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Direct measurement by secondary-ion mass spectrometry of self-diffusion of boron in $Fe_{40}Ni_{40}B_{20}$ glass

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The available methods for measuring diffusion rates of various metalloids in metallic glasses are critically reviewed, and the advantages of studying boron diffusion by secondary-ion mass spectrometry (SIMS) set out.

A surface coating of chemical composition similar to that of the glass but enriched in ^{10}B was deposited on the polished, preannealed, glass by sputtering in an ultra-clean environment. The samples were diffusion-annealed and profiled by SIMS. Subsequent tests showed that some samples had partly crystallized and these had anomalously low diffusion rates. In the range between 340 and 370° C, D for boron varied between about 2×10^{-19} and 7×10^{-18} m^2 sec^{-1}. The values did not obey an Arrhenius relationship.

It is concluded that the method is feasible, and a number of improvements in technique are proposed in the light of experience.

1. Introduction

Only three measurements of diffusion rates in metallic glasses have been published to date [1–3] and these all refer to diffusion of metallic solutes. No measurement of *metalloid* diffusion in a metallic glass has been reported; yet such information is desirable since it is generally assumed that crystallization rates, as well as the kinetic of various pre-crystallization changes in physical and mechanical properties, are determined by metalloid diffusion rates. Extensive estimates of metalloid diffusivities in various Fe/B, Fe/B/C and Fe/Ni/B alloys have been made indirectly [4, 5] from the isothermal growth rates of spherical crystals in such glasses, on the basis of the approximate relation $r = 2\sqrt{(Dt)}$ (r = crystal radius, D = diffusivity of slowest diffusing metalloid, t = time). These estimates show that D increases at a fixed temperature as boron is replaced by carbon.

The present study has been undertaken to establish the feasibility of directly determining metalloid diffusivities in a metallic glass over a range of temperatures, with a view to later systematic studies of such diffusivities in a range of different glasses – for instance, as a function of metalloid content in a series of glasses.

2. Experimental strategy

The reason why diffusion measurements in metallic glasses have been so few is that the standard experimental methods are useless. D is generally below 10^{-18} m^2 sec^{-1} and moreover annealing times are limited by the need to avoid incipient crystallization. Accordingly, solute penetration is

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limited to some hundreds of nanometres at most and no standard method dependent on sectioning or absorption of radiation emitted by an isotope is sensitive enough.

The experiments published to date on metal-in-glass diffusion made use of: (a) ion-implantation of gold and analysis by ion back-scattering of the as-implanted and the diffused samples to establish changes in solute profile [3]; (b) ion-implantation of lithium followed by a neutron-induced nuclear reaction *in situ* of the implanted species and subsequent assessment of lithium profiles in diffused samples by energy analysis of the emitted radiation [2]; (c) micro-profiling by sputter-etching of a diffused sample containing radioactive silver tracer and measurement of the radioactivity of successive emitted fractions [1]. The first method is suitable only for heavy solute atoms in a matrix of lighter atoms and thus cannot be used for the study of metalloid diffusion. The second approach may be suitable for the study of boron diffusion and at least three attempts to exploit this method are currently in progress. The third method may be applicable to the study of the diffusion of radioactive ^{14}C if the available level of specific activity proves sufficiently high. This last technique has been successfully used to measure *Ds* as low as 10^{-22} m^2 sec^{-1} in crystalline metals [6, 7], but such measurements are not subject to limited diffusion times as are those in metallic glasses.

The most important metalloid solutes in metallic glasses are C, B, P and Si. The indirect studies already cited [4, 5] suggest that C diffusion may be just fast enough at the highest accessible temperatures to permit measurement of diffusion profiles on transverse sections by electron microprobe analysis, and experiments on these lines are under way at Sussex University. This method would not be applicable to B (diffusion is probably too slow and X-ray emission too weak), but it may prove useful for P, which is suspected of being a fast diffuser. The diffusion of Si, which is a relatively large atom, is probably far too slow for this approach, but the radioactive method mentioned above may prove appropriate for this element.

