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5 Quantitatively defining free-volume,
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8 interconnecting-zone and cluster in metallic glasses
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ABSTRACT

The free-volume and interconnecting-zone (i-zone) can be quantitatively determined by distances between the nearest atoms based on the investigation on the pair distribution function data, which were obtained at a cryogenic temperature of 15 K using a neutron scattering source on the $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ bulk metallic glass and its crystallized counterpart. Accordingly, the atomic cluster regions can be determined, i.e. the atoms are regarded in the cluster regions if it is not in i-zones and free volumes. This approach not only helps us for qualitatively analyzing local atomic packing, but also enables us to quantitatively characterize local atomic structures in amorphous alloys.

Keywords:

A. Bulk metallic glass

D. Amorphous structures, atomic clusters

The concept of the dense random packing of hard spheres, which was based on the John Bernal's 'dense random packing' of hard spheres in liquids [1-4], has been in a dominated position for a long period since the first discovery of the amorphous alloy in 1950s [5]. Entering the 21st century, the cluster-based atomic models [6] [7] have been introduced and well studied since scientists have found that the amorphous alloys are not actually randomly packed at an atomic level. Furthermore, the concept of the interconnecting-zone (i-zone) has been also introduced and adopted [8]. With the variation of the random to cluster packing and the introduction of the i-zone concept for the amorphous models, the free volume concept, as one of the most important concept in amorphous alloys, has been constantly used to explain physical and mechanical properties since the amorphous alloy has been born. The free volume concept is so important, but often farfetched to explain some physical and mechanical properties of amorphous alloys. The free volume is actually not quantitatively defined based on atomic bond lengths, and this results in an insufficiency in conducting some detailed analyses. For example, how to explain the glass transition with accompanied mechanical changes: differential scanning calorimetry measurements revealed an energy absorption of 0.79 W/g during the glass transition, and an exothermic release of 14.43 W/g during the crystallization. Yet, the small energy absorption dramatically changes its mechanical properties, such as the yield strengths are reduced from ~2000 MPa with a limited plastic deformation at room temperature to ~70 MPa with superplasticity above the glass-transition temperature

(T_g) in Zr-based BMGs. How does the small energy absorption change the atomic structure of BMGs and result in the liquid like mechanical properties?

A quantitative study on their local atomic structures is important and necessary for understanding this kind of materials. For doing so, quantitatively defining free-volume, i-zone and cluster at the atomic level is important. We conducted neutron scattering experiments on as-cast and its counterpart of the fully crystallized (for 1.8 ks at 1,000 K) specimens of the $Zr_{55}Cu_{35}Al_{10}$ (at. %) bulk metallic glass (BMG) at 15 K using the high-resolution neutron scattering source (HRNS) at the Neutron Powder Diffractometer (NPDF) of the Los Alamos National Laboratory. This technology enables us to quantitatively understand the bond nature of the free-volume, i-zone and atomic clusters.

Atomic vibration is reflected by its constant volume specific heat capacity, C_V , at any given absolute temperature (T) from a macroscopic thermodynamic description. The C_V is proportional to $\exp(-\varepsilon/kT)/[\exp(-\varepsilon/kT)-1]^2$ in the Einstein solid model or $(T/T_D)^3$ in the Debye model, where k is the Boltzmann constant, T_D the Debye temperature. The specific heat quickly goes to zero as an $\exp(-\varepsilon/kT)$ or T^3 a power law. Therefore, neutron data collection at a low temperature of 15 K minimizes the thermal induced atom vibration effect effectively, and the temperature effect may be ignored and atom position or atomic distance in the PDF (pair distribution function) can thus be accurately measured.

The peaks of the PDFs contain information about the thermal, zero-point motion of atoms and the static displacement of the atoms away from their ideal lattice sites,

the atom-pair probability distribution [9]. The peaks for the nearest atom pairs reveal the detailed information about the short-range order, which is of primary importance to understand amorphous structures. The investigation on the nearest atom pairs is the focus of this analysis, and we thus present the PDF curves in the enlarged area on the distance axis for quantitative analyses.

