Relation Between Time and Temperature Dependence of Diffusion and the Structural State in ZrTiCuNiBe Bulk Glasses

Thomas Zumkley¹, Volkmar Naundorf¹, Michael-Peter Macht¹, Peter Fielitz^{1*} and Günter Froberg²

¹Department Materials Sciences, Hahn-Meitner-Institute Berlin, Glienicker Str. 100, D-14109 Berlin, Germany

²Institute of Materials Sciences and Technology, Technical University Berlin, Hardenbergstr. 36, D-10623 Berlin, Germany

Time and temperature dependence of impurity diffusion is measured in detail for several ZrTiCuNiBe bulk glasses in a wide temperature range. We find that neither the quenched-in free volume nor a small volume fraction of crystals have a significant effect on the diffusivity. It is shown that the composition of these glasses has a much weaker effect on the diffusion coefficients than have structural changes of the glass. By long time relaxation the reversible metastable equilibrium of the glass structure could be reached at temperatures below the calorimetric glass transition. For this metastable equilibrium state a single set of diffusion parameters, activation enthalpy and pre-factor of the diffusion coefficient, is derived in the entire temperature range above and below the glass transition. This indicates that the usually observed non-linear Arrhenius behavior of diffusion coefficients in the ZrTiCuNiBe bulk glasses is caused by insufficient structural relaxation at temperatures below the calorimetric glass transition.

(Received February 22, 2002; Accepted March 12, 2002)

Keywords: diffusion, structural state, long time relaxation, reversible metastable equilibrium, arrhenius behavior, zirconium based beryllium bearing bulk glass

1. Introduction

Metallic bulk glasses are multi-component alloys comprising at least four components. This new class of materials includes alloys of the PdCuNiP, ZrCuNiAl and ZrTiCuNiBe type¹⁻³⁾ and can be produced in bulky form because the crystallization is bypassed during solidification of the liquid melt at relatively low critical cooling rates which can be as low as 0.1 K/s.¹⁻⁴⁾ Metallic bulk glasses are stable, *i.e.* they resist the general tendency to crystallize in a wide temperature range above the glass transition for rather long times. Based on their favorable physical and mechanical properties and excellent processing capabilities metallic bulk glasses have considerable potential as advanced engineering materials for technical application.^{1-3,5)}

ZrTiCuNiBe bulk glasses are prominent representatives and are well suited for fundamental investigations of these new materials. They can be rather easily produced at cooling rates of 1–20 K/s, which is generally sufficient to obtain rods with diameters up to 50 mm.^{2,3)} Be, which is the smallest and most mobile atom in the alloy, seems to play a key role for the glass forming ability and the stability of the ZrTiCuNiBe-bulk glasses.⁶⁾ One of the best glass formers of the ZrTiCuNiBe-family is the $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ alloy (here called V1).⁷⁾ However, it is known that the V1 glass decomposes already at temperatures below 620 K, *i.e.* near the calorimetric glass transition, within a few hours,⁸⁻¹¹⁾ and isothermal crystallization of the undercooled melt starts after less than 1 h at 650 K.¹²⁾ The decomposition of V1 causes a nanosized microstructure of two phases, one of them enriched in Be and Zr, and depleted of Ti and Cu, the other enriched in Ti and Cu, and depleted of Be and Zr.^{13,14)} The two alloys, $\text{Zr}_{41}\text{Ti}_{8.7}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{27.8}$ (here called D1) and

$\text{Zr}_{41}\text{Ti}_{16.5}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{20}$ (here called D2), lie together with the V1 glass on a common line of the pseudo-ternary (Zr, Ti)–(Cu, Ni)–Be phase diagram and differ only in their Be/Ti ratio.¹⁵⁾

A higher Be-content is expected to improve the thermal stability of the ZrTiCuNiBe glasses.^{16,17)} In fact, the $\text{Zr}_{46.8}\text{Ti}_{8.2}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass (here called V4) shows an exceptionally extended region of the supercooled liquid phase, with the calorimetric glass transition at 603 K, and the first crystallisation at 730 K.¹⁸⁾ Detailed investigations of the microstructure have revealed, however, the existence of a small fraction of primary crystals which could be identified as a modified Be_2Zr phase.¹⁹⁾ These crystals can be observed by optical microscopy, but they cannot be detected in the Cu– K_α X-ray diffraction (XRD) spectrum since generally their volume fraction is lower than about 3%.²⁰⁾ The number density of these primary crystals increases steeply with decreasing cooling rate.¹⁸⁾ Their formation during the production indicates general limitations of the glass forming ability of the ZrTiCuNiBe glasses.

Although the V4 glass is not the most stable of the ZrTiCuNiBe family¹⁷⁾ it is sufficiently stable in order to perform extended experiments in the supercooled liquid state below temperatures of about 670 K before a massive crystallization sets in. It is this property which makes the bulk glasses in general and the ZrTiCuNiBe glasses in particular attractive for fundamental investigations of the behavior of supercooled liquids, because the temperature range is now extended well above the calorimetric glass transition which was up to now not accessible with the conventional melt-spun glasses.

Most of the unavoidable structural changes of the metastable bulk glasses at higher temperatures, *e.g.* decomposition connected with the formation of other amorphous phases or crystallization, require long range atomic transport. Hence any interest in the static properties of state and stability

*Present address: Institute of Metallurgy, Technical University Clausthal, Robert-Koch-Str. 42, D-38678 Clausthal-Zellerfeld, Germany.

of the glasses implies at the same time a fundamental interest in the dynamic property of diffusion. This paper reports on measurements of impurity diffusion around the calorimetric glass transition temperature in four ZrTiCuNiBe bulk glasses, namely the glasses V1, D1, D2, and V4. It focusses on the effects of composition and of time dependent structural changes on the diffusivity in these glasses. We use B, Fe, Co, Al, and Hf impurities as probes which in these glasses are in part chemically similar to the alloy components and cover their size spectrum, so that the behavior of these impurities ought to reflect self diffusion. The experimental details will be described in ch. 2. In ch. 3 we present the time and temperature dependent diffusion coefficients. A thorough discussion of these results in ch. 4 will show that diffusion in the ZrTiCuNiBe bulk glasses is strongly affected by at least two different structural changes which the glasses undergo during isothermal annealing in the supercooled liquid and amorphous state.