An approach which can in principle be tried for all four metalloids is profiling of a diffused couple by sputter-etching (ion-erosion). Here, material is removed very gradually by directing an ion beam at the surface of the sample so that atoms are sputter-etched away. Failing the radioactive tracer method used by Gupta *et al.* and others [1, 6, 7]—and this requires an appropriate isotope of high specific activity—the concentration profile for the diffusing species can be measured either by analysing successive atoms as they are sputtered away, or else by periodically analysing the freshly exposed surface. The various ways of performing such analyses, and the problems associated with securing accurate and reproducible rates of sputter-etching, are critically compared in a review by Coburn and Kay [8]. It is clear that analysis of sputtered material is preferable to the surface-analysis approach, and of the various techniques available for analysing sputtered species, SIMS is plainly the most highly developed and accurate. This method was used in the present study.

Three published investigations have used SIMS to measure diffusivities. Contamin and Slodzian [9] have examined oxygen diffusion in UO_2, at one temperature, while Brebec *et al.* [10] have measured the diffusivity of silicon in glassy SiO_2 at a range of temperatures. (SiO_2 only crystallizes with extreme sluggishness, so that there is no effective limitation of annealing times). To measure *self*-diffusion of a species which is already present as solute in the experimental material, it is necessary to use as tracer a separated stable isotope of the diffusing species: for the UO_2 study, ^{18}O was used, and for the SiO_2 study, ^{30}Si. In the first, $U^{18}O_2$ was coated on to a polished UO_2 crystal and in the latter, $^{30}SiO_2$ was sputtered on to polished SiO_2. Another recent study used SIMS to determine diffusion of Mg and Ca in $Na_2O{-}Al_2O_3{-}SiO_2$ glasses [25].

The choice of this method limits the experimenter to a study of diffusion of boron or silicon, among the common metalloids; both of these have suitable, readily available stable isotopes. Phosphorus has only a single stable isotope and is thus ruled out of court, while carbon, though ^{13}C is available, has a low sputter-yield (about 20 times lower than that of boron [11]) and thus is not suitable for this approach. Since boron is expected to diffuse faster than silicon and is also of greater practical importance, our choice fell on boron. We decided to use a glass with a substantial boron content; the aim was to measure the self-diffusion of boron in a system with a constant boron content.

3. Experimental procedure

The glass chosen for this initial study was $Fe_{40}Ni_{40}B_{20}$, obtained as 45 μm thick ribbon from

Vacuumschmelze, Hanau, Germany (registered trade name VITROVAC E0040). The temperature of incipient crystallization of glass of this composition has been measured as a function of isothermal annealing time by Luborsky [12]; his measured times were taken as upper limits of permissible annealing times. The onset of crystallization, T_x, was found by our own DSC experiments to be at ~410 K for a heating rate of 10 K min^{-1}. According to Luborsky, T_g is 7 K below T_x, but our slow DSC runs showed no sign of a glass transition. T_g presumably almost coincides with T_x.

The isotope-labelled surface coating was made to be as close as possible in chemical composition to the substrate glass; in this way, the total boron concentration should be unaltered after diffusion at all points in the composite specimen and premature crystallization should be prevented. Boron powder (300 mesh) enriched to 95.7% in ^{10}B–as compared with the natural abundances of 19.8% ^{10}B, 80.2% ^{11}B–was purchased from Centronic, New Addington, Croydon, UK. This powder was mixed with 300-mesh iron and nickel powders of high purity in the proportions corresponding to $Fe_{40}Ni_{40}B_{20}$, sheathed and cold-pressed isostatically and vacuum-sintered at 850 K for 15 min, to form a sputtering target. An electric lead was incorporated at the time of cold-pressing. (Subsequent SIMS analysis showed that the target did not sputter true and the deposits had a somewhat higher boron content than the target.)

