

Diffusion in metallic glasses

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Abstract. Rutherford α -particles backscattering technique was employed for measurements of diffusion rates in metallic glasses. Effects of relaxation, crystallization and plastic deformation on diffusion rates were also investigated.

It has been observed that the diffusion rates of a metallic solute are of the same orders of magnitude in both metal-metal and metal-metalloid glasses. A higher diffusivity is likely if there is a large difference between melting points of the solute and matrix. Relaxation has no effect on diffusion, however, diffusivity increases on crystallization. An increase in diffusivity is also observed on plastic deformation of metallic glass.

Keywords. Metallic glass; diffusion; relaxation; crystallization; plastic deformation; activation energy.

1. Introduction

An understanding of crystallization behaviour and various pre-crystallization changes in physical and mechanical properties of metallic glasses requires a knowledge of diffusion rates in the glassy state. Though a few investigations have been made in this direction in the recent years (Gupta *et al* 1975; Birac and Lesuer 1976; Chen *et al* 1978; Cahn *et al* 1980; Koster *et al* 1980; Kijek *et al* 1980, 1982; Valenta *et al* 1981; Edelin and Tete 1981; Baer *et al* 1981; Luborsky and Bacon 1982), it is difficult to interpret the data because a random group of different diffusing atoms in different glasses have been studied. For a meaningful comparison of the data, a systematic study of diffusion of a single solute in different glasses and different solutes in a single glass is essential. Measured diffusion rates in a metallic glass might depend on the structural state of the matrix as well. An investigation on this aspect is also desirable as the structural state of the glassy phase could alter by one or more of the various treatments like thermal relaxation, crystallization and plastic deformation.

Extensive investigations of diffusion rates in metallic glasses were therefore undertaken at the University of Sussex, England. Solute depth profiles were determined by means of backscattering of 2 MeV α -particles obtained from a van de Graff accelerator. Aim of the studies was three fold.

(i) Diffusion of a single metallic solute in different glasses: diffusion rates of Au in two metal-metal (NiZr_2 and $\text{Ni}_{64}\text{Zr}_{36}$) and two metal-metalloid ($\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ and $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$) glasses were measured.

(ii) Diffusion of different solutes in a single metallic glass: diffusion rates of Pb, Pt and Au in a NiZr_2 glass were measured.

(iii) Effect of structural state of the matrix on diffusion rates: measurements were made on as-quenched, relaxed, crystallized and plastically deformed glasses.

2. Experimental

Three alloys (NiZr_2 , $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$) were prepared by induction melting high purity components over a water cooled silver hearth under a dynamic argon atmosphere, and melt-spun into glassy ribbons over a rotating (5000 rpm) polished copper wheel (150 mm dia.) using a quartz nozzle (1 mm orifice diameter) and an ejection pressure of ~ 12 psi. $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ glass ribbons were obtained from Vacuumschmelze, Hanau, Germany (registered trade name Vitrovac E0040). In all cases, the thickness of the ribbons was between 30 and 50 μm . At a heating rate of 10 K min^{-1} , $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ exhibited glass transition temperatures, T_g , of 823 and 633 K respectively. NiZr_2 and $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$, however, did not show any glass transition, so T_g was taken as the temperature of onset of crystallization, at 660 and 673 K, respectively.

Details of the experimental procedure are given elsewhere (Akhtar *et al* 1982a). For relaxation treatment, the NiZr_2 and $\text{Ni}_{64}\text{Zr}_{36}$ glasses were heated for 10 min at 613 and 773 K, respectively and the $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ and $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ ribbons for 5 min at 658 and 623 K, respectively. Few NiZr_2 ribbons were partially crystallized by heating for 10 min at 673 K and a few were partially deformed at room temperature.

Lower surface (*i.e.* the surface in contact with the copper wheel during melt-spinning) of each ribbon was mechanically polished to 1 μm finish using diamond paste and sputter coated with thin (100 Å) films of solute elements. Samples were sealed in quartz tubes under vacuum and diffusion annealed. It was made sure that the ribbons did not crystallize due to diffusion annealing. Diffusion concentration profiles were determined by means of backscattering of 2 MeV α -particles obtained from a van de Graff accelerator. The incident beam area was 1 mm^2 and the total number of incident α -particles was 6.25×10^{14} in each case. The backscattered α -particles were detected at an angle of 150° with a silicon surface barrier detector. These α -particle pulses were amplified and fed through a pulse height analyzer and a PDP 11 computer for on-line data analysis.

