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POINT DEFECTS AND ATOMIC DIFFUSION IN METALLIC GLASSES

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ABSTRACT

In this paper we review the theoretical and experimental data concerning point defects and diffusion in metallic glasses. We shall show that even though simulations seem to indicate that point defects could exist under certain conditions in glassy alloys there is not yet clear experimental evidence for their existence ; in addition their role in atomic transport is not clear since the diffusion mechanisms are not known todate. To conclude, we propose specific experiments and simulations which could be helpful for a better understanding of these phenomena.

INTRODUCTION

Defects and atomic transport in metallic glasses is an important field both for technological applications and fundamental research. There are several review papers on this topic *. Chaudhari et al. [1], Greer [2], Limogé et al. [3], Cantor et al. [4], Cantor [5].

Our main goal here is to answer the following questions :

- Is the existence of localized or point defects in glassy alloys clearly demonstrated ?
- Are there properties of these possible defects which can compare with those of defects in crystals ?
- What is the role of defects in atomic transport ?

To answer these questions we shall present :

- 1) The theoretical study of defects in amorphous alloys
- 2) The identification and role of defects from experimental studies.

* Because of the very large number of publications relating to "point defects" and transport phenomena in metallic glasses our bibliography is far from exhaustive.

I - THEORETICAL STUDY OF DEFECTS IN AMORPHOUS SOLIDS

It is impossible to define defects in a material if we do not know its underlying structure. So we have first to look at the structure :

1) Modelling of the structure

A - The models

In order to classify the different structural models we introduce the distinction between topological and "physical" models.

In the first category we need some guiding principles to build the amorphous structure, in the second we start from the crystal, we melt it and then quench it from the liquid state to get an amorphous solid.

a) Topological models

There is a large diversity of such models developed either "by hand" or on the computer. They are frequently classified as :

Continuous random network (CRN) (Zachariasen [6], Polk [7], Gaskell [8], Dubois et al. [9,10]) proposed mainly for covalent and oxide glasses, where we start from "structural units" close to those of the corresponding crystalline compounds. The network is characterized by the length of the bonds, the angles between bonds and the distribution of rings of the structural units.

Dense random packing (DRP) derived from the hard spheres Bernal model [11]. They differ by :

- the packing rules
- the interaction potential
- the relaxation technique (Molecular Dynamics is used by some authors)
- the boundary conditions
- the technique used to analyse the structure

More informations on these models can be found in review papers by Gerl [12], Hoare [13].

b) "Physical models"

All these models use the molecular dynamics technique to build the amorphous structure and we simply give as examples the simulation of :

- Silica by Woodcock et al. [14], Soules [15], Doan [16]
- Argon by Rahman et al. [17], Kristensen et al. [18], Nose et al. [19]
- Iron by Vitek et al. [20]
- Binary systems in two dimensions by Lançon et al. [21]

B - Parameters used to analyse the structure

Some DRP models relaxed with the molecular dynamics technique are very close to the "physical models" ; in most of them the number of atoms is comprised between a few hundreds and a few thousands.

Many parameters can be obtained, from these models, which allow the determination of the structure, ; we quote as examples :

- the radial distribution function $g(r)$
- the density
- the holes of the structure

- the Voronoi's polyedra
- the atom trajectories
- some local parameters as, for instance, the local stress tensor

2) Defect studies and diffusion

From the simulated amorphous solid, defect and diffusion parameters have been deduced in the following different ways :

- calculation of the local stress tensor
- removal or addition of atoms to create defects
- direct observation of atomic migration during annealing

A - Fluctuations of local pressure

Egami et al. [22] were the first to consider that local variation of stress could characterize the amorphous state (see also Srolovitz et al. [23], Egami et al. [24], Egami et al. [25]). They chose the local pressure fluctuation $\langle p^2 \rangle$ and have done calculations both with DRP and physical models using Johnson potential corresponding to Fe. We see in figure 1 the distribution corresponding to local pressure calculated on every atom. Because this distribution is almost gaussian, the $\langle p^2 \rangle$ decrease which could be expected, when the structure is relaxed by annealing after quenching from the liquid state, is obtained by elimination of sites characterized by a large positive or negative pressure. So the density fluctuations p^- and n^- are considered by the authors as thermal defects (see figure 2). However such results on structural relaxation are not confirmed by the simulations of Kobayashi et al. as we shall see later. In our opinion these pressure fluctuations cannot be considered as thermal defects, they are more likely correlated to the thermodynamical driving force for the microscopic evolution towards an "ideal glass structure" and their role in atomic transport is far from evident.

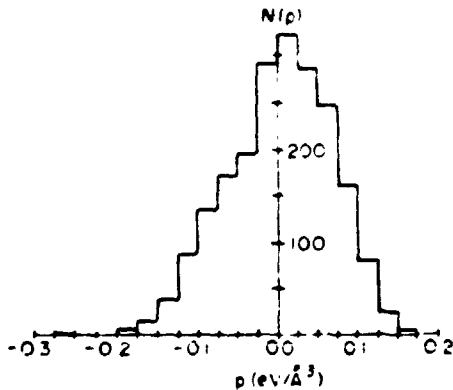


Fig. 1 : Distribution histogram for the atomic level hydrostatic stress p , after Srolovitz et al. [23]

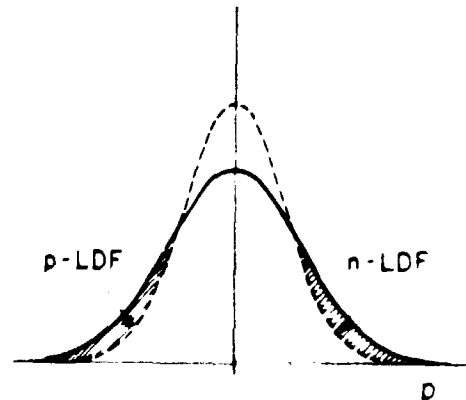


Fig. 2 : Effect of annealing on $\langle p^2 \rangle$ after Egami et al. [25]