In view of the observation of anomalous diffusivities in crystalline metals when the substrate had been polished only with 25 μm diamond powder [7], special care was taken to produce a mechanically polished surface both optically flat and as nearly as possible free of damage. (Electrolytic polishing was found to give too undulating a surface.) Samples of the glass were first annealed for 5 min at 385° C in order to create a standardized relaxed structure, following the procedure first used by Chen *et al.* [3]. The samples were cemented to a metal block and mechanically polished on emery (to 1200 grit), diamond (to 1 μm grade) and finally overnight on alumina (0.05 μm grade), and released from the block.

Several samples were then placed in the UHV sputtering unit together with the ^{10}B-enriched target. After evacuation to 10^{-8} Torr, ultra-pure argon was admitted to a pressure of 0.3 Torr and repeatedly flushed. The electric connections were inverted and the samples made cathodic, in order to clean them by bombardment with argon ions. This was essential, since the glass oxidizes readily and even a monolayer of boron-rich oxide at the surface might suffice to inhibit diffusion entirely (Dearnaley [13]). Immediately after cleaning, the electrodes were reversed and the sintered target bombarded with argon ions at 800 V to form a coating 0.4 to 0.7 μm thick on the samples.

Coated samples were cut into pieces 3 mm square and each piece was isothermally annealed in flowing argon in a Du Pont 990 Differential Scanning Calorimeter. This method of annealing has the advantage that, because of a very small thermal inertia, the temperature rises rapidly (about 150 K min^{-1}) to the desired level, with negligible overshoot, and is then held constant to ± 0.5 K, in a protective atmosphere. The annealing times ranged from 14880 sec at 340° C to 450 sec at 385° C.

SIMS was performed in the Harwell CAMECA IMS 300 ion analyser. Sputter-etching was performed by means of a primary beam of O_2^+ ions at 5.5 kV; the use of oxygen ions is known to enhance the sputter-yield of many species. The defocused primary beam etched an area 300 μm square but analysis was restricted to secondary ion ions emitted by a central circular region 100 μm in diameter. In this way, interference from the sloping sides of the pit was prevented. The mass spectrometer was set to 4 alternative settings, to count singly ionised atoms of ^{10}B, ^{11}B, ^{56}Fe and ^{58}Ni, and the instrument adjusted to cycle automatically between these settings, 8 sec on each, with a 32-sec cycle time. All counts were stored electronically and could be displayed on a CRO after completion of a run; a complete set of counts for all cycles was also printed out after each run and used for calculation of diffusion coefficients.

The rate of sputter-etching was calibrated by measuring several pits, about 1 μm deep, by means of multiple-beam interferometry [9]. This is the least accurate part of the procedure; the mean of the 3 most precise measurements was 0.66 ± 0.08 nm sec^{-1}. Use of a Talystep instrument would be an alternative to interferometry but would be unlikely to be more accurate.

Plots were prepared for each sample of the ratio $R = (^{10}\text{B counts})/(^{10}\text{B counts} + {}^{11}\text{B counts})$ in each counting cycle, as a function of time (or

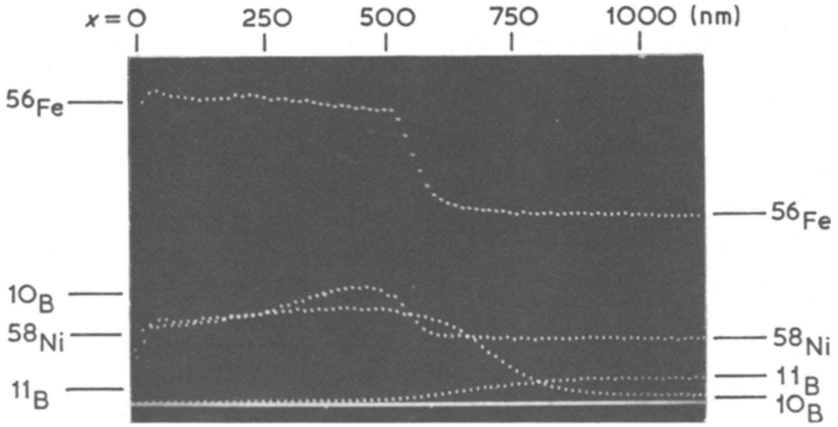

Figure 1 CRO displays of counts during sputter-etching of sample 5 in the ion-probe. The ordinate represents mass spectrometric counting-rates. The abscissa represents time, converted into distance, x. (The height of signal for different elements is not proportional to their relative concentrations, since they have different sputter-yields.)

