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Free-volume changes in the bulk metallic glass $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ and the undercooled liquid

C. Nagel, K. Rätzke, E. Schmidtke, and J. Wolff
Technische Fakultät der Christian-Albrechts-Universität Kiel, Lehrstuhl für Materialverbunde, Kaiserstraße 2, D-24143 Kiel, Germany

U. Geyer
Technische Fakultät der Christian-Albrechts-Universität Kiel, Lehrstuhl für Materialverbunde, Kaiserstraße 2, D-24143 Kiel, Germany and I. Physikalisches Institut, Universität Göttingen, Bunsenstraße 9, D-37073 Göttingen, Germany

F. Faupel*
Technische Fakultät der Christian-Albrechts-Universität Kiel, Lehrstuhl für Materialverbunde, Kaiserstraße 2, D-24143 Kiel, Germany

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Volume changes in $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ bulk metallic glass have been observed by positron-annihilation and density measurements. Excess volume of the order of 1% is quenched in the bulk glass at cooling rates as low as 1–2 K/s. The isothermal relaxation kinetics obey a Kohlrausch law with β exponents of ~ 0.3 between 180 and 230 °C. The effective activation energy is ~ 0.7 eV. Structural relaxation is not accompanied by severe embrittlement. The outer surface is shown to play a crucial role in annealing of excess volume. Relaxed excess volume is restored completely after heat treatment in the undercooled liquid state. The observed free-volume changes contrast with the behavior of perfectly strong glasses. [S0163-1829(98)09017-1]

Metallic glasses essentially exhibit a frozen-in liquidlike structure that gives rise to a unique combination of properties including high flow stress and fracture toughness as well as extreme wear and corrosion resistance.[1] Usually, the production of metallic amorphous alloys requires rapid quenching at $\sim 10^6$ K/s. Hence, it is not possible to obtain bulk samples. Recently, Zhang, Inoue, and Masumoto[2] and Peker and Johnson[3] introduced Zr-based bulk metallic glasses offering a variety of new applications. Results on other bulk-glass-forming alloys have been reported earlier.[4,5] As a consequence of the high cooling rates, rapidly quenched conventional metallic glasses are prone to irreversible structural relaxation that affects almost all properties and particularly may lead to severe embrittlement.[6–9] Irreversible structural relaxation is related to annealing of excess volume.[6–9] In addition, chemical short-range ordering that requires only local rearrangement of atoms occurs mainly prior to excess volume elimination.[10–12] The new slowly cooled bulk glasses are not *a priori* expected to exhibit a significant amount of excess volume. Moreover, unlike conventional amorphous alloys they are stable enough in the undercooled liquid state[3] to allow one to study changes in free volume concomitant with the glass transition. From the practical point of view the question arises whether free volume can be restored in bulk glasses by annealing above T_g and slow cooling.

In this paper we report results from positron annihilation measurements on free-volume changes during structural relaxation and through the glass transition for the ''Johnson'' glass $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ (Zr-Ti-Cu-Ni-Be). This alloy was chosen rather than the glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ to avoid phase separation upon annealing.[13] A conventional amorphous $Fe_{78}Si_9B_{13}$ alloy was studied for comparison. Density measurements confirm the interpretation in terms of volume changes.

After injection and thermalization positrons in condensed matter preferentially reside in regions of reduced atomic density and undergo annihilation with electrons. The positron lifetime τ is very sensitive to differences in electron density. In metallic glasses one single lifetime is generally observed and interpreted in terms of complete trapping of positrons into the high number of cavities of different size on the atomic scale, representing irregular arrays of potential wells with different binding strength. The annihilation characteristics are regarded as statistically averaged quantities over the annihilation sites.[14–18] The positron lifetime is thus a measure of the mean local free volume, whereas changes in the chemical short-range order are not expected to have a major influence,[14–18] as confirmed in this paper.