2. Experimental Details

Four alloys of the ZrTiCuNiBe family with different compositions, namely the alloys $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ (V1), $\text{Zr}_{41}\text{Ti}_{8.7}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{27.8}$ (D1), $\text{Zr}_{41}\text{Ti}_{16.5}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{20}$ (D2), and $\text{Zr}_{46.8}\text{Ti}_{8.2}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ (V4) were produced in the form of bulk glasses by levitation melting of the pure elements under purified Ar atmosphere, and cooling the melt by contact with a water cooled copper surface. Estimated cooling rates for these as-cast glasses range between 10 K/s and 30 K/s. From the resulting ingots of oblate spherical shape (principle diameters: about 15 mm thick, 20 mm wide) plates of $10 \times 10 \times 1 \text{ mm}^3$ were cut. Part of the V4 glass was remelted and splat cooled in order to obtain sample material which has undergone a considerably higher cooling rate estimated to about 10^6 K/s . The surface of all these samples was mechanically polished to 1 μm grade. The XRD spectrum of the specimens showed no indication of any crystalline peak. Inspection by optical microscopy showed, however, the presence of primary crystals with number densities of typically 10^{14} m^{-3} in the slowly cooled samples. DSC scans of the material indicated a reproducible state of the glass. XRD and DSC were generally also used in order to characterize the glass after diffusion and the various other annealing treatments.

The layer structure required for the diffusion measurements was prepared under ultra-high vacuum conditions in three steps. First the surface was cleaned by sputtering with 4 kV Ar ions in order to remove any contaminations and oxides left over from the polishing procedure. Next a layer of about one nanometer thickness of the impurity to be investigated, *i.e.* Hf, Al, Co, Fe, and B, was sputter deposited onto the surface. Finally a layer of the base material was sputter deposited on top of the specimens to protect the thin impurity layer. Each specimen was cut into four pieces of $5 \times 5 \text{ mm}^2$. Only three of these were diffusion annealed so that the non-annealed reference state was always available for an evaluation of the penetration depth profiles. Generally the annealing was performed in a resistance furnace under vacuum better than 10^{-4} Pa , annealing temperatures were controlled to better than $\pm 1.5 \text{ K}$. Annealings for times shorter than 2000 s were performed in a differential scanning calorimeter (DSC,

Perkin Elmar Pyris 1).

The concentration depth profiles of the impurity atoms before and after annealing were obtained by sputter sectioning with 4 kV O_2^+ ions in combination with secondary ion mass spectrometry (SIMS). Details of this technique are given elsewhere.²¹⁾ Figure 1 shows, as an example, depth profiles of Al in V4 glass before and after annealing for 2 h at 624 K. For such measurements we assume that the intensity measured for the impurities by SIMS is proportional to their atomic concentration.²²⁾ The width of the Al peak from the as-prepared state indicates a depth resolution of about 10 nm full width at half maximum which is characteristic of the SIMS technique when using 4 kV O_2^+ ions. The magnitude of this depth resolution results mainly from ion mixing and surface roughening due to the sputter process.²³⁾ Broadening of the concentration depth profile due to diffusion of the Al is also visible in Fig. 1. The slight increase of the Ni matrix signal in the vicinity of the peak position is caused by an enhanced ionization probability in the layer region.^{21–23)}

The design of the specimens satisfies the boundary conditions of the thin film solution of the diffusion equation. Hence the spatio-temporal evolution of the impurity concentration, $C(x, t)$, along the x -axis perpendicular to the thin layer originally positioned at x_0 is given by

$$C(x, t) = A(\sqrt{\pi Dt})^{-1} \exp(-(x - x_0)^2/4Dt). \quad (1)$$

Here A is the amount of originally deposited impurities, D is the diffusion coefficient (assumed to be independent of time and concentration), and t is the diffusion time. The diffusion coefficient can be determined from the slope s of a plot of $\ln C$ vs. $\Delta x^2 = (x - x_0)^2$ as

$$D = (s^{-1} - s_0^{-1})/4t. \quad (2)$$

Fig. 1 Concentration depth profile as measured by sputter sectioning and secondary ion mass spectrometry (SIMS): sketch of the layer structure representing the diffusion sample (upper part), example of measured Al and Ni concentration depth profiles (lower part). Note the diffusional broadening of the Al layer after a 2 h, 624 K diffusion anneal.

With s_0 in eq. (2) the instrumental broadening of the impurity profile (depth resolution of the SIMS technique) is taken into account. It is derived from the depth profile of the non-annealed reference specimen. If the diffusion coefficient depends on time as may happen, for instance, by structural changes (relaxation) of the material in the course of the diffusion anneal, then eqs. (1) and (2) remain valid when D is replaced by the time averaged diffusion coefficient

$$\bar{D}(t) = \frac{1}{t} \int_0^t dt' D(t'). \quad (3)$$

The conversion procedure from sputter time during serial sectioning in the SIMS apparatus to absolute depth coordinates, *i.e.* the depth calibration, determines the accuracy of the diffusion coefficients.²²⁾ This depth calibration was performed with a Dektak 3030 (Veeco Instruments Inc.) profilometer after the sectioning process was finished. Due to the wavy surface structure of the specimens the calibration factor between depth and sputter time could be determined only with an uncertainty of about $\pm 15\%$, which results in an uncertainty of the diffusion coefficients of typically $\pm 30\%$.

Figures 2(a), (b) present typical penetration depth profiles of Fe, B, Al and Hf in V4.^{24,25)} The steep apparent increase of the concentration near the original position of the layer at $\Delta x = 0$ is caused by an enhanced ionisation probability due to contaminations in the layer region.^{21,22)} This part of the curve was not considered for the evaluation of diffusion coefficients from the slopes which are marked by full lines.

Fig. 2 Gaussian penetration plots of Al (open symbols) and Hf (closed symbols) diffusion in V4 bulk glass. Note the different scales for Δx^2 .

