

## Characterization of fatigue-induced free volume changes in a bulk metallic glass using positron annihilation spectroscopy

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Depth-profiled Doppler broadening spectroscopy of positron annihilation on the cyclic fatigue-induced fracture surfaces of three amorphous  $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$  metallic glass specimens reveals the presence of a 30–50 nm layer of increased free volume that is generated by the propagating fatigue crack tip. The presence and character of this *fatigue transformation zone* is independent of the initial amount of bulk free volume, which was varied by structural relaxation via annealing, and the voids generated in the zone by intense cyclic deformation are distinct from those typical of the bulk. © 2007 American Institute of Physics. [DOI: 10.1063/1.2825427]

Bulk metallic glasses (BMGs) have a wide array of attractive properties for structural applications, including high specific strength combined with good corrosion resistance, low damping, large elastic strain limits, and the ability to precisely process into complex geometries in a highly efficient manner.<sup>1,2</sup> Although metallic glasses do not have a traditional microstructure like their crystalline counterparts, other structural features can strongly affect their mechanical behavior. A review of the structural aspects of BMGs may be found in Ref. 3, and it is well known that the deformation of metallic glasses requires extra “free” volume relative to a fully dense glass that allows physical space for atomic movement under mechanical loading.<sup>4</sup> Accordingly, the amount of free volume affects the mechanical properties of bulk metallic glasses,<sup>5–7</sup> and recent studies have demonstrated a pronounced effect on the fatigue life.<sup>8,9</sup> Current research efforts are focused on understanding this latter effect by studying the fatigue crack growth properties, which surprisingly have been found to be largely *unaffected* by bulk free volume differences in the absence of hydrogen.<sup>9</sup>

Noting that the free volume increases in shear bands during inhomogeneous flow of metallic glasses,<sup>4</sup> it may be expected that the intense deformation near a fatigue crack tip will generate a *local* increase in free volume that determines the local flow properties, rendering fatigue crack growth behavior relatively insensitive to bulk free volume differences. Accordingly, spatially resolved characterization of free volume differences in BMGs is paramount if one wants to fundamentally understand the mechanisms controlling fatigue failure. Positron annihilation spectroscopy (PAS) has been used to qualitatively assess bulk (spatially unresolved) structural changes associated with sub- $T_g$  annealing,<sup>10,11</sup> plastic deformation,<sup>12,13</sup> and cooling rate variations.<sup>14</sup> In this work, we utilize depth-profiled PAS, which uses a focused beam of positrons to examine spatial variations in free volume on the

scale needed to study the deformation associated with fatigue-induced cracks in BMGs.

Doppler broadening spectroscopy (DBS) of positron annihilation is a standard PAS technique to characterize open volume defects in materials (e.g., vacancies in crystals and packing defects in polymers).<sup>15</sup> Positron beams with variable low positron implantation energies are also widely used to depth profile near sample surfaces where significant deviations from bulk behavior occur.<sup>15</sup> In the present experiments, a focused positron beam spot of <2 mm diameter was used to depth profile and compare both the cyclically deformed fracture surfaces and the undeformed (polished) faces of three fully amorphous  $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$  compact tension  $C(T)$  specimens (2.2 mm thick). In addition, positron annihilation lifetime spectroscopy (PALS) was performed on the undeformed bulk by depositing <sup>22</sup>Na positron source between two identical samples. The three samples are discussed in detail elsewhere,<sup>9</sup> but briefly, one sample was isothermally relaxed at 610 K for  $10\tau$ , where  $\tau$  represents the structural relaxation time ( $\tau=438$  s at 610 K).<sup>16</sup> After annealing for  $10\tau$ , the BMG was confirmed to be fully amorphous by high resolution transmission electron microscopy and is assumed to be fully relaxed into its metastable equilibrium, or lowest free volume state with a normalized free volume difference relative to the original as cast state  $\Delta v_f/v_m$  of 0.044%.<sup>16</sup> Here,  $\Delta v_f$  is the average free volume difference per atom and  $v_m$  is the atomic volume near the liquidus.<sup>17</sup> A residual stress relief annealing treatment (573 K for 2 min) was applied to the second sample [stress relieved (SR)] but, unlike the  $10\tau$  sample, no free volume relaxation occurred at the low temperature and short time, as confirmed by differential scanning calorimetry (DSC) experiments.<sup>9</sup> A third sample was studied in its as-cast condition without stress relief or relaxation. Fatigue crack growth experiments were conducted in general accordance with ASTM standard E647 (Ref. 18) using a computer controlled servohydraulic test machine, 25 Hz sine wave cyclic loading, and a load ratio, the ratio of minimum to maximum applied load, of  $R=0.1$ . Using depth-profiled DBS, free volume was characterized on the cyclically deformed fracture surface where the

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applied stress intensity range was  $\Delta K \approx 1.5 \text{ MPa}\sqrt{\text{m}}$ ,<sup>19</sup> a value near the fatigue threshold.

