Ten reflections of each Guinier De-Wolff powder pattern were chosen, with $Pb(NO_3)_2$ as the internal standard.

Lattice parameters of hexagonal barium hexaferrite were found to be $a = 5.907$, $c = 23.187$, in agreement with reported single-crystal data [3]. The lattice parameters of composition 5 were found to be $a = 5.904$, $c = 23.154$.

Examination of the diffraction patterns of the other samples in the single-phase region was not indicative of any distortion of the cell parameters. No appreciable solubility was found along the join $BaO \cdot 6Fe_2O_3$–$CaO \cdot Fe_2O_3$. In all the samples of that line, the presence of three phases was determined: barium hexaferrite-type solid solution, calcium monoferrite and barium calcium ferrite. Examination of compositions 3, 8, 13, 16, 21, 42, 44, 45, 46, 47 and other compositions of the previous work [1] permitted two further ternary fields to be determined (see Fig. 2).

Adjacent to the single-phase region, three single pseudobinary fields are formed, with iron oxide, calcium monoferrite and barium calcium ferrite as the equilibrium phases (see Fig. 2).

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Diffusion in some iron-based metallic glasses

Iron-rich metallic glasses have been reported to crystallize by primary crystallization of α-iron followed by polymorphous crystallization of Fe_3B. The diameter of the α-iron crystals in $Fe_{86}B_{14}$ alloys obeys a √time-law [1, 2]. This parabolic relationship indicates that the growth is controlled by volume diffusion, and it should be possible to calculate diffusion data from primary crystallization. The aim of this communication is to discuss such an indirect method for predicting diffusion coefficients from primary crystallization data in more detail and to present first results from some iron-based metallic glasses.

For precipitation in supersaturated solid solutions Aaron *et al.* [3] calculated the radius r of spherical particles in volume diffusion-controlled particle growth to be proportional to √ time such that

$$r = \alpha\sqrt{(Dt)}, \qquad (1)$$

where α is a dimensionless parameter evaluated from the compositions at the particle interface and the composition of the sample and D is the diffusion coefficient. Knowing α and the particle radius, the diffusion coefficient can be estimated. Using this approach and assuming boron concentrations of about 1 at% in the primary α-iron crystals and about 25 at% at the crystal/amorphous interface (this concentration is indicated by the polymorphous crystallization of the matrix into Fe_3B), it is calculated that for $Fe_{86}B_{14}$ alloys $\alpha = 2$, for $Fe_{84}B_{16}$ $\alpha = 1.6$ and for $Fe_{80}B_{20}$ $\alpha = 1.0$.

Fig. 1 shows diffusion rates* estimated by this method versus temperature for these three Fe–B alloys (nominal composition). Within the accuracy of our measurements the diffusivity is independent of boron concentration at least for the temperature and concentration range so far investigated. At

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*Older data [2], indicating a boron-dependent diffusion coefficient, were calculated with a concentration-independent $\alpha = 2$ in Equation 1. These data are included in Fig. 1, but recalculated using the exact numbers of α.

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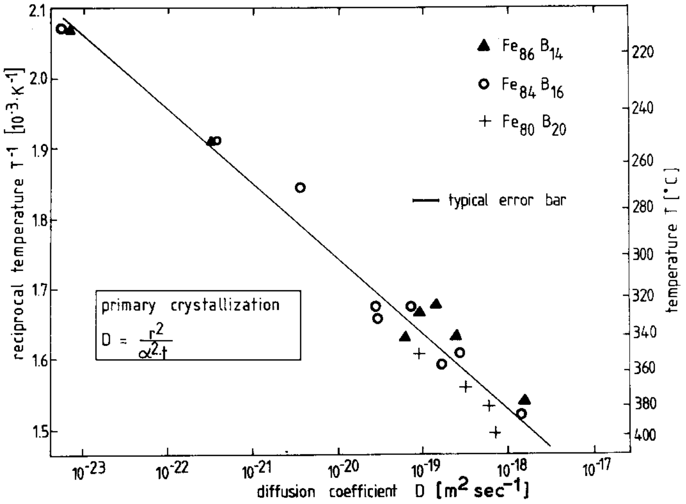

Figure 1 Diffusion coefficients in amorphous iron–boron alloys.

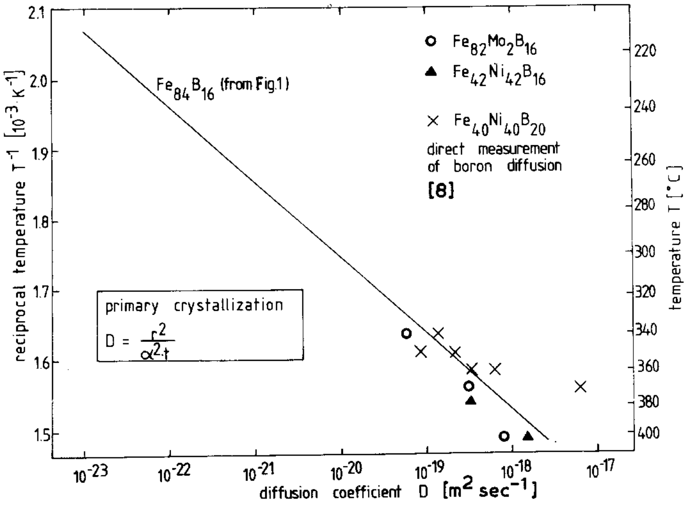

Figure 2 Diffusion coefficients in amorphous (iron, metal)–boron alloys.

