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Size dependence of tracer-impurity diffusion in amorphous $Ti_{60}Ni_{40}$

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Tracer diffusion coefficients (D) of several impurity atoms, namely, B, Be, Fe, and Si, in the metallic glass $Ti_{60}Ni_{40}$ were measured at 604 and 690 K using the technique of secondary-ion mass spectrometry for concentration depth profiling. The results showed that the small boron atoms diffused about 2 orders of magnitude faster than the big silicon atoms while the diffusivities of Be and Fe had intermediate values following the trend $D_B > D_{Be} > D_{Fe} > D_{Si}$, which is opposite to the trend of the atomic radius (r) of the respective diffusing species, i.e., $r_{Si} > r_{Fe} > r_{Be} > r_B$. The data are compared with the reported data in other metal-metal-type amorphous alloys and in the crystalline α-Ti and α-Zr.

INTRODUCTION

Diffusion investigations in amorphous alloys are important for understanding basic kinetic processes such as structural relaxation, crystallization, and also the changes in their structure-sensitive properties. Additionally, these investigations are of great academic interest from the point of view of establishing any distinct differences in the diffusion behavior in amorphous and crystalline media.[1] Despite the inherent experimental difficulties associated with the measurement of small diffusion distances of the order of a few nanometers,[1] a considerable volume of diffusion data in amorphous alloys has so far been reported in the literature.[2] Moreover, fewer diffusion investigations have been reported in metal-metal (m-m) type of amorphous alloys as compared to those in metal-metalloid (m-me) type of amorphous alloys.[2] Among the metal-metal-type amorphous alloys, Zr-based alloys, e.g., Zr-Ni,[3,4] Zr-Fe,[5] Zr-Co,[6] and amorphous Ni-Nb,[1,7] have mostly been considered for diffusion investigations. In contrast to this, only two investigations pertaining to the direct measurement of diffusion rates in Ti-containing m-m type of amorphous alloys have so far been reported in the literature.[8,9] These include the measurement of diffusivities of Si (Ref. 8) in $Ti_{60}Ni_{40}$ and of B (Ref. 9) in $Co_{74}Ti_{26}$.

Among the Ti-based amorphous alloys, Ti-Ni constitutes an important alloy system wherein amorphous alloys over a wide composition range have been produced.[10] Some of the attractive features of these alloys are their good thermal stability, excellent mechanical properties and low mass density. Moreover, the ternary additions of Be and Si to Ti-based alloys [e.g., Ti-Zr-Be (Ref. 11) and Ti-Ni-Si (Ref. 10)] have been found to result not only in high strength amorphous alloys with good thermal stability, but also in their easy quenchability in amorphous forms.[10] Though much attention has been paid to study the crystallization and relaxation behavior of amorphous Ti-Ni alloys,[12,13] detailed diffusion behavior still remains uninvestigated. Recently[8] we studied the diffusion of Si in the amorphous $Ti_{60}Ni_{40}$ using secondary-ion mass spectrometry (SIMS) for concentration depth profiling. In the present paper, our results for the diffusion of B, Be, and Fe in amorphous $Ti_{60}Ni_{40}$ are reported.

In addition to the fact that the diffusion measurements in Ti-based amorphous alloys are lacking in the literature,[2] the motivation for carrying out diffusion measurements in amorphous $Ti_{60}Ni_{40}$ also came from the following. It has been shown that the diffusivities in Zr-based amorphous alloys depend on the size of the diffusing atom.[3-6] A similar size dependence of D has also been found to hold in crystalline α-Zr and α-Ti.[14,15] Therefore, it was considered worthwhile to check the size effect in amorphous $Ti_{60}Ni_{40}$ as well and to compare the diffusion data in amorphous $Ti_{60}Ni_{40}$ and those available in other metal-metal-type amorphous alloys. The diffusing species B, Be, Fe, and the earlier investigated Si (Ref. 8) possess an appreciable difference in their atomic sizes[16] for checking the size dependence of D. Moreover, these species should be of additional interest due to their drastic influence on the thermal stability of Ti-Ni amorphous alloys.[10,11]