A series of positron beam implantation energies ranging from 1.1 to 8.0 keV was used in the depth-profiled DBS experiments. The corresponding mean implantation depths of the positrons into the metallic glass (density  $\sim 6 \text{ g/cm}^3$ ) varied from less than 10 to 190 nm. The undeformed faces and the fracture surfaces of the three samples were all depth profiled. For each sample, the two fractured edges were stacked side by side with their corresponding surfaces aligned to give a total width of 4.4 mm, ensuring that no positrons missed the fracture surface. The 511 keV annihilation photopeak in the energy spectrum of a high purity Ge gamma detector was fitted to two Gaussian functions and a step-changing background, and the  $S$  parameter was defined as the fraction of all 511 keV events within a central region of  $\pm 0.88 \text{ keV}$  from the peak.

The  $S$  parameter at deepest implantation on each undeformed face (0.522–0.526) is assumed to be the *bulk*  $S$  for each sample. For the fatigue fracture surface, the  $S$  parameter shows a significant depth-dependent deviation from the bulk  $S$  that is much stronger than the rather superficial effect on the polished (undeformed) surfaces (Fig. 1). All three samples, regardless of stress relief or structural relaxation, exhibit higher  $S$  parameters near the fatigue-cracked surface. At the lowest positron depth, an ubiquitous drop in  $S$  parameter is commonly attributed to positron diffusion back to and annihilation from a surface state. At the higher implantation depths up to 190 nm,  $S$  asymptotically approaches the bulk value. These  $S$  parameter profiles into the fracture surface are consistent with a thin surface layer of enhanced free volume generated by the intense deformation of the propagating crack.

Increased  $S$  parameter typically means that fewer positrons annihilate with high-momentum core electrons, suggesting that there are more open-volume (free volume) defects in the surface layer. However, all three samples have the same bulk  $S$  parameter despite the fact that the bulk free volume determined by DSC is distinctly lower for the long-relaxed  $10\tau$  sample.<sup>9,16</sup> Thus, DBS is evidently not sensitive to the typical free volume changes from structural relaxation observed by DSC. This is also true for the bulk positron lifetime, a measure of the average void size. As shown in the insets of Fig. 1, PALS indicates no statistically significant difference in the positron lifetime between the  $10\tau$  and the SR samples, while an increased positron lifetime ( $\sim 1.5 \text{ ps}$ ) was found for the as-cast sample. Such results are similar to Nagel and co-workers,<sup>10,11</sup> who found a decrease of several picoseconds in the positron lifetime upon heating through the 100–200 °C range. In both cases, the decreased lifetime is not due to free volume reduction by structural relaxation (long time scale relaxation) since (1) DSC studies on the kinetics of the Zr–Ti–Cu–Ni–Be amorphous system have shown that free volume reduction by structural relaxation cannot occur at temperatures below 200 °C in readily achievable annealing times,<sup>16,20</sup> and (2) there is no free volume difference between the as-cast and SR samples with shorter positron lifetime.<sup>9</sup> All this implies that the definite increase in  $S$  within the fatigue fracture surface layers indicates that those regions have voids/defects that are different in nature to the free volume defects associated with structural relaxation in the undeformed bulk. This is consistent with