3. Results and discussion

3.1 Analysis of backscattering spectra

Typical backscattered energy spectra for Au coated NiZr_2 , $\text{Ni}_{64}\text{Zr}_{36}$, $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ and $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ metallic glass specimens before diffusion annealing are shown in figure 1. Different elements are easily identified by their backscattered energies. B and Si which correspond to lower backscattered energies are excluded in the figure. On annealing, Au energy maxima broadens as Au diffuses into the glassy matrix and a typical example of broadening is shown in figure 2 for $\text{Ni}_{64}\text{Zr}_{36}$ glass.

A computer programme was formulated to determine the Au concentration profiles directly from the backscattered energy spectra with the help of a PET 2001 computer. Details of the analysis are given elsewhere (Akhtar *et al* 1982a). Estimated Au concentration profiles for the observed backscattering spectra of figure 2 are shown in figure 3.

In a thin film solution of the diffusion equation the concentration of the solute at a depth x is given by the Gaussian equation (Shewmon 1963),

$$C(x) = C_0 \exp(-x^2/2b^2),$$

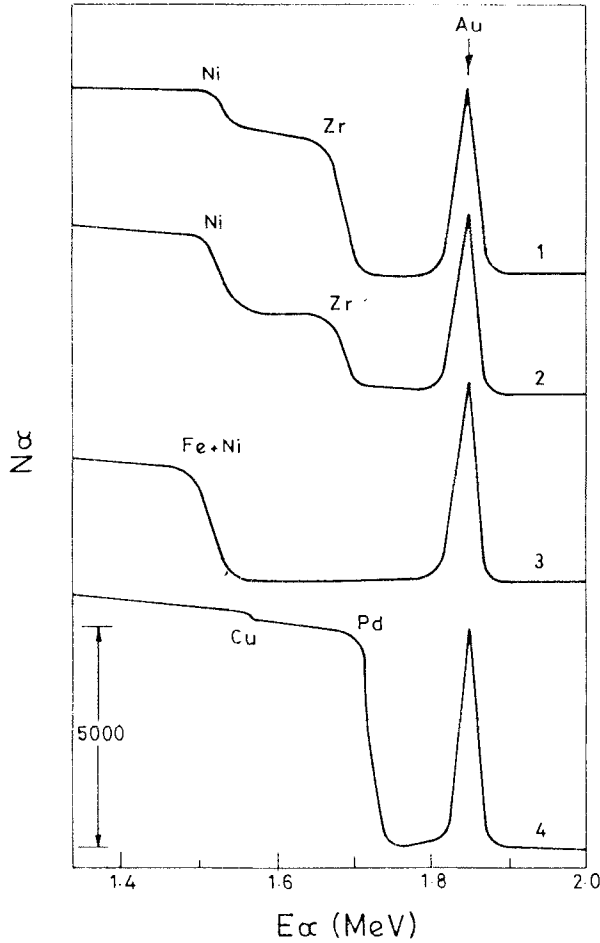


Figure 1. Backscattered α -particle energy spectra from Au coated 1. NiZr_2 2. $\text{Ni}_{64}\text{Zr}_{36}$ 3. $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ and 4. $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ glasses.

where $b = \sqrt{2Dt}$ is the standard deviation, D is the diffusion coefficient, t is the annealing time and C_0 the surface solute concentration after time t . For the above equation to be applicable for calculation of D , a plot of $\ln C$ vs x^2 should yield a straight line. A plot of $\ln C$ vs x^2 for a diffusion annealed specimen of $\text{Ni}_{64}\text{Zr}_{36}$ is shown in figure 4, and in general, the fit to the above equation was reasonable. Diffusion coefficients were therefore calculated from

$$D = (b^2 - b_0^2)/2t,$$

where b_0 and b are standard deviations before and after diffusion annealing.

3.2 Diffusion of a solute in different glasses

Figure 5 shows a plot of log diffusion rate vs inverse temperature for Au diffusion in two metal-metal glasses, NiZr_2 and $\text{Ni}_{64}\text{Zr}_{36}$. Figure 6 shows a similar plot for two metal-metalloid glasses, $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ and $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$. It is apparent from the figures

