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CHARACTERIZATION OF PLASTICALLY-INDUCED STRUCTURAL CHANGES IN A Zr-BASED BULK METALLIC GLASS USING POSITRON ANNIHILATION SPECTROCOPY

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Characterization of plasticity-induced structural changes in a Zr-based bulk metallic glass using positron annihilation spectroscopy

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Abstract

Flow in metallic glasses is associated with stress-induced cooperative rearrangements of small groups of atoms involving the surrounding free volume. Understanding the details of these rearrangements therefore requires knowledge of the amount and distribution of the free volume and how that distribution evolves with deformation. The present study employs positron annihilation spectroscopy to investigate the free volume change in $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ bulk metallic glass after inhomogeneous plastic deformation by cold rolling and structural relaxation by annealing. Results indicate that the size distribution of open volume sites is at least bimodal. The size and concentration of the larger group, identified as flow defects, changes with processing. Following initial plastic deformation the size of the flow defects increases, consistent with the free volume theory for flow. Following more extensive deformation, however, the size distribution of the positron traps shifts, with much larger open volume sites forming at the expense of the flow defects. This suggests that a critical strain is required for flow defects to coalesce and form more stable nanovoids, which have been observed elsewhere by high resolution TEM. Although these results suggest the presence of three distinct open volume size groups, further analysis indicates that all groups have the same line shape parameter. This is in contrast to the distinctly different interactions observed in crystalline materials with multiple defect types. This similarity may be due to the disordered structure of the glass and positron affinity to particular atoms surrounding open-volume regions..

Introduction

Bulk metallic glasses (BMGs) exhibit an impressive array of mechanical properties with unusual manufacturing flexibility, making them attractive for numerous applications {Johnson, 1999 #22;Loffler, 2003 #24;Telford, 2004 #39;Wang, 2004 #30;Lemley, 2004 #21}. Structural applications are currently limited, however, in part due to the limited understanding of the micromechanisms of flow and mechanical failure. At low temperatures and high strain rates, plastic deformation in BMGs is highly localized in shear bands. Under tensile stress states, strain localization can result in catastrophic failure without significant macroscopic plastic deformation, limiting the structural reliability of these alloys. Control and optimization of the deformation behavior requires an understanding of atomic level structural changes during flow and their role in shear band formation and multiplication mechanisms.

Flow in metallic glasses is thought to be a diffusion-like process involving the stress-induced cooperative rearrangement of small groups of atoms referred to as “flow defects” or “shear transformation zones” [1, 2]. These flow defects are associated with atomic scale open spaces, or “free volume” sites, which are distributed throughout the structure. Thus, it is usually assumed that the amount and distribution of the free volume controls plastic flow. While studying plastic flow in metallic glass ribbons, Spaepen proposed that free volume is created as an atom squeezes into a neighboring free volume site with slightly smaller volume [1]. Competing with this creation process is a relaxation process in which subtle structural rearrangements annihilate free volume. At sufficiently high stresses the free volume creation rate exceeds the annihilation rate, resulting in the characteristic softening behavior. While this free volume model for flow is generally accepted and experimental results confirm an increase in free volume with deformation [3-5], the details of the flow defect structure and the atomic rearrangements required for flow are areas of active research.

Recently, high resolution TEM imaging techniques have revealed the formation of nanovoids within shear bands [6-9]. These nanovoids have been shown to be more thermodynamically stable than the distributed excess free volume, and presumably form due to the accelerated kinetics of mass transport within the shear band [10]. However, the details of free volume coalescence and nanovoid formation during inhomogeneous deformation remain unclear due to a lack of quantitative information about changes in the free volume distribution with plastic strain.

Positron annihilation spectroscopy (PAS) techniques have been used to gain unique insight into the size and distribution of open volume sites in metallic glasses [4, 11-21]. Positron

lifetime and Doppler broadening spectroscopy studies confirm that the size or amount of open volume in the structure increases after moderate room temperature deformation [4]. 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. Suh et al. suggests that these may be stable Bernal holes in the densely packed structure and larger unstable flow defects [19].

