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Abstract

The free volume model for flow in metallic glasses predicts a significant increase in free volume at the onset of plastic deformation. The details of these structural changes are unclear, however, particularly during strain localization in shear bands. In this study, the free volume changes associated with inhomogeneous plastic deformation of a Cu-based bulk metallic glass were examined using positron annihilation spectroscopy (PAS). PAS results indicated that there was a distribution of free volume site sizes in both the as-quenched and rolled glasses, and that the concentration of larger sites increased with deformation. Differential scanning calorimetry (DSC) was also used to observe the glass transition behaviors of Cu- and Zr-based glasses after rolling and annealing. Annealing resulted in an increase in the height of the endothermic glass transition peak, consistent with structural relaxation relative to the as-quenched material. Deformation resulted in both a lower endothermic peak height and an earlier and deeper exothermic peak associated with structural relaxation, indicating a more disordered structure with more free volume.

Introduction

The development of bulk forming metallic glasses with minimum dimensions of several millimeters has resulted in renewed interest in the mechanical behavior of this unique class of materials [1-13]. Plastic flow in metallic glasses is believed to occur via a diffusional process involving the rearrangement of a small number of atoms and their surrounding free volume [14-16]. At low temperatures and high strain rates, flow is highly localized in shear bands. Characteristic vein patterns are visible on failure surfaces, indicating that the glass viscosity

within the shear band has been greatly reduced. This observation is consistent with the free volume model which predicts a dramatic increase in the average free volume at the onset of flow [14, 16]. While this model has achieved general acceptance, the details of free volume evolution during flow and structural relaxation remain unclear.

Recently, several researchers have used positron annihilation spectroscopy (PAS) to obtain a more detailed picture of the distribution of open volume in metallic glasses [17-20]. Positrons injected into crystalline or glassy samples seek out regions of open volume, where they become trapped until they annihilate with electrons from surrounding atoms. Analysis of the resulting radiation provides information about the open volume site. PAS studies of Zr-based glasses have revealed decreases in the amount open volume after annealing below the glass transition temperature, consistent with the relaxation of free volume towards an equilibrium value [17, 18, 20, 21]. Conversely, moderate room temperature deformation resulted in an increase in the open volume [19, 22]. Furthermore, by varying the thermal energy of the positrons, it has been shown that both shallow and deep positron traps exist in bulk metallic glasses, corresponding to at least two different size open volume sites [17, 20]. Suh et al. suggested that these may be stable Bernal holes and larger unstable flow defects [20].

While PAS provides information about the distribution of free volume, it is currently not possible to make quantitative statements about the amount of atomic-scale free volume in noncrystalline systems using this technique. Numerous attempts have been made to use differential scanning calorimetry to characterize free volume changes in metallic glasses, particularly after structural relaxation [23-27]. Van den Beukel and Seitsma presented a quantitative model relating the relaxation of free volume towards equilibrium to the glass transition phenomenon observed during constant heating rate DSC experiments [23]. Subsequent work applied this model to examine the influence of annealing time and temperature on the degree of relaxation [24, 25, 27]. De Hay et al. used this model to quantify the amount of structural disordering associated with high temperature (homogeneous) plastic deformation [28].

In this work, we examine the changes in free volume associated with shear band formation in Cu- and Zr-based bulk metallic glasses. PAS has been used to obtain detailed information about the open volume in as-cast and rolled $Cu_{60}Zr_{30}Ti_{10}$ glass. These results are compared to previously published data on $Zr_{41.25}Ti_{13.75}Cu_{12.5}Ni_{10}Be_{22.5}$ [19, 20]. In order to obtain more quantitative information, we applied van den Beukel and Sietsma's analysis to determine the average free volume from DSC data [23]. Preliminary DSC data for as-cast, rolled, and

annealed $Cu_{60}Zr_{30}Ti_{10}$ and $Zr_{58.5}Nb_{2.8}Cu_{15.6}Ni_{12.8}Al_{10.3}$ glasses are presented and discussed in light of the PAS results.

Free Volume and Deformation

After inhomogeneous deformation, metallic glass failure surfaces exhibit characteristic vein and void patterns indicative of significant softening on the failure plane. Thus, flow models that lead to strong softening in shear bands have been proposed. Argon introduced the concept of the shear transformation zone [15]. These zones begin as small regions where the local atomic structure is capable of rearrangement under an applied shear stress. The ability of a region to undergo a shear transformation depends on the local atomic density; that is, the amount of free volume. The free volume is defined as that part of an atom's nearest neighbor atomic cage in excess of its hard sphere atomic volume. The free volume is assumed to be distributed statistically among all the atoms in the material. This implies that there is a similar statistical distribution of "flow defects" with sufficient free volume to enable shear transformation at a given stress.

