Positron-annihilation studies of free-volume changes in the bulk metallic glass $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ during structural relaxation and at the glass transition

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(Received 7 December 1998)

Volume changes in $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ bulk metallic glass have been observed by positron annihilation and density measurements. Excess volume of the order of 0.1% is quenched in the bulk glass at cooling rates as low as 1–2 K/s. The isothermal relaxation kinetics below the glass transition temperature obey a Kohlrausch law with β exponents of $\cong 0.3$ between 230 and 290 °C. The effective activation energy for relaxation is (1.2 ± 0.2) eV. Stress-strain measurements indicate that structural relaxation is not accompanied by embrittlement. It is shown that the outer surface plays a crucial role in the annealing of excess volume. Free volume can be restored by a heat treatment in the undercooled liquid state. The observed free volume changes contrast with the behavior of perfectly strong glasses. The temperature dependence of the positron lifetime can be explained by thermal detrapping of the positrons from shallow traps. [S0163-1829(99)14133-X]

Metallic glasses, also termed amorphous metals, have a frozen-in liquidlike structure and exhibit a unique combination of properties including high flow stresses and fracture toughness as well as extreme wear and corrosion resistance.[1] Due to the high quenching rates for the production of conventional metallic alloys (10^6 K/s) only thin samples (≈ 50 μm) can be prepared. After the first reports[2] Zhang, Inoue, and Masumoto[3] and later Peker and Johnson[4] established bulk metallic glasses, which can be produced using low cooling rates and which are stable above the caloric glass transition temperature on experimentally accessible time scales. These Zr-based alloys offer a variety of technical applications,[5] and, on the other hand, allow detailed investigations of the glass transition and the supercooled liquid state.

As a consequence of the high cooling rates, rapidly quenched (conventional) metallic glasses undergo irreversible structural changes during the first annealing after preparation. Structural relaxation is accompanied by changes in many properties, e.g., the density increases, and the diffusivity decreases and many glasses show severe embrittlement. Generally these phenomena are separated into changes of the chemical short-range order (CSRO) and changes of the topological short-range order (TSRO). Whereas the former incorporate minor changes of the local chemical surroundings and are mostly reversible, the latter involve larger rearrangements of all atoms and are mainly irreversible. For the new metallic glasses one might be tempted to expect little structural relaxation for bulk samples due to low cooling rates during preparation. However, significant changes have been observed for density and for free volume[6] in bulk samples of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$, which are similar to changes in conventional rapidly quenched glasses. Furthermore, it was demonstrated that free volume, which anneals out during structural relaxation,[6] can be restored as in conventional metallic glasses.[7] Since the new metallic glasses are quite stable in the supercooled state they have been used as relatively simple systems to study the glass transition. In particular, the variation of the atomic dynamics at the glass transition, e.g., atomic vibrations, relaxation,[8] and diffusion,[9] were measured. The viscosity shows a marked change of the effective activation energy at the caloric glass transition T_g.[8] The same holds for the diffusivity in $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ of selected elements.[9] On the other hand, isotope effect measurements in the latter alloy indicate that the underlying diffusion mechanism does not change around T_g.[10]

Positron annihilation has proven to be a suitable tool for investigations of open volume in amorphous materials.[11–13] In glassy systems, structural relaxation and nonlinear changes of free volume at the glass transition can be detected.[6,14] 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, only one single lifetime is generally observed and interpreted in terms of trapping of positrons into the high number of cavities of different sizes on the atomic scale, representing irregular arrays of potential wells with different binding strength. Around a cavity, the electron density and especially the core electron density will be reduced, resulting in a prolonged positron lifetime compared to the positron lifetime for perfect crystals. Additionally, the reduced core electron density causes a deficit of annihilations with electrons having large momenta. This results in a narrowing of the electron-positron momentum density spectrum, which is actually measured as the Doppler-broadened 511 keV annihilation line (for a detailed description see, e.g., Ref. 15). In amorphous metals, the annihilation characteristics are regarded as statistically averaged quantities over the annihilation sites.[6,16,17]

In this paper we report results from positron annihilation measurements on free-volume changes during structural re-

laxation and through the glass transition for the ''Inoue'' glass $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$. Density measurements confirm the interpretation in terms of volume changes. The temperature dependence of positron lifetime and Doppler broadening is interpreted in terms of a distribution of shallow traps and temperature-dependent trapping and detrapping of positrons.