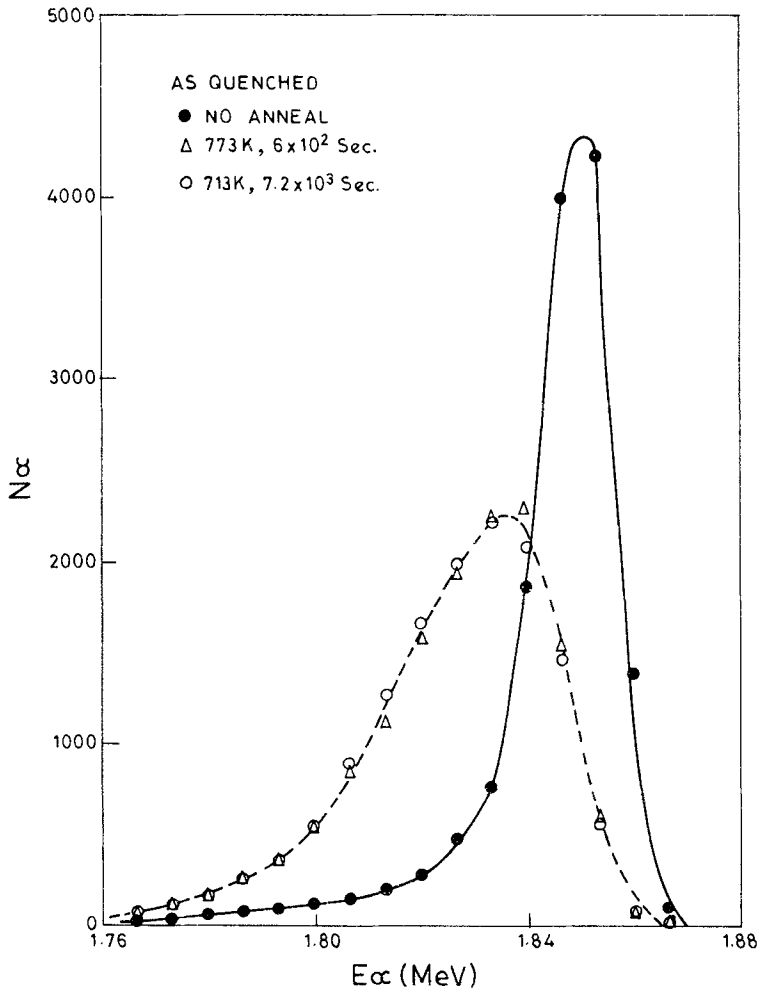
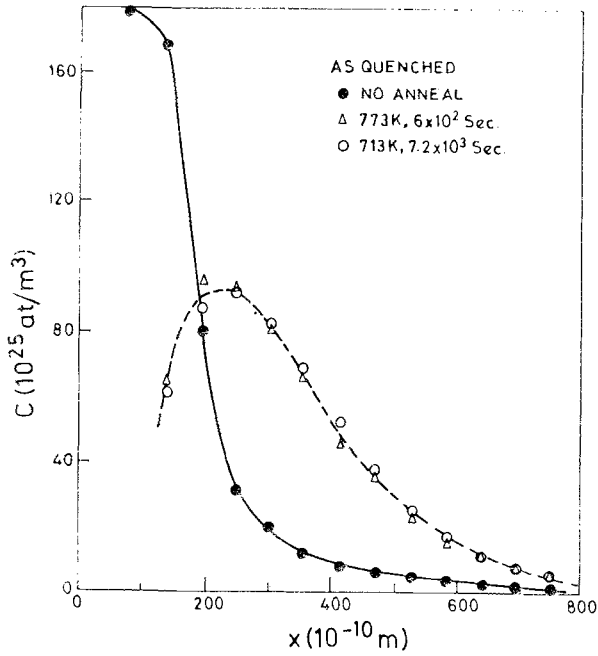
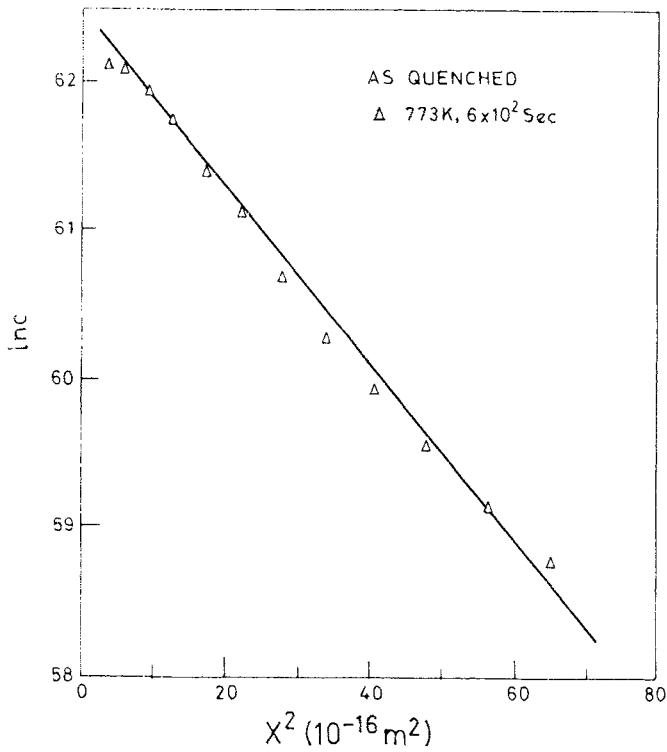