The penetration depth of the impurities as measured in terms of $\sqrt{Dt}$ is usually small and does not exceed about 200 nm.¹⁸⁾ For the examples shown in Fig. 2(a) it ranges from about 5 nm (Hf at 588 K) to 50 nm (Al at 683 K). Since the annealing times must be kept short because of the potential instability of the glass small penetration depths have to be accepted which only slightly exceed the resolution limit of the experimental method of about 3.5 nm. Small penetration depths are, on the other hand, of advantage because they largely reduce the possible influences of the primary crystals on the diffusivity. Taking a number density of primary crystals of about $2 \times 10^{16} \text{ m}^{-3}$ ¹⁸⁾ the average jump distance of an atom in order to encounter one of these crystals is estimated to be larger than 10^6 nm . This is indeed many orders of magnitude larger than the largest penetration depths employed in the present diffusion experiments. It indicates a negligible influence of the primary crystals for these investigations.

3. Results

During isothermal treatment the glasses can change their structure towards the “metastable equilibrium” by relaxation, resulting in a time dependent diffusivity.^{21,26)} Since the reliable measurement of a diffusion coefficient requires always a certain minimum annealing time such measurements when performed during relaxation would yield a poorly defined average over various different states of the glass which is a result not very useful as a characteristic parameter for transport in the material. Hence, as a first step of a diffusion investigation on glasses it is always necessary to establish for any temperature an appropriate time range in which measurements can be made without significant structural changes occurring during the diffusion anneal. This situation is achieved either for measurements performed on well relaxed glasses which have already acquired their “metastable equilibrium”, or for situations when the necessary diffusion time is small compared to the inherent relaxation time of the material. In the following we will characterize a relaxation towards the “metastable equilibrium” as being irreversible, if the relaxation effect cannot be recovered by annealing the material at a different temperature, as is true for instance with the annealing of quenched-in “free volume” in melt-spun glasses.^{21,26)}

The structure of the supercooled liquid in “metastable equilibrium” is very likely temperature dependent. In the following we will characterize a relaxation as being reversible, if the relaxation effect is caused by adjustment of the structure belonging to a “metastable equilibrium” at one temperature to that at another temperature. Since the diffusion coefficients are affected by the glass structure we expect that the measured diffusion parameters, activation enthalpy Q and pre-factor D_0 , are effective ones, reflecting both the temperature dependence of the structural state as well as that of the diffusivity.

In the next two sections we present measurements of the time and temperature dependent diffusion coefficients of different impurities in the four bulk glasses V1, D1, D2, and V4 which were processed partly in different ways. The results include measurements on samples containing a small amount of crystalline phase.

Table 1 Time dependence of B, Fe, and Al diffusion coefficients D and square of penetration depths Dt in V1.

Diffusion time (ks)	Temperature (K)	$Dt(\text{B})$ (nm ²)	$D(\text{B})$ ($10^{-19} \text{ m}^2 \text{ s}^{-1}$)	$Dt(\text{Fe})$ (nm ²)	$D(\text{Fe})$ ($10^{-19} \text{ m}^2 \text{ s}^{-1}$)	Diffusion time (ks)	Temperature (K)	$Dt(\text{Al})$ (nm ²)	$D(\text{Al})$ ($10^{-22} \text{ m}^2 \text{ s}^{-1}$)
2.68	643	1560	5.82	270	1.01	6.9	624	12.75	18.5
4.9	643	1792	3.66	392	0.8	18.42	624	18.17	9.86
10.3	643	3019	2.93	579	0.56	28.62	624	28.15	9.84
21.1	643	5531	2.62	1034	0.49	58.44	624	40.15	6.87
53.2	643	20839	3.92	1733	0.33	110.1	624	44.4	4.03
107.32	643	25095	2.34	1675	0.16	230.4	624	46.95	2.04
0.36	643	287	7.97	37	1.03	368.82	624	42.6	1.16
0.72	643	552	7.67	93	1.29	368.82	624	42.6	1.16
1.44	643	1024	7.11	186	1.29	749.22	624	48.9	0.65
2.7	643	1719	6.37	293	1.09	1302.48	624	29.99	0.23

Table 2 Time dependence of B, Fe, and Al diffusion coefficients D and square of penetration depths Dt in V4.

Diffusion time (ks)	Temperature (K)	$Dt(\text{B})$ (10^3 nm^2)	$D(\text{B})$ ($10^{-19} \text{ m}^2 \text{ s}^{-1}$)	$Dt(\text{Fe})$ (10^3 nm^2)	$D(\text{Fe})$ ($10^{-19} \text{ m}^2 \text{ s}^{-1}$)	Diffusion time (ks)	Temperature (K)	$Dt(\text{Al})$ (nm ²)	$D(\text{Al})$ ($10^{-21} \text{ m}^2 \text{ s}^{-1}$)
2.68	643	4.51	16.6	1.45	5.21	5.34	625	20	3.65
6.4	643	9.07	14.2	2.7	4.22	16.86	625	66	3.9
20.8	643	33.88	16.3	11.05	5.29	25.74	625	118	4.58
64.3	643	88.93	13.8	22.98	3.57	79.26	625	327	4.12
						228.6	625	800	3.5

3.1 Time dependence of diffusion

Indications for irreversible structural changes during a few hour's annealing of the V1 glass at temperatures above about 600 K were already deduced from small angle neutron scattering (SANS) results.^{8–10} These were interpreted as isothermal decomposition of the glass into two phases. In Table 1 we present diffusion coefficients of Al, Fe, and B in this glass obtained at 624 K and 643 K using different diffusion times. The diffusion coefficients were derived according to eq. (3) as averages over the annealing time t , which is also given in the table. These data show a significant decrease of the Al, Fe and B diffusion coefficients at diffusion times of more than one hour. This time scale is compatible with the time scales derived from the isothermal structural changes of the same glass observed by SANS.^{8,15} The behavior of the V1 glass is in contrast to time averaged diffusion coefficients for the same impurities obtained in the V4 glass. These are summarized in Table 2. They show no significant time dependence during the annealing times used here, in accordance with recent SANS investigations which did not show decomposition in the V4 glass.¹¹ The data for the two glasses are compared in Fig. 3. The time dependence of the impurity diffusion coefficients in the investigated time-temperature range is characteristic for each glass indicating that it is indeed possible to perform time independent diffusion measurements even in those glasses which undergo irreversible relaxation.