While studying plastic flow in metallic glass ribbons, Spaepen modeled the strain rate in terms of a diffusion-like mechanism of atomic motion [14]. If the applied shear stress is large enough, Spaepen further proposed that free volume could be created as an atom with volume v* squeezes into a neighboring free volume site with slightly smaller volume v, increasing the free volume by v*-v. Competing with this creation process is a relaxation process in which subtle structural rearrangements annihilate free volume. At low stresses, the annihilation rate exactly balances the creation rate and the free volume remains constant. However, at high stresses the creation rate exceeds the annihilation rate, resulting in catastrophic softening as the free volume increases dramatically. As the stress drops, the driving force for free volume creation declines until a new, larger steady state free volume is established. Steif et al. [16] went on to show that if one assumes that a band of material is perturbed to a slightly higher initial free volume than its surroundings, the catastrophic softening event is associated with strain localization in the band. Thus, after the localization event, the free volume within the shear band should be measurably greater than in the undeformed material, increasing the average free volume overall.

Examination of open volume using positron annihilation spectroscopy

Positrons are repelled by positively charged atomic nuclei and therefore preferentially occupy open volume sites in the material. Upon annihilation with an electron from the

surrounding atoms, two γ-rays with characteristic energies of 511 keV are emitted. However, the momentum transfer from the electron-positron pair to the γ-ray in the direction of propagation will result in a Doppler broadened energy spectrum that describes the electron momentum distribution in the material. The shape of the spectrum is determined by the momentum distribution of electrons with which the positron interacts, i.e. valence or core, and the type of atom donating the electron. If the annihilation occurs in a large open volume site such as a defect in a crystalline material, the fraction of low momentum conduction and valence electrons participating in the process increases relative to the fraction of high momentum core electrons, and the energy shift is smaller. Thus, a defect rich material will have a narrower electron momentum distribution (as seen by positrons) than would a defect free material. It is common to compare the normalized area under the central, low momentum portion of the distribution, called the S parameter, with the normalized area in a fixed interval under the high momentum tail of the curve, called the W parameter. An increase in S and reduction in W corresponds to either more or larger open volume regions. Additional details about PAS are available elsewhere [29].

Free volume and the glass transition

Figure 1 schematically illustrates the change in the average free volume per atom, v_f, as a function of temperature during quenching from the liquid state followed by heating at a constant rate, such as during a DSC experiment. As the glass cools and atomic mobility decreases an excess amount of free volume, v_{fi}, corresponding to the equilibrium free volume at the fictive temperature, T_f, is frozen into the system. When the system is heated at a constant rate, the structure relaxes towards equilibrium, and v_f decreases with temperature. This is observed as an exothermic dip in the DSC trace. At the same time, the metastable equilibrium free volume of the supercooled liquid, v_{feq}, increases approximately linearly with temperature. Thus, once v_f reaches v_{feq}, the average free volume should begin to increase with temperature. However, in a constant heating rate experiment the kinetics of free volume production are too sluggish to keep up with the constantly increasing temperature, and hence v_f undershoots the equilibrium behavior. As the temperature continues to increase, atomic mobility increases sufficiently to bring the system back to equilibrium. This rapid production of free volume is observed as an endothermic peak on the DSC trace, and is identified as the glass transition. Van den Buekel and Seitsma [23] noted that the glass transition is thus a purely kinetic phenomenon, observable only due to the finite heating rate of the DSC experiment. They further noted that the change in free volume is proportional to the energy released during

relaxation or required during production. Noting that the specific heat, c_p, is the change in enthalpy, H, with respect to temperature, we find that the specific heat determined during a constant heating rate DSC experiment is related to the free volume:

$$c_p = \frac{dH}{dT} = A\frac{dv_f}{dT}, \quad (1)$$

where A is a scaling factor. Based on Tsao and Spaepen's model for the rate of free volume creation and annihilation, it can be shown that [23, 25, 30, 31]:

$$\frac{dv_f}{dT} = -\frac{\nu}{\beta}\exp\left(\frac{-Q_f}{kT}\right)v_f^{\,2}\left[\exp\left(-\frac{1}{v_f}\right) - \exp\left(-\frac{1}{v_{feq}}\right)\right] \quad (2)$$

where β is the heating rate (dT/dt), ν is a frequency parameter, Q_f is the activation energy for structural changes, k is Boltzman's constant, and v_{feq} is the equilibrium value of the average free volume at temperature T. Equation 2 may be solved for initial condition $v_f(T = T_i) = v_{fi}$ using an explicit incremental temperature step method with linear interpolation. Using v_{fi} as a fitting parameter, it is then possible to use Equations 1 and 2 to quantify the initial free volume from the specific heat data obtained during a constant heating rate DSC experiment.

Using this method, it has been shown that annealing processes, which relax the quenched in free volume, result in an increase in the height of the c_p peak [24, 25, 27]. This is understood by considering the severity of the undershoot when v_f first intersects v_{feq} during heating. If the initial free volume is lowered by structural relaxation, v_f will intersect v_{feq} at a lower temperature where the kinetics of free volume creation are slow. This results in a larger undershoot, and consequently a larger driving force and more rapid free volume creation when the kinetics finally accelerate. In contrast, homogeneous deformation of a fully relaxed glass is expected to increase the initial free volume and results in a decrease in the c_p peak [28]. The present work attempts to qualitatively apply this model to the free volume changes associated with the inhomogeneous deformation of the as-quenched glass. Efforts to quantify the free volume changes are ongoing.