Figure 2. Broadening of the Au backscattered energy maximum on diffusion annealing of an as-quenched, Au coated $\text{Ni}_{64}\text{Zr}_{36}$ glass.

that the measured diffusion rates obey an Arrhenius relationship in all the alloys. In $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ and $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$, studied above the glass transition, T_g as well, the same Arrhenius relationship is obeyed both below and above T_g . It is also noteworthy that the diffusivity at a given temperature is lower in a glass of higher T_g . Average activation energies for diffusion in NiZr_2 and $\text{Ni}_{64}\text{Zr}_{36}$ glasses are 1.97 and 1.92 eV, respectively, which suggests that the activation energy for diffusion of Au is independent of relative proportions of Ni and Zr in NiZr glasses. Activation energies in $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ and $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ glasses are 2.07 and 1.80 eV, only slightly higher and lower, respectively than in NiZr glasses. This similarity suggests that in metal-metal



(3)



(4)

Figures 3 and 4. 3. Au concentration profiles corresponding to the spectra of figure 2 for Au diffusion into an as-quenched $Ni_{64}Zr_{36}$ glass. 4. Au concentration profile of figure 3 showing a fit to the thin film diffusion solution for Au diffusion into an as-quenched $Ni_{64}Zr_{36}$ glass.

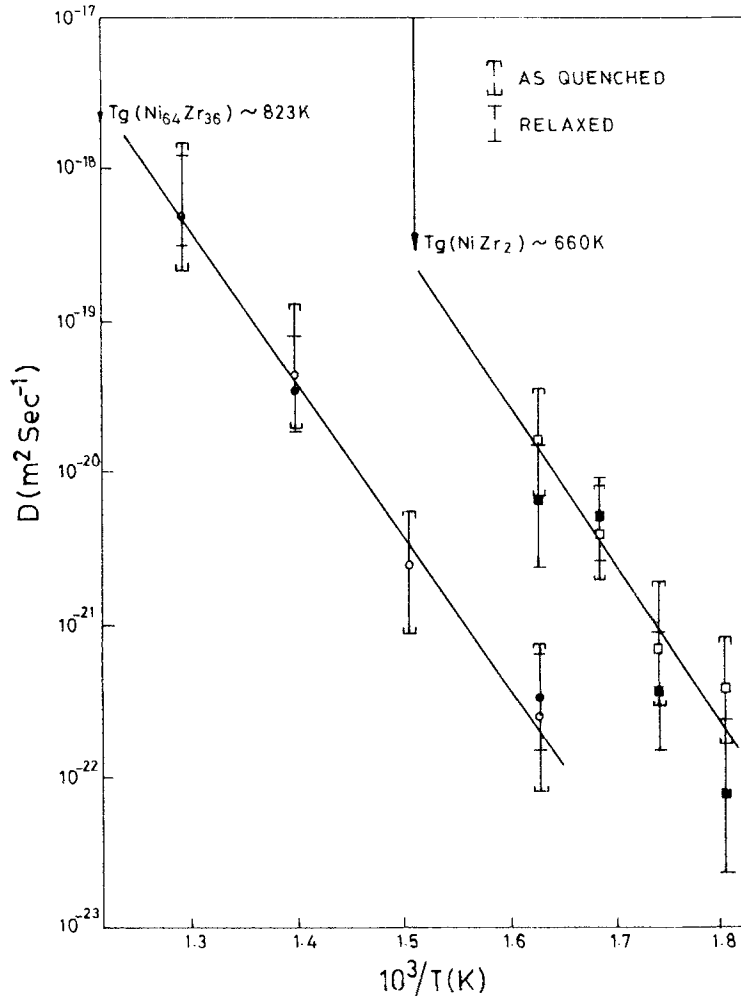


Figure 5. Diffusivities of Au in $NiZr_2$ (squares) and $Ni_{64}Zr_{36}$ (circles) glasses. Open and filled data points for as-quenched and relaxed glasses respectively.

and metal-metalloid glasses, diffusion of a metallic solute occurs by a similar mechanism.