Although the V4 glass is structurally stable at temperatures between about 620 K and 640 K for several hours (see Fig. 3) long term reversible structure changes are observed by their effect on the diffusivity at temperatures below about 600 K. Table 3 summarizes the B and Fe diffusion coefficients obtained at 553 K on the V4 glass which was long time pre-annealed (relaxed). Both diffusion coefficients decrease by a factor of about three when the glass is pre-annealed at 553 K

Fig. 3 Time dependence of the Al, Fe and B diffusion coefficients in the V1 bulk glass (open symbols) and in the V4 bulk glass (closed symbols). The diffusion coefficients were derived according to eq. (3) of the text as averages over the annealing time t , details are given in Tables 1 and 2.

for 1.6×10^7 s before the diffusion measurement, and the values of the as-cast glass are recovered when this relaxed material is annealed again for only 8.7×10^4 s at the higher temperature of 606 K. This reversible structural relaxation was verified by DSC.²⁷ Figure 4 shows a series of DSC scans around the calorimetric glass transition at about 603 K which demonstrate reversible enthalpy recovery of the glass first relaxed at 553 K for 6 months and then annealed again at 606 K for one day. The total enthalpy gain of the underlying structural

Fig. 4 Differential scanning calorimetric (DSC) plots of a V4 bulk glass sample which has been successively heat treated at different temperatures for different times as indicated in the figures. The heating rate was 0.067 K/s.

Table 3 Long time relaxation of B and Fe diffusion coefficients in V4. All diffusion coefficients were measured at 553 K with a diffusion time of 1.12×10^6 s.

Annealing procedure	$D(\text{B})$ (m^2s^{-1})	$D(\text{Fe})$ (m^2s^{-1})
Non-annealed (as-cast)	1.75×10^{-21}	1.23×10^{-22}
As-cast + 6 months at 553 K	6.31×10^{-22}	3.6×10^{-23}
As-cast + 6 m/553 K + 1 day at 606 K	1.68×10^{-21}	1.01×10^{-22}

changes was very small, only about 0.01 eV/at, the relaxation time was about 10^6 s.

3.2 Temperature dependence of diffusion

The temperature dependence of B and Fe diffusion coefficients in the V1 glass was measured for the as-cast state, *i.e.* the diffusion times were short enough to avoid decomposition at high temperatures and long term relaxation at lower temperatures. Table 4 shows a compilation of these data. The corresponding data for the D1 and D2 glasses are given in Tables 5 and 6, respectively. A comparison of all these data is presented as Arrhenius plot in Fig. 5. It shows that the temperature dependences of B and Fe diffusion coefficients in these three glasses is very similar, respectively.

For a single thermally activated process the diffusion coefficients D should follow a linear Arrhenius behavior, *i.e.* we expect that the relation $D = D_0 \exp(-Q/k_B T)$ is valid, with D_0 the pre-factor, Q the activation enthalpy, k_B the Boltzmann constant and T the temperature. Figure 5 shows, however, a non-linear Arrhenius behavior with different activation enthalpies at high ($T > 600$ K) and low ($T < 580$ K) temperatures, *i.e.* above and below the calorimetric glass transition. Activation enthalpies Q and pre-factors D_0 of the dif-

Table 4 Temperature dependence of B and Fe diffusion coefficients D in V1.

Temperature (K)	Annealing time (ks)	$D(\text{B})$ ($10^{-20} \text{m}^2\text{s}^{-1}$)	$D(\text{Fe})$ ($10^{-21} \text{m}^2\text{s}^{-1}$)
513	10260.0	0.00331	0.00199
533	3081.6	0.0217	0.0143
554	264.4	0.0711	0.0492
573	85.9	0.283	0.198
593	172.3	0.18	0.654
611	21.1	4.38	5.44
628	53.5	12.2	18.8
643	2.1	75.8	120.0
658	1.44	237.0	621.0

fusion coefficients derived in the different temperature ranges are compiled in Table 7.

The temperature dependence of B, Fe, Co, Al, and Hf diffusion in the as-cast V4 glass was measured between 513 K and 673 K. The results are summarized in Table 8 and presented in the form of Arrhenius plots in Fig. 6. For the B, Fe, and Co diffusion these also indicate a non-linear Arrhenius behavior with significantly different activation enthalpies at high ($T > 580$ K) and at low ($T < 580$ K) temperatures. The Al and Hf diffusion coefficients showed a linear Arrhenius behavior, however, they were measured only down to 588 K. The activation enthalpies Q and pre-factors D_0 for impurity diffusion in V4 are collected in Table 7.

As has been shown above long term annealing of V4 at 553 K reduces the B and Fe diffusion coefficients by a factor of about three due to reversible structural relaxation. The temperature dependence of the diffusion coefficients of this long term relaxed glass was measured between 533 K and 638 K.

Table 5 Temperature dependence of B and Fe diffusion coefficients D in D1.

Temperature (K)	Diffusion time (ks)	$D(B)$ ($10^{-20} \text{ m}^2 \text{ s}^{-1}$)	$D(Fe)$ ($10^{-21} \text{ m}^2 \text{ s}^{-1}$)
513	8314.8	0.0014	0.0021
533	3883.0	0.0061	
551	1631.6	0.0456	0.018
555	348.2	0.0671	0.0233
573	516.2	0.183	0.246
585	88.4	0.573	1.18
612	86.4	3.38	5.04
628	53.5	10.7	27.0
642	57.0	40.5	62.8
651	2.1	69.4	237
657	1.2	69.2	322

Table 6 Temperature dependence of B and Fe diffusion coefficients D in D2.