In this work, we examine the free volume changes associated with inhomogeneous deformation of a $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ BMG using Doppler broadening PAS. Inhomogeneous deformation is achieved via cold rolling through various thickness reductions. Results indicate that the open volume distribution is at least bimodal, in contrast to the continuous distribution assumed by the free volume model [22]. The size of the flow defects increases with initial deformation, which is consistent with the free volume increase predicted by this model. Rather than exhibiting a monotonic increase in free volume with plastic strain, more extensive deformation shifts the size distribution of the open volume in a direction consistent with the coalescence of moderate sized flow defects into less numerous, larger scale defects. Annealing of the as-cast and deformed structures reduces the size of the flow defects.

Examination of open volume using positron annihilation spectroscopy

Details about defect analysis using PAS and its application to metallic glasses are described elsewhere (e.g. [16, 23]). A summary of the technique is included here for completeness. After implantation in a solid, a positron thermalizes rapidly and then diffuses through the specimen until it is trapped in an energy well. Positrons are repelled by positively charged atomic nuclei and therefore preferentially occupy open volume sites in the material. The positron annihilation rate is determined by the electron density seen by the positron, which in turn is a function of the size of the trapping site. The two γ particles resulting from the positron-electron annihilation have a characteristic energy of 511 keV. However, the momentum transfer from electron-positron pair to the γ particles in the direction of propagation results in Doppler broadening of the 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 annihilates, 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 momentum

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distribution 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.

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While positron trapping does depend on the chemical nature of the trapping site, previous results indicate that the volume of a trapping site is a larger factor in determining where the positron is trapped. Experimental and first principle theoretical studies on numerous systems including semiconductors, ionic crystals and metallic compounds show positrons are in a delocalized state [24] and localization around a particular atom is enhanced only in the presence of an associated open volume or when Rydberg states are formed around negatively charged states. Previous PAS studies of glassy $Zr_{52.5}Ti_5Al_{10}Cu_{17.9}Ni_{14.6}$ and $Zr_{41.25}Ti_{13.75}Cu_{12.5}Ni_{10}Be_{22.5}$ alloys indicated that positrons annihilated primarily in free volume sites surrounded by Zr and Ti atoms, even though Zr and Ti have lower positron affinities when compared to the other elements in these alloys [4, 16, 25]. Thus, PAS provides a unique probe of free volume site size.

By varying the thermal energy of the positrons, and thus their ability to escape or "detrap" from shallow energy wells, positron traps of different binding energies may be sampled. The trapping behavior, characterized by S, as a function of temperature provides a picture of the size distribution of open volume sites in the specimen. Changes in S with T are indicative of the competition among multiple traps with different binding energies, e.g. different sized open volume sites. At low temperatures, positrons are not agitated by phonons and are less likely to detrap, thus annihilating in both shallow (small) 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, as indicated by an increase in S. In crystalline materials, where the ordered atomic structure is well defined, quantitative measurements are possible. However, in the present amorphous system we are limited to qualitative statements about the quantity and distribution of open volume in the specimen.

Experimental

Strips of $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ (nominal at%) were prepared by arc-melting in an argon atmosphere and suction casting 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 from 20 – 30 mm. The strips were cleaned with 300-grit SiC paper to remove a thin crystalline surface layer formed due to interaction with the mold. X-ray diffraction and DSC measurements confirmed that the cleaned strips were amorphous. The thicknesses of the cleaned strips were ~0.50 mm. A control specimen was cut from each as-cast strip and saved for later comparison with the deformed and annealed material to limit artifacts due to variations in cooling rate and composition. One as-cast strip was deformed by cold rolling to 14% and 36% thickness reductions. Several rolling passes were performed, with the thickness reduction of a single pass not exceeding xx%. Following initial PAS measurements, the 36% rolled specimen was annealed at 585 K for 50 minutes in an argon atmosphere. Additional as-cast strips were annealed at 460 K for 23 hours and 585 K for 50 minutes, also in argon.

The free volume changes associated with plastic deformation and annealing were examined using the positron beam facility at Lawrence Livermore National Laboratory. Details of this technique are described elsewhere for a Zr-based bulk metallic glass [4, 16, 17, 19, 21]. 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. In my opinion we don't need this, since we have enough references.The temperature dependence of positron annihilation in the glass was examined over a temperature range of 50 K to 300 K. These measurements were performed under vacuum to prevent water condensation on the specimen surface.