Rapidly quenched $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ glasses of 40 μm thickness were produced by melt spinning (cooling rate $\sim 10^6$ K/s). Bulk samples of amorphous $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ were produced as a hollow cylinder (inner diameter, 2.5 mm; outer diameter, 3.5 mm) by slow cooling (100 K/s) and cut into pieces. Positron lifetime measurements were carried out as described previously.[6] Low-temperature measurements were performed with the same samples, using a self-made liquid-nitrogen-cooled sample holder. Part of the measurements were carried out in a commercial He cryostat. Except for the measurements in the He cryostat, all temperature-dependent lifetime and Doppler experiments were carried out simultaneously on one sample. The positron sources (^{22}Na, 1 MBq) have directly been deposited onto the sample surface. To ensure complete positron capture, several ribbons were stacked. After source and background corrections, lifetime spectra containing about 3×10^6 counts were best fitted by one single lifetime component, hereafter denoted as average positron lifetime τ_{av}, using PATFIT88.[18] The intensity of the source term was typically 4%. The error in relative changes of τ_{av} always proved to be <0.5 ps. Doppler-broadening spectra were evaluated in terms of S and the W parameters.[15]

X-ray measurements after heat treatments showed amorphousness or the degree of crystallinity of the samples. Microprobe analysis was performed to check the homogeneity and concentration differences between different batches. 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. Error bars are from the usual calculations taking into account variations in sample area and temperature. However, as can be seen in Fig. 1(b), the reproducibility for different samples shows that these estimations are very conservative.

Mechanical testing was performed by standard stress-strain measurements on 5×40-mm^2 thin ribbons. Strain at fracture was calculated by averaging over up to four independent measurements.

As shown in Fig. 1(a), isochronal annealing up to T_g leads to a decrease in τ_{av}, measured at room temperature, in all samples. A second annealing run up to T_g [dashed line in Fig. 1(a)] leads to no further decrease in lifetime and demonstrates the irreversible nature of the changes as well as the excellent reproducibility of the data. This irreversible decrease in the average positron lifetime upon annealing is a well-known phenomenon that can be attributed to annealing of the excess volume quenched in from the liquid state. The annealing of excess volume is also reflected in the density measurements revealing an increase in density of about 0.1% during irreversible structural relaxation and 0.6% upon crystallization [Fig. 1(b)]. Similar values have been reported for conventional melt-spun metallic glasses[19] and the Johnson glass $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$.[6] In the latter alloy, there was a larger change in lifetime for the splat-cooled sample than

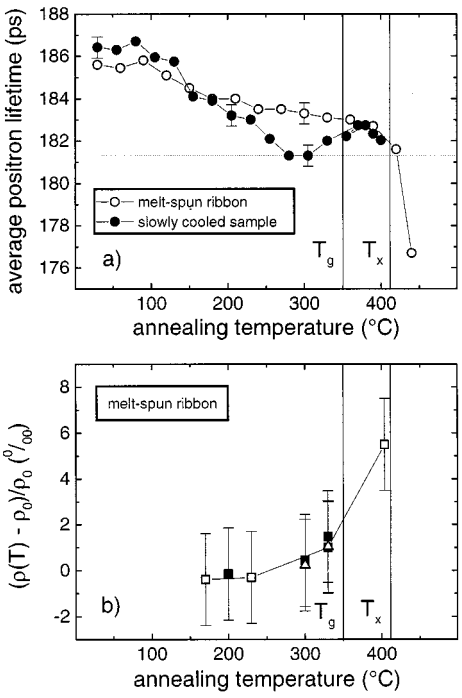

FIG. 1. (a) Room-temperature average positron lifetime, (b) relative change of density for cumulative annealing of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ bulk glass at indicated temperatures. Different symbols denote different samples. Lines between data points are to guide the eye. Straight lines denote approximate values for the caloric glass transition temperature T_g (DSC at 2 K/min, Ref. 25) and the crystallization temperature T_x. Dashed line indicates the positron lifetime for the fully relaxed state, obtained from a second annealing run of the bulk sample.

for the bulk sample, which reflects the smaller amount of excess free volume quenched in the bulk sample due to its lower cooling rate. Obviously, this is not the case in the Inoue glass under investigation. One possible explanation might be that the cooling-rate difference between bulk sample (10^2 K/s) and the ribbon (10^6 K/s) is much smaller in the present Inoue alloy compared to the Johnson alloy (10^1 K/s for the bulk and 10^8 K/s for the splat). Therefore, less excess volume could be quenched in the ribbon. In contrast to most conventional glasses, where drastical embrittlement occurs with increasing degree of relaxation, no change in strain at fracture [$\varepsilon_f=(3.7\pm0.1)\%$] was observed within error bars. This is in agreement with the behavior of the Johnson glass.[6]