equivalent as a function of depth of etching). Fig. 1 shows the CRO display of all the counts for sample 5, annealed 960 sec at 370° C, and in Fig. 2 the equivalent plot of R against depth is shown for sample 5 and two others. The great advantage of basing the analysis on the boron isotopic ratio rather than, say, the ^{10}B/Fe ratio, is that errors resulting from inhomogeneities in solute concentration or from changes of the relative sputter-yield (i.e. the number of emitted ions of a particular species per incident primary ion) as between different elements are avoided. Such changes are always apt to arise, because sputter-yield is very structure-sensitive and the influence of structural and compositional changes is different for different elements [8]. However, the sputter-yield of ^{10}B and ^{11}B should always be very nearly the same, whatever the local condition of the sample. The value of this feature is demonstrated by considering Fig. 3, run 13; here the boron counts vary much less smoothly from cycle to cycle than in Fig. 1 (and this is certainly due to inhomogeneities, not counting statistics), yet the plot of R against depth derived from these data (Fig. 2), while less smooth than that for specimen 5, is quite acceptable. The smoothness of the other profiles fell between these extremes. Quite apart from the above considerations, the use of the boron isotopic ratio is inescapable when substrate and coating have the same boron concentration.

A profiling run was also performed with a coated but undiffused sample. The R/depth profile calculated from the measurements is also shown in Fig. 2 (run 15) and it can be seen that the interface is quite sharp. Three factors tend to limit the apparent sharpness of what should ideally be a step-profile: (a) an insufficiently flat substrate surface; (b) an uneven etching rate across the pit (a

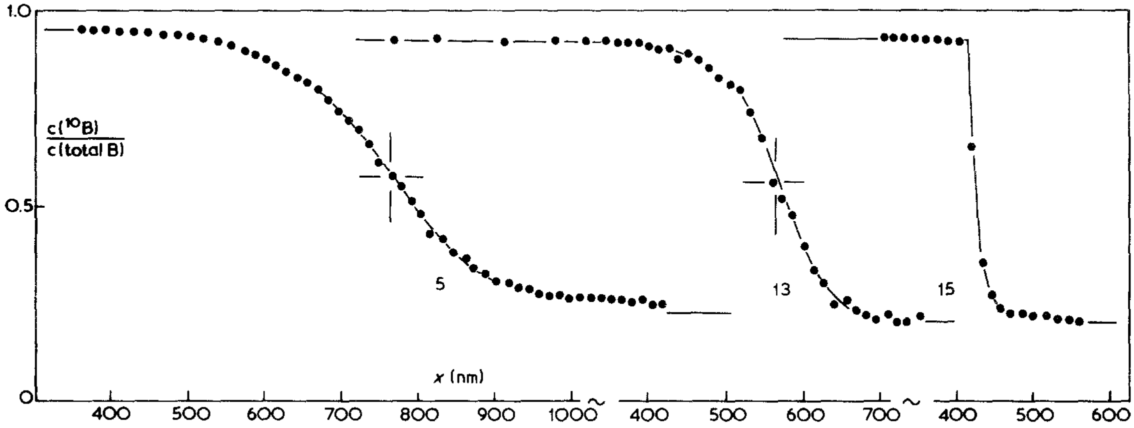

Figure 2 Profile for the boron isotopic ratio for sample 5 (370° C, 960 s), sample 13 (350° C, 8580 s) and sample 15 (undiffused).