Temperature (K)	Diffusion time (ks)	$D(B)$ ($10^{-20} \text{ m}^2 \text{ s}^{-1}$)	$D(Fe)$ ($10^{-21} \text{ m}^2 \text{ s}^{-1}$)
513	8314.8	0.00445	0.00397
533	3883.0	0.0202	0.0151
551	1631.6	0.0986	0.0293
555	348.2	0.149	0.353
573	516.2	0.366	0.423
585	88.4	0.901	0.635
612	86.4	3.79	2.29
628	53.5	11.9	7.77
642	57.0	44.5	80.7
653	2.1	71.1	78.0
657	1.2	164	212

The data are collected in Table 9 and plotted in Fig. 7. Comparison with the diffusion coefficients of the as-cast V4 glass indicates that after long term annealing the diffusion coefficients of B and Fe show linear Arrhenius plots in the entire temperature range with activation enthalpies corresponding to those of the high temperature branch.²⁵⁾

Splat-cooling with quenching rates comparable to those of melt-spun glasses should produce an enhanced fraction of “free volume”^{28,29)} which can give rise to an increased diffusivity.^{21,26)} The B and Fe diffusion coefficients obtained in the splat-cooled V4 glass are collected in Table 10 and compared with those obtained for the as-cast bulk glass in Fig. 8. The two data sets agree in the entire temperature range within the experimental uncertainties indicating a small if any effect of fast cooling rates on the diffusivity in V4.

Some samples of the V4 glass were annealed at 643 K for 6 h and 9 h in order to completely relax the material and partly crystallize it. While the XRD pattern of the material after 6 h annealing was indistinguishable from that of the as-cast glass Bragg peaks were observed after 9 h annealing which indicated the presence of less than 10% of a quasicrystalline icosahedral phase.^{30,31)} The B and Fe diffusion coefficients obtained on this material are summarized in Table 11 and compared with the results on the as-cast V4 glass in Fig. 9. We find agreement within the experimental uncertainties between the two data sets. This indicates a negligible effect

Fig. 5 Arrhenius plot of B (closed symbols) and Fe (open symbols) diffusion coefficients in the three bulk glasses D1 (squares), D2 (triangles) and V1 (circles). Details are given in the text and in Tables 4, 5 and 6.

Table 7 Activation energy Q and pre-factor D_0 of B, Fe, Co, Al, and Hf diffusion coefficients in V1, V4, D1, D2. Typical random errors are 0.2 eV for Q and 1,5 for $\log D_0$.

Glass	Tracer	D_0 ($\text{m}^2 \text{ s}^{-1}$)	Q (eV)	D_0 ($\text{m}^2 \text{ s}^{-1}$)	Q (eV)
		Low temperature regime		High temperature regime	
V1	Fe	1.08×10^{-5}	1.91	2.26×10^8	3.48
	B	1.73×10^{-5}	1.80	1.22×10^5	2.97
V4	Fe	1.98×10^{-3}	2.11	2.76×10^6	3.16
	B	1.89×10^{-4}	1.87	2.84×10^2	2.59
	Co	7.3×10^{-4}	2.01	3.05×10^5	3.00
	Al			3.19×10^{12}	4.09
	Hf			3.76×10^{10}	3.76
D1	Fe	2.05×10^{-2}	2.27	7.24×10^5	3.17
	B	3.14×10^{-2}	2.18	1.24×10^1	2.50
D2	Fe	4.80×10^{-6}	1.85	4.58×10^7	3.44
	B	1.19×10^{-4}	1.87	2.11×10^3	2.77

of the quenched-in “free volume” on diffusivity in this bulk glass. It moreover shows that small amounts of crystals and the accompanying local decomposition have likewise no detectable effect on the diffusivity in V4.

4. Discussion

Upon annealing above about 600 K the V1 bulk glass decomposes into a two-phase structure.^{8–10)} Of these phases one is rich in Be and Zr and poor in Ti and Cu, the other rich in Ti and Cu and poor in Be and Zr.^{13,31)} Furthermore ZrTi enriched regions have been found in annealed V1.³³⁾ Volume fractions of more than 10% of nanoparticles in the decomposed matrix

Fig. 6 Arrhenius plot of B (full squares), Fe (up-triangles), Co (down-triangles), Al (crossed circles) and Hf (full circles) diffusion coefficients in the V4 bulk glass. Lines are least-mean-squares fits to all data points (Al), or separately to four data points (B, Fe, Co) at lower temperatures (< 580 K) and six data points at higher temperatures (> 580 K).

Fig. 7 Arrhenius plot of B and Fe diffusion coefficients (full symbols) in long term annealed (1.58×10^7 s, 553 K) V4 bulk glass. The full lines are least-mean-squares fits to the data. Open symbols and dashed lines indicate the behavior of the as-cast V4 bulk glass as given in Fig. 6.

have been derived from SANS results.³⁴⁾ In general, the rate of decomposition becomes smaller with time and a limiting degree of decomposition is found.^{9,15,35)} At higher temperatures the decomposition is faster and slows down at a higher level of decomposition.⁹⁾ Having reached its final degree of decomposition at one temperature, further decomposition occurs when the sample is annealed at a higher temperature than before.³⁴⁾

A decrease of the B and Fe diffusion coefficients in the V1 glass with increasing diffusion time at 643 K is demonstrated in Fig. 3. Similar results were obtained in this glass at 623 K.¹⁵⁾ The D1 and D2 bulk glasses are also unstable quite

Table 8 Temperature dependence of B, Fe, Co, Al, and Hf diffusion coefficients D in V4.

Temperature (K)	Diffusion time (ks)	$D(B)$ ($10^{-20} \text{ m}^2 \text{ s}^{-1}$)	$D(Fe)$ ($10^{-21} \text{ m}^2 \text{ s}^{-1}$)
513	10260.0	0.00849	0.00214
534	923.2	0.0418	0.026
554	348.7	0.177	0.115
574	172.9	0.777	0.613
593	83.5	2.90	3.88
613	51.7	15.9	29.2
630	10.0	55.5	151
643	6.4	142	422
658	3.1	411	1660
672	3.58	1200	5980

Temperature (K)	Diffusion time (ks)	$D(Co)$ ($10^{-21} \text{ m}^2 \text{ s}^{-1}$)
513	9219.0	0.0132
533	3081.1	0.0405
554	665.5	0.486
573	349.9	1.41
593	172.9	8.98
614	52.9	52.7
628	11.2	251
642	3.1	920
658	4.3	2880
673	2.2	11000