Rapidly quenched $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ glasses of 50 μm thickness were produced by splat quenching ($\sim 10^8$ K/s). Bulk samples (10 mm diameter) of amorphous $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ were produced by slow cooling (1–2 K/s) and cut into 600 μm disks. Commercial melt-spun amorphous $Fe_{78}Si_9Be_{13}$ (Goodfellow) ribbon of 20 μm thickness was used. Positron lifetime measurements were carried out by means of a conventional fast timing coincidence setup consisting of ORTEC components and HAMAMATSU photomultiplier tubes (FWHM is 230 ps). Isochronal (15 min) and isothermal annealings were performed under high vacuum (10^{-7} mbar) in a water-cooled sample holder allowing heating and cooling rates of 1–2 K/s. Lifetime spectra were measured at room temperature using positron sources (^{22}Na, 1 MBq) directly deposited onto the sample surface. For complete positron capture, several ribbons and splat-quenched samples were stacked. After source and background corrections, all spectra, each involving about 3 $\times 10^6$ counts, were best fitted by one single lifetime component, hereafter denoted as average positron lifetime τ_{av}, using PATFIT88.[19] The intensity of the source term was typically 4%. The error in relative changes of τ_{av} always proved to be <0.5 ps. X-ray measurements after heat treatments showed

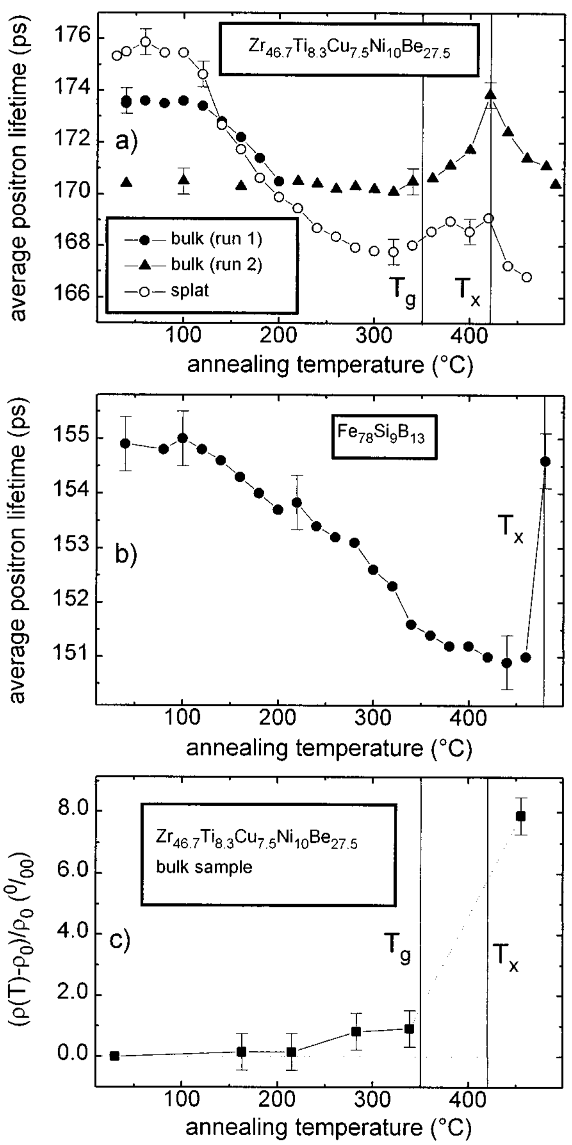

FIG. 1. Average positron lifetime (a), (b), and relative change of density (c), measured at room temperature, for cumulative annealing of different metallic glasses at indicated temperatures. The melt-spun conventional Fe-Si-B glass was measured for comparison. Straight lines denote approximate values for the glass transition temperature T_g (DSC at 2 K/min) and the crystallization temperature T_x of the corresponding alloy. Lines between data points are to guide the eye.

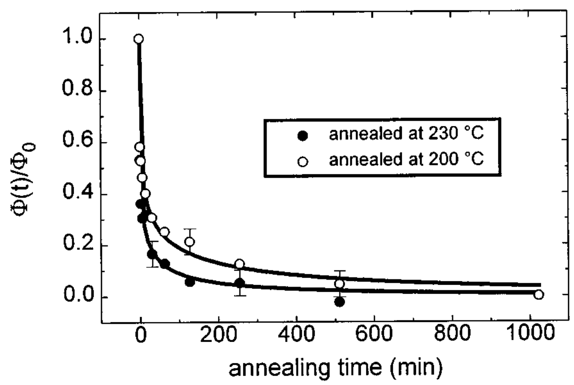

FIG. 2. Representative normalized changes in average positron lifetime, measured at room temperature, during annealing of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ bulk glass at different temperatures. Solid lines are fits according to the Kohlrausch law.

amorphousness of the samples. Density measurements were carried out after ultrasonic cleaning by means of a gravimetrical method using a modified Mettler M3 microbalance. Samples were measured in the as-quenched state and after 1 h heat treatment under vacuum (10^{-6} mbar) at various temperatures.