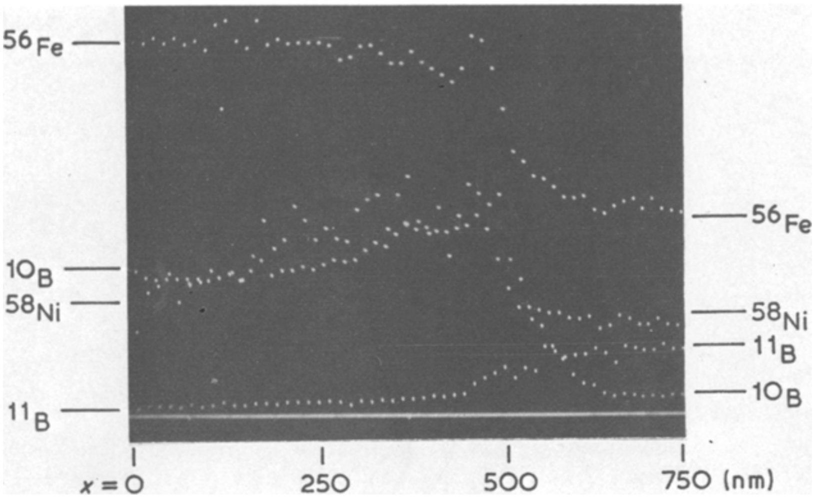

Figure 3 CRO display for sample 13 (350° C, 8580 (nm) sec).

problem which is more serious with polycrystals than with glasses); (c) "sputter-broadening" by the knock-in effect [14]. The sample surface had been polished to an optical standard of flatness and moreover the pit floor was adequately flat-bottomed, judging from interferometry, but SEM showed that a few per cent of the pit floor were covered by characteristic sputter-cones (Fig. 4), known to be associated with dust particles on the original surface [8]; the photograph was located to show an untypically high local density of cones. Knocking-in of atoms by incident primary ions in effect mixes all atoms over a depth equal to the primary ion range, which in our tests was roughly 10 nm. The profile of run 15 fitted rather closely the asymmetrical shape expected to result from sputter-broadening, and fitting it to an approximate theoretical formula [10] gave a sputter-broadening depth of 13 nm. This is not large enough—in comparison with other error sources—to make it worthwhile to apply corrections, which can be quite involved [10, 14], to the observed diffusion profiles; such corrections would tend to steepen the profile and slightly reduce the derived value of *D*. The good curve fit to the theoretical sputter-broadening profile indicates that error sources (a) and (b) were negligible. Coburn and Kay [8] express the general view, however, that features such as the cones of Fig. 4 are the principal sources of error in SIMS profiling and it would thus be good routine practice to photograph the topography of each experimental pit as a precaution.

The CRO displays (such as those of Figs. 1 and 3) showed two curious features: (a) the total boron counts, $^{10}B + {}^{11}B$, always fell sharply on going from coating to substrate. This could imply that the coating contained more than the intended 20 at % boron — which would mean that the sputtering target was subjected to sustained preferential sputtering of boron—or it could be due to differences in the sputter-yield in the ion-probe as

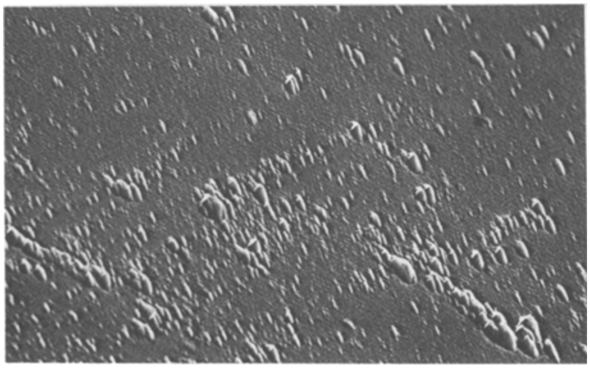

Figure 4 SEM photograph of part of the floor of the sputter-etched pit on sample 9 (570 X).