Experimental

Strips of $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ and $Cu_{60}Zr_{30}Ti_{10}$ were prepared by arc-melting in an argon atmosphere and suction cast into a copper mold at the Air Force Research Laboratory, Wright-Patterson Air Force Base, Dayton, OH. The 0.55 mm thick strips had nominal widths of 5 mm and varied in length. The strips were cleaned with 300-grit SiC paper to remove surface artifacts. X-ray diffraction confirmed that the cleaned samples were amorphous. The thickness

of the cleaned samples was ~0.50 mm. The as-cast strips were sectioned in order to retain a control specimen from each casting. The remaining material was then either relaxed or plastically deformed. Plastic deformation was accomplished by rolling the specimens to ~0.35 mm in multiple passes. Relaxed specimens were annealed at 200°C for 24 hours under an argon atmosphere.

The free volume changes associated with plastic deformation of the $Cu_{60}Zr_{30}Ti_{10}$ strip was examined using PAS at Lawrence Livermore National Laboratory. Details of this technique are described elsewhere for Zr-based bulk metallic glasses [19, 20]. Positrons emitted from a radioactive Na^{22} source were confined and transported to the specimen using a strong magnetic field (~1.0 kG). The positrons had energies up to 540 keV, resulting in implantation into the specimen up to a depth of ~100 μm. The temperature dependence of positron annihilation in the $Cu_{60}Zr_{30}Ti_{10}$ glass in both as-cast and rolled forms was examined over a temperature range of 50 K to 300 K. These measurements were preformed with the specimen under vacuum to avoid water freezing on the specimen surface.

In an effort to more directly assess the changes in free volume associated with relaxation and plastic deformation, the glass transition behavior of as-cast, rolled, and annealed $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ and $Cu_{60}Zr_{30}Ti_{10}$ specimens were observed using a TA Instruments temperature modulated DSC 2920 with constant argon flow. Specimens ranged from 5 mg to 15 mg. DSC data was obtained in two heating scans. The specimens were first equilibrated at 50°C for 1 minute to avoid any sudden temperature change effects. They were then heated to 600°C at a constant heating rate of 20 K/min. The crystallized specimens were cooled to 25°C and again scanned at 20 K/min in order to obtain a baseline. This baseline was subtracted from the first scan in order to obtain the final result.

Results

An SEM image of a rolled $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ specimen is shown in Figure 2. The rolled $Cu_{60}Zr_{30}Ti_{10}$ had a similar appearance. Numerous shear bands are apparent throughout the specimen volume, indicating that the ensuing investigations of the deformed structure indeed sampled a significant fraction of deformed material. PAS Doppler broadening results for the $Cu_{60}Zr_{30}Ti_{10}$ glass are presented in Figure 3. In Figure 3(a), the fraction of positrons annihilating with high momentum electrons, W, is plotted versus the fraction annihilating with low momentum electrons, S, at room temperature for both the as-cast and rolled specimens. It is clear from this data that W decreased and S increased after plastic deformation. This is the

same trend observed in a Zr-based glass following much lighter deformation [19]. This behavior is consistent with an increase in the size or number of open volume sites with deformation.

The temperature dependence of the S parameter is presented in Figure 3(b) for the $Cu_{60}Zr_{30}Ti_{10}$ specimens. As has been observed previously for Zr-based bulk metallic glasses [20, 32], S initially increased over the temperature range of 50 to ~200 K, followed by a plateau between 200 and 300 K. This temperature dependence is associated with the increased thermal energy of the positrons enabling them to avoid shallow trap sites and diffuse to "deep" trap sites. This suggests that there are multiple free volume site sizes. With plastic deformation, the entire curve shifted to higher S values, indicating an increase in the free volume as discussed in the following section.

The heat capacity data calculated from the DSC scans of the as-cast, rolled, and annealed $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ specimens are presented in Figure 4. It is apparent that the exothermic dip indicating the onset of structural relaxation of the rolled specimen began at ~475 K while the as-cast and annealed specimens began to relax at ~520 K. Although the rolled data reached a slightly lower depth, it overlapped with the as-cast data between the bottom of this exothermic peak and the glass transition peak. Note that the rolled peak appears sharper than in the as-cast condition. The annealed data was higher than the as-cast and rolled states throughout structural relaxation and the glass transition.