As shown in Fig. 1(a), isochronal annealing up to T_g leads to a decrease in τ_{av} in all samples. A second run in Fig. 1(a) illustrates the irreversible nature of the changes, which were also detected by means of Doppler broadening measurements, and demonstrates the excellent reproducibility of the data. The irreversible decrease in the average positron lifetime τ_{av} upon annealing is a well-known phenomenon for rapidly quenched conventional metallic glasses[14,15,17,20] and was also observed in the amorphous Fe-Si-B ribbon at hand [Fig. 1(b)]. It can be attributed to annealing of the excess volume quenched in from the liquid state.[6,7,21] This interpretation is strongly supported by the higher absolute τ_{av} value in the splat-quenched Zr-Ti-Cu-Ni-Be glass [Fig. 1(a)] and the larger relative change in τ_{av} in the splat-quenched vs the slowly cooled glass. Moreover, annealing of excess volume is directly reflected in our density measurements revealing an increase in density of about 0.1% during irreversible structural relaxation and 0.8% upon crystallization in bulk samples of Zr-Ti-Cu-Ni-Be [Fig. 1(c)]. The density changes in the Fe-Si-B ribbon are of the same order of magnitude. Similar values have been reported for conventional melt-spun metallic glasses.[22–24]

We note that even though the observed density changes and the corresponding changes in τ_{av} are small, the resulting effect on properties may be drastic, as mentioned earlier. In agreement with these expectations, the amorphous Fe-Si-B ribbon was severely embrittled after irreversible structural relaxation. In contrast, first bending measurements did not show severe embrittlement for the Zr-Ti-Cu-Ni-Be glass. Apparently, deformation in the Johnson glass is not significantly facilitated by quenched-in structural defects. After crystallization the Johnson glass proved to be strongly embrittled. Further details of the ongoing mechanical tests will be reported elsewhere.

After heating above T_g and cooling at 1–2 K/s, the average positron lifetime, measured at room temperature, shows a distinct increase in the bulk Zr-Ti-Cu-Ni-Be material reaching about the same value measured in the as-quenched state [Fig. 1(a)]. The corresponding increase is much smaller in the splat-quenched sample. The drop of τ_{av} near T_x in the Johnson glass was identified as the onset of crystallization by means of x-ray diffraction. In Fe-Si-B, τ_{av} increases upon crystallization due to positron trapping in vacancies and/or grain boundaries. Evidence of the formation of such defects comes from the appearance of a second component of $\tau_2 = 250$ ps and $I_2 = 20\%$ in the lifetime spectra.[25] The Zr-Ti-Cu-Ni-Be glass, on the other hand, is known to crystallize partially under the present conditions.[26] The material should hence not contain intercrystalline boundaries. Here, the decrease of the positron lifetime may be a net effect because the reduced lifetime due to increasing crystal density over-

TABLE I. Parameters according to the Kohlrausch law fitted to the data depicted in Fig. 2.

T_a (°C)	t_0 (min)	β
180	25 ± 8	0.32 ± 0.06
200	17 ± 7	0.27 ± 0.06
230	4 ± 1	0.28 ± 0.04

compensates the longer lifetime due to the amorphous-crystalline interphase.[27]