Comment [KMF1]: Stephen or Ashok: some details about the DBS detection might be appropriate here.

Results

Preliminary PAS measurements conducted on as-cast strips at selected temperatures indicated that the distribution of open volume was similar in all three castings. Detailed measurements were made on specimen A in the as-cast condition for comparison with the deformed and annealed material from all of the strips.

The fraction of positrons annihilating with valence electrons, S, is plotted as a function of the measurement temperature, T, for the as-cast, annealed, and deformed specimens in Figure 1-Figure 3. Curves have been drawn through each data set to guide the eye. Each specimen initially exhibits the same trend of increasing S with temperature. This indicates that a range of open volume site sizes exists in the glass, since the positron is able to detrap from shallow (small) traps and diffuse to deeper (larger) traps with increasing temperature, thus increasing the annihilation fraction with valence electrons. If only a single size open volume site was present, S would remain constant, independent of temperature [26]. The increase in S is

not monotonic throughout the temperature range examined; most of the specimens reach a plateau in S, while one clearly exhibits a peak followed by a decrease in S with temperature.

The as-cast and annealed specimens are compared in Figure 1. Data obtained from the lightly annealed specimen (460 K for 23 hours) were similar to that for the as-cast specimen for temperatures below 230 K. At 300 K, the annealed specimen exhibited a lower S, indicating a reduction in open volume sampled at that temperature. Annealing at 585 K for 50 minutes shifted the entire curve to lower S values at all the temperatures.

PAS data for the 14% and 36% deformed conditions are compared with the as-cast state in Figure 2. For the 14% rolled specimen, the entire curve shifts to higher S values, indicating an increase in the size or amount of open volume. Note that the temperature at which S reaches a plateau is similar to that of the as-cast material. In the case of the 36% rolled specimen, the curve again shifts to higher S values compared to the as-cast specimen. However, over the temperature range examined in this study, the 36% rolled data falls below that for the 14% rolled material. Additionally, the low temperature slope of S versus T is more shallow, and the plateau is no longer clearly discernable.

The effect of structural relaxation on the open volume distribution in a previously deformed material is examined in Figure 3. Following annealing, the curve shifted to a lower S value compared to the 36% rolled material, consistent with a decrease in the amount of open volume. This shift was larger at higher temperatures, where the deformed + annealed material exhibits a plateau in S. Note that the data for the annealed and deformed + annealed specimens overlap between 230-300 K, while for lower temperatures the deformed + annealed data lies between the deformed only and annealed only data.

Discussion

We note that there are three different S(T) trends observed in the present data. One specimen (36% rolled) exhibits an increasing S with T over the entire temperature range. As the temperature increases, the positrons are able to escape the traps with lower binding energy and retrap in larger, deeper defects, thus increasing the annihilation fraction with valence electrons. One specimen (460 K, 23 hr anneal) exhibits a peak S value below room temperature. At temperatures greater than the peak, positrons are unable to find a sufficient number of traps with a large enough binding energy to localize them and thus they annihilate as they diffuse through the bulk, resulting in a decrease in S. While this existence of shallow and deep traps in metallic glasses has been suggested previously based on similar S(T) trends [17,

19], this basic description is not inconsistent with a continuous size distribution of open volume sites, such as described by Cohen and Turnbull's free volume model [22].

The remaining specimens all exhibit a plateau in S beginning below room temperature. The presence of a plateau indicates that the positrons are trapping in a similar distribution of open volume sites, regardless of temperature. Thermally activated detrapping does not change the annihilation characteristics, so there is no longer a competition between shallow and deep traps or deep traps and the bulk. The concentration of deep traps is large enough to localize a constant fraction of the positrons as the temperature increases. The transition from increasing S with T at low temperatures to a plateau at high temperatures implies that concentration of deep traps must be higher than the concentration of active shallow traps, and thus the open volume distribution in the present alloy must be at least bimodal rather than continuous, as sketched in Figure 4. Recently, positron lifetime spectroscopy studies have revealed multiple lifetime components for the same Zr-based glass, confirming the existence of distinct groupings of trap sizes [27]. It is reasonable to assume that the smaller set of open volume sites are the bulk or Bernal holes, while the larger set corresponds to flow defects, as suggested previously [17, 19]. Prior to the plateau, open volumes of sufficient depth from the entire size distribution may act as trapping centers in proportion to their concentration. As the temperature increases, fewer Bernal holes and more flow defects localize the positrons, and S increases. On the plateau the larger flow defects are numerous enough to mask the presence of other trapping centers. As long as the concentration and binding energy of flow defect traps are high enough to prevent detrapping to the bulk, and as long as no larger traps become available, S will remain constant. Although not observed here, we do not expect the plateaus to continue indefinitely. At sufficiently high temperatures, thermally activated detrapping from the flow defects will occur, with the positrons migrating to even deeper traps if available or annihilating in the bulk.