B - Removal or addition of atoms

We shall consider two cases :

a) In Continuous Random Network (CRN) a point defect is described by the breaking of a bond in an elementary ring. The result is a strong electronic perturbation which can be identified experimentally ; as an example an oxygen vacancy in silica can trap an electron or a hole and can be identified by spectroscopic techniques (Friebele et al. [26]). The study of the stability of vacancies in covalently bonded systems represented by the Polk's model has been carried out by Bennett et al. [27] who have computed the static relaxation after removing a group of atoms. A Keating potential (an empirical potential with non-central interactions) has been used in this simulation. They establish in this case that vacancy-type defects are stable. Such defects could contribute to the atomic transport but no detailed mechanisms have been proposed to date ; in addition in processes such as structural relaxation other less localized defects could play a role.

b) In Dense Random Packing (DRP) or in "physical" models
There are two typical simulations (done on DRP models) where the defect stability is studied by removing or adding atoms or atom clusters.

- In the first, developed by Bennett et al. [27], a dense random packing is obtained by a progressive densification of a few thousand atoms with periodic boundary conditions. Metallic glasses are described by a Lennard-Jones potential. In order to study the defect stability an atom or a cluster of atoms is removed, the structure is statically or dynamically relaxed and its evolution is followed directly from the trajectories of all the atoms for different time steps.

- In the second category developed by Brandt [28] metallic glasses are described by a Johnson potential corresponding to Fe and the fluctuations of density and pressure are calculated. The presence of a defect is characterized by the variation of some averaged local density or pressure when the defect is introduced. The stability is claimed if after static relaxation this variation has not disappeared.

The conclusions of these two simulations are the following :

- In the first, vacancies are not stable with a Lennard-Jones potential as shown in figure 3 which represents a slice of width of one atomic diameter. Solid circles and vectors represent atoms the centres of which are in the slice both initially and at the end. The initial positions are indicated by the circles. Dotted circles and vectors represent atoms the centres of which have either left or entered the middle of the slice ; we see that the vacancy disappears in a short time.

- In the second the point defects are stable but unfortunately there is no direct evidence of this stability from the atom trajectories. However it is probably true because vacancies were observed by chance in a simulation done by Egami et al. [22] in regions of high symmetry and also by Doyama et al. [29] with irradiation of iron as we shall see later.

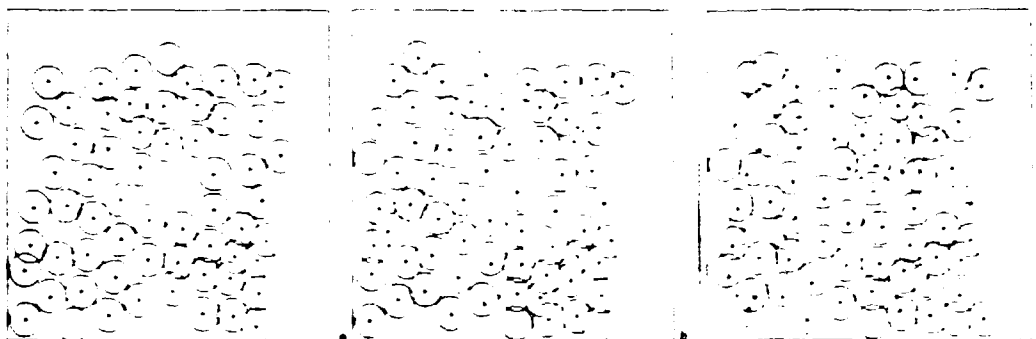


Fig. 3 : Plots showing the relaxation which occurs after the removal of an atom. a) 6 K b) 12 K c) 24 K, after Bennett et al. [27]

C - Direct observation of atomic migration during annealing

Now we consider the direct observation of atomic migration during annealing ; this has been done just above T_g in binary systems by :

- Lançon et al. [21] in a two-dimensional glass prepared by a simulated quenching from the liquid state using a modified Johnson potential.

- Kobayashi et al. [30] in a three dimensional system representing the metallic glass $\text{Cu}_{57}\text{Zr}_{43}$ which was obtained from DRP with a modified Lennard-Jones potential fitted to the experimental data.

In both cases we notice that the diffusion is heterogeneous (see figure 4) ; the homogeneous regions are about 5 to 15 atomic distances large.

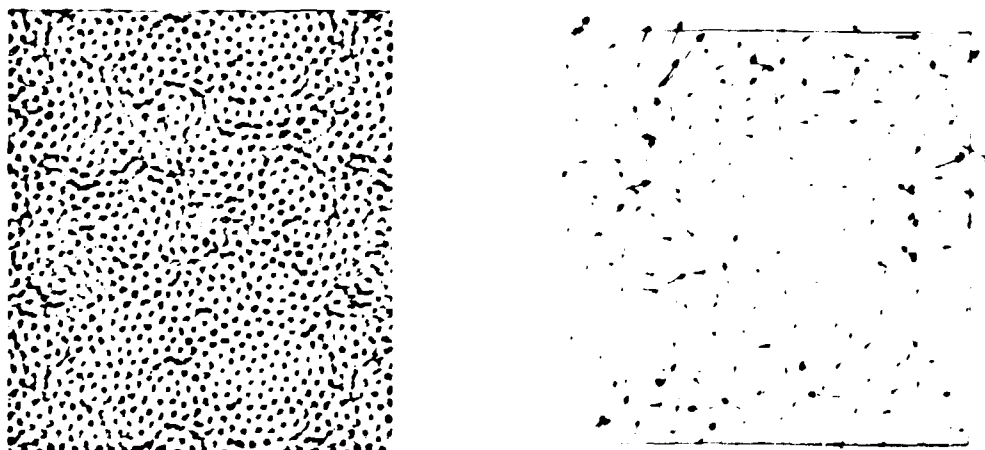


Fig. 4 : Atomic displacements during annealing. Left) after Lançon et al. [21]; Right) after Kobayashi et al. [30].