EXPERIMENT

The specimens (each of dimensions measuring 11 mm × 11 mm × 30 μm) were cut from a melt-spun ribbon of $Ti_{60}Ni_{40}$. A characterization of the alloy ribbon by x-ray diffraction (XRD) and transmission electron microscopy (TEM) revealed the presence of some crystalline traces on the air side (shiny side) while the wheel side (nonshiny side) was found to be completely amorphous. The diffusion investigations were carried out on the wheel side which was mechanically polished to a mirror finish using 3 and 1 μm diamond abrasives, respectively. These polished specimens were thermally relaxed at 620 K for 2 h in a high-vacuum furnace. A ~2-nm-thick film of Be or Fe tracer was sputter deposited on the polished side of each of the specimens in an UHV chamber under argon pressure of 10^{-4} Pa. In order to evaluate the diffusivities of B, a tracer layer of FeNiB was sputter deposited from a target which consisted of the metallic glass $Fe_{40}Ni_{40}B_{20}$. It was felt that this procedure would permit the simultaneous evaluation of the diffusivities of both B and Fe from the same specimen. An independent check of the correctness of the diffusivities of Fe was made from the diffusion rates obtained from the specimens on which a tracer layer of pure Fe was sputter deposited. It is assumed here that the effect of any interaction between the constituents of the FeNiB tracer layer in their dilute concentration on the diffusion rates of the respective tracers is quite insignificant. Prior to sputter deposition the specimen was cleaned by argon-ion etching in order to remove residual contaminations. After sputter deposition the tracer was covered by about 50 nm of the sputter-deposited $Ti_{60}Ni_{40}$ base material.

The concentration depth profiles of the as-deposited pure tracer layers of Be or Fe, or those of B and Fe from the FeNiB tracer layer on each of the diffusion specimens, were obtained by using the technique of secondary-ion mass spectrometry with a primary beam of 4-keV O_2^+ ions which resulted in a sputter crater of 1×1 mm^2 on the specimen surface after the analysis. The specimens were subsequently diffusion annealed at two selected temperatures of 604 and 690 K for 40 min and about 6 days, respectively, in a high-vacuum ($\leq 10^{-4}$ Pa) furnace with a temperature accuracy of ±1.5 K. These temperature values lie on the lower and the higher sides of the temperature range of 600–690 K used for the measurement of Si diffusion rates in this alloy.[8] No crystallization was detected after the diffusion annealing by XRD and TEM. The concentration depth profiles of the tracers Be, B, or Fe after the diffusion annealing were again obtained by SIMS under identical experimental conditions. The necessary depth calibration of the concentration profiles was achieved by mechanically probing the depth of the sputter crater by a surface profilometer (DECTAC, Veeco). This calibration procedure had an accuracy of ±20%. As the specimen geometry employed here for diffusion measurements corresponds to a thin-film couple, the diffusion coefficients were evaluated using the thin-film solution of the diffusion equation.[17] The logarithm of the SIMS intensity of the diffusing tracer was plotted against the square of the depth $(\Delta x)^2$ to yield the diffusion penetration plots. The depth $\Delta x = (x - x_0)$ represents the distance measured from the position of the intensity maximum at x_0 in the corresponding concentration versus the depth plot. The diffusion coefficients D were calculated from the relation

$$D = (1/s - 1/s_0)/4t , \qquad (1)$$

where s_0 and s are the mean slopes of the linear fits to the background corrected penetration plots of B, Be, or Fe tracer obtained from the same specimen before and after the diffusion annealing for a time t, respectively. The estimated errors in the D values reported here were about ±40% and resulted mainly from the error in depth calibration.

RESULTS AND DISCUSSION

Some typical penetration plots and the corresponding Gaussian fits for the diffusion of B, Be, and Fe into amorphous $Ti_{60}Ni_{40}$ at 604 K are shown in Fig. 1. A noticeable feature in Fig. 1 is the slight curvature in the tail region of some of the penetration plots and strikingly steep slopes around the concentration maximum. The former is the result of atomic mixing during the SIMS analysis while the latter is probably caused by contamination with residual oxygen during the specimen preparation.[18] Such contamination, however, does not influence the diffusion behavior of the tracer Be, B, or Fe. In order to minimize the effect of these disturbances, the data evaluation was restricted to intensity values which were higher by at least a factor of 2 than the respective background values and