For those specimens exhibiting a plateau, the onset temperature and $S_{plateau}$ vary with the processing conditions. The plateau value indicates the relative size of the flow defect sites; a higher $S_{plateau}$ corresponds to a larger volume (i.e. higher binding energy). The onset temperature indicates the temperature at which trapping in Bernal holes becomes insignificant, which is a function of the concentration of the flow defects. Thus, for a constant plateau value, an increase in the onset temperature indicates a lower defect concentration, since a larger sampling volume is required to obtain the same annihilation conditions.

With these interpretations in mind, we now examine the specific changes of the S(T) curves as a function of the processing state. In their PAS study of structural relaxation of a similar Zr-based BMG, Suh et al. noted that annealing resulted in a significant decrease in S

only for the higher measurement temperatures, while at low temperatures the S parameter was similar for the relaxed and unrelaxed alloys [19]. They suggested that the overlapping data at low temperatures indicated that the positrons were sampling the more numerous inherent Bernal holes in the structure, while the deviation at higher temperatures was due to the removal of larger deep traps, i.e. flow defects, with annealing. Suh et al.'s data exhibited definite peaks, but no plateau values. In the present study, a low temperature anneal (460 K, 23 hr) caused a small decrease in S at room temperature, but no effect for positrons with lower thermal energies. This suggests that the concentration of the larger open volume sites was reduced with annealing, as evidenced by the loss of the plateau and onset of detrapping to the bulk. However, some large sites remain, such that the peak S value for the annealed material is the same as the plateau value for the as-cast. Annealing at 585 K for 50 min, similar to the conditions in Suh et al.'s study, resulted in a decrease in S at all measurement temperatures and the emergence of a lower plateau. This suggests that the concentration of flow defects was high enough to be sampled in the as-cast condition even at low temperatures, and the size of these deep traps was subsequently reduced by the higher temperature annealing process. The substantial decrease in S at low temperature differs from Suh et al.'s work, perhaps due to the higher quench rates achieved in the 0.5 mm thick strips used in the present study versus the thick plates examined by Suh et al. A slower quench rate is expected to result in a more relaxed glass structure with less free volume.

A free volume increase with deformation has been modeled by various researchers {Cohen, 1959 #49;Johnson, 2002 #59;Cohen, 1979 #65;Turnbull, 1961 #52;Turnbull, 1971 #51;van den Beukel, 1990 #10;Spaepen , 1977 #48}. Most of the models suggest that free volume increases with increase in deformation [refs?]. In the present study, the increase in S for the rolled specimens relative to the as-cast state clearly indicates that deformation is associated with an increase in open volume. Both the as-cast and 14% rolled specimens exhibit plateaus with similar onset temperatures. The higher $S_{plateau}$ for the rolled specimen indicates that the size of the flow defects has increased, while the similar onset temperature suggests that the defect concentration was unchanged. However, it is surprising that over most of the temperature range examined, $S_{36\%} < S_{14\%}$. The monotonic increase in the 36% rolled data indicates that positrons continue to detrap from relatively shallow traps and retrap in deeper ones even at higher temperatures. One possible explanation for this is that the concentration of sites with sizes intermediate to the Bernal holes and flow defects has increased sufficiently such that they compete with the larger flow defects. Alternatively, the distribution may have become trimodal, as a high enough concentration of nanovoids form to compete with

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Comment [KMF3]: Biraja: This is a bold statement. According to my implementation of Spaepen's model, the free volume increases to a point and then reaches a plateau, which corresponds to the rapid softening and plateau flow stress. Have you actually seen a model that predicts that the free volume increases without limit prior to failure?

the smaller flow defects as trapping sites. This latter explanation is consistent with quantitative high resolution TEM evidence of nanovoids preferentially forming within shear bands as a result of deformation [6-9] as well as more recent positron lifetime measurements [27]. The lower S value in the 50-300 K temperature range suggests that the nanovoids formed at the expense of the more numerous, moderate sized flow defects present after 14% rolling. At the lowest temperature (50 K) the positrons sample similar environments in both deformed specimens, indicating that the smallest, most numerous open volume sites are unchanged with further deformation.