3) Diffusion mechanisms

All the diffusion mechanisms proposed are either very qualitative or based on phenomenological considerations and we could quote without being exhaustive the following :

A - Models from the liquid structure

In the Cohen and Turnbull's "free volume model" (Cohen et al. [31], Turnbull et al. [32,33]) we assume that one atom vibrates in the cage of its first neighbours and there is a translational displacement only if there appears a void with a volume larger than v^* , the critical free volume. Although the equation given for D is not able to describe the diffusion in solids, the "free volume" concept is often used since it involves a dependence of D on the specific volume. In fact this dependence has nothing to do with the Turnbull-Cohen's model itself.

B - Models from the topological structure

In this type of models it is assumed that atoms diffuse as "interstitials" in the biggest holes of the dense random packing. This is extensively discussed by Ahmazadeh et al. [34]. Chains of Bernal's holes (see Yamamoto et al. [35]) could be paths of easy diffusion but, up to date, such models remain qualitative.

C - Models of hopping with a variable energy

In crystals the atomic distances, for a given direction, are constant, which is not the case in amorphous solids and hence, in these materials, the activation energy of migration is likely to vary. All the models which have been used to describe the migration in amorphous solids (diffusion, relaxation...) are based on the hypothesis that there is a spectrum of activation energies. Gibbs et al. [36], Cost et al. [37], Kronmüller [38] have developed such models mainly for the relaxation phenomena, Belashchenko [39] for diffusion (see also simulations of hopping transport by Schönher et al. [40,41]). According to these models the "effective activation energy" has to vary with temperature, in agreement with the "latent vacancy mechanism" of Kiritani [42]. We have to point out that Belashchenko and Kiritani assume a vacancy-type mechanism while the other models are purely phenomenological.

D - Atomic models from computer simulations

Starting from irradiation effect simulations, Doyama et al. [29] suggest that diffusion could proceed without the help of vacancies, by an open ring mechanism (arc mechanism) similar to the Zener mechanism [43]. In the same manner one could think that the Doan-Adda mechanism [44] of open rings induced by density fluctuations (that is an unstable Frenkel pair) could produce atomic transport. In addition the heterogeneities in migration we have mentioned above would suggest that diffusion proceeds by vacancy jumps in regions of high symmetry (vacancies have been observed in these regions by Egami et al. [22], Doyama et al. [29]) and by cooperative mechanisms, probably induced by density fluctuations (unstable Frenkel pairs), in the loosely packed regions. Finally we have to note that the heterogeneous media has been described by Finney [45], Hoare [13] and Yamamoto et al. [35] as formed by icosahedral clusters in loosely packed media. However, in the absence of direct experimental observation (by high resolution electron microscopy, for instance) this description remains speculative.

4) Radiation effects

Computer simulations which have played such an important role in the study of radiation effects in crystals are very few for glasses. The only ones seem to be those from Doan [16] on Silica and Doyama et al. [29] on amorphous Iron. The striking result in these two simulations is the occurrence of collision sequences very similar to the replacement collision sequences in crystals. In Silica, prepared by quenching from the melt, a large number of stable defects are observed (Oxygen and Silicon vacancies/interstitials and more complex defects).

In amorphous Iron obtained by dense random packing and relaxation it is observed that most of the defects created relax with the exception of those which are surrounded symmetrically with 8 or 12 neighbours. Figure 5 shows collision sequences in Silica created by a primary of oxygen of 150 eV (Doan [16]) and in amorphous iron (Doyama et al. [29]).

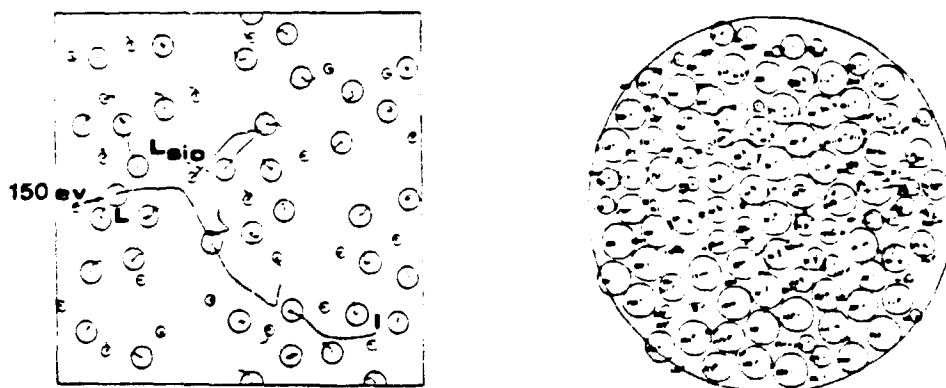


Fig. 5 : Collision sequences in : left) : Silica after Doan [16]; right) : Iron after Doyama et al. [29]. Initiated by 50 eV knock-on.

II - IDENTIFICATION AND ROLE OF DEFECTS FROM EXPERIMENTAL STUDIES

We shall discuss experimental techniques and experimental results.

1) Experimental techniques

We shall not describe here the experimental techniques which are used for diffusion, relaxation, viscosity and positron measurements and which are detailed in several review papers, for instance, Philibert [46], Limoge et al. [3], Hillairet [47], Gopinathan et al. [48] (this last one is a review on positron techniques).