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 $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ material, but not in the ribbon. The increase in the lifetime for the bulk sample shows that the free volume increases upon annealing above T_g and free volume can be quenched in at least partially, even at cooling rates as low as 1–2 K/s. One notes in Fig. 1(a) that the increase in free volume appears to start somewhat below the T_g values from viscosity measurements;[8] however, these experiments might probe different time scales compared to the experiments here. Additionally, it has to be mentioned that T_g as probed, e.g., by differential scanning calorimetry (DSC) is heating-rate de-

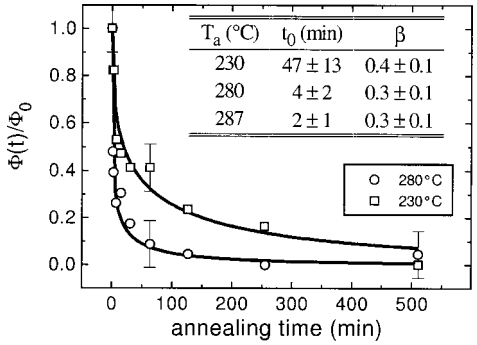

FIG. 2. Normalized changes in average positron lifetime, measured at room temperature, during annealing of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ ribbon at 280 °C and 230 °C. The data for 287 °C are not shown for the sake of clarity. Solid lines are fits according to the Kohlrausch law (see text for details).

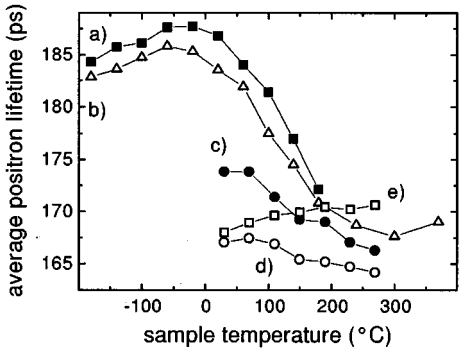

FIG. 3. Average positron lifetime for $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ ribbon as function of sample temperature for (a) as prepared sample, (b) structurally relaxed sample, (c) and (d) partially crystallized sample, (e) fully crystallized sample. Every second data point has been omitted.

pendent, i.e., the transition temperature in the DSC trace increases with increasing heating rate. However, here isothermal measurements were performed. This explains why the transition metallic glass→supercooled liquid starts at somewhat lower temperature as in the DSC measurements referred to in Fig. 1(a). Judging from well-established empirical relations between free volume and diffusivity or viscosity[20] 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. This is clearly in contrast with the characteristics of almost perfectly strong glasses like covalently bound amorphous oxides or semiconductors.[21] As mentioned above, changes in the effective activation energy at the glass transition have indeed been reported for viscous flow in the Inoue glass under consideration here[8] and for some diffusants like Be, B, or Fe in the Johnson glass $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$.[9] No changes were found for Al diffusion in the latter system. However, T_g might be located below the temperature range under consideration, because Al, as a slow diffusant, probes a different time scale compared to Be, B, and Fe.

The comparison of bulk sample and ribbon additionally shows that the sample geometry, in particular the surface, plays an important role for the restoration of excess free volume after annealing above T_g. In the thin ribbon the excess free volume generated above T_g cannot be quenched in at a cooling rate of 1–2 K/s, whereas quenching is possible in the bulk sample. Therefore, it is self-evident that excess free volume annihilates at the surface of the sample and contributions from annihilation mechanisms, based on the recombination of regions of higher and lower density, the so-called *n* and *p* defects[22,20] are of minor importance in these alloys. This is in accord with our observations in the Johnson glass $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$.[6] The drop in τ_{av} near T_x in the Inoue alloy was identified as the onset of crystallization by means of x-ray diffraction. The partial crystallization leads to a decrease of lifetime due to the reduced lifetime in the cystalline phase.

Isothermal annealing below T_g revealed the well-known Kohlrausch behavior,[21] $\Phi(t)=\Phi_0 \exp(-[t/t_0]^{\beta})$ for structural relaxation with the relaxation function $\Phi(t)=\tau(t)-\tau_{\text{relaxed}}$ and $\Phi_0=\tau_{\text{as-quenched}}-\tau_{\text{relaxed}}$. (See Fig. 2.) The small value of β for the present glass suggests a broad distribution of activation energies, whereas $\beta=1$ would reflect a single activation energy.[21] The effective activation energy E_a for structural relaxation can be estimated from the temperature dependence of the relaxation time according to $t=t_0 \exp(E_a/k_BT)$. The low value of $E_a=1.2\pm0.2$ eV either suggests that annealing of excess volume requires no long-range mass transport, which involves much higher activation energies,[9] or that mass transport is strongly facilitated through the presence of the excess volume.