Temperature (K)	Diffusion time (ks)	$D(Al)$ ($10^{-21} \text{ m}^2 \text{ s}^{-1}$)
588	1394.7	0.0176
600	397.5	0.138
607	346.62	0.253
616	74.4	1.25
624	16.86	3.90
624	5.34	3.92
624	79.26	4.12
625	228.6	3.50
625	25.74	4.02
636	12.3	16.4
649	1.5	38.5
661	1.6	210
670	1.57	510
683	0.95	1500

Temperature (K)	Diffusion time (ks)	$D(Hf)$ ($10^{-21} \text{ m}^2 \text{ s}^{-1}$)
585	6739.2	0.0357
661	1.5	159
667	1.2	291

similar to the V1 glass.⁶⁾ This is to be expected since these two glasses do not represent true decomposition phases of V1 at a temperature of 643 K.¹⁴⁾ The B and Fe diffusion coefficients obtained in the time independent range and shown in Fig. 5 were each found to be very similar for the V1, D1, and D2 glasses. Moreover, comparison with Fig. 6 shows that in the V4 glass the B and Fe diffusion coefficients are higher by only a factor of about three. These results indicate that the com-

Table 9 Temperature dependence of B and Fe diffusion coefficients D after pre-annealing for different times t_{pa} at 553 K. The uncertainty of the diffusion coefficients is generally about $\pm 30\%$, except for $D(\text{Fe})$ measured at 535 K and 533 K, where it amounts up to about $\pm 80\%$.

t_{pa} (s)	Diffused		$D(\text{B})$ (m^2s^{-1})	$D(\text{Fe})$ (m^2s^{-1})
	T/K	t/s		
1.12×10^6	551	1.73×10^6	6.1×10^{-22}	3.5×10^{-23}
	555	1.22×10^6	9.5×10^{-22}	5.7×10^{-23}
5.27×10^6	553	1.79×10^6	7.5×10^{-22}	4.0×10^{-23}
1.58×10^7	533	1.79×10^6	1.2×10^{-22}	5.0×10^{-24}
	546	1.73×10^6	4.5×10^{-22}	2.4×10^{-23}
	553	1.79×10^6	6.3×10^{-22}	3.6×10^{-23}
	606	8.67×10^4	8.9×10^{-20}	1.8×10^{-20}
	634	5.20×10^3	8.1×10^{-19}	2.5×10^{-19}
	638	6.90×10^3	1.1×10^{-18}	3.3×10^{-19}
2.37×10^7	535	2.60×10^6	1.6×10^{-22}	7.1×10^{-24}

Table 10 Temperature dependence of B and Fe diffusion coefficients D in splat-cooled V4.

Temperature (K)	Diffusion time (ks)	$D(\text{B})$ ($10^{-20} \text{m}^2\text{s}^{-1}$)	$D(\text{Fe})$ ($10^{-21} \text{m}^2\text{s}^{-1}$)
554	1119.6	0.235	0.142
576	86.4	0.802	1.33
591	88.5	3.82	6.48
623	75.2	35.7	106
654	5.4	312	1250

position of the glasses or of the decomposition phases cannot be responsible for the strong time dependence of the diffusivity during decomposition of the V1 glass. We believe that some not yet identified structural alterations which occur during decomposition cause the observed irreversible relaxation of the diffusivities. We note that a small fraction of crystals assumed to form polymorphously during decomposition⁸⁾ is most likely not the reason for time dependent diffusion coefficients, since we have found that partial crystallization has a negligible effect on diffusivity in the V4 glass.

Structural relaxation in rapidly quenched melt spun metallic glasses, *e.g.* in the metal-metalloid FeNiB glass, is usually accompanied by a volume density increase of the order of a few tenths of a percent.^{28,36)} This effect has been attributed to the elimination of excess of free volume retained from the fast quenching of the liquid state during the production process. It is proposed that during this irreversible relaxation units of free volume, so-called quasi-vacancies, anneal via thermally activated migration resulting in the observed decrease of the diffusion coefficients by more than one order of magnitude.^{21,26)}

The B and Fe diffusion coefficients obtained for the splat cooled V4 glass fit well to those of the as-cast V4 glass (see Fig. 8) indicating a negligible influence of the cooling rate on the diffusivity. This is a result not to be expected. The positron life time and density measurements performed by Nagel *et al.*²⁹⁾ showed that a considerable amount of excess volume which is of similar magnitude as that observed for an amorphous melt-spun FeSiB ribbon can be quenched-in in the

Fig. 8 Arrhenius plot of B and Fe diffusion coefficients in splat-cooled V4 glass. The lines indicate the behavior of the as-cast V4 bulk glass as given in Fig. 6.

Fig. 9 Arrhenius plot of B and Fe diffusion coefficients in V4 bulk glass annealed at 643 K for 6 h (closed symbols) and 9 h (open symbols). The lines indicate the behavior of the as-cast V4 bulk glass as given in Fig. 6.

V4 metallic glass. After annealing the V4 glass at 643 K for 6 h this glass should contain a negligible amount of quenched-in free volume. This assumption should also hold for the partially crystallized state after annealing at 643 K for 9 h when the volume fraction of crystals was smaller than 10%.³¹⁾ The results shown in Fig. 9 indicate agreement between the B and Fe diffusion coefficients of the pre-annealed and partly crystallized V4 glass with the data of the as-cast glass over the entire temperature interval of the investigation, *i.e.* impurity

Table 11 Temperature dependence of B and Fe diffusion coefficients D in V4 pre-annealed at 643 K.