We should however like to emphasize the following points :

- the low values of the diffusion coefficients in amorphous solids (from 10^{-18} to 10^{-27} $\text{m}^2 \text{s}^{-1}$) make the diffusion measurements very difficult ;
- in our opinion the ion abrasion in conjunction with a method of analysis (radioactivity counting or mass spectrometry) yields the more precise values of diffusion coefficients, even though it is not the most sensitive method.

It has been shown (Gupta et al. [50], Maier et al. [51]) that data obtained by this method are in close agreement with the extrapolations of high temperature measurements obtained by other techniques. Figure 6, Horvath et al. [49], shows the quality of the $C(x)$ plots which can be obtained. The smallest diffusion coefficients which can be measured by this technique are about $10^{-24} \text{ m}^2 \text{ s}^{-1}$.

- the more sensitive techniques are those where D is determined from the evolution of a film (by X-rays or resistance measurements) which has a periodic composition. The film is prepared by evaporation or sputtering and the periodicity of the composition is some 10 Angstroms . It is then possible to measure diffusion coefficients as low as $10^{-27} \text{ m}^2 \text{ s}^{-1}$, Rosenblum et al. [52], Greer et al. [53], Reda et al. [54]. Because of the neighbourhood of surfaces and the possibility of the presence of a large number of defects one can wonder whether the values which are obtained in such thin films are representative of the bulk material. According to Cook et al. [55], who carried out such experiments in polycrystals (Au-Ag), the answer is yes (the values obtained are in good agreement with the ones extrapolated from the high temperature data); on the contrary Turner et al. [56], Wagendristel [57], Weaver [58] found a large increase in the diffusivity; but in these latter cases the diffusion samples were not films with a periodic composition but classical diffusion arrangements A/B some hundred Angstroms thick.

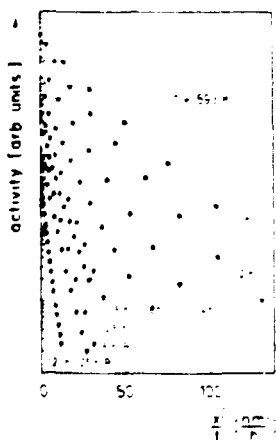


Fig. 6 : Penetration plots for ^{59}Fe diffusion in $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ alloy. The parameters denote the annealing time after Horvath et al. [49]

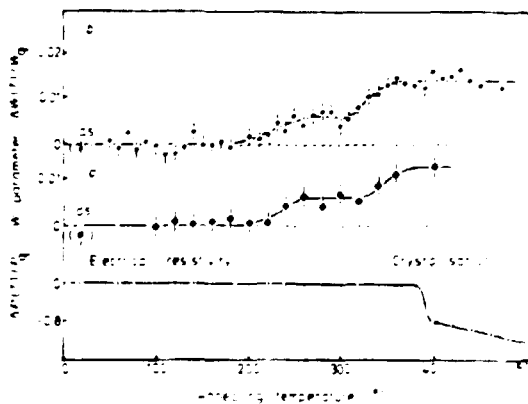


Fig. 7 : a and b : relaxation stages as observed by positron techniques in metglas 2826; lower curve : corresponding resistivity measurements after Mihara et al. [59]

- Local order studies by anelasticity, magnetic anisotropy or resistivity measurements are very sensitive and precise techniques for the determination of D but they also need a precise knowledge of atomic mechanisms for local order. In amorphous alloys where these mechanisms are not known it is not possible to obtain D from a measurement of the local order time τ . Nevertheless relations between D and τ established for crystals are often used for amorphous alloys although they are not theoretically founded. In

addition local ordering and long range diffusion can involve different parts of the material if metglas presents the heterogeneous structure mentioned above.

- In contrast to what has often been said the positron annihilation technique seems sensitive enough, so that different stages during relaxation are observed with positrons but nothing with resistivity (after Mihara et al. [59]) as shown in figure 7.

2) Experimental results

We shall review in this section the main results in relaxation, diffusion, viscosity and irradiation experiments.

A - Structural relaxation

- The amorphous alloys are always prepared by a method analogous to that of a very brutal quenching, so on annealing an as-quenched metallic glass many properties vary ; density increases, Young modulus increases, viscosity increases, diffusion decreases... As expected from the phenomenological models (see above) relaxation phenomena display a spectrum of activation energies (Balanzat [60], Cost et al. [61]) ; these models are also able to explain cross-over phenomena, $\text{Log}(t)$ kinetics which are often observed and reversible evolutions near "equilibrium". Even when the thermodynamical properties change only by a few percent during annealing, dynamical ones (viscosity, diffusion) can vary by several orders of magnitude. For example in figure 8 we can see the variation of viscosity as a function of annealing time for Pd-Si-Cu alloy, after Taub et al. [62].