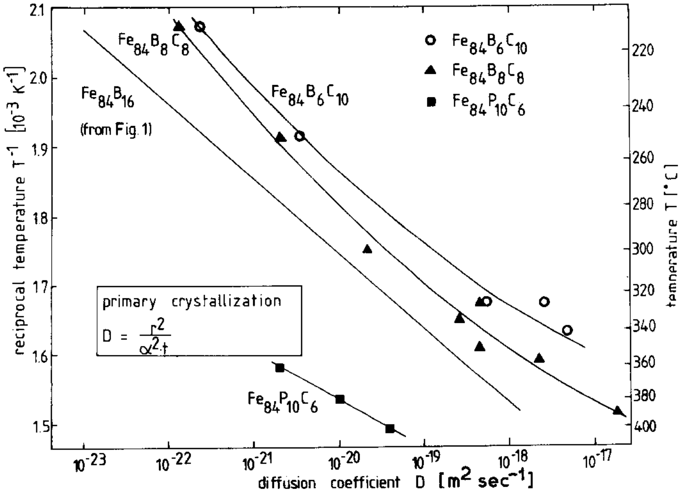

Figure 3 Diffusion coefficients in amorphous Fe–B–C and Fe–P–C alloys.

350° C the diffusion coefficient has been found to be $2 \times 10^{-19}\,\mathrm{m^2\,sec^{-1}}$. The calculated diffusion coefficients obey quite reasonably an Arrhenius relationship with a slope corresponding to an activation energy of $180\,\mathrm{kJ\,mol^{-1}}$ and a pre-exponential factor $D_0 = 2 \times 10^{-4}\,\mathrm{m^2\,sec^{-1}}$.

The data can be compared with diffusion data in crystalline iron–boron alloys: self-diffusion in α-iron has been measured only down to temperatures of about 500° C ($D^{511°\mathrm{C}} \approx 10^{-22}\,\mathrm{m^2\,sec^{-1}}$; $Q \approx 290\,\mathrm{kJ\,mol^{-1}}$) [4] indicating an extrapolated diffusion coefficient of about $10^{-27}\,\mathrm{m^2\,sec^{-1}}$ at 350° C. Extrapolating diffusion data for γ-iron, which is thought to have a structure similar to that of the amorphous phase, gives an even smaller diffusivity (about $10^{-28}\,\mathrm{m^2\,sec^{-1}}$). In boron-segregated grain boundaries in b c c iron which might act as a two-dimensional model for Fe–B metallic glasses, grain-boundary diffusion can be estimated to be about $2 \times 10^{-19}\,\mathrm{m^2\,sec^{-1}}$ at the same temperature ($D_0 = 0.8\,\mathrm{m^2\,sec^{-1}}$; $Q = 220\,\mathrm{kJ\,mol^{-1}}$) [5]. Data for boron diffusion in α-iron have been published only by Busby *et al.* [6, 7] with $D_0 = 10^2\,\mathrm{m^2\,sec^{-1}}$ and $Q = 260\,\mathrm{kJ\,mol^{-1}}$; the high activation energy indicates a substitutional diffusion mechanism in the α-phase. Extrapolating these data to 350° C, one obtains $D \approx 2 \times 10^{-20}\,\mathrm{m^2\,sec^{-1}}$. Boron diffusion in γ-iron is assumed to occur by an interstitial mechanism; extrapolating Busby's data [6] to 350° C one obtains $D \approx 10^{-14}\,\mathrm{m^2\,sec^{-1}}$ which is much faster than the observed diffusion coefficient in amorphous Fe–B alloys. This means that boron volume diffusion in b c c iron and iron diffusion in boron-segregated grain boundaries are in reasonable agreement with the measured data in iron–boron metallic glasses. With increasing boron content, progressive filling of the holes in the Bernal structure of an amorphous metal should lead to a reduction of available empty holes to sustain diffusion. However, diffusivity does not drop with increasing boron content. Assuming that the boron diffusion out of the crystallizing regions is the rate-determining process, we think that boron diffusion occurs, not by an interstitial mechanism but as in crystalline α-iron by a substitutional one, i.e. iron and boron diffusion occurs by the very same mechanism. The activation energy for the eutectic crystallization which reflects diffusion of iron and boron has been found to be about $200\,\mathrm{kJ\,mol^{-1}}$ [1], and is in good agreement with this assumption.