	Temperature (K)	Diffusion time (ks)	$D(B)$ ($10^{-20} \text{ m}^2 \text{ s}^{-1}$)	$D(Fe)$ ($10^{-21} \text{ m}^2 \text{ s}^{-1}$)
Pre-annealed for	533	2476.8	0.0308	0.0296
6 h	553	119.6	0.114	0.0779
	625	14.4	34.2	69.9
Pre-annealed for	533	2476.8	0.0291	0.0235
9 h	553	119.6	0.118	0.0977
	625	14.4	28.2	71.0

diffusion in the V4 bulk glass seems to depend neither on the cooling rate with which the glass was produced nor on an annealing above the calorimetric glass transition. It can be concluded that the amount of excess free volume in the present experiments is of minor importance for the magnitude of the diffusion coefficients. If the total effect of free volume on the diffusion coefficients in V4 is of similar magnitude as that observed in melt-spun $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ (in which it is about $5 \times 10^{-21} \text{ m}^2/\text{s}$ for the Fe diffusion coefficient at 615 K^{21,26)}) then we expect that this effect is hidden in the experimental error bar of the diffusion coefficients (about $10^{-20} \text{ m}^2/\text{s}$ for Fe diffusion at 615 K) in V4.

The striking feature of the diffusivities measured in the as-cast bulk glasses is their non-linear Arrhenius behavior, which was described by different parameters in the high and low temperature range (see Figs. 5, 6, and Table 7). Moreover the magnitude of the diffusion parameters Q and D_0 obtained in the high temperature range is noteworthy. These parameters are much higher than expected from diffusion in crystals.³⁷⁾ The reason for this as well as for the specific correlation between D_0 and Q found universally in glasses³⁸⁾ are up to now unknown. A non-linear Arrhenius behavior of diffusion coefficients was also reported for three other members of the class of bulk glasses, $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$,³⁹⁾ $\text{Zr}_{55}\text{Cu}_{25}\text{Ni}_{10}\text{Al}_{10}$,⁴⁰⁾ and $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$,^{41,42)} indicating that such behavior is a general feature of these materials. With the results shown in Figs. 4 and 7 we answer the long standing question whether the different branches of temperature dependent diffusion coefficients are due to diffusion mechanisms which are different above and below the calorimetric glass transition.^{41,43,44)} Our results clearly indicate a reversible structural relaxation effect, *i.e.* the influence of the thermal history on the diffusion coefficients in the V4 bulk glass at and below 575 K. This reversible relaxation leads to a reduction of the diffusion coefficients of about 50% at 553 K and of 70% to 80% at 535 K if the results of the as-cast material and those of the relaxed are compared (see Fig. 7). Above 575 K no effect of a pre-annealing at 553 K was observed because reversible relaxation at these temperatures is fast and the glass attains its metastable equilibrium in times which are short compared to usual experiment times. Quite similar results were recently obtained for Fe diffusion in the $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ bulk glass.⁴²⁾

It is obvious from these results that even slow cooling rates as are applied during glass production (and leading to the “as-cast” glass) or furnace cooling of diffusion samples quench the glass structure at a temperature in the vicinity of

the calorimetric glass transition. Since the B and Fe diffusion coefficients derived from the reversibly relaxed V4 fit to the high temperature ($>575 \text{ K}$) data of the as-cast material our results support the interpretation that the non-linear Arrhenius behavior of the diffusion coefficients is caused by structural changes alone, *i.e.* by insufficient adjustment of the actual structure to that of the supercooled liquid state at low temperatures.³⁹⁾ Hence the diffusion coefficients which are measured in the as-cast material at these temperatures reflect merely the transport properties of a configurational state representing the supercooled liquid structure frozen from a higher temperature. It is remarkable that the structural changes during the reversible relaxation are characterized by an enthalpy change of only $0.01 \text{ eV}^{27)}$ while the difference of effective activation enthalpies of diffusion obtained from the high and low temperature branch of the Arrhenius plots is roughly 1 eV (see Table 7). This large difference reflects the general observation that small changes of the glass structure by relaxation becoming visible *e.g.* in its radial distribution function,⁴⁵⁾ can have a huge influence on the glass dynamics as is illustrated here by their effect on the diffusivity.

5. Summary

Bulk glasses of the ZrTiCuNiBe family are sufficiently stable above the calorimetric glass transition to allow measurements for extended time periods in this temperature range. Detailed investigations in a large temperature range around the calorimetric glass transition revealed a non-linear Arrhenius behavior of the diffusivity in these bulk glasses. At high temperatures the diffusivity is only weakly dependent on the composition of these glasses, and is practically not affected by the amount of quenched-in free volume or a small volume fraction of crystals. The diffusivity is, however, strongly affected by structural changes of the glass. These are either due to chemical decomposition of the glass which leads to an irreversible decrease of the diffusivities, or due to the reversible adjustment of the actual structure to its metastable equilibrium state. The reversible relaxation becomes detectable only at temperatures below the calorimetric glass transition. Our results indicate that the non-linear Arrhenius behavior of the diffusivity is caused by insufficient relaxation of the glass at the diffusion temperatures. The diffusion parameters Q and D_0 found for the metastable equilibrium state of the glass at temperatures above the calorimetric glass transition are valid also below the glass transition if the

glass is properly relaxed at these lower temperatures. These parameters are much larger than would be expected from diffusion in crystals. This points to their effective nature and is probably caused by a strong influence of the temperature dependent structure on the atomic transport mechanism.

Acknowledgements

We are grateful to Drs. Elisabeth Budke and Jörg Rüsing who were involved in an early stage of the here described work, and to Dr. C. Abromeit for critically reading the manuscript. Financial support of the DFG under project nos. Fr 223/10-1-4; Ma 1832/2-1-2 is acknowledged.