Wright et al. argues that the excess amount of quenched in free volume increases the free energy of the system relative to the fully relaxed glass, providing a thermodynamic driving force for free volume coalescence to form nanovoids [10]. Nanovoids are not observed in undeformed glass, however, due to sluggish mass transport kinetics. Flow within the shear bands significantly increases the mass transport rate, enabling the free volume sites to coalesce. A critical radius, r^*, and a critical energy, G^*, are required to form these nanovoids. For example, for a $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ glass, at ~400K, $r^* \sim 0.24$ Å and $G^* \sim 2 \times 10^{-21}$ J. While these values would increase with shear band temperature, both are quite small, such that void formation is spontaneous with minimal deformation. Our evidence suggests that a significant amount of deformation is required for the subsequent growth of nanovoids and the shift of the S(T) curve in the direction of large open volume sites.

Annealing the 36% rolled specimen at 585 K for 50 minutes shifts the S(T) curve to lower S values, with a plateau value equivalent to that of the material annealed at the same conditions. The similarity of the plateau values indicates that the size of the flow defects are similar for both the annealed and the deformed + annealed conditions, while the earlier onset of the plateau suggests that the concentration of flow defects is higher in the deformed + annealed specimen. This effect could be due to the break up and redistribution of nanovoids. However, since the nanovoids are thermodynamically more stable than the distributed free volume, this is unlikely. Indeed, TEM studies of shear bands following annealing still reveal the presence of nanovoids [9]. Alternatively, the increase in the contribution of flow defects to annihilation may be due to the relaxation of a wider distribution of larger flow defects formed during initial deformation, resulting in a higher, narrower distribution of smaller flow defects with concentration high enough to mask the presence of the nanovoids.

The fraction of positrons annihilating with core electrons, W, versus the fraction annihilating with valence electrons, S, for all the specimens at all measurement temperatures are compared in Figure 5. It is notable that all of the data falls along the same slope, formally

described as the line shape parameter. In crystalline materials, a constant slope indicates that positrons are only annihilated at two types of sites, most likely a single type of open volume defect and in the bulk [23, 26]. Different positions along the line correspond to different concentrations of the defect contributing to the annihilation process. For the glass this suggests that there is only a single "type" of open volume, and that the concentration changes with deformation and annealing. This is somewhat counterintuitive in light of the bi- or trimodal open volume distributions suggested herein. It may be an effect of the disordered nature of the glass that the line shape parameter depends more on the total amount of open volume than the details of the size distribution. Finally, it should be noted that crystallization results in a completely different line shape parameter than the creation and annihilation of free volume, as observed elsewhere [4]. Thus, it is unlikely that one of the positron signature we associate with the open volume group is related to crystallization.

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Conclusion

The structural changes associated with inhomogeneous deformation of a Zr-based bulk metallic glass have been investigated using positron annihilation spectroscopy. The variation in the annihilation characteristics with measurement temperature indicates that the distribution of open volume is at least bimodal, in contrast to the continuous size distribution inherent to the free volume model. The smaller open volume regions were identified as inherent Bernal holes in the otherwise dense structure, while the larger regions were identified as flow defects. Deformation and annealing change the size and concentration of the flow defects. The size of the flow defects increases with initial deformation, while PAS evidence combined with high resolution TEM studies performed elsewhere suggest that the flow defects coalesce to form larger nanovoids after more severe deformation. Low temperature annealing reduces the concentration of the largest flow defects, while a higher temperature anneal reduces the size of these defects. While the size distribution of the open volume is not continuous, further examination of the line shape parameter indicates that Bernal holes, flow defects, and nanovoids are all the same "type" of defect with simply different concentrations. This may be a result of the disordered nature of the glass structure.

