DIFFUSION MECHANISMS IN AMORPHISATION BY S-S REACTION

R.W. CAHN

*Department of Materials Science and Metallurgy, University of
Cambridge, Pembroke Street, GB-Cambridge CB2 3QZ, Great-Britain*

Résumé — Pendant l'amorphisation en état solide, la diffusion à travers la couche croissante d'alliage amorphe qui sépare les réactifs métalliques doit limiter la vitesse de réaction. Alors, la compréhension du processus de diffusion aidera l'interprétation de la cinétique de réaction. Ce court article a pour but d'esquisser les généralisations qui sont maintenant bien établis pour la diffusion dans les verres métalliques, y compris l'effet de la taille des atomes, les énergies d'activation et l'effet de la relaxation du verre sur la diffusion. On discute les informations à propos de la vitesse de diffusion pendant l'amorphisation en état solide.

Abstract — In SSAR, diffusion through the growing thickness of amorphous material separating the reacting metals is likely to be rate-determining for the speed of reaction. Accordingly, understanding of diffusion rates helps in interpreting reaction kinetics. This presentation outlines the principal generalizations now established for diffusion in metallic glasses, including effects of atom sizes, activation energies, and the effect of relaxing the glass structure on diffusion. Evidence about the rate of diffusion during SSAR is outlined.

1. — INTRODUCTION

At this conference, we are treating two distinct types of solid-state amorphisation reaction: SSAR by interdiffusion of metals in a multilayer, and SSAR by mechanical milling. In the second form, the crucial feature appears to be the destruction of atomic order prior to spontaneous amorphisation, and diffusion in the amorphous state should not be relevant. In the first form, the fast-diffusing constituent metal has to reach the other metal by diffusing through the amorphous layer as this grows, and it is likely that this diffusion process will be rate-limiting. For this reason, a brief overview of diffusion in metal-metal glasses is relevant to the purposes of this conference.

A number of reviews of the general topic of diffusion in metallic glasses have appeared in recent years [1-4]. These deal not only with the phenomenological features but also with the contentious issue of diffusion mechanisms; this last is only marginally relevant in the present context, and I refer the reader to two papers which specifically discuss various models [5,6], and to my own recent review [4].

2. — DIFFUSION, ATOMIC SIZES AND CHEMICAL CHARACTER

It is well known that the diffusive variant of SSAR is entirely dependent on rapid diffusion of *one* of the two atomic species through the amorphous layer, combined with very slow diffusion of the other. For instance, it is known that in Ni-Zr glasses, Ni diffuses several powers of ten faster than Zr. Barbour et al.[7] cited a disparity factor of 10^4 , while Greer [private communication] has measured a ratio of around a million to one in this system at 250°C. In this connection, it is important to note that the relative diffusivities of different solutes in the same metallic glass at the same temperature are inversely related to the atomic radii of the solutes. Thus, the standard atomic radii (calculated from atomic volumes) of Ni and Zr are 1.377 and 1.771 Å, respectively, a ratio of 1.286; the ratio of atomic volumes (which would probably be a more apposite measure in connection with diffusion) is 2.13.

The clearest set of results concerning the effect of solute atom size on diffusivity come from the work of Hahn et al.[8] (the particular reference cited discusses these findings in connection with SSAR) and from that of Sharma [9,10]. Table 1, from Hahn et al., gives details of diffusion of different solutes in $\text{Ni}_{50}\text{Zr}_{50}$ glass.

TABLE 1: Tracer diffusivities in amorphous $\text{Ni}_{50}\text{Zr}_{50}$ (ref.12)

Tracer	Atomic radius (nm)	Q (eV/atom)	D (573K) ($10^{-18}\text{cm}^2\text{s}^{-1}$)
Co	0.126	1.40	1852.0
Ni	0.125	1.45	318.0
Cu	0.128	1.57	29.8
Fe	0.128	1.64	30.2
Au	0.144	1.77	0.044
Ti	0.147	—	0.160

The extreme sensitivity to atom size is evident. Fig. 1 shows Sharma's data on diffusion of 4 solutes in another Ni-Zr glass, of composition $\text{Ni}_{61}\text{Zr}_{39}$. The figure comes from ref. 9, with a value for Al, from ref. 10, inserted. Here the dependence on atomic size is less pronounced. — Further evidence, in the same direction, comes from a comparison of diffusivities of metallic and metalloid solute species in the same kinds of glasses; Fig. 2 shows this for B,

Si, Au, P, Ag and Fe in several rather similar metal-metalloid glasses, from a compilation by Cantor[1]. — Irrespective of the exact mechanism of diffusion in such glasses, the greater ease with which smaller atoms move is just what one would expect.