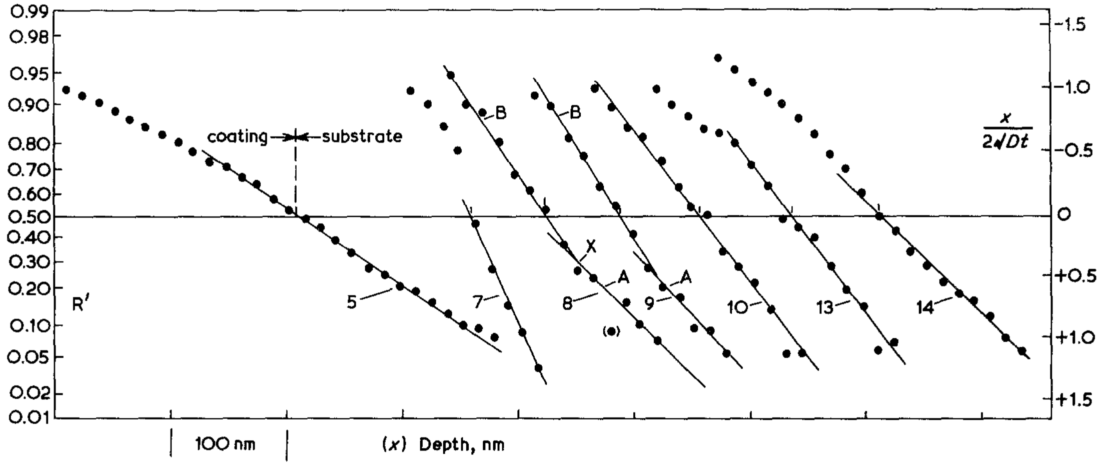

Figure 5 Plots of R' against sputter-etching depth, x, for the successful ion-probe runs. (x is here taken from the coating surface as origin.) The ordinate is also calibrated in terms of $x/2\sqrt{(Dt)}$. Run 5; 370° C, 960 sec. Run 7; 350° C, 5700 sec. Run 8; 385° C, 450 sec. Run 9; 360° C, 3960 sec. Run 10; 370° C, 1440 sec. Run 13; 350° C, 8580 sec. Run 14; 340° C, 14880 sec.

between coating and substrate. (b) There was always a fairly sharp change in Ni and Fe counts, not generally coinciding with the coating–substrate interface. This might well be due to a change in ionization efficiency of Fe and Ni in the ion-probe because of some unknown change in operating conditions. These two features are not at present well understood, but fortunately they do not affect the analysis because the use of the $^{10}\text{B}/^{11}\text{B}$ ratio to calculate diffusivities.

Several of the diffusion samples were examined subsequently to test for possible partial crystallization. Some were thinned for TEM, others were heated in the DSC so that the temperature, T_{mx}, of the peak of the heat output due to crystallization could be compared with that for the as-received glass; T_{mx} is very sensitive to small percentages of pre-existing crystallities (Greer [15]). The as-coated, undiffused sample was completely amorphous, showing that the brief stabilizing anneal at 385° C and subsequent ion-cleaning had not initiated crystal growth. Samples 8 and 10 proved to be partially crystalline (see Fig. 6); samples 7, 9 and 13 were wholly amorphous. The other samples were not available for testing.

4. Calculation of diffusion coefficients

The appropriate solution of the diffusion equation for the circumstances of the present experiments, treating the coating as a semi-infinitely thick source, is [16]:

$$R' = \frac{R(x) - R(\text{s})}{R(\text{c}) - R(\text{s})} = \tfrac{1}{2}[1 - \operatorname{erf}(x/2\sqrt{(Dt)})].$$

Here $R(x)$ is the concentration ratio, $c(^{10}\text{B})/[c(^{10}\text{B}) + c(^{11}\text{B})]$, at depth x from the initial interface; $R(\text{s})$ is the isotopic ratio in the substrate (0.198) and $R(\text{c})$ is the ratio in the coating (0.957).

To fit this equation to profiles such as those of Fig. 2, the best procedure is to plot R' as a function of x on probability graph paper [17]. Such paper has as ordinate a quantity y satisfying the relation $2R' = 1 - \operatorname{erf}(y)$ for R' in the range 0 to 1, and for our purposes, $y = x/2\sqrt{(Dt)}$.