Acknowledgements

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Figures

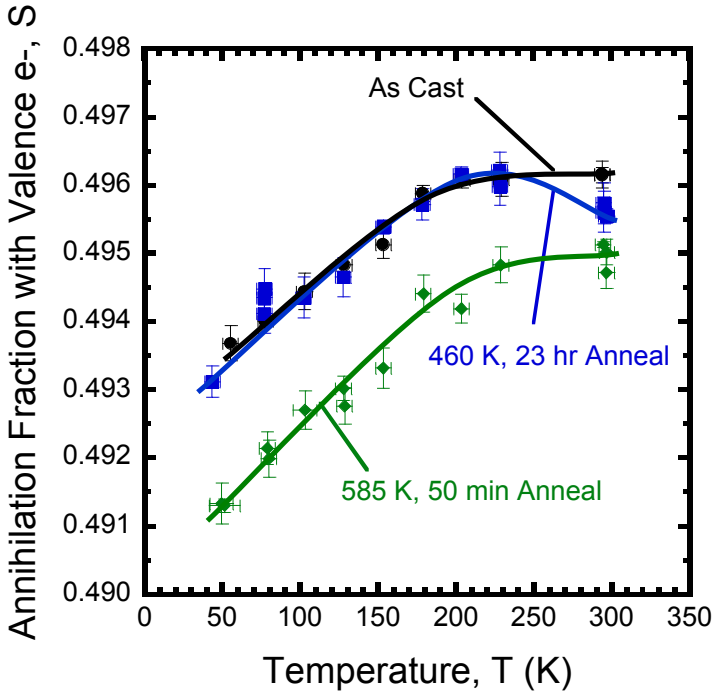

Figure 1. The fraction of positrons annihilating with the valence electrons, S, is plotted versus the measurement temperature for the as-cast, annealed at 460 K for 23 hours, and annealed at 585 K for 50 minutes specimens. Low temperature annealing results in a slight decrease in the flow defect concentration, while the higher temperature anneal reduced the size of the flow defects.

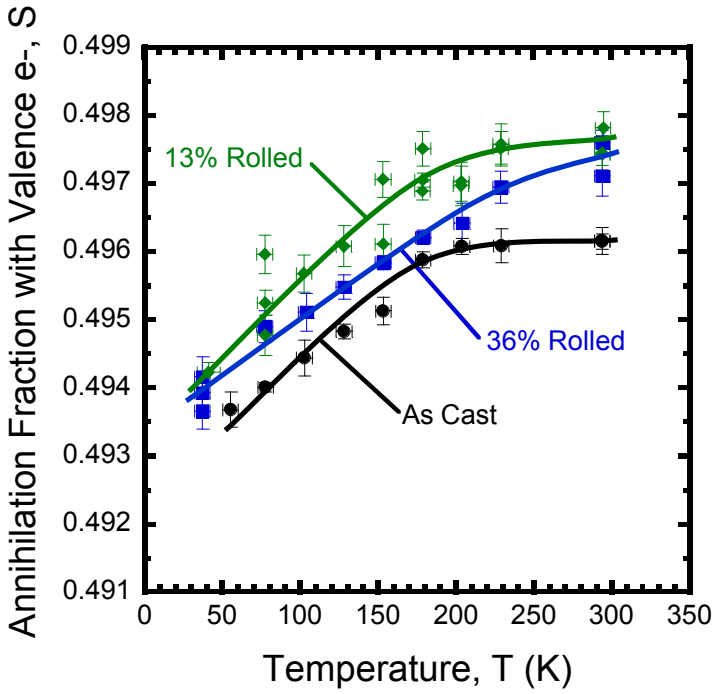

Figure 2. The fraction of positrons annihilating with the valence electrons, S, is plotted versus the measurement temperature for the as-cast, 14% rolled and 36% rolled specimens. Initial deformation increases the size of the flow defects, while more severe deformation results in flow defects coalescing to form nanovoids.