The data for the $Cu_{60}Zr_{30}Ti_{10}$ were obtained from two different strips. Data from the same as-cast and rolled specimens used for the PAS work are presented in Figure 5(a). In this case, the rolled specimen exhibited a much deeper structural relaxation peak, although the onset temperature was only ~5 K lower than in the as-cast case. It is interesting to note that this exothermic event appears much sharper than that observed in previous studies where a faster heating rate was used [33, 34]. However, examination of the full DSC scan revealed that this structural relaxation peak was much smaller in magnitude than those associated with crystallization (not shown). The as-cast glass clearly exhibited a higher glass transition peak than the rolled specimen. The effect of annealing was examined using a second strip, and the results are presented in Figure 5(b). As observed for the Zr-based glass, the data for the annealed glass was greater than the as-cast data throughout the scan. In fact, this as-cast strip appeared to exhibit a subtle exothermic effect beginning at ~480 K, possibly associated with chemical reordering [23], followed by the more severe relaxation exothermic event beginning at ~690 K. The annealed specimen only exhibited the deeper exotherm. Subsequent rolling of the annealed specimen deepened this higher temperature relaxation peak but had no effect at lower temperatures. The glass transition peak for the annealed + rolled specimen was at an

intermediate height between the as-cast and annealed states. This is in good agreement with prior work on homogeneous deformation of a structurally relaxed glass [28].

Discussion

The pronounced increase in S parameter with temperature has been observed previously during PAS examination of a $Zr_{41.25}Ti_{13.75}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk glass [20, 32]. An increase in positron lifetime, which is a function of the local electron density at the annihilation site, has also been noted for a $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ glass ribbon [17]. In both cases, the increase has been interpreted as resulting from thermally activated positron detrapping from shallow (small) traps. At low temperatures, positrons are not agitated by phonons and are less likely to detrap, thus annihilating in both shallow and deep (large) sites. The relative partition between these traps is determined by their concentrations. At higher temperatures, the positrons are able to detrap from shallow traps and are localized only by deep traps, resulting in an increase in annihilation with low momentum electrons (i.e. an increase in S). Thus, the data presented in Figure 3(b) is indicative of an open volume site size distribution in the glass. Additionally, in both Zr-based systems, the contribution of the larger traps reached a peak and dropped off for higher temperatures, indicative of positrons detrapping from even the large open volume sites and annihilating in the bulk. This detrapping was not observed in the Cu-based glass, although the trend line fit to the data does suggest that detrapping may begin slightly above room temperature. This increase in the detrapping temperature suggests that the smaller traps in the Cu-based glass may be deeper in energy than those in the Zr-based systems. While this may be associated with composition dependant topological differences, it should be noted that the specimens were prepared with different cooling rates, which would have a strong effect on the amount of free volume frozen into the material.

Suh et al. [20] examined the effect of annealing on positron trapping. They found that at low temperatures, the annealed and as-cast specimens exhibited similar S parameters, indicating that the numerous shallow traps were unaffected by structural relaxation. They identified these shallow traps as intrinsic Bernal holes in a dense, randomly packed hard sphere (DRPHS) model. However, they observed a significant decrease in S at higher temperatures and a shift in the detrapping temperature from ~200 K in the as-cast glass to ~170 K following relaxation. This was interpreted as resulting from the removal of large, unstable flow defects during annealing.

In the present work, the PAS results clearly indicate an increase in the open volume in the Cu-based glasses after heavy plastic deformation. A similar room temperature Doppler

broadening spectroscopy study on the $Zr_{41.25}Ti_{13.75}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk glass revealed that plastic deformation led to an increase in the open volume, while a low temperature annealing treatment resulted in a reduction of the same type of open volume [19]. In contrast to Suh et al.'s results after annealing, plastic deformation resulted in a shift to higher S values over the entire temperature range. The fact that the low temperature end of the curve shifts indicates that the concentration of deep traps has increased. This would be consistent with a cascade effect in the creation of flow defects due to the operation of shear bands. It is unclear from the present data if the flow defects have increased in number or in size as well. Higher temperature measurements and the determination of the temperature required for detrapping may shed light on this issue.

DSC results for the $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ glass indicate that structural relaxation of the rolled specimen began at a lower temperature than the as-cast and annealed glasses. This is consistent with an increase in free volume due to plastic deformation, which pushes the system further out of equilibrium and provides a larger driving force for relaxation. Once the system relaxed to the same extent as the as-cast glass, the rolled and as-cast specimens exhibited similar glass transition behavior, reaching approximately the same peak height. In contrast, the annealed specimen does not reach the same exothermic depth as the other specimens, consistent with a lower initial free volume. The annealed specimen also exhibits a higher glass transition peak, as suggested by prior studies [24, 25, 27].

The dominant structural relaxation peak in the $Cu_{60}Zr_{30}Ti_{10}$ glasses always began at ~690 K, regardless of specimen preparation. Only the depth of the peak varied from the rolled to as-cast to annealed states. The rolled specimen exhibited the deepest exothermic peak, followed by the as-cast and annealed states, again consistent with the deformed structure being a more disordered, higher energy state (i.e. more free volume) and the annealed structure being a relaxed, lower energy state. It should be noted that the constant onset temperature and depth of this exothermic peak suggests that it may be associated with a more significant structural change than just the annihilation of free volume. Future work will consider the possibility of the formation of a metastable crystalline phase at this temperature.

