unique type of unit- to account for a large domain of amorphous compositions or for the concentration variations that are known to occur within a specimen during preparation.

The interesting point here, however, is at an even more microscopic scale as it shows how minute shifts of the constituents profile with respect to that of an ideal -possibly metastable- crystalline state may induce positional disorder (without requiring point defects, i.e. empty prisms, which of course may also appear). Conversely, it also points towards why such disordered materials may form.

In section 4, use was made of only four examples that can be classified as:

1. change of direction of the structural operation
2. change of periodicity of the structural operation
3. intermixing of structural operations
4. restriction of the domain of application of the structural operation.

The author is nonetheless convinced that many other possibilities can be imagined from the crystalline configurations shown in [17]. Obviously, several of these effects may operate simultaneously. Case 1 is the most "efficient" in introducing disorder and case 2 in changing the composition. It must be noted that in the pictorial descriptions of this paper, the regularity of the structure is overemphasized for the sake of clarity. In fact, an average correlation length is associated with the structural operation and accounts for the linear dimension of the volume over which it applies without changing its direction or/and periodicity. It is just a few times larger than a unit length which smoothes out the "planar" picture suggested in the figures and -more seriously- defines essentially 2D regions where angular deficits (direction change) or/and variations in the \( X \)-number density are concentrated.

Elimination of one or both effects to recover crystallinity requires atomic transport and defect mobility because the \( \text{X} \) atoms is supposed to force always the formation of a unit and therefore transports also its own connection. The reason why clusters of atoms, organized according to a single direction of the structural operation, do not grow further during the glass transition and form a glass may thus be understood if the time constants associated with these diffusion effects are larger than the time basis imposed by the quenching process. In the liquid alloys considered here, diffusion is likely to be slowed down by i - the strong interaction between \( \text{X} \) and \( \text{M} \) species and ii - by the tendency to form clusters (associates) which enhances the local concentration fluctuations, especially in a liquid with a mean composition in between that of the associates (or of the crystalline phases). Note that in case 4, the formation of pure \( \text{M} \) regions works opposite to this as the absence of \( \text{X} \) atoms rapidly balances the stabilizing effect due to the interface with the surrounding amorphous phase.

Of course, in the present model which does not take into account electronic contributions explicitly, atoms which are too small to form units and do fit into usual interstitial sites or atoms too large which substitute for \( \text{M} \) atoms are not relevant as they may diffuse (rapidly) without affecting the defect network inherent to the glass. The classification of glass formers (\( \text{X} \) atoms) with respect to a structural operation [3b] and the knowledge of their transport properties in a amorphous structure (and not in a crystalline solid solution) are thus essential to the understanding of the glass formation from a structural point of view.
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