Fig. 5 shows seven experimental profiles plotted in this way. When the points lie very close to a straight line, as for run 5, then a single diffusion coefficient accurately fits the profile*. When there is a change of slope, as in run 8, then different values of D apply at different depths. In the case of sample 8, which was substantially crystalline according to TEM, there was presumably a rapid rise in the crystalline fraction when diffusion had reached "X". Alternatively, the value of D can change progressively during anneal as crystallites grow. On either view, the value of D deduced from such a plot can only give a rough indication. The same applies to sample 9, which was wholly amorphous according to our tests.

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*The random scatter of individual points from the best straight line on run 5 can be accounted for entirely in terms of counting statistics; the probable error of R' was somewhat less than 0.01.

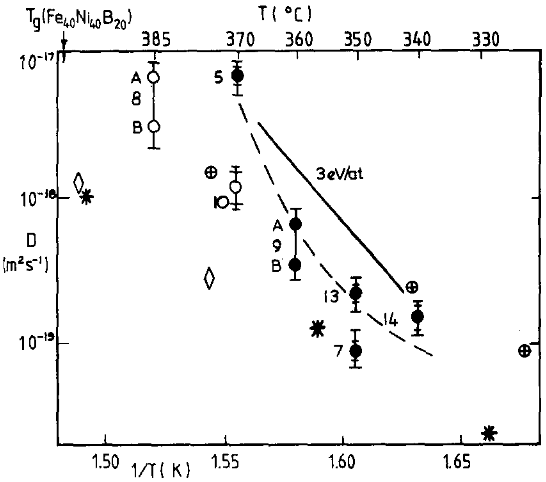

Figure 6 Values of D calculated from plots of Fig. 5. (A and B represent values calculated from the two alternative straight lines fitted to runs 8 and 9 in Fig. 5). ● amorphous samples; ○ partially crystallized samples (T_g has been marked at 400° C); ⊕ D calculated from growth rates of crystallites in $Fe_{86}B_{14}$ [4]; ◇ D calculated from growth rates of crystallites in $Fe_{42}Ni_{42}B_{16}$ [4]; D calculated from growth rates of crystallites in $Fe_{84}B_{16}$ [5].

Each set of points, except those for sample 7, shows deviations from a straight line well inside the coating region. This was to be expected, since the coating does not usually have exactly the same density and composition as the substrate, and D in a glass is known [3, 18] to be sensitive to very small changes in free volume. Consequently, the best straight line was fitted along the part of the plot lying within the substrate (but for runs 8 and 9, two straight lines were fitted to each.)

In Fig. 6, the deduced values of D are plotted as log D against $1/T$. Two error bars are marked: the broad bars show the error due to the uncertainty (± 12%) in the sputter-etching rate in the ion-probe; the narrower bars show the estimated random error in fitting straight lines to the plots of Fig. 5. (For the sake of clarity, the two errors were not statistically combined.) The partially crystalline samples have been distinguished by open circles. Samples 5 and 14 are assumed to have remained amorphous.

5. Discussion

The values of D plotted in Fig. 6 indicate that the degree of uncertainty of individual values is quite acceptable, in view of the low absolute diffusivities being measured, but the two measurements at 350° C show that reproducibility still requires improvement.

The five non-crystallized samples (nos. 5, 7, 9, 13, 14), of which sample 5 gave the straightest R'/x plot, do not lie along a straight line in Fig. 6. This may well prove in due course to be a generally valid conclusion for diffusion in metallic glasses, at any rate near T_g: the same is also true of the D values for gold diffusing in $Pd_{77}Cu_6Si_{17}$ following a short relaxation anneal just below T_g [3]. Plainly, the effect of various relaxation anneals on diffusion rates is one of the issues which requires systematic examination, and boron diffusion would be a good basis for this. The recent creep experiments by Taub and Spaepen [18] have shown clearly that *long* anneals at temperatures well below T_g cause very large changes—several orders of magnitude—in viscosity as deduced from creep rates. It is by no means clear whether the Stokes–Einstein relationship between viscosity η and diffusivity D ($D = (k/3\pi a)T/\eta$, where a is the atomic diameter) continues to apply as a glass structure relaxes and atomic transport mechanisms perhaps change. This doubt arises because (a) a long diffusion anneal well below T_g still appears to give an isoconfigurational *diffusivity* [1]; (b) a long anneal well below T_g changes *viscosity* sharply [18]; (c) a short anneal just below T_g changes both glass configuration and diffusivity sharply [3]. The ambiguities concerning the different measures of atomic mobility—viscous flow and diffusion—have been set out clearly by Spaepen and Turnbull [19]. Recent findings also indicate that ion-irradiation of a metallic glass, which decreases free volume, drastically lowers the crystallization temperature and thus (by implication) enhances diffusivity [20].