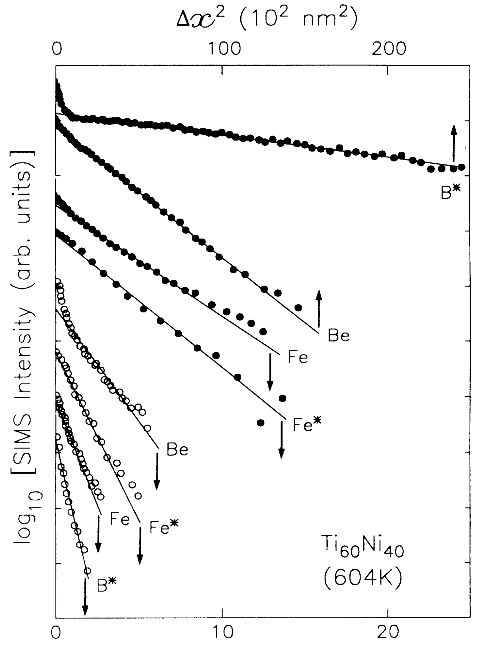

FIG. 1. Typical penetration plots corresponding to the diffusion of B, Be, and Fe in amorphous $Ti_{60}Ni_{40}$ at 604 K. The logarithm of the intensity of the tracer (indicated on the figure) as measured by SIMS is given after background subtraction as a function of $\Delta x^2 = (x - x_0)^2$, where x_0 is the position of the maximum in the concentration profile. The lower four curves correspond to the nonannealed states. The curves for Fe and B marked with an asterisk represent the plots obtained from the tracer layer of FeNiB. The arrows point to the depth scales for the respective profiles.

TABLE I. Impurity tracer diffusion coefficients D in $Ti_{60}Ni_{40}$ and other metal-metal amorphous alloys.

Alloy	Diffusant	D at 604 K (m^2s^{-1})	D at 690 K (m^2s^{-1})	References
$Ti_{60}Ni_{40}$	B	5.2×10^{-21}	7.3×10^{-19}	
	Be	8.5×10^{-22}	1.5×10^{-19}	
	Fe	8.3×10^{-23} $5.0\times10^{-23\,a}$	2.0×10^{-20} $2.2\times10^{-20\,a}$	This work
	Si	1.4×10^{-23}	4.0×10^{-21}	
$Zr_{50}Ni_{50}$	Fe	1.6×10^{-20}	7.9×10^{-19}	4
$Co_{74}Ti_{26}$	B	4.4×10^{-21}	2.2×10^{-19}	9
$Ni_{59.5}Nb_{40.5}$	B	5.4×10^{-24}	2.1×10^{-21}	7

[a] Data obtained from FeNiB tracer layer on $Ti_{60}Ni_{40}$.

which were lying well outside the contaminated zone. A detailed discussion on these disturbances can be found elsewhere.[18] The calculated values of the diffusion coefficient [according to Eq. (1)] are mentioned in Table I. These have also been plotted against the atomic (metallic) radius[16] r of the diffusion atoms in Fig. 2.

It can be observed from Fig. 2 that the D values of the smaller B atoms (radius 0.098 nm) are higher than those of the bigger Si atoms (0.132 nm) by more than 2 orders of magnitude and the diffusion rates of Be (0.112 nm) and Fe (0.126 nm) are intermediate between those of B and Si. This observation is consistent with the trend of decreasing diffusivity ($D_{Si} < D_{Fe} < D_{Be} < D_B$) with the increasing atomic radius[16] of the diffusing atoms ($r_B > r_{Be} > r_{Fe} > r_{Si}$). Previous investigations on diffusion in amorphous alloys have shown the occurrence of the size dependence of D in Zr-based amorphous alloys.[3-6] Furthermore, it has recently been shown that a similar size dependence seems to hold in amorphous $Fe_{40}Ni_{40}B_{20}$ (metal-metalloid type) alloy with some exceptions.[19] Despite the availability of a good amount of diffusion data in amorphous alloys,[2] only a few systematic diffusion investigations[3-6] have been carried out. Therefore, it remains an open question whether the size effect of D applies only to a certain type of amorphous alloys, such as those which are Zr- or Ti-based, or whether this is a general feature of all amorphous alloys. In regard to the Zr- or Ti-based amorphous alloys, it is interesting to note here that a similar size dependence of D has earlier been reported in crystalline α-Zr and α-Ti.[14,15]