Isothermal annealing measurements in the Zr-Ti-Cu-Ni-Be glass below the glass transition temperature revealed the well-known Kohlrausch behavior,[28] $\Phi(t)=\Phi_0\exp(-[t/t_0]^{\beta})$, for structural relaxation with the relaxation function $\Phi(t)=\tau(t)-\tau_{\text{relaxed}}$ and $\Phi_0=\tau_{\text{as-quenched}}-\tau_{\text{relaxed}}$ (Fig. 2). The corresponding parameters are shown in Table I. The resulting small value of $\beta\sim0.3$ for the Johnson glass suggests a broad distribution of activation energies. It should be noted that the present value of $\beta\sim0.3$ refers to temperatures (180–230 °C) far below T_g ($\sim$350 °C), and the deviation from previously reported values of $\beta\sim0.8$ (Ref. 29) near T_g is in accord with the expected temperature dependence of β.[30] The effective activation energy E_a for structural relaxation, estimated from $t_0=t_0^*\exp(E_a/k_BT)$, is $E_a=0.7\pm0.2$ eV. This low value suggests that either annealing of excess volume requires no long-range mass transport, which involves much higher activation energies,[31] or that mass transport is strongly facilitated through the presence of the excess volume.

The observed substantial irreversible structural relaxation of the slowly cooled Zr-Ti-Cu-Ni-Be Johnson glass calls for further discussion. It clearly shows that cooling rates as low as 1 K/s do not prevent quenching of excess volume in the bulk metallic glass and suggest the outer sample surface plays an important role in annealing of excess volume. The crucial role of the outer surface is also reflected in the striking differences in free-volume restoration after annealing above T_g between bulk samples of Zr-Ti-Cu-Ni-Be and thin splat-quenched material [Fig. 1(a)]. As indicated by the increase in τ_{av} above T_g in Fig. 1(a) the equilibrium free volume generated in the undercooled liquid state is quenched in the Zr-Ti-Cu-Ni-Be bulk sample at cooling rates of 1–2 K/s. The same free-volume restoration was also observed in bulk samples after annealing above T_g and quenching in water. On the other hand, very little volume is restored in the splat-quenched [Fig. 1(a)] samples. The effect of geometry also manifests itself in the different minima of τ_{av} around 300 °C for bulk and splat-cooled samples [Fig. 1(a)]. After very slow cooling ($\sim$1 K/min), τ_{av} for the bulk material approached the value for the splat-quenched samples.

The present geometry effect in free-volume annihilation rules out major contributions from annihilation mechanisms that are based on the recombination of regions of higher and lower density, so-called n and p defects, on a microscopic scale. Here the net reduction in free volume arises from the anharmonicity of the interatomic potentials.[32,33] The strong geometry effect in free-volume recovery after annealing above T_g and slow cooling further shows that the positron lifetime is not significantly influenced by changes in chemical short-range order, which requires only local rearrangement of atoms on a very small scale,[10–12] and is hence independent of the sample size.

The increase in the average positron lifetime in the Johnson glass above T_g, depicted in Fig. 1(a), shows that the equilibrium free volume in this glass increases significantly above the glass transition temperature. The volume increase already shows up somewhat below the T_g value from the differential scanning calorimetry (DSC) (heating rate 2 K/min) because of the time scale dependence of T_g.[28,34] Judging from well-established empirical relations between free volume and diffusivity or viscosity (see, e.g., Ref. 33), the observed increase in free volume above T_g implies significant changes in the effective activation energies for diffusion and viscosity at the glass transition. It is well known, e.g., from measurements during structural relaxation,[6,7] that a density variation of a few percent may change the diffusivity by more than one order of magnitude. The expected changes in the effective activation energies for diffusion and viscosity clearly contrast with the characteristics of almost perfectly strong glasses like covalently bound amorphous oxides or semiconductors.[35,28] Changes in the effective activation energy at the glass transition have indeed been reported for viscous flow in an Inoue glass[36] and for Be diffusion in the present Johnson glass.[37] No change was found for Al diffusion in the latter system.[31] However, T_g might be located below the temperature range of the Al diffusion measurements, since Al is a very slow diffusant.

In conclusion, the present positron annihilation studies and density measurements show that excess free volume can be quenched in the new bulk metallic glasses even at cooling rates of the order of 1 K/s. Excess volume starts to anneal out above 100 °C. The kinetics depend on the sample size and involve the outer surface. Relaxed free volume in the bulk glasses can be restored by heat treatment above T_g and slow cooling. While the new bulk glasses are certainly much stronger than typical fragile glasses,[29] the free-volume changes observed in the present Johnson glass at the glass transition clearly distinguish them from perfectly strong glasses.

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*Author to whom correspondence should be addressed.

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