In situ positron lifetime and simultaneous Doppler-broadening experiments have also been performed at different temperatures with different samples using a specially designed liquid-nitrogen-cooled sample holder. These simultaneous measurements were carried out to check for differences in the variation of τ_{av} and the *S* parameter vs temperature. Differences would indicate that changes of the momentum density spectrum are governed by changes in the chemical surrounding of the annihilation site. Otherwise, one may conclude that free-volume changes play a major role. Furthermore, linearity among the *S* and *W* parameters indicates that one single type of defect is detected in the annihilations.[16,23]

Representative lifetime values are shown in Fig. 3. For the fully crystallized sample the usual reversible increase of the average lifetime with increasing temperature is observed, which is generally attributed to the reduced average electron density due to thermal expansion.[24] For the amorphous samples, the behavior is rather complicated. Starting at low temperature, the lifetime first increases up to a maximum at ~ -50 °C and then decreases to a minimum at about 300 °C. This behavior is reversible. The slightly lower τ_{av} values for the relaxed sample are expected because of the annealing of excess volume (see above).

Similar lifetime experiments have already been performed above room temperature by Dittmar *et al.*[14] These authors interpret the reversible change of the lifetime with temperature by thermal detrapping of the positrons from free-volume traps at elevated temperatures thereby reducing the average lifetime. This model can be adapted to explain the present data assuming the trapping centers for positrons and their binding energies are distributed around a mean value. At very low temperatures the positrons annihilate from shallow

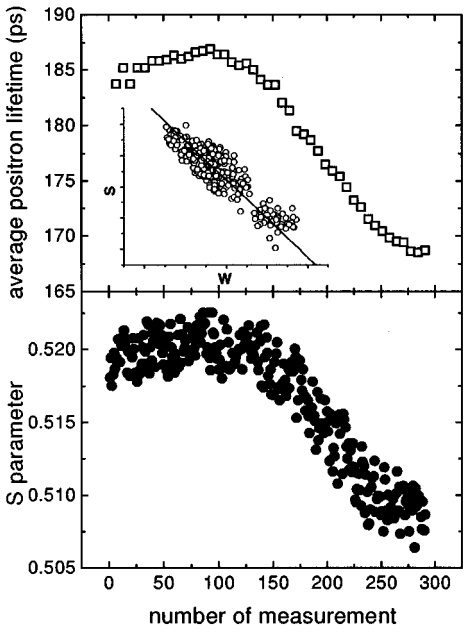

FIG. 4. Simultaneously measured average positron lifetime and S parameter for $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ ribbon. Inset: S parameter vs W parameter from Doppler-broadening experiments (for explanation see text).

traps with a distribution of binding energies. The positrons are not able to find the deepest traps, and the average lifetime is below its maximum value. With increasing temperature, a detrapping of positrons from the shallow traps is possible, which results in an increase in lifetime. With further increase in temperature also detrapping from deeper traps occurs, and annihilation mainly takes place between the atoms, resulting in a decrease of lifetime. Using the simplifying assumption that the lifetime distribution can be represented by an effective value, we have estimated the binding energy of the traps to be of the order of some tenth of eV.

While the above model nicely explains the observed temperature dependence of the average positron lifetime, one may also consider an explanation in terms of changes in chemical short-range order. Changes in CSRO are reversible and could lead to different chemical surroundings of the positrons and therefore to different lifetimes depending on temperature. For changes in the chemical environment of the positrons, however, one would expect a different variation of the S parameter compared to the variation of τ_{av}. As seen in Fig. 4, this is not the case, and therefore, changes in CSRO obviously do not affect positron annihilation significantly. Additionally, linearity between S and W parameters (inset in Fig. 4), as found in our experiments, indicates that there is only one type of defect.[15] The free-volume distribution is represented by an effective positron lifetime within experimental accuracy.

In conclusion, the present positron annihilation studies and density measurements in the Inoue glass show that 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 150 °C. Structural relaxation is not accompanied by embrittlement. 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. The temperature dependence of the lifetime experiments shows an unusual behavior that can be explained by a temperature-dependent redistribution of the positrons among the trapping centers.

The authors would like to thank R. Krause-Rehberg (Halle, Germany) and his group for making available the He cryostat and a lifetime spectrometer for our low-temperature lifetime experiments. We are also indebted to R. Gerling, Forschungszentrum Geesthacht, for providing the microbalance and for various hints.

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