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DIFFUSION IN SOME IRON-NICKEL-BORON GLASSES

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In metallic glasses the standard experimental methods for measuring diffusion rates \( D \) are useless: \( D \) is very small and annealing times and temperatures are strongly limited in order to avoid crystallization. Therefore, only very few measurements \(^1\ldots^4\) have been published so far. Very recently, boron diffusion rates calculated from measurements of concentration gradients by SIMS in a \( \text{Fe}_{40}\text{Ni}_{40}\text{B}_{20} \) glass \(^4\) have been reported. These data agree reasonably with some roughly estimated diffusion rates deduced indirectly from measured crystal growth rates \(^5\) in \( \text{Fe}_{42}\text{Ni}_{42}\text{B}_{16} \).

Kinetics of crystallization are generally assumed to be determined by diffusion rates and should be useful for calculating diffusion data. The aim of this paper is to discuss the prediction of diffusion rates from crystallization data in more detail and to present data on diffusion in some \( (\text{Fe}_{5}\text{Ni}_{5})_{100-x}\text{B}_{x} \) metallic glasses. Such glasses with \( 16\leq x \leq 22 \) were prepared by melt spinning in a He-atmosphere of about 0.5 bar. Crystallization has been investigated by light and transmission electron microscopy of specimens annealed in the bulk state \(^6\) prior to any thinning procedure. Depending on composition these glasses exhibit primary, eutectic, and polymorphous crystallization.

During primary crystallization occurring in \( (\text{Fe}_{5}\text{Ni}_{5})_{100-x}\text{B}_{x} \) glasses with \( x \leq 20 \) the radii of \( \gamma-(\text{Fe},\text{Ni}) \) crystals have been found to obey a \( \sqrt{\text{time}} \)-law as shown for example in fig. 1a. This parabolic relationship indicates that growth is controlled by volume diffusion. Assuming a concentration independent diffusion rate \( D \), Aaron et al. \(^7\) calculated the radius \( r \) of spherical particles in volume diffusion controlled particle growth to be proportional to \( \sqrt{\text{time}} \), i.e.

\[
r = a \sqrt{D \cdot \text{time}}
\]

where \( a \) is a dimensionless parameter evaluated from the compositions at the particle interface and the composition of the sample. The concentration gradient over

![Graph of \( r = a \sqrt{D \cdot \text{time}} \) for the largest observed crystallites in an \( \text{Fe}_{41}\text{Ni}_{41}\text{B}_{18} \) glass aged at 430 °C](image-url)
the glass - crystallite interface is shown schematically in fig. 1b. Such a concentration gradient which would be expected to exist near the interface of a region growing with parabolic growth kinetics was observed recently by Freed et al.\(^8\) in a Cu\(_{56}\)Zr\(_{44}\) glass. Knowing \(\alpha\) and the particle radius, the diffusion rate can be estimated. Using this approach and assuming boron concentrations of less than 1 at.\% in the primary crystals and about 25 at.\% at the glass/crystallite interface (this concentration is indicated by the polymorphous crystallization of the matrix into (Fe,Ni\(_3\))B), we calculate for \(x = 16, 18,\) and 20 \(\alpha = 1.6, 1.3,\) and 1.0, respectively.

Fig. 2 shows diffusion rates estimated by this method versus temperature for these three Fe-Ni-B glasses (nominal composition). These data are in astonishingly good agreement with the direct measured boron diffusion rates in Fe\(_{40}\)Ni\(_{40}\)B\(_{20}\)\(^4\). As in Fe-B metallic glasses\(^9\) within the the accuracy of our measurements the diffusivity is independent of boron concentration at least for the temperature and concentration range investigated so far. 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. Boron diffusion in \(\gamma\)-iron is assumed to occur by an interstitial mechanism; extrapolating Busby's data\(^10\) to 350 °C one obtains \(D = 10^{-14}\) m\(^2\)/s which is much faster than the observed diffusion rate in amorphous Fe-Ni-B alloys at this temperature. The calculated diffusion rates obey quite reasonable an Arrhenius relationship with a slope corresponding to an activation energy of \(Q = 210\) kJ/mole which is much higher than expected for an interstitial mechanism. Assuming that the boron diffusion out of the crystallizing regions is the rate determining process, we guess.
that boron diffusion occurs by a substitutional mechanism. Such behaviour would be in accordance with a structure of Fe-B glasses recently concluded from XPS studies: boron atoms occupy interstitial-like sites only below some critical boron concentration, probably below 14 at.% and excess boron atoms occupy substitutional-like sites.

Eutectic crystallization has been found in Fe₄₀Ni₄₀B₂₀ as well as Fe₃₉Ni₃₉B₂₂ glasses. The decomposition necessary to occur during crystallization is described schematically in fig. 3a & b; the diffusion processes involved may occur in the crystallization front or in the amorphous matrix ahead of them. If diffusion occurs in the amorphous phase, the growth rate \( u = \lambda^{-1} \), where \( \lambda \) is the interlamellar spacing; if diffusion occurs along the amorphous/crystalline interface, \( u = \lambda^{-2} \). Therefore, the following equations can be set up assuming a driving force \( \Delta G >> RT \), i.e. for large undercooling:

\[
\text{volume diffusion: } u = 4D\lambda^{-1} \\
\text{interfacial diffusion: } u = 8D\delta\lambda^{-2}
\]

where \( \delta \) is the thickness of the crystallization front.

Fig. 4 shows the growth rates during eutectic crystallization. The interlamellar spacings have been found to decrease slightly with increasing temperature (\( \lambda = 24 \) nm at 320 °C and \( \lambda = 13 \) nm at 430 °C). Using these data one can estimate diffusion rates as shown in fig. 2 which depend on the diffusion mechanism assumed: if volume diffusion is rate determining, diffusion rates are much faster than those estimated from primary crystallization.
Therefore, we suggest that interfacial diffusion is the rate limiting process during eutectic crystallization. For such a reaction a higher diffusivity is expected than for volume diffusion. Assuming $\Delta G >> RT$, the growth rate for polymorphous crystallization can be written as:

$$u = \delta \cdot v_0 \cdot \exp \left( \frac{-Q}{RT} \right)$$  \hspace{1cm} (3)

A diffusivity for this growth process may be defined by $D = v_0 \cdot \delta^2 \cdot \exp \left( \frac{-Q}{RT} \right)$ and equation (3) becomes:

$$u = \delta^{-1} \cdot D$$  \hspace{1cm} (4)

First results from the polymorphous crystallization following the primary crystallization in $Fe_{42}Ni_{42}B_{16}$ glass show surprisingly small diffusion rates which are in good agreement with the data for volume diffusion of boron. The diffusion rates estimated from polymorphous crystallization, however, were expected to reflect interfacial diffusion. At the moment we cannot explain this different behaviour:

If the condition for equation (3) is not fulfilled, the calculated data may be much too small. Another possibility could be the influence of the volume change during crystallization producing some internal stress which may be reduced by relaxation (volume diffusion) processes ahead of the crystallization front. Or growth may be controlled by processes at the interface, for example atoms may be unable to transfer from the amorphous to the crystalline phase with a relatively complicated structure at all parts of the interface, but only at certain active sites.

The foregoing shows that volume diffusion rates of boron in $Fe-Ni-B$ glasses can be estimated from primary crystallization. Diffusion rates have been found to be independent of boron content and indicate a substitutional-like mechanism for boron diffusion. Whereas interfacial diffusion with higher diffusion rates is suggested to be rate determining during eutectic crystallization, the understanding of data estimated from polymorphous crystallization needs further investigation.

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