A different correlation was proposed by Böttiger et al. [11,12], who compared diffusivities of W, Au, Hg, Pb and Bi in two Ni-Zr glasses and the diffusivities of Bi, Pb, Ti, Hg, Au, W, Pt and Ir in $\text{Pd}_{78}\text{Cu}_6\text{Si}_{16}$ glass. In the first study [11] they found changes in diffusion with time (not due to relaxation) which they could rationalize by postulating that oxygen complexes form round metal atoms during annealing, the more strongly so, the larger the

Fig. 1. The dependence of diffusion coefficient on the atomic radius of the diffusing species in a metallic glass. (After Sharma et al.).

Fig. 2. Comparison of different diffusing species in metal-metalloid glasses. After Cantor).

formation enthalpy of the metal oxide in question. In accord with this, there was no time dependence at all for the diffusivity of gold, the oxide of which has low stability. — In the second study [12], the normal inverse relationship between diffusivity and solute atom size was not obeyed by W and Ir, and these particular metals from very stable oxides. — It is in accord with this approach that M. Nastasi and R.W. Cahn (unpublished research) were unable to observe any diffusion at all of C in a Ni-Nb glass.

Sharma et al.[9] also succeeded in establishing a regularity concerning the diffusional activation energy, Q , of various solutes in the same glass; he found these to be related to the formation energy of a 'hole' in the corresponding glass, computed according to a model due to Miedema. That energy, in turn, is proportional to the crystallization temperature of the glass, T_x .

Sharma et al. found that Q is proportional to T_x when a correction is made for the size of the diffusing atoms. Sharma interprets this as implying that the larger the solute atom and the harder it is to form holes (i.e., vacanc-like entities) in the glass, the harder the solute finds it to migrate. This assumes that there are recognizable holes in a metallic glass, which is hotly disputed by some.

3. — REDUCTION OF DIFFUSIVITY BY RELAXATION

The very first investigators of diffusion in a metallic glass[13], in 1978, reported a steep decrease in diffusivity with time of holding at the measurement temperature. Since then, this feature has been investigated many times, with very variable results. It now appears that this decrease is observed only if the metallic glass has been made by a very drastic quenching process, so that there is plenty of scope for structural relaxation; otherwise, relaxation takes place during the quench. The apparent magnitude of the effect also depends on the sensitivity of the technique for measuring diffusivity. For this purpose, by far the most sensitive technique is that based on x-ray diffraction from multilayers[14]: structural relaxation implies an increase in density with a consequent change in multilayer periodicity, which shows up by a change in Bragg angle. Fig. 3, constructed from the data of a study by Chason and Mizoguchi, using this method[15], shows how the interdiffusivity between the constituents of a Fe-Ti multilayer varies as the atomic volume (and therefore the free volume) changes during annealing at various temperatures. This figure shows what is probably the largest relaxation-induced change in diffusivity to date.

Fig. 3. Interdiffusivity, D , against change in atomic volume, $\Delta V/V$, in an amorphous Fe-Ti multilayer: the solid line is a fit to the free volume theory of diffusion. (After Chason and Mizoguchi).

Fig. 4. Time dependence of Fe self-diffusion in $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ glass at 673K. (After Ulfert et al.).

Fig. 4 is an example of relaxation-induced change in diffusivity deduced from a precision study made with the aid of a radioactive diffusant, using a sputtering technique for serial sectioning[16]. As befits this less sensitive technique, the change is smaller than that revealed by Fig. 3.

It is interesting to note that amorphous alloy films made by co-deposition of two elements on to a substrate show no reduction of diffusivity with time. This was shown by Hoshino et al.[17], who made a near-equiatom NiZr glass by coevaporation and found that even an anneal as long as 48h at 295°C did not alter the diffusivity of Co tracer. This is in accord with earlier measurements on amorphous films made in this way. It appears that co-evaporated films are not subject to relaxation in the way that melt-quenched glasses are, though it is not obvious why this should be so.

It would be most interesting to know whether there is any possibility of

relaxation in the amorphous layers created by SSAR in multilayers...i.e., in glasses which grow by an interdiffusion process, and may therefore be in a fully relaxed condition...i.e., in metastable structural equilibrium. There have been no explicit measurements of diffusivity in such SSAR-generated amorphous alloys as a function of annealing time, but so far as the indirect evidence to be summarised in the next Section goes, it would appear that here, also, there is *no* relaxation.

4. — KINETICS OF SSAR AS RELATED TO DIFFUSION IN AMORPHOUS LAYERS

Early studies on SSAR by diffusion in multilayers commonly assessed the kinetics of the process by examining the multilayers destructively by electron microscopy after various annealing periods. More recently, non-destructive methods have been used, using either RBS[18] or measurements of electrical resistance of the multi-layers[19,20]. The first two papers deal with Zr-Co multilayers: The thickness of the amorphous layers was found[18] to be proportional to $\sqrt{t}$ (where t = time), as would be expected for a layer thickness entirely controlled by diffusion, but since no direct measurements of diffusion have been made in CoZr glass, no comparison of the klayer thickness kinetics with those predicted from known diffusivities is here possible. However, a recent study by Rubin and Schwarz[20] of SSAR in a multilayer designed to generate equiatomic NiZr amorphous layers, using resistivity measurements during continuous slow heating, combined with a sophisticated analysis to derive amorphous layer thickness from the resistivity values, gave a plot as shown in Fig. 5. The '1X' points are derived from multilayers with initial elemental layers 132 nm thick, '2X' refers to layers 264 nm thick and '4X', to layers 529 nm thick. The diffusion distances are of course greater for the thicker initial layers. Rubin and Schwarz's analysis for the steady-state stage, when the initial layers have turned into equilibrium solid solutions by early diffusion, is that $\ln[x_{\text{am}}(dx_{\text{am}}/dt)]$, where x_{am} is the thickness of the amorphous layers, is equal to the instantaneous diffusivity at the temperature reached during the steady heating process.