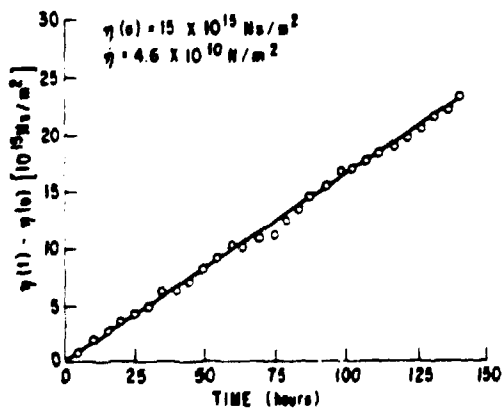


Fig. 8 : Viscosity versus annealing time in $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ alloy at 534 K after Taub et al. [62]

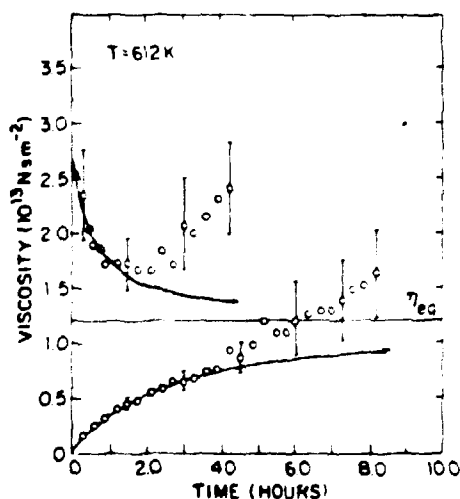


Fig. 9 : Relaxation of the viscosity of $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ alloy at 612 K from both sides of the equilibrium state; deviations from the curves are due to the crystallization. After Tsao et al. [63]

- At a high temperature ($\sim T_g$) amorphous alloys can relax to the corresponding metastable equilibrium ; the reality of such an equilibrium is

shown in figure 9 which represents the evolution of viscosity from both sides of the equilibrium state for a Pd-Si-Cu alloys, after Tsao et al. [63]. Generally crystallization disturbs these experiments.

- At low temperature (below T_g) "equilibrium" cannot be achieved but it is possible to reach structural states which evolve very slowly ; when this evolution is practically null (on the time scale of an experiment) one is said to be in an isoconfigurational state (see figure 10).

- The relaxation could depend on the measured property ; this is shown in figure 11 where viscosity and diffusion (D_{Fe}) in $Fe_{40}Ni_{40}B_{20}$ are represented as a function of annealing time. We can see that the diffusion coefficient becomes constant after 100 hours while the viscosity is still changing after 300 hours. Viscosity measurements are due to Van den Beukel et al. [64] and diffusion to Horvath et al. [49].

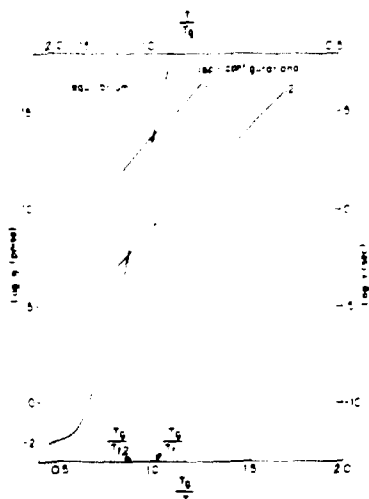


Fig. 10 : Schematic representation of the equilibrium and isoconfigurational viscosity of an amorphous system. Tf_1 and Tf_2 are the fictive temperature of the configurations corresponding to the isoconfigurational viscosities (1) and (2) after Spaepen et al. [91].

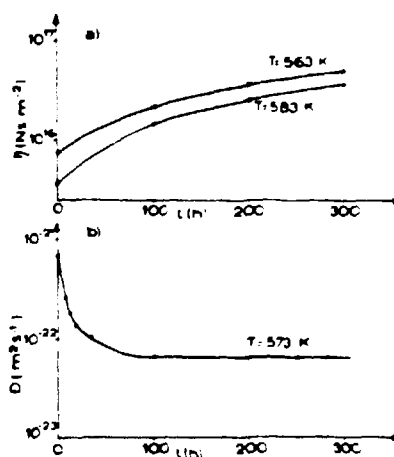


Fig. 11 : Viscosity and diffusion versus annealing time in

$Fe_{40}Ni_{40}B_{20}$.

a) Viscosity after Van den Beukel et al. [64]. The same sample has been used at 523 K, 543 K, 563 K and 583 K (300 hours for each of these temperatures) ⁵⁹Fe after Horvath et al. [49].

- Simulation of relaxation by molecular dynamics has been done by Egami et al. [25] and Kobayashi et al. [30]. These two studies yield rather contradictory results. According to Egami the irreversible part of the relaxation (i.e. the one which cannot be restored by thermal treatments) would be due to annihilation of positive and negative pressure fluctuations. In contrast Kobayashi shows that the distribution of local pressures remains almost unchanged during annealing. In addition in this model topological and chemical short range orders (CSRO) are linked and the relaxation is correlated to CSRO. In spite of these contradictory results obtained here, this type of studies are necessary for the understanding of these complicated phenomena.

B - Diffusion

We want to emphasize the following points :

- It is difficult to compare quantitatively diffusion in amorphous and crystalline materials since very few systems have the same composition in the two states. When they do exist, for instance, Se, SiO_2 , Si..., either the diffusion is known in only one of the materials or, when it is known for each material, the values are questionable. Cantor [5] compares diffusion in a range of Fe, Ni and Pd amorphous alloys with self- and impurity-diffusion in fcc and bcc Fe and in Ni (see figure 12). We see that :

$$D_{\text{GB}} > D_{\text{amorphous}} > D_{\text{c}}^{\text{S}}$$

D_{GB} is the grain boundary diffusion and D_{c}^{S} the substitutional or self-diffusion in crystals. In a recent experiment, Barbour et al. [65], it has been shown that Ni diffusion in amorphous $\text{Ni}_{50}\text{Zr}_{50}$ is about 4 orders of magnitude smaller than in crystalline Zr. We must point out here that Ni is a fast diffuser in crystalline Zr.