The influence of rolling on a previously annealed Cu-glass specimen shows that while the deformation did move the structure towards the as-cast condition, it did not result in the same level of disorder. This may be due to the highly localized nature of the deformation. While the shear band density is high (see Figure 2), there is still a significant volume of material outside of the shear bands. The free volume outside of the shear bands should remain virtually unaffected by the deformation process.

In agreement with the PAS results, these DSC observations clearly show that plastic deformation increases structural disorder and thus the free volume, while annealing results in a free volume decrease and a higher level of structural order prior to the glass transition. Following the glass transition, one would expect the as-cast, rolled, and annealed specimens of each glass to exhibit similar supercooled liquid behavior. However, the specific heat values for the varying conditions are shifted relative to each other in this region for both glasses and do not reach any obvious plateau value prior to crystallization. This may indicate that the heating rate is too high to permit complete relaxation to equilibrium before crystallization. Alternatively, Slipenyuk and Eckert suggest that this shift may be due to an instrument error that may be subtracted out as a linear correction [27]. Work to clarify the behavior of the supercooled liquid as well as to quantify the free volume changes using van den Beukel and Seitsma's model is ongoing.

Conclusions

The free volume changes associated with inhomogeneous deformation of Cu-based and Zr-based bulk metallic glasses have been investigated using positron annihilation spectroscopy and differential scanning calorimetry. Consistent with free volume models for flow and previous studies of Zr-based systems, PAS results indicated that the open volume in the Cu-based glass increased after deformation by rolling. This is contrasted with other studies of annealing effects on Zr-based glasses, which result in structural relaxation and show the opposite PAS trend. The temperature dependence of the positron annihilation suggested that there is a distribution of open volume site sizes, with a high concentration of small sites. The concentration of the larger open volume sites, believed to be flow defects, increased following plastic deformation.

The PAS results are confirmed by the DSC observations. The deformed Zr-based glass exhibited structural relaxation at a lower temperature, indicative of a higher initial free volume, while deformation of the Cu-based glass pushed the structure to a higher energy state, resulting in a deeper exothermic effect prior to the glass transition. Furthermore, following deformation the height of the endothermic peak associated with the glass transition decreased relative to the as-cast Cu-based glass, and remained unchanged for the Zr-based glass. This was contrasted with an increase in peak height following annealing, consistent with several prior studies and indicative of a lower initial free volume.