At least three possible diffusion processes should be considered in a metallic glass; vacancy, cooperative and interstitial mechanisms. Computer modelling studies (Ahmadzadeh and Cantor 1981) indicate that the individual vacancies are not stable in metallic glasses, and hence vacancy diffusion is ruled out. As in crystals, there is a large energy barrier to prevent a large atom such as Au to remain in an interstitial site. Thus a possible diffusion mechanism seems to be a cooperative process and, a correlated jump mechanism has indeed been proposed previously for diffusion of Au in the $Pd_{77.5}Cu_6Si_{16.5}$ glass (Chen *et al* 1978).

Figure 7 shows our results plotted against inverse temperature normalised to T_g . For $Fe_{40}Ni_{40}B_{20}$, $Pd_{77.5}Cu_6Si_{16.5}$ and $NiZr_2$ glasses, which have similar values of T_g (673, 633 and 660 K, respectively), the diffusivity values are very close and lie almost on one line. However, diffusivity values for $Ni_{64}Zr_{36}$ ($T_g \sim 823$ K) do not normalise in the

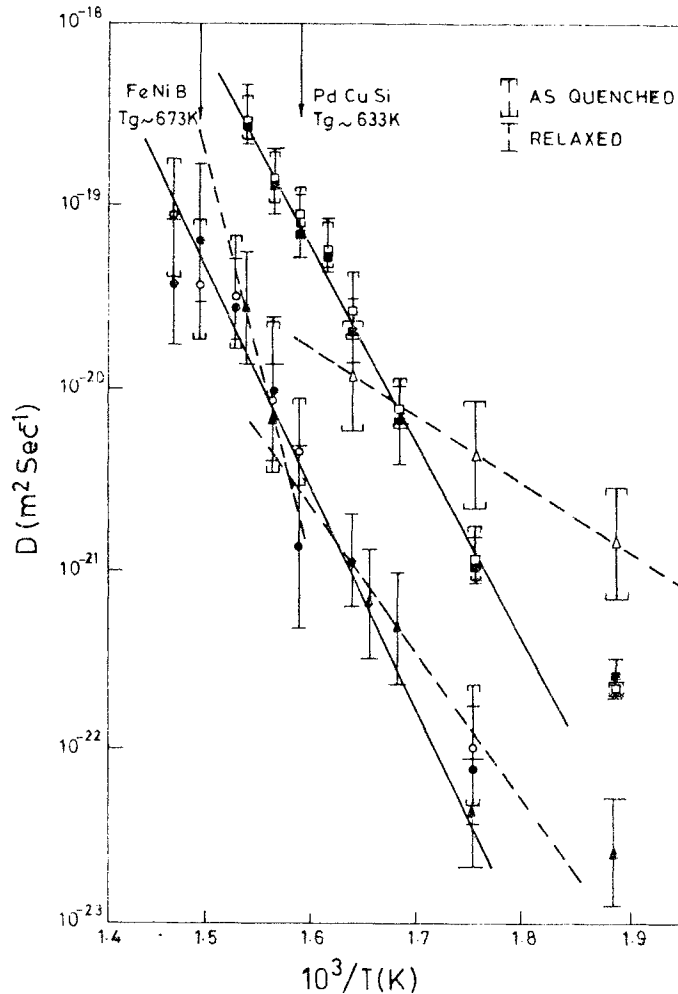


Figure 6. Diffusivities of Au in $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ (squares) and $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ (circles) glasses along with Chen *et al.*'s (1978) data (triangles with dashed lines) for the $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ glass. Open and filled data points for as-quenched and relaxed glasses respectively.

same way. At a given fraction of T_g , the diffusivity of Au is higher for this glass, with a higher T_g . Similar behaviour has also been observed (Kijek *et al* 1982) in a NiNb glass with high T_g .

For diffusion of metalloid in these glasses, the only available data of Cahn *et al* (1980) for diffusion of B in $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ are included in figure 7 and it is apparent that the small atom, B, does indeed diffuse faster than the large atom, Au in the same glass at the same temperatures.