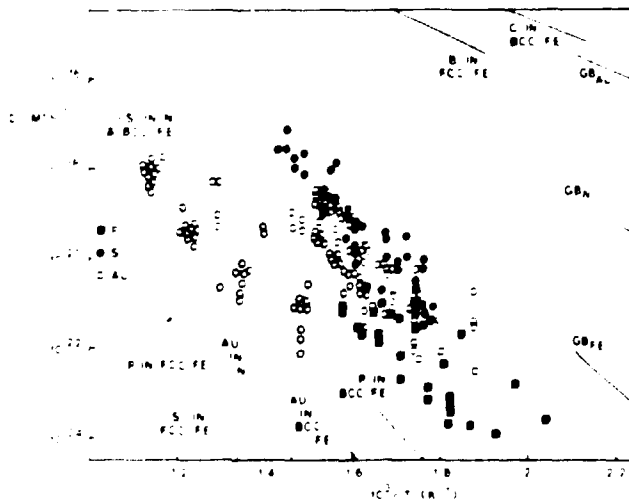


Fig. 12 : Au, P and Si diffusion coefficients in amorphous alloys, together with comparable crystalline data after Cantor [5].

- Diffusion in amorphous alloys is more similar to diffusion in crystals (Q and D_0 of the same order of magnitude) than in liquids.

- In contradiction with the model of Belashchenko [39] the activation energy for diffusion seems to be constant in the experimental range of measurements; since this range is always narrow (about 100°C) one wonders if the experimental precision is high enough to detect a curvature in the Arrhenius plot.

- According to Cantor et al. [4], Akhtar et al. [66] it seems that the behaviours are not different below and above T_g : Arrhenius plots are straight lines in the limit of the experimental precision. In fact since the range of temperatures explored above T_g is very small this statement is questionable.

- One Kirkendall effect experiment has been done on the NiZr amorphous alloy by Hahn et al. [67]. It gives us useful information on the diffusion mechanism; in this system Ni is more mobile than Zr and has to diffuse

through the skeleton of the Zr atoms. As has been previously pointed out Ni is a fast diffuser in crystalline Zr (α and β) and it seems that this is also true in the amorphous state.

- Indirect measurements of diffusion under hydrostatic pressure, by kinetic studies of the crystallization in metglas 2826 (Limoge [68]), yield a volume of activation of the order of an atomic volume. Thus a defect or a fluctuation of volume is involved in the diffusion process. To go further we need a direct measurement of self diffusion under pressure.

- As seen previously D depends on the thermal history of the sample ; generally it is larger for as-quenched samples than for relaxed ones ; some exceptions to this behaviour have been observed by Akhtar et al. [66] (in this case D did not depend on preannealing). For as-quenched samples the diffusivity can depend on the face of the amorphous ribbon as shown by Edelin et al. [69] ; this difference of behaviour for the two faces of the sample may be due to the difference in the quenching rate.

- D depends on the mechanical treatments ; it seems to increase after plastic deformation, Akhtar et al. [70].

- There are few experiments on diffusion under irradiation ; for instance Cahn et al. [71] have reported that after neutron irradiations of $Ni_{64}Zr_{36}$ the Au diffusivity decreased and this was explained by assuming that irradiation favours the relaxation ; Hillairet et al. [72] showed that local ordering in $Cu_{50}Ti_{50}$ was slightly enhanced after electron irradiation and more stronger after proton irradiation. Finally Barbu et al. [73] and Limoge [68] have interpreted :

- the acceleration of nucleation in metglas 2826
- the acceleration of the growth of crystals (NiNb) in Ni_6Nb_4 amorphous alloy (see figure 13).

as an enhancement of diffusion under electron irradiation :

- There are many studies on hydrogen diffusion in metallic glasses ; as in metals, hydrogen is a fast diffuser, D increases with hydrogen content. For more details see the reviews by Cantor et al. [4], Limoge et al. [3], Kirchheim et al. [74].

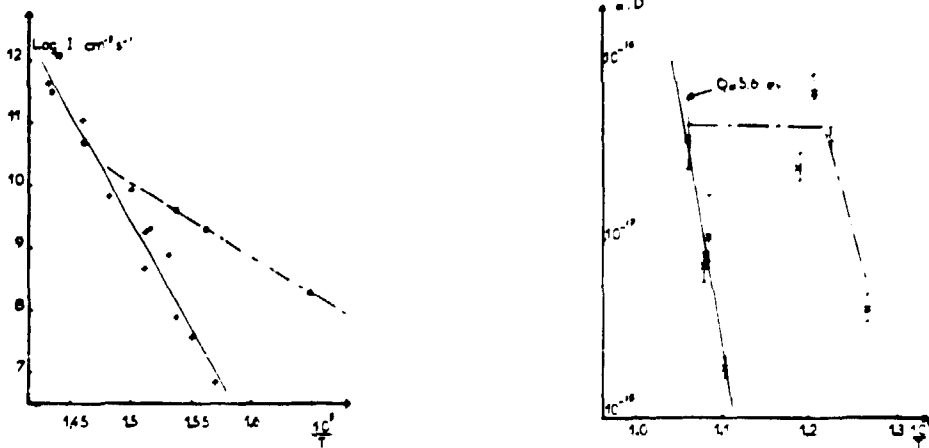


Fig. 13 : Irradiation effect on crystallization. Left) : in metglas 2826 after Barbu et al. [73]. I is the nucleation rate which is proportional to D.

+ : without Irradiation. O : with Irradiation

Right) : in $Ni_{60}Nb_{40}$ after Limoge [68].

D is the chemical diffusion coefficient $m^2 s^{-1}$, α a numerical factor = 45.2
 full line : without Irradiation. dashed-dotted line : with Irradiation

C - Viscosity

- It has been observed that around or above T_g equilibrium values of viscosity can be reached as shown in figure 9 ; in this range of temperature the Stokes-Einstein relation : $\eta = kT/(6\pi Da)$ seems to be obeyed as for liquids, Chen et al. [75], Brébec et al. [76].