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Figures

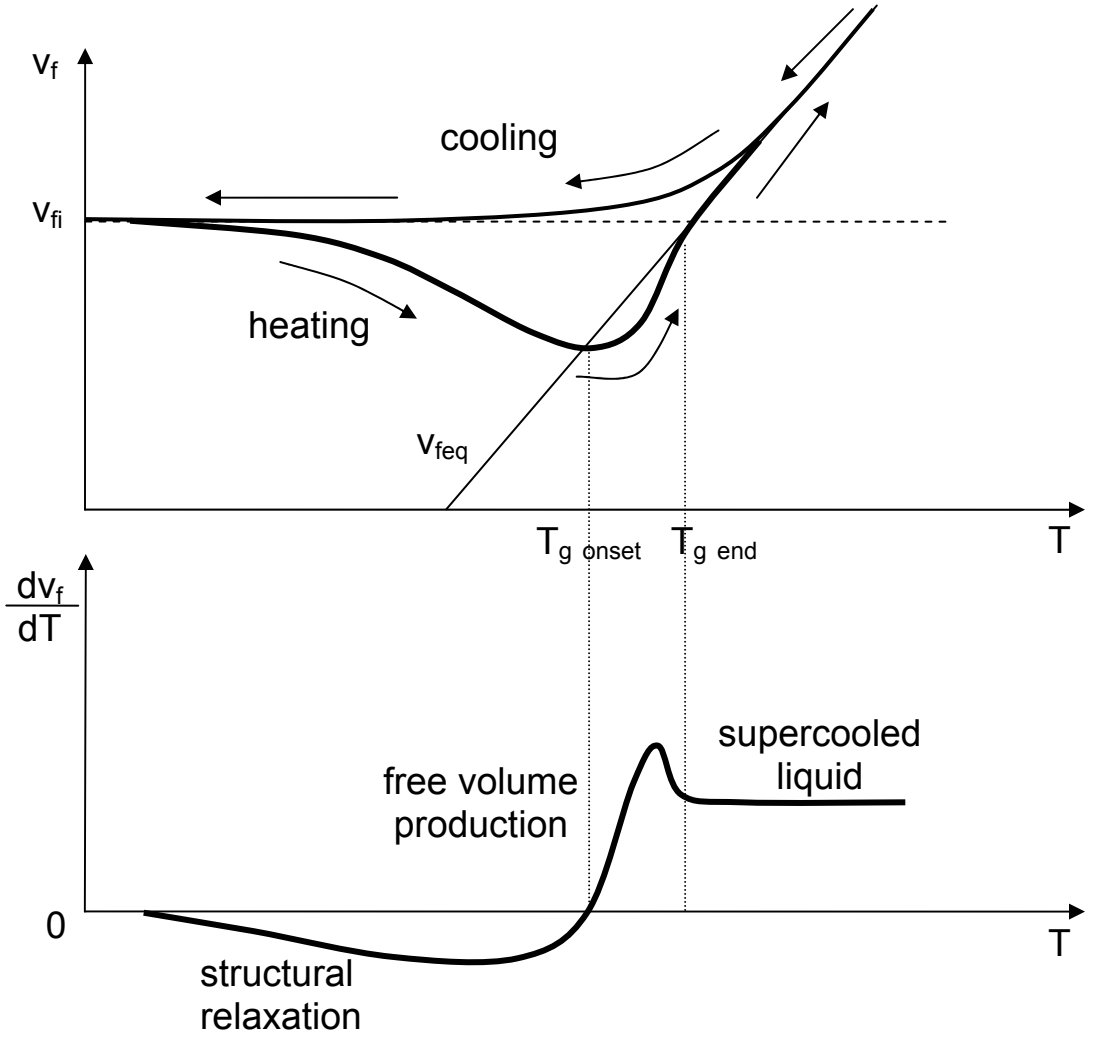
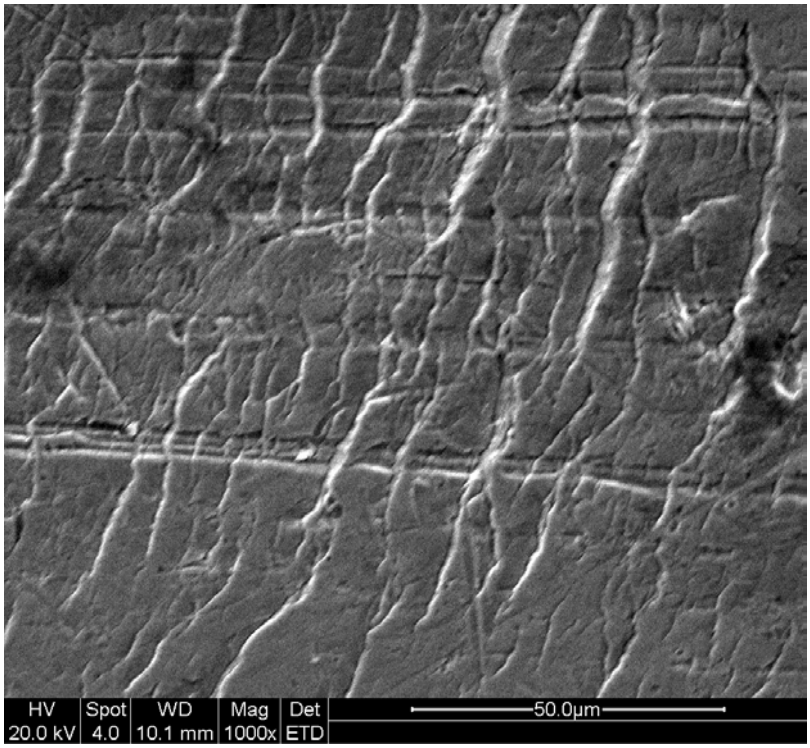
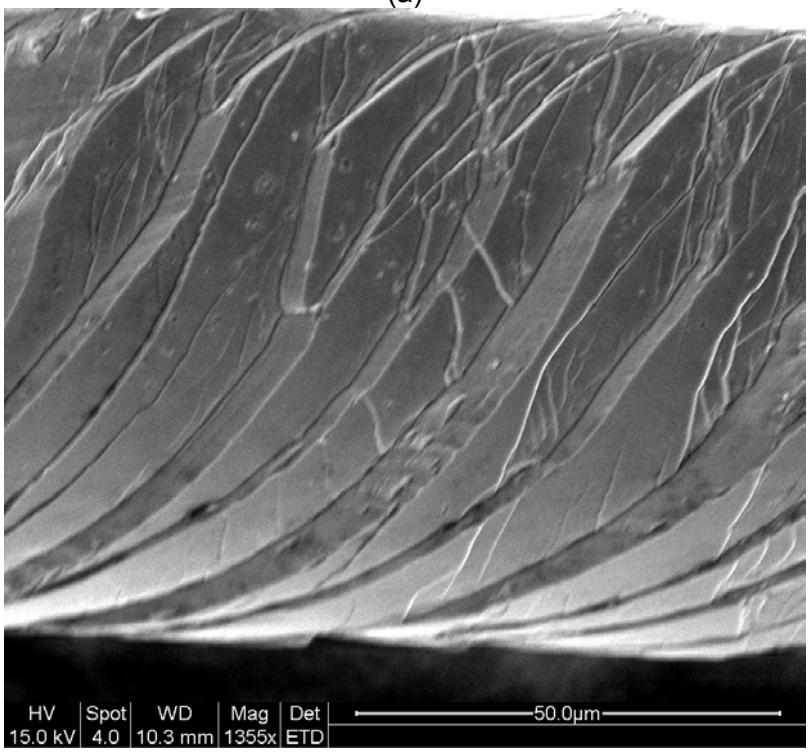