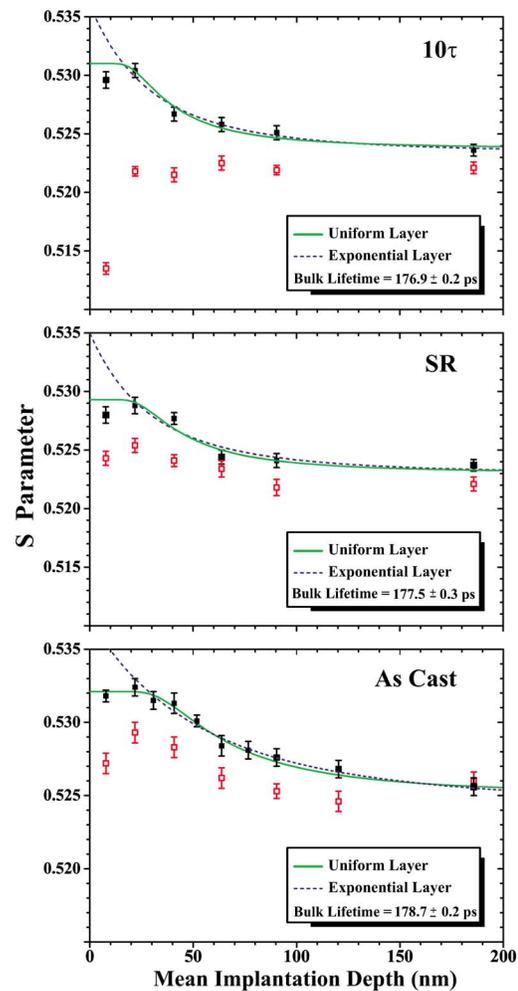


FIG. 1. (Color online) Depth-profiled Doppler broadening spectroscopy  $S$  parameter results for the  $10\tau$ , stress relieved (SR), and as cast samples. The  $S$ -parameter near the fatigue-fractured surface (solid symbols) is significantly larger than  $S$  for the undeformed face (open symbols) at equivalent depth. Fits of the depth profiles to simple models of  $S$  parameter depth dependence (uniform  $S$  layer—solid line and exponentially decreasing  $S$ —dashed line) are shown.

recent PAS results that suggest that the size distribution of the free volume elements is bi- or trimodal, and that defects of a specific size range, denoted as flow defects, are predominantly produced during deformation.<sup>13,21</sup>

The fracture surface  $S$  profiles in Fig. 1 can be fitted using simple models of how the  $S$  parameter might depend on depth. The solid curve uses a two-layer model with a uniformly deformed surface layer of thickness  $t$  which has a constant  $S$  ( $\sim 0.531$ ) on top of an infinite layer with the bulk  $S$  value. The second model (dashed curve) has  $S$  decaying exponentially in depth from some high value at the surface to the bulk value. Both models give indistinguishably good fits with a layer thickness or exponential depth of 30–35 nm for both the  $10\tau$  and SR samples, and 50 nm for the as-cast material.

The 30–50 nm depth of this layer corresponds well with the expected extent of plastic deformation due to the fatigue cycling. For plane strain conditions, the overall plastic zone extent normal to the crack plane (i.e., into the fracture surface) is three times the extent in the direction ahead of the crack tip, i.e.,<sup>22</sup>

$$r_p = \frac{1}{2\pi} \left( \frac{K}{\sigma_Y} \right)^2, \quad (1)$$

where  $K$  is the maximum stress intensity of the loading cycle ( $\sim 1.67 \text{ MPa}\sqrt{m}$ ) and  $\sigma_Y$  is the yield stress of the material ( $\sim 1900 \text{ MPa}$ ),<sup>23</sup> giving a value of 122 nm. Furthermore, during cyclic loading there is a smaller *cyclic* plastic zone where reversed plastic flow occurs each cycle. It is generally accepted that this cyclic plastic zone is roughly  $\frac{1}{4}$  the total plastic zone size,<sup>24</sup> or in this case 31 nm, corresponding well with the depth-profiled DBS results. Thus, it appears that fatigue cycling induces a *fatigue transformation zone* ahead of the crack tip that has distinctly higher free volume than the bulk. The fatigue crack then propagates through this zone of higher free volume which appears to dominate the local flow behavior based on the insensitivity of fatigue crack growth rates to free volume reduction by structural relaxation.

In conclusion, depth-profiled DBS has been used to demonstrate the presence of a fatigue transformation zone of higher free volume that is generated by the propagating crack tip. All three samples, regardless of bulk free volume differences due to different structural relaxations, present similar surface layers of increased free volume that is qualitatively different from that of the bulk. Comparison of the measured transformation zone size to the deduced cyclic fatigue plastic zone size show these both occur on the same size scale. This localized transformation zone provides a structural basis to support the surprising findings<sup>9</sup> that fatigue crack growth propagation is largely unaffected by bulk free volume differences.

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