- Below T_g viscosity evolves linearly with annealing time as previously shown in figures 8 and 11. In this range Stokes-Einstein relation is not satisfied as was already pointed out by Limoge et al. [3] and Greer [2] ; but in the few cases where experimental values are available, the activation energy for viscosity remains close to the self diffusion one [3].

- The relation between diffusion and viscosity is of prime interest for the understanding of atomic transport. In liquids and supercooled liquids the "free volume" phenomenological theory gives a description of diffusion and viscosity with the same mechanism and, as we have seen, the Stokes-Einstein relation is obeyed, in contrast to the glassy domain. In this domain we have shown earlier [3] that the mechanism of the Nabarro-Herring creep is able to reproduce the experimental behaviours. In that case $\eta = kTd^2/40D\Omega$, with d being the "grain size" and the atomic volume. By using Taub et al. [77], Tsao et al. [78] and Greer et al. [53] results, a value of d of the order of 20 Angströms could be derived in the Pd-Si class of metglasses (for an annealing time of 20 hours) [3]. In the most recently studied alloy ($Fe_{40}Ni_{40}B_{20}$) Van den Beukel et al. [64], Horvath et al. [49] an even larger value can be derived in the same way : d is found to be 3900 Å (after some hundred hours of annealing for viscosity measurements).

In fact the heterogeneous structure of metallic glasses (i.e. well "ordered" atom clusters imbedded in more loosely packed medium) could support this approach. One can therefore imagine deformation mechanisms similar to those of polycrystals, where the "ordered clusters" would play the role of the grains in polycrystals. Because diffusion in a loosely packed medium is thought to be generally faster than in a denser one, one can also think of other diffusion controlled mechanisms. Namely :

- Superplasticity deformation mechanism controlled by diffusion in the loosely packed medium.

- Coble creep, i.e. Nabarro-Herring creep controlled by diffusion in the loosely packed medium (in this case the viscosity depends on d^3/δ , where δ is the thickness of the grain boundary, instead of d^2 for Nabarro creep). In that case, assuming $\delta = 5 \text{ Å}$, the previous d values would reach the order of 18 Å for Pd-Si alloys and 600 Å for FeNiB alloys.

These results on the whole raise three important points to be discussed:

- If this kind of approach is sound, one can wonder if such large ordered domains (600-4000 Å) cannot be directly evidenced in samples which would have been "dynamically recrystallized", using improperly the vocabulary of crystals. If these ordered domains are crystals or quasicrystals they should be easily observed by electron microscopy.

- If other mechanisms are involved the analysis we have done is not correct and the relation between D and η is not so simple.

- Finally we have to keep in mind that the different behaviours of D and η with respect to annealing (η continuously increases, D becomes constant) may be due to experimental conditions : diffusion is always measured near a surface where relaxation could be faster than in the bulk, while the viscosity measurements inherently involve the whole sample. Thus it is important to strain a very thin specimen (if possible !) and/or improve D measurements by local ordering techniques to find bulk mobility.

D - Irradiation effects

In this field there are many experimental results which seem rather contradictory, see for instance the review by Nandedkar et al. [79]. To summarize we classify the data in :

- Annealing stages after low temperature irradiation
- Irradiation with heavy ions of high energy
- Structural changes and related phenomena

(the effect of irradiation on diffusion has been discussed above).

a) Annealing stages after low temperature irradiation

Two types of behaviours are observed when electrical resistivity is used to measure the "defect" concentration :

- In some alloys such as Fe-B, Cu-Ti, Cu-Zr, Ti-Be-Zr... there are several stages during annealing, Audouard et al. [80], Hillairet et al. [81].
- In PdSi alloys annealing is continuous, Klaumunzer et al. [82]

The stages are interpreted by some authors (Audouard et al. [80]) as point defects annealing, but this interpretation is controversial :

- * during annealing short range order complicates the analysis
- * the curves representing the variation of the positron lifetime with annealing temperature are in general continuous (see figure 14 where is shown the difference of behaviour between resistivity and positron measurements). Nevertheless the annealing after low temperature irradiation is interpreted as an evidence of interstitial-vacancy "close-pairs" or vacancy-like defects; as the biggest vacancy seems to be the less stable, they could be the density fluctuations increased by irradiation (Yli et al. [83], Moser et al. [84]). They also could be vacancies or Frenkel pairs, created in densely packed zones where the symmetry is high, as observed in the simulations of Doyama et al [29].

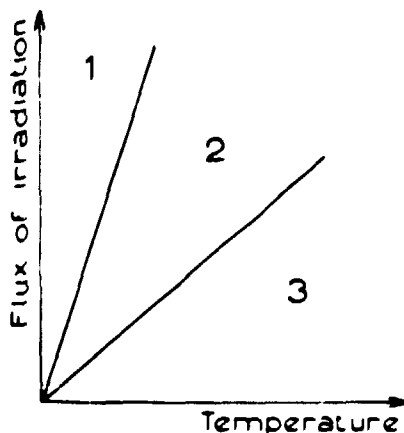
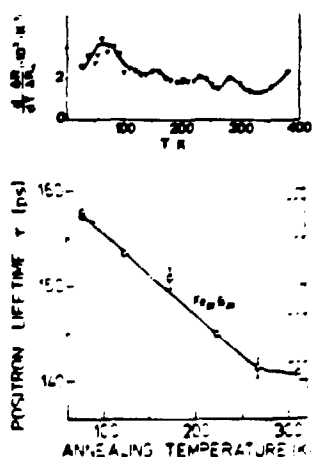


Fig. 14 (Left) ; - Isochronal annealings of Fe₈₀B₂₀ after electron irradiation at 20 K. Upper curve : derivation annealing curves as obtained by resistivity measurements after Audouard et al. [80]. Lower curve : positron life time after Moser et al. [84].