An influence of exchange of iron by nickel or molybdenum on diffusion in $\mathrm{Fe_{84}B_{16}}$ has been found in our first experiments to be negligible, as shown in Fig. 2. The only known *direct* boron diffusion data (measured in $\mathrm{Fe_{40}Ni_{40}B_{20}}$ [8]) are in astonishingly good agreement with our data, confirming the assumption of metalloid diffusion as rate-determining process.

The influence of some metalloid exchange, however, has been found to be quite significant (Fig. 3). Whereas the replacement of boron by phosphorus produces only minor changes, replacement of two-thirds of the boron by carbon increases diffusivity by about one order of magnitude. Approximating the data for $\mathrm{Fe_{84}B_8C_8}$ and $\mathrm{Fe_{84}B_6C_{10}}$ by Arrhenius plots, activation energies of about 180 and $190\,\mathrm{kJ\,mol^{-1}}$, respectively, are obtained. But, as indicated in Fig. 3, there is some evidence for a deviation to higher diffusivities at low temperatures than would be expected from extrapolation from the high-temperature part. So far, however, measurements are not exact enough to draw any conclusions. Diffusion in $\mathrm{Fe_{84}P_{10}C_6}$ has been found to be much slower. In α-iron, phosphorus diffusion is assumed to occur by a substitutional reaction as indicated by the high activation energies ($Q = 230\,\mathrm{kJ\,mol^{-1}}$ in α-iron and $290\,\mathrm{kJ\,mol^{-1}}$ in γ-iron) [9], but carbon diffusion occurs by an interstitial mechanism and has been found to be very fast with a diffusion coefficient of about $10^{-13}\,\mathrm{m^2\,sec^{-1}}$ [10]. Therefore, an increase in diffusivity in amorphous iron–boron alloys could be expected by steadily replacing boron by the much smaller carbon, but it is far too early for any further speculation.

The foregoing shows that volume diffusion of metalloids in metallic glasses can be estimated from primary crystallization data. Using this method, metalloid diffusion rates have been found to be of the same order as metalloid diffusion in b c c iron, indicating a substantial mechanism for boron diffusion. Further experiments, however, have to be conducted under more controlled conditions, knowing the exact composition and thermal history of the ribbons used. In addition, there is a great need for direct measurements, like Cahn's, to ascertain that the indirect method described here, which is experimentally so much easier, is a useful approach.

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Polymorphic transition of $GaNbO_4$ under high pressures

The crystal structure of $GaNbO_4$ under atmospheric pressure was studied by Morosin and Rosenzweig [1] and found to be $AlNbO_4$-like with a non-centric space group C2 ($a = 12.660$, $b = 3.7921$, $c = 6.6147$ Å, $\beta = 107.90°$ and $Z = 4$ unit formulae/cell). The co-ordination about gallium and niobium is a highly distorted octahedral one. The idealized structure of $GaNbO_4$ at standard pressure is shown in Fig. 1.

A hexahedral anvil type apparatus and a piston–cylinder type apparatus were used for generating pressure ranging over 7 to 50 kbar, and an internal heating type apparatus using the argon gas was used for generating pressure ranging over 1 to 1.5 kbar.

A mixture of Nb_2O_5 ("spectrographically standardized", chemical analysis in the previous paper [2]) and Ga_2O_3 (99.999% pure) was sealed in a platinum capsule to prevent reduction. The procedures for the runs were given in the previous paper [2], when the piston–cylinder and hexahedral anvil type apparatuses were used. When the internal heating type apparatus using argon gas was used, the samples were quenched at a rate of approximately $60°\,C\,min^{-1}$ before the pressure was released. After the run, each sample, was analysed by X-ray diffraction, using nickel-filtered copper radiation.

The X-ray powder patterns are shown in Table I, which indicates that the high-pressure structure is very likely of the wolframite type (Fig. 1) that

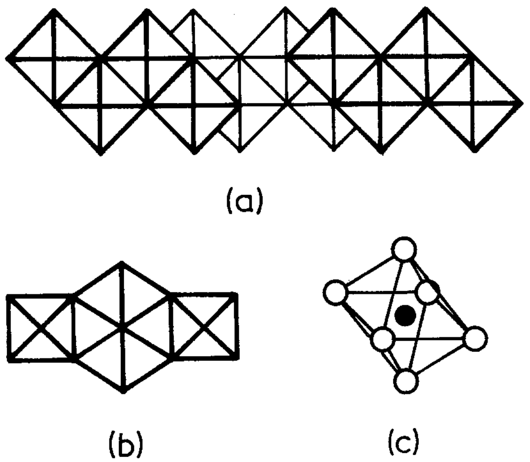

Figure 1 (a) The idealized structure of $GaNbO_4$ at standard pressure; each square represents an octahedron in projection as viewed from a corner, the lighter lines indicate displacement downwards by half an octahedral diagonal. (b) The idealized structure of wolframite type. (c) Each octahedron consists of oxygen ions at the corners and a metal ion at the centre.