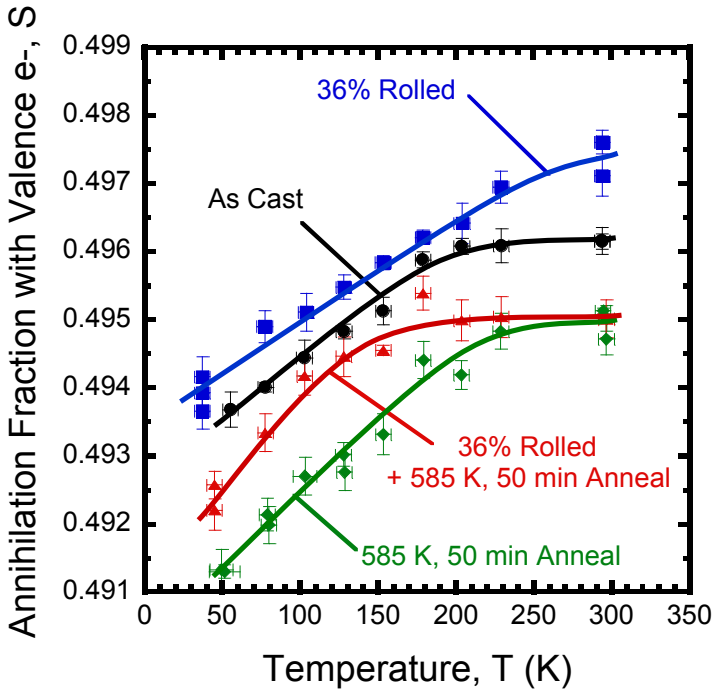

Figure 3. The fraction of positrons annihilating with the valence electrons, S, is plotted versus the temperature for the as-cast, 36% deformed, 585 K 50 minute annealed, and deformed + annealed specimens. Annealing following deformation reduces the median size and increases the concentration of flow defects.