A great deal of systematic work needs to be done to understand just how diffusion in a metallic glass depends on the state of relaxation of the glass.

In Fig. 6, some estimated diffusion rates deduced indirectly from crystal growth rates in $Fe_{42}Ni_{42}B_{16}$ and $Fe_{80}B_{20}$ [4, 5] are also indicated. These rates agree quite well with those directly measured in the present work between 340° C and 370° C, but tend to fall away from extrapolated expectations at higher temperatures (370 to 400° C); however, little significance should be attributed to these discrepancies which are at temperatures close to T_g, since the various glasses have different T_g's.

If the present results are plotted in terms of reduced temperatures, T/T_g, and compared with a corresponding plot for *metal* diffusion in Pd–Si or Pd–Cu–Si glasses [1, 3], then boron diffusion in $Fe_{40}Ni_{40}B_{20}$ proves to be between 2 and 4 orders of magnitude higher at a given T/T_g. This is not surprising, in view of the much smaller size of the boron atom.

The curved line in Fig. 6 represents an approximate join of observed diffusivities. For comparison, the straight line is drawn with a slope corresponding to an activation energy of 3.0 eV $atom^{-1}$, which is the activation energy for crystallization of $Fe_{40}Ni_{40}B_{20}$ found by Luborsky [12]. The activation energies deduced from the indirect D values are smaller than this.

It remains to be seen whether, further below T_g, a straight-line Arrhenius plot applies. Köster [21] has found that in Fe–B–C alloys there is a deviation to higher (indirectly estimated) diffusivities at low temperatures than would be predicted by extrapolation from a high-temperature Arrhenius plot. Provided diffusion does *not* take place by the migration of well-defined vacancies or holes of size invariant with temperature, there is no intrinsic reason why there should be a straight Arrhenius plot for diffusivities in a metallic glass. For a discussion of possible diffusion mechanisms, see a recent review by Cahn [22].

Our results indicate that diffusion is slower in a partly crystallized sample than in wholly glassy ones, contrary to a view expressed in the past. This finding is however consistent with the observations of Birac and Lesueur [2] who measured the diffusion of lithium, another small atom, in $Pd_{80}Si_{20}$.

6. Improvements in experimental technique

Several lessons were learnt from the experiments which point the way to changes that should reduce experimental scatter:

(1) Since the sputter-etching rate is the principal source of error, long etching times to make deep pits could be used for more precise measurement. Ideally, this should be done separately in coating and substrate, since the values are not necessarily exactly the same.

(2) Care needs to be taken to clean the samples of all dust before insertion in the ion-probe in order to minimize formation of sputter-cones, and a SEM photograph should be taken of the pit at the conclusion of each run to check smoothness of the pit floor.

(3) Since incipient crystallization of the samples is plainly a danger at the longer annealing times, it is important to prevent preferential crystallization in the coating, which could propogate into the substrate. This aim could be achieved by depositing a coating with a higher T_x than the substrate. Recent measurements on Fe–Si–B alloys [23, 24] indicate that addition of about 3 at % Si to the coating should raise T_x by 80 to 100 K. Since silicon is likely to be a slow diffuser, it should not interfere in the diffusion experiment. An alternative approach is to use a thin (~ 30 nm) coating of pure ^{10}B and analyse the profile in terms of the thin-film solution of the diffusion equation.

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