REFERENCES

- 1) A. Inoue: *Bulk Amorphous Alloys*, Materials Science Foundations, Vol. 4, (Trans Tech Publ., Zürich, 1998).
- 2) W. L. Johnson: MRS Bulletin **24** (1999) 2.
- 3) A. Peker and W. L. Johnson: Appl. Phys. Lett. **63** (1993) 2342.
- 4) A. Inoue, N. Nishiyama and T. Matsuda: Mater. Trans., JIM **37** (1996) 181.
- 5) T. Masumoto: Sci. Rep. RITU A **39** (1994) 91.
- 6) M.-P. Macht, V. Naundorf, P. Fielitz, J. Rüsing, Th. Zumkley and G. Froberg: Mater. Sci. Eng. A **304–306** (2001) 656.
- 7) C. C. Hays, C. P. Kim and W. L. Johnson: Appl. Phys. Lett. **75** (1999) 1089.
- 8) A. Wiedenmann, U. Keiderling, M.-P. Macht and H. Wollenberger: Mater. Sci. Forum **225–227** (1996) 71.
- 9) A. Wiedenmann and J. M. Liu: Solid State Comm. **100** (1996) 331.
- 10) S. Schneider, P. Thiagarajan, U. Geyer and W. L. Johnson: in MRS Symp. Proc Vol. 455 (MRS Pittsburgh, PA, USA, 1997) p. 295.
- 11) J. F. Löffler, P. Thiagarajan and W. L. Johnson: J. Appl. Cryst. **33** (2000) 500.
- 12) J. Schroers, R. Busch, A. Masuhr and W. L. Johnson: J. Non-Cryst. Solids. **250–252** (1999) 699.
- 13) M.-P. Macht, N. Wanderka, A. Wiedenmann, H. Wollenberger, Q. Wei, S. Klose, A. Sagel and H.-J. Fecht: in MRS Symp. Proc. Vol. 398, (MRS Pittsburgh, PA., USA, 1996) 375.
- 14) A. Hoell, F. Bley, A. Wiedenmann, J. P. Simon, A. Mazuelas and P. Boesicke: Scr. Mater. **44** (2001) 2335.
- 15) M.-P. Macht, V. Naundorf, P. Fielitz, J. Rüsing, E. Budke and G. Froberg: Mater. Sci. Forum **343–346** (2000) 140.
- 16) M. P. Macht, N. Wanderka, Q. Wei, I. Sieber and N. Deyneka: Mater. Sci. Eng. A **304–306** (2001) 701.
- 17) T. A. Waniuk, J. Schroers and W. L. Johnson: Appl. Phys. Lett. **78** (2001) 1213.
- 18) Th. Zumkley, V. Naundorf and M.-P. Macht: Z. Metallkd. **91** (2001) 901.
- 19) N. Wanderka, Q. Wei, I. Sieber, U. Czubyko and M.-P. Macht: J. Metastable and Nanocrystalline Materials **2–6** (1999) 369.
- 20) M.-P. Macht, N. Wanderka, I. Sieber and Q. Wei: in *Materials Development and Processing-Bulk Amorphous Materials, Undercooling and Powder Metallurgy*, EUROMAT99-Vol. 8 (Wiley-VCH, Weinheim, 2000) p. 10.
- 21) K. Tyagi, M.-P. Macht and V. Naundorf: Acta Metal. Mater. **39** (1991) 609.
- 22) M.-P. Macht and V. Naundorf: J. Appl. Phys. **53** (1982) 7551.
- 23) M.-P. Macht, R. Willecke and V. Naundorf: Nucl. Instr. Meth. Phys. Res. **B43** (1989) 507.
- 24) Th. Zumkley, M.-P. Macht, V. Naundorf, J. Rüsing and G. Froberg: Mater. Sci. Forum **343–346** (2000) 135.
- 25) Th. Zumkley, V. Naundorf, M.-P. Macht and G. Froberg: Scr. Mater. **45** (2001) 471.
- 26) J. Horvath and H. Mehrer: Crys. Latt. Def. and Amorph. Mat. **13** (1986) 1.
- 27) Th. Zumkley, V. Naundorf, M.-P. Macht and G. Froberg: Mater. Sci. Forum **386–388** (2002) 65–70.
- 28) R. Gerling, F. P. Schimansky and R. Wagner: Acta Metall. **35** (1987) 1001.
- 29) C. Nagel, K. Rätzke, E. Schmidke, J. Wolff, U. Geyer and F. Faupel: Phys. Rev. B **57** (1998) 224.
- 30) N. Wanderka, M.-P. Macht, M. Seidel, S. Mechler, K. Stahl and J. Z. Jiang: Appl. Phys. Lett. **77** (2000) 3935.
- 31) Th. Zumkley, V. Naundorf, M.-P. Macht and G. Froberg: Defect and Diff. Forum **194–199** (2001) 801.
- 32) M.-P. Macht, N. Wanderka, A. Wiedenmann, H. Wollenberger, Q. Wei, H. J. Fecht and S. G. Klose: Mater. Sci. Forum **225–227** (1996) 65.
- 33) M. Miller: Mater. Sci. Eng. A **250** (1998) 133.
- 34) J.-M. Liu, A. Wiedenmann, U. Gerold and H. Wollenberger: Mater. Sci. Forum **235–238** (1997) 523.
- 35) N. Wanderka, Q. Wei, R. Dole, M. Jenkins, S. Friedrich, M.-P. Macht and H. Wollenberger: Mater. Sci. Forum **269–272** (1998) 773.
- 36) F. Faupel: Phys. Status Solidi A **134** (1992) 9.
- 37) P. Shewman: *Diffusion in Solids*, (Mc Graw-Hill, New York, 1963).
- 38) V. Naundorf, M.-P. Macht, A. S. Bakai and N. Lazarev: J. Non-Cryst. Solids **224** (1998) 122.
- 39) K. Knorr, M.-P. Macht and H. Mehrer: in *Materials Development and Processing-Bulk-Amorphous Materials, Undercooling and Powder Metallurgy*, EUROMAT99-Vol. 8 (Wiley-VCH, Weinheim, 2000) p. 22.
- 40) H. Nakajima, W. Sprengel and K. Nonaka: Defect and Diff. Forum **143–147** (1997) 803.
- 41) H. Nakajima, T. Kojima, T. Zumkley, N. Nishiyama and A. Inoue: *Proc. Int. Conf. on Solid-Solid Phase Transformations '99 (JIMIC-3)* eds. by M. Koiwa, K. Otsuka and T. Miyazaki (Japan Inst. Metals, 1999) p. 441.
- 42) Th. Zumkley *et al.*, to be published.
- 43) U. Geyer, W. L. Johnson, S. Schneider, Y. Qiu, T. A. Tombrello and M.-P. Macht: Appl. Phys. Lett. **69** (1996) 2492.
- 44) P. Tang, U. Geyer, R. Busch, W. L. Johnson and Y. Wu: Nature **402** (1999) 160.
- 45) D. Srolovitz, T. Egami and V. Vitek: Phys. Rev. B **24** (1981) 6936.