3.3 Diffusion of different solutes in a glass

Measured diffusion rates of Pb, Pt and Au in NiZr_2 glass are plotted in figure 8. It is apparent that Arrhenius relationship is valid for diffusion of Pb and Pt also. Average activation energies for diffusion of Pb, Pt and Au are 2.72, 2.43 and 1.97 eV,

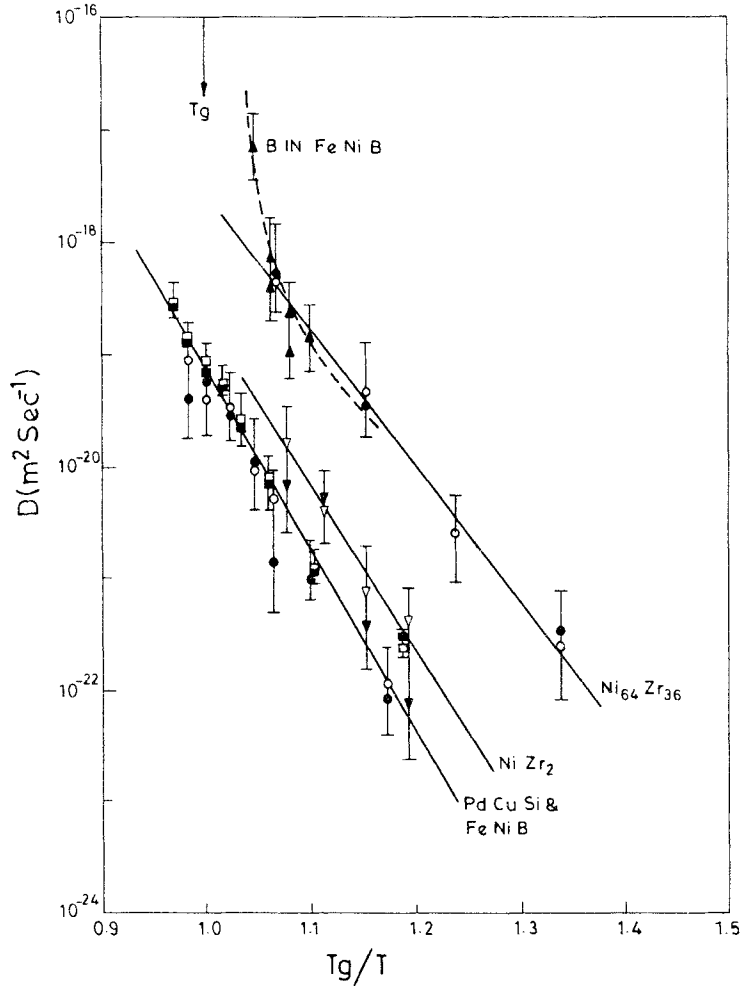


Figure 7. Diffusivities of Au vs normalized inverse temperature, together with Cahn *et al's* (1980) data for B in $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$. Open and filled data points for as-quenched and relaxed glasses respectively.

respectively. It should be noted that both the diffusivities and the activation energies decrease in the same order Pb to Pt to Au.

At first sight, a high diffusivity of Pb would seem rather surprising since the atomic size of Pb is larger than that of Pt or Au. Even in crystalline metals, correlations between the characteristics of solutes diffusing in a matrix and the rates of diffusion are not well understood. In general, the more dissimilar the solute and the matrix, faster is the rate of diffusion (Le Claire 1949). This similarity may be described in terms of crystal structure, atomic sizes, melting points and electronic configurations of the pure solutes and matrix materials. The melting point of crystalline NiZr_2 is 1140°C , Au melts at 1064°C , Pt at 1772°C and Pb at 327°C (Hansen and Anderko 1958). Thus the absolute difference in melting points between solute and matrix increases in the order Au, Pt, Pb and the solute diffusivities increase in the same order. Our results are therefore qualitatively in agreement with earlier suggestions (Le Claire 1949) for