Figure 1. The upper plot is a schematic illustration of the variation in average free volume per atom, v_f, with temperature, T, during cooling from the liquid and reheating at a constant rate. The lower plot illustrates the corresponding behavior of dv_f/dT with temperature. Van den Beukel and Seistma [23] noted that dv_f/dT exhibits the same form as the specific heat, c_p, during a constant heating rate DSC experiment.

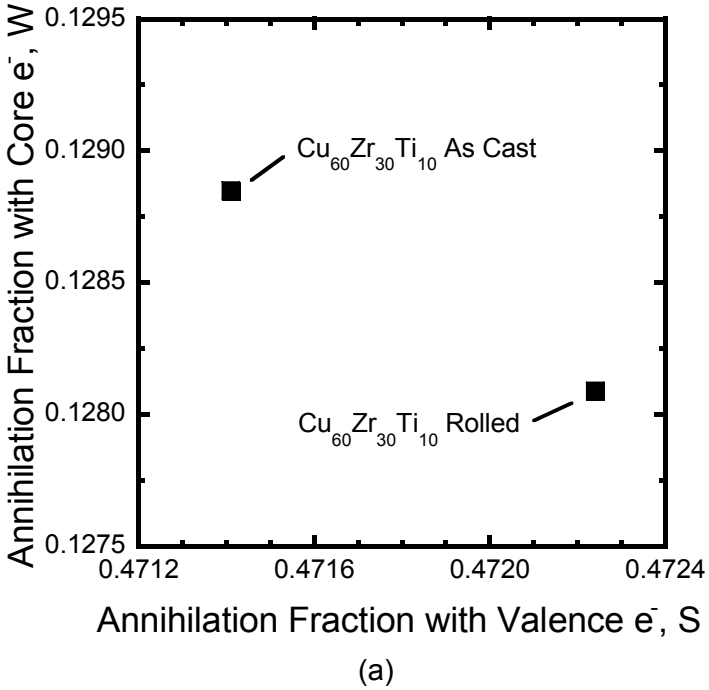


(a)

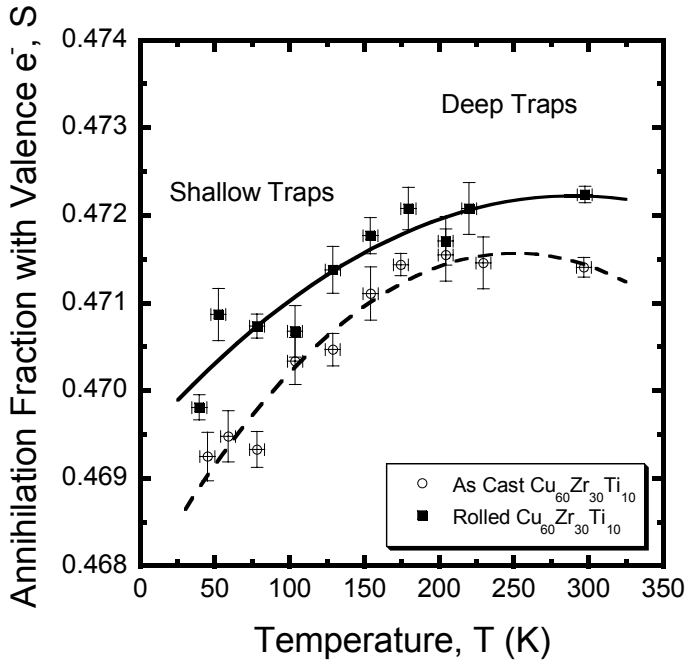


(b)

Figure 2. Top (a) and edge (b) views of a rolled $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ specimen are shown in these SEM images. Note the high density of shear bands in both views. The horizontal markings in (a) are scratches formed during the rolling process.