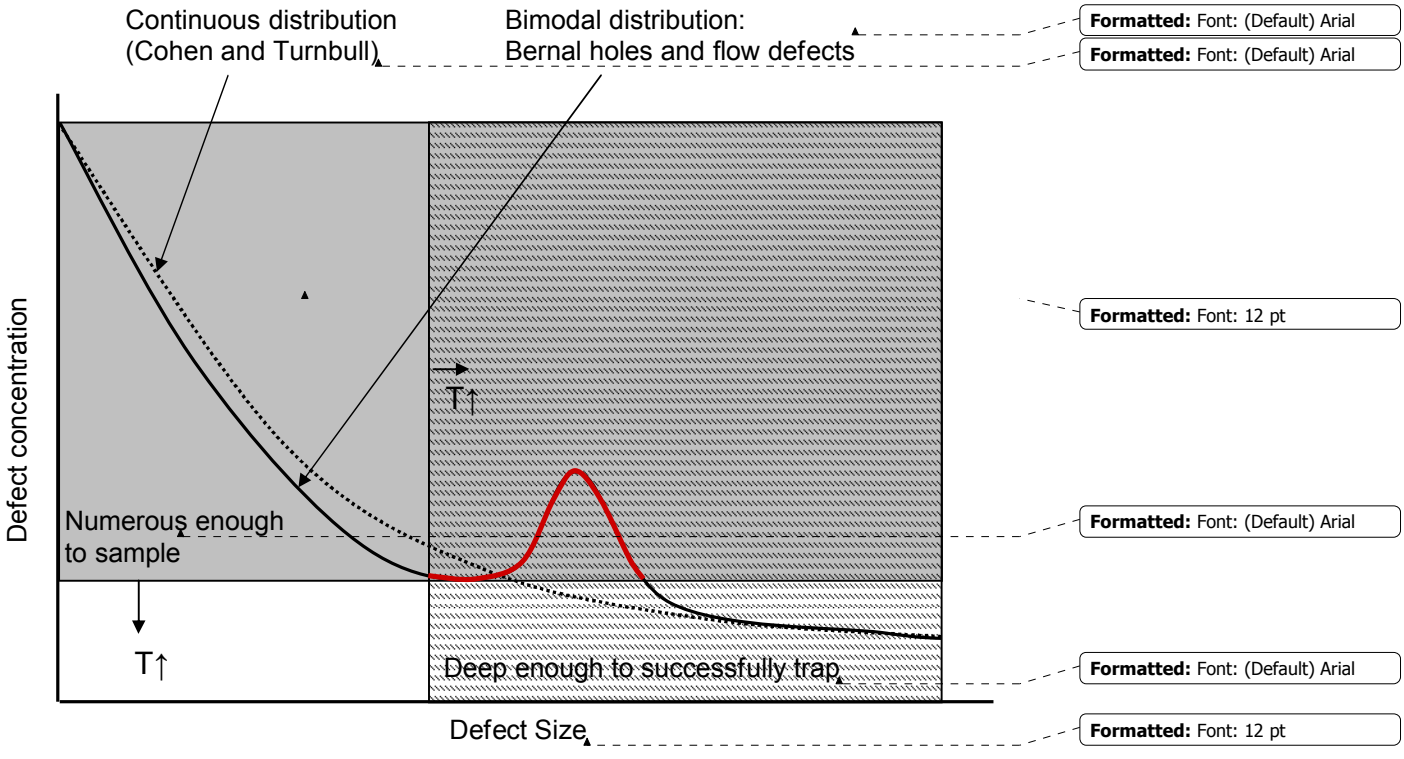

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Figure 4. Schematic comparison of the continuous free volume distribution described by Cohen and Turnbull [22] and the proposed bimodal free volume distribution indicative of a separation between Bernal holes and flow defects. Shaded regions illustrate the open volume size range with high enough concentration to be sampled and binding energy greater than the thermal energy of the positron. As shown, at the onset of $S_{plateau}$, only flow defects contribute to annihilation.

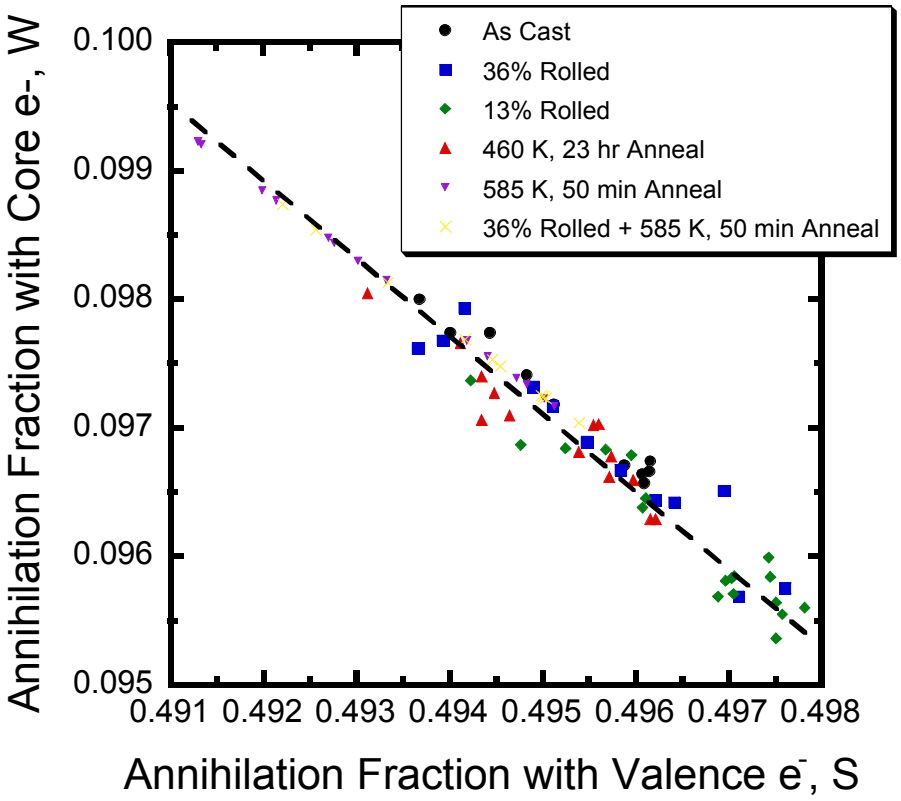

Figure 5. The fraction of positrons annihilating with the valence electrons, S, is plotted versus the fraction of positrons annihilating with the core electrons, W, for all the specimens at all temperatures. All data fall along the same line, indicating that the same type of trap contributes to annihilation in all cases. Only the concentration of the trap changes with processing and measurement temperature.