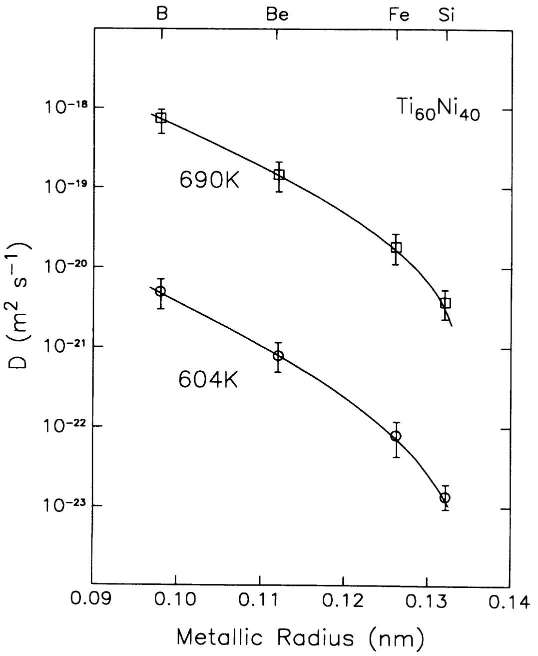

FIG. 2. Plots showing the size dependence of the diffusion coefficients D of B, Be, Fe, and Si in amorphous $Ti_{60}Ni_{40}$ at 604 and 690 K.

We now compare the data obtained in amorphous $Ti_{60}Ni_{40}$ with those available for impurity diffusion in other metal-metal-type amorphous alloys. While data for diffusion on B (Refs. 7 and 9) in amorphous $Ni_{59.5}Nb_{40.5}$ and $Co_{74}Ti_{26}$ and for the diffusion of Fe (Ref. 5) in $Zr_{50}Ni_{50}$ exist in the literature, no data for diffusion of Be or Si are available in a metal-metal-type amorphous alloy. We prefer to restrict the comparison here to metal-metal-type amorphous alloys only in order to make it more meaningful in view of differences in the diffusion rates in metal-metalloid and metal-metal-type amorphous alloys[1] and the fact that the observed systematics for diffusivity trends in metal-metalloid-type amorphous alloys has many notable exceptions.[1,3,19] It can be observed from Table I that there is good agreement between the B diffusivity values in amorphous $Ti_{60}Ni_{40}$ and $Co_{74}Ti_{26}$ alloys. On the other hand, B diffusion in $Ti_{60}Ni_{40}$ is 2–3 orders of magnitude faster than in $Ni_{59.5}Nb_{40.5}$ while Fe diffusion in $Ti_{60}Ni_{40}$ is about 2 orders of magnitude slower than in $Zr_{50}Ni_{50}$. The much slower diffusion of B in $Ni_{59.5}Nb_{40.5}$ could be attributed to its higher thermal stability as is also revealed by its significantly higher crystallization temperature[7,20] T_x (T_x is equal to 953 K for $Ni_{59.5}Nb_{40.5}$ as compared to 770 K for $Ti_{60}Ni_{40}$). As the crystallization temperatures[20] of $Ti_{60}Ni_{40}$ and $Zr_{50}Ni_{50}$ do not differ considerably from each other ($T_x = 770$ K for $Ti_{60}Ni_{40}$ and 750 K for $Zr_{50}Ni_{50}$), the faster diffusion of Fe in $Zr_{50}Ni_{50}$ than in $Ti_{60}Ni_{40}$ by about 1–2 orders of magnitude is quite noteworthy. It is interesting to note further that this observation is in line with the reported higher diffusion rates of Fe in the crystalline α-Zr than in α-Ti.[15,21] A detailed comparison in the amorphous and the crystalline cases will be presented elsewhere.[22]

To summarize the discussion, it has been shown in this paper that the size dependence of D is found to hold in amorphous $Ti_{60}Ni_{40}$ and possibly it may be a general feature of Zr- or Ti-based amorphous alloys. The observed similarity of the diffusivity trends in amorphous $Ti_{60}Ni_{40}$, $Zr_{50}Ni_{50}$, and crystalline α-Zr,α-Ti is quite noteworthy.

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