Fig. 5. Plot of $\ln[x_{\text{am}}(dx_{\text{am}}/dt)]$ against $1/T$ for Ni/Zr multilayers of various periodicities. The straight line is a least-squares fit to the linear (equilibrium) portions of the various curves. (After Rubin and Schwarz).

The fitted straight line in Fig. 5, then, represents a plot of diffusivity, D , against temperature, T , for Ni diffusing in amorphous NiZr. (The straightness of the line seems to imply that there was no relaxation-induced change of diffusivity during the heating ramp). From this line, Rubin and Schwarz determined the prefactor, D_0 , to be $(2.5 \pm 4) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, while the activation energy, Q , is $1.01 \pm 0.04 \text{ eV/atom}$. This can be compared with experimentally measured diffusivity values for Ni in am-NiZr, determined by Hahn et al.[8]: in their work, D_0 was determined as $1.7 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ while Q is 1.45 eV/atom . The difference between the two pairs of numbers is considerable, and suggests that there is some unrecognized difference between the diffusion process in an SSAR-generated amorphous alloy and tracer diffusion in an amorphous foil made by melt-spinning (which was the way that Hahn et al. made their experimental glass). — It is to be hoped that further comparisons of this type will become possible as a result of future experiments along the lines of Rubin and Schwarz's work.

REFERENCES

- [1] Cantor, B., in: Haasen, P., Jaffee, R.I., editors, *Amorphous Metals and Semiconductors* (1986) p. 108.
- [2] Cahn, R.W., *J. Vac. Sci. Technol. A* **4** (1986) 3071.
- [3] Cahn, R.W., in: *Second Supplementary Volume of Encyclopedia of Materials Science and Engineering*, Oxford: Pergamon (1988) 308.
- [4] Cahn, R.W., in: *Basic Features of the Glassy State*, J. Colmenero, editor. Singapore: World Scientific (1990), in press.
- [5] Kirchheim, R. and Stolz, U., *J. Non-Cryst. Solids* **70** (1985) 323.
- [6] Frank, W., Horváth, J. and Kronmüller, H., *Mat. Sci. & Eng.* **97** (1988) 415.
- [7] Barbour, J.C., Saris, F.W., Nastasi, M. and Mayer, J.W., *Phys. Rev. B* **32** (1985) 1363.
- [8] Hahn, H., Averback, R.S. and Shyu, H.-M., *J. Less-Comm. Metals* **140** (1988) 345.
- [9] Sharma, S.K., Banerjee, S., Kuldeep and Jain, A.K., *J. Mater. Res.* **4** (1989) 603.
- [10] Sharma, S.K. and Mukhopadhyay, P. *Acta metall.* **38** (1990) 129.
- [11] Böttiger, J., Dyrbye, K., Pampus, K. and Torp, B., *Int. J. Rapid Solid.* **2** (1986) 191.
- [12] Böttiger, J., Dyrbye, K., Pampus, K., Torp, B. and Wiene, P.H., *Phys. Rev. B* **37** (1988) 9951.
- [13] Chen, H.S., Kimerling, L.C., Poate, J.M. and Brown, W.L., *Appl. Phys. Lett.* **32** (1978) 461.
- [14] Greer, A.L. and Spaepen, F., chapter on 'Diffusion' in: *Synthetic Modulated Structures*, Chang, L.L. and Giessen, B.C. editors. New York, Academic Press (1985) p. 419.
- [15] Chason, E.H. and Mizoguchi, T., *MRS Symp. Proc. Vol. 80* (1987) p. 61.
- [16] Ufert, W., Horváth, J., Frank, W. and Kronmüller, H., to be published.
See also: Horváth, J., Ott, J., Pfahler, K. and Ufert, W., *Mater. Sci. & Eng.* **97** (1988) 409.
- [17] Hoshino, K., Averback, R.S., Hahn, H. and Rothman, S.J., *J. Mater. Res.* **3** (1988) 55.
- [18] Pampus, K., Böttiger, J., Torp, B., Schröder, H. and Samwer, K., *Phys. Rev. B* **35** (1987) 7010.
- [19] Samwer, K., Schröder, H. and Pampus, K., *Mat. Sci. & Eng.* **97** (1988) 63.
- [20] Rubin, J.B. and Schwarz, R.B., *Appl. Phys. Lett.* **55** (1989) 36.