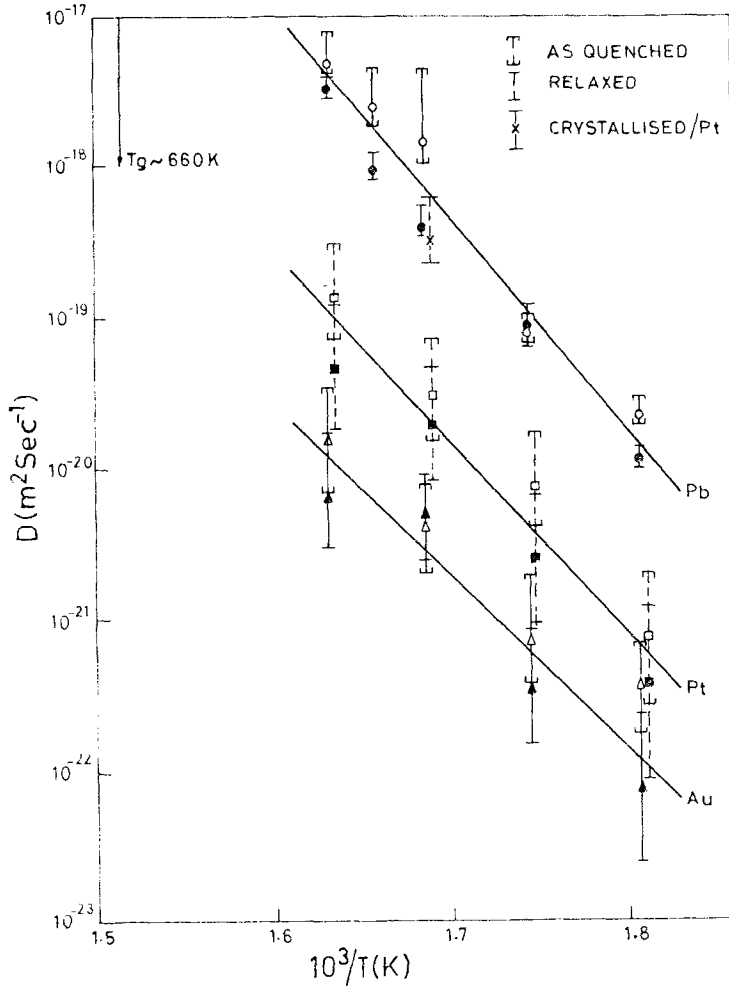


Figure 8. Diffusivities of Pb (circles), Pt (squares) and Au (triangles) in NiZr_2 glass. Open and filled data points are for as-quenched and relaxed glass respectively. Diffusivity of Pt in partially crystallized NiZr_2 is shown by a cross.

crystalline alloys that a high diffusion rate is likely when there is a large difference between the solute and matrix melting points.

3.4 Effect of structural state of the matrix

3.4a Relaxation: All measurements were made on two sets of samples (i) as-quenched and (ii) thermally relaxed. These measurements are presented by open and filled data points, respectively in figures 5–8. It is clear from these figures that the relaxation treatment used in the present experiment had no significant effect on the measured diffusion rates and activation energies of diffusion. Our observations are in agreement with previous measurements by Kejek *et al* (1982) on metal-metal glasses and by Luborsky and Bacon (1982) on metal-metalloid glasses.

The only previous measurement of diffusion of the solutes in the glasses investigated

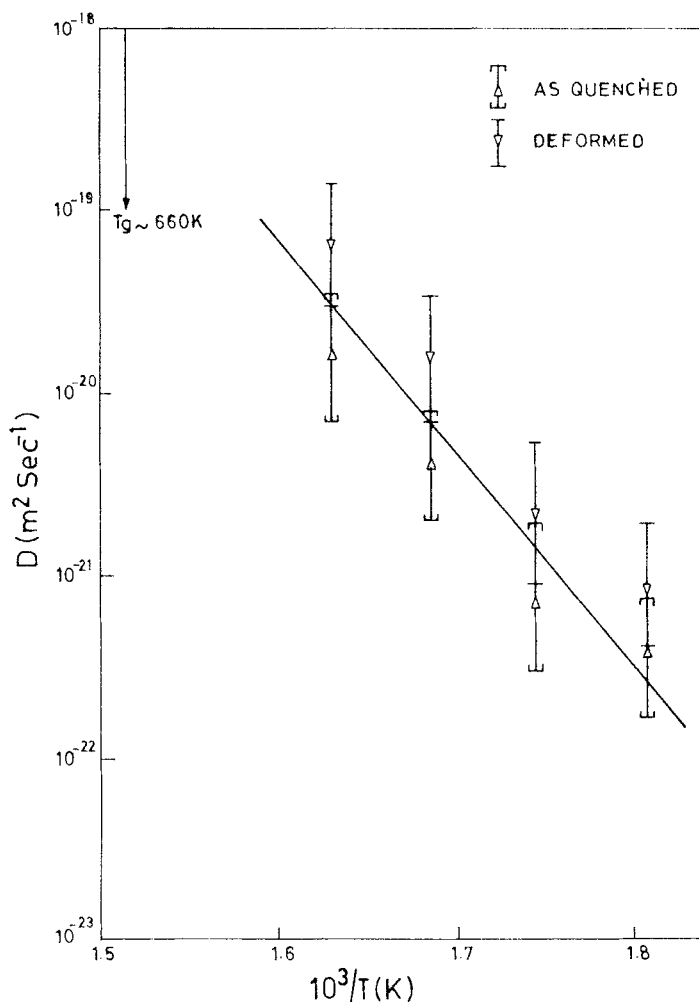


Figure 9. Diffusivities of Au in as-quenched and deformed $NiZr_2$ glasses.

here is due to Chen *et al* (1978) for diffusion of Au in $Pd_{77.5}Cu_6Si_{16.5}$ glass and their data has been included in figure 6. Though the relaxation treatment, temperature of measurements and measured values of T_g were same for the $Pd_{77.5}Cu_6Si_{16.5}$ glass in the two sets of experiments, our measurements are different from those of Chen *et al* (1978) who observed significantly higher diffusivity and lower activation energy in as-quenched glass as compared with relaxed glass. Possible reasons for these discrepancies are discussed elsewhere (Akhtar *et al* 1982a) and may be an anomalous effect caused by Chen *et al*'s (1978) experimental technique.