Fig. 15 (Right) : - Diagram flux/temperature (see text). We give this very schematic diagram although, as in crystals, it is likely that the boundaries between domains do not go through the origin.

b) Irradiation with heavy ions of very high energy

Irradiation of strips of metallic glasses with heavy ions of energy between a few hundred MeV and a few GeV under conditions such that there is no implantation, shows a "growth" phenomenon, similar to the growth in anisotropic crystals, which is linearly dependent on the dose and increases as the temperature is lowered. The origin of this phenomenon could be :

- the strong damage anisotropy produced by the few elastic recoils of high energy in a direction perpendicular to the beam, Klaumünzer et al. [85], Sunmacher et al. [86].

- the electronic excitations, Audouard et al. [87].

In our opinion it could be creep by diffusion induced by the sub-threshold collisions due to the very high flux of electrons ejected in the direction perpendicular to the beam (i.e. delta rays) in the stress field due to the damage anisotropy. This has to be analysed in more detail.

c) Structural evolution (see Limoge et al. [88])

Data from the literature are rather contradictory. They become more coherent if we assume, as in crystals, that irradiations modify both kinetics and thermodynamics. For a given temperature and damage rate, expressed in dpa s^{-1} for instance, we assume that there is a stationary state which could be considered as if it were in a thermodynamical equilibrium under irradiation. Then using mainly data from Nandedkar et al's review [79] we can represent the structural modifications in a flux/temperature diagram as in figure 15 where we observe * :

- In zone 1 : density decrease, destruction of short order, slowing down of crystallization kinetics or increase of crystallization temperature, increase of local fluctuations, helium in solution ?, modification of $g(r)$, ductility increase.

- In zone 2 : ductility decreases ?, density increases ?, short range order increases, formation of helium bubbles, enhancement of crystallization kinetics or decrease of crystallization temperature, modification of $g(r)$, decrease of local density fluctuations.

- In zone 3 : no structural modifications compared to thermal treatments without irradiation.

It is important to emphasize here that such a description is, of course, more speculative than in crystals and has to be considered at the present time only as a guide. Furthermore we have to insist on the crucial importance of the study of diffusion enhancement by irradiation which seems to be one of the best tests of diffusion mechanisms. So the increase of short range order kinetics should be probably observed only :

- if diffusion proceeds by more or less localized defects the concentration of which is increased by irradiation.

- or if the diffusion mechanism is of the type proposed by Doyama et al. [29] or Doan et al. [44] but in this case it has to be the radiation induced-diffusion. In these conditions the kinetic energy of atoms in rings or elementary jumps has to be of the order of magnitude of the interaction energy in the short range order and if it is not the case irradiation should destroy short range order.

* ? means that it is not well established or not yet observed

III - DISCUSSION

We have now to answer the questions we put at the beginning.

1°) To the question "is it possible to define point defects in metallic glasses" the answer is yes if :

a) the structure can be described by structural units in a continuous random network ; this has not been demonstrated to date.

b) the local symmetry in the D.R.P. is high enough in some places so as to impose a symmetrical relaxation around the defect and thus allows its localization.

It should be emphasized that the results of the simulations are very sensitive to the interatomic potential used; it is desirable to carry out simulations with more realistic and reliable potentials.

2°) Is there experimental evidence of localized defects of an atomic size ? The answer is controversial because it is based on positron annihilation data the interpretation of which differs with authors. This point would be clarified by a theoretical model of positron trapping in metallic glasses (Gupta, to be published).

Nevertheless computer simulations of defects in metallic glasses seem to indicate that such defects could exist (see question 1).

3°) If localized defects exist (question 2) is there some information about their lifetime ?

The answer is yes. Computer simulations and positron annihilation experiments seem to indicate that their lifetime is much shorter than the lifetime of defects in crystals.

4°) Do we know the role of these possible defects in atomic transport in metallic glasses ?

The answer is no, whatever is the defect (vacancy or local pressure) since the diffusion mechanism is not known. We think that this problem could be solved by :

- * experiments (see 5°))

- * computer simulations with more realistic models :

- better atomic interactions by a combination of molecular dynamics and tight-binding calculations of forces on the atoms, Legrand [89], Legrand et al. [90].

- systems with pressure and temperature constant, Nose [19].

5°) Is it important to pursue experimental work on diffusion ?

The answer is yes, but if the aim is to clarify diffusion mechanisms we have to use as simple alloys as possible, measure all diffusion coefficients of the components of the glass, compare different experimental techniques and concentrate the experimental effort in specific areas :

- Effect of pressure on self diffusion

- Study of the diffusion below and above T_g (to know if there is a change in the mechanism)

- Comparison between D and η

- Effect of irradiation (SRO kinetics and direct measurements as discussed before).

IV - CONCLUSION

In the last few years some progress was made in the study of defects and atom transport in glassy alloys. The consequence is that this field seems even more difficult. The "quasi-vacancy" approach was very useful in trying to understand the first results because glassy alloys were more similar to crystals than to liquids. But this analogy has nothing to do with the scientific proof and sticking too long to the analogy arguments could kill any real progress.

So the first priority seems to be to concentrate now on computer simulations and experiments which could help to clarify diffusion mechanisms and "medium range" structure in the Gaskell sense. To end this review, a glance on the evolution of the knowledge of defects and atom transport in crystals from 1940 up to now shows that, even at the very beginning, very good theoretical models were used to guide experimental work. In the much more complicated field of amorphous alloys it is hopeless to expect much progress without a very large use and development of computer simulations and associated theoretical work. Fortunately, from the work done during the last few years, one could be optimistic for progress in the future.

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