(a)



(b)

Figure 3. PAS Doppler broadening results for the as-cast and rolled $Cu_{60}Zr_{30}Ti_{10}$ strips are plotted in (a) as the fraction of positrons annihilating with core electrons, W, versus the fraction annihilating with valence electrons, S. The variation in S with temperature is shown in (b)

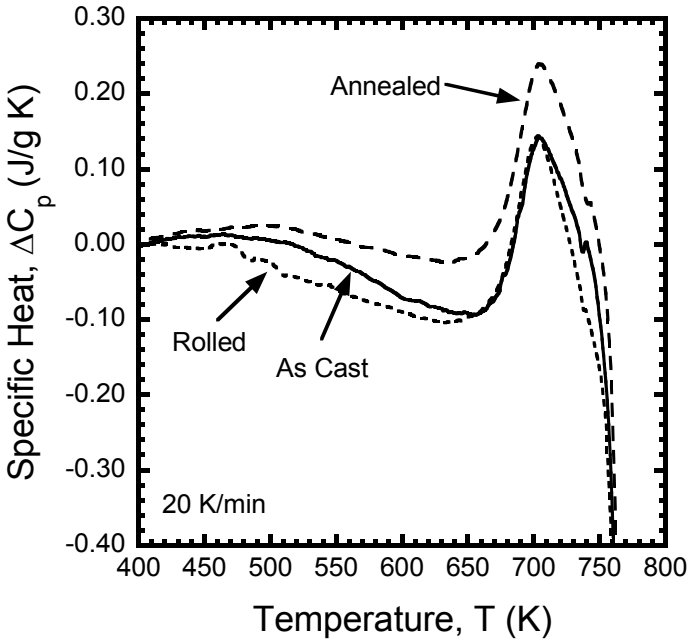
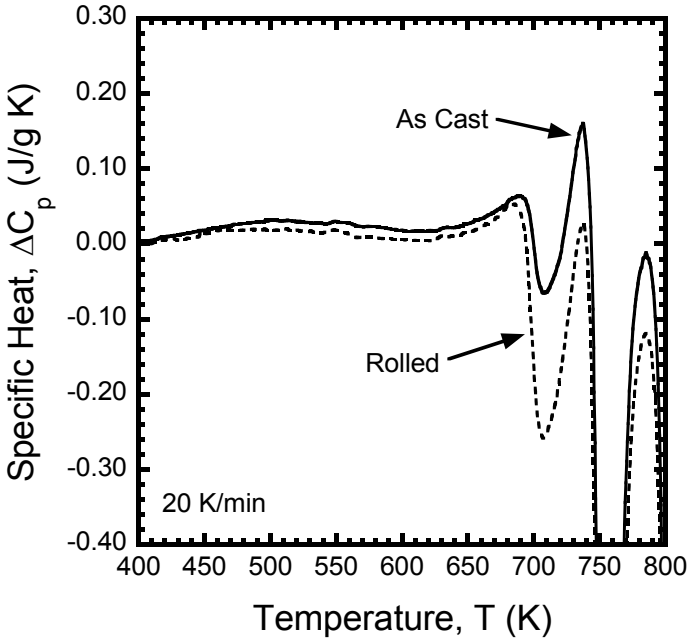
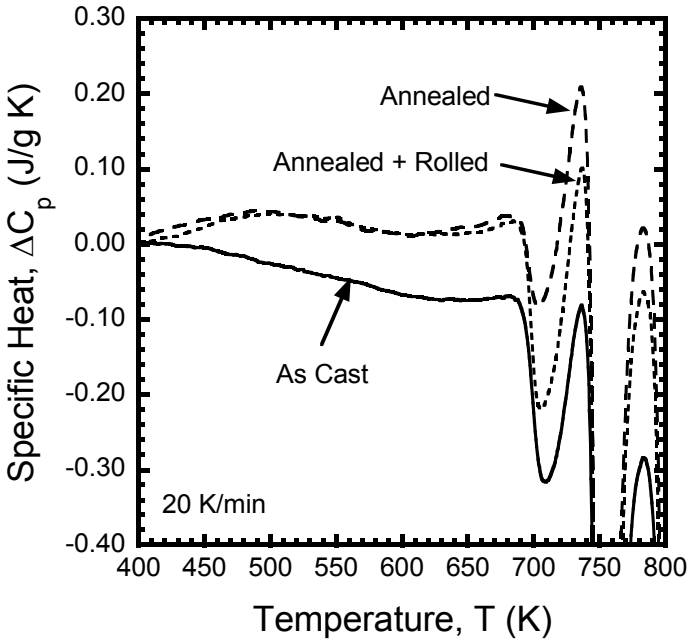


Figure 4. The specific heat data calculated from DSC scans of the $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ in the as-cast, annealed, and rolled conditions are presented. The data have been shifted to 0 at 373 K. The rolled specimen begins to structurally relax at a lower temperature than the as-cast. In contrast, the annealed specimen relaxes at a higher temperature. The rolled and as-cast specimens exhibit similar glass transition behaviors while the annealed specimen reaches a higher endothermic peak.



(a)



(b)

Figure 5. The specific heat data calculated from DSC scans of the $Cu_{60}Zr_{30}Ti_{10}$ glass are presented. The data have been shifted to 0 at 373 K. As-cast and rolled conditions are compared in (a). The rolled specimen exhibits a significantly deeper structural relaxation exothermic peak as well as a lower glass transition peak than in the as-cast condition. The effect of annealing is examined in (b). Annealing reduces the depth of the exothermic peak and increases the glass transition peak height relative to the as-cast state. Subsequent rolling shifts the trace towards the as-cast data.