3.4b Crystallization: Crystallized ribbons were brittle and hence not very suitable for handling during backscattering experiment. Only one measurement could therefore be performed for diffusion of Pt in partially crystallized $NiZr_2$, which is shown by a cross in figure 8. It appears that the diffusion rate of Pt in glassy $NiZr_2$ increases when the glass is partially crystallized. This observation is in agreement with Chen *et al*'s (1978) Au diffusion measurements in glassy $Pd_{77.5}Cu_6Si_{16.5}$.

3.4c *Plastic deformation*: Figure 9 shows the observed diffusion rates of Au in as-quenched and deformed NiZr_2 glass. Though the difference is not large, a systematic higher diffusivity at all temperatures is observed in deformed samples. This observation suggests that diffusion rate is enhanced on deformation. Pratten (1980) observed a decrease in density on deformation of a $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ glass and attributed it to increased free volume associated with the formation of shear bands. Our observation of enhanced Au diffusivity after deformation may be explained by the same deformation induced increase in free volume.

4. Conclusions

Diffusion rates of Au in NiZr_2 , $\text{Ni}_{64}\text{Zr}_{36}$, $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ and $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ glasses obey an Arrhenius relationship. Our observations suggest that Au diffusion rates are of the same orders of magnitude in both metal-metal and metal-metalloid glasses. At a given temperature, Au diffusion rate is lower in a glass of higher T_g .

Diffusion rates and activation energies of diffusion for Pb, Pt and Au in NiZr_2 glass decrease in the order Pb, Pt, Au. This observation suggests that a higher diffusion rate is likely when there is large difference in melting points of solute and matrix.

Relaxation has no significant effect on measured diffusion rates. Partial crystallization of the glass increases the solute diffusivity considerably and higher diffusion rates are also observed after deformation of the glass.

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References

- Ahmadzadeh M and Cantor B 1981 *J. Non-Cryst. Solids* **43** 189
 Akhtar D, Cantor B and Cahn R W 1982a *Acta Metall.* **30** 1571
 Akhtar D, Cantor B and Cahn R W 1982b *Scr. Metall.* **16** 417
 Baer D R, Pederson L R and Thomas M T 1981 *Mater. Sci. Eng.* **48** 283
 Birac C and Lesuer D 1976 *Phys. Status Solidi* **A36** 247
 Cahn R W, Evetts J F, Patterson J, Somekh R E and Kenway J C 1980 *J. Mater. Sci.* **15** 702
 Chen H S, Kimmerling L C, Poate J M and Brown W L 1978 *Appl. Phys. Lett.* **32** 461
 Edelin G and Tete C 1981 *Scr. Metall.* **15** 739
 Gupta D, Tu K N and Asai K W 1975 *Phys. Rev. Lett.* **35** 796
 Hansen M and Anderko K 1958 *The constitution of binary alloys* (New York: McGraw-Hill)
 Kijek M, Ahmadzadeh M, Cantor B and Cahn R W 1980 *Scr. Metall.* **14** 1337
 Kijek M, Akhtar D, Cantor B and Cahn R W 1982 *Proc. 4th Int. Conf. on Rapidly Quenched Metals* (eds T Masumoto and K Suzuki (Sendai: The Japan Institute of Metals) vol 1 573
 Koster U, Herold U, Hillenbrand H G and Denis J 1980 *J. Mater. Sci.* **15** 2125
 Le Claire A D 1949 *Progress in metal Physics I*, (ed.) B Chalmers (London: Butterworths Scientific Publication)
 Luborsky F E and Bacon F 1982 *Proc. 4th Int. Conf. on Rapidly Quenched Metals* (eds T Masumoto and K Suzuki (Sendai: The Japan Institute of Metals) vol 1 561
 Pratten N 1980 Ph.D. Thesis, Sussex University
 Shewmon P G 1963 *Diffusion in solids* (New York: McGraw-Hill)
 Valenta P, Maier K, Kronmuller H and Freitag K 1981 *Phys. Status. Solidi* **105** 537 and **106** 129