Figure 1 shows the $G(r)$ s (PDFs) measured at 15 K for as-cast $\text{Zr}_{60}\text{Cu}_{35}\text{Al}_{10}$ BMG and its crystallized counterpart, where r is the distance of atoms away from a central atom.

$$G(r) = 4\pi r \rho_0 [g(r) - 1] = \frac{2}{\pi} \int [S(Q) - 1] \sin(Qr) Q dQ \quad (1)$$

Where $Q = 4\pi \sin(\theta)/\lambda$, λ is the neutron wavelength.

With $r > 3.27$ Å, the light blue color shadowed area indicates that more atom pairs have longer bonding lengths in the $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ BMG, as compared with those in its crystallized counterpart structure. They should be associated with interconnecting pairs and free volumes. The atomic radius is 1.62 Å for Zr, 1.28 Å for Cu and 1.43 Å for Al, and the characteristic atom pair distances can be estimated by these atomic radius as shown in Fig. 1. The Zr-Zr has the largest atom pair distances since Zr is the largest atom in size. The nearest Zr-Zr pairs in the crystallized structure end at the intersection of the dotted horizontal line and the crystallized PDF curve in Fig. 1, which is about 3.4 Å. The tangent line (a dotted line) as shown in the Fig. 1 intersects with the horizontal line, which is marked as C at $r = 3.33$ Å (the tangent line intersects the horizontal axis in Fig. 2 is also at $r = 3.33$ Å). Beyond 3.4 Å, no Zr-Zr

nearest neighbor pairs exists within the crystallized crystals. When $3.33 < r < 3.4 \text{ \AA}$, the possibility for the nearest neighbor atoms is very small because of the normal distribution of the PDF. Thus the point C can be considered as the starting point for the i-zone. The Zr-Zr has the pair distance with the characteristic value of $3.24 \text{ \AA}$. Note that the atomic distances of $3.33 \text{ \AA}$ and $3.4 \text{ \AA}$ are 2.8% and ~5% greater than the $3.24 \text{ \AA}$, respectively. Deducing the concept, the initiating atom pair distance for i-zone can be defined as that they are at least 2.8% greater than that calculated from their characteristic atomic radius.

The number of nearest atom pairs can be calculated by the following equation:

$$N = \int_{r_1}^{r_2} R(r) dr \quad (2)$$

$R(r)$ is the radial distribution function (RDF), $R(r) = 4\pi r^2 \rho_0 g(r) = rG(r) + 4\pi r^2 \rho_0$, The quantity of $R(r)dr$ gives the number of atoms in an annulus of thickness, dr , at a distance, r , from another atom.

Further investigating the RDF as shown in Fig. 2, about 4% (N/N_{total}) of the nearest neighbor atoms within the range of $3.33 \text{ \AA} < r < 3.55 \text{ \AA}$ still remains in the completely crystallized samples (it is a polycrystal structure, which contains grain boundaries between crystals), and when $r > 3.55 \text{ \AA}$, there are no nearest neighbor atoms. On the contrary, there are nearest neighbor atoms existing in the metallic glass when $r > 3.55 \text{ \AA}$. The free volume is a very important concept in metallic glasses [10, 11], and does not exist in the fully crystallized structures of metallic glasses. Therefore, it is reasonable to consider that the nearest neighbor atoms in the

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5 amorphous structure form free volumes when $r > 3.55 \text{ \AA}$. The $r = 3.55 \text{ \AA}$ is 9.6 %
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7 larger than $3.24 \text{ \AA}$ of the characteristic distance of Zr-Zr, close to the 10% of the
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9 Lindemann's melting criterion [12]. Thus, free-volumes might be considered as
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11 liquid-like bonds. Deducing from the concept, the initiating distance of the nearest
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13 neighbor atoms for free volumes can be defined as that they are at least 9.6 % greater
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15 than the calculated one from their characteristic atomic radius.
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20 Based on the analyses above, the free-volume, i-zone and cluster in metallic
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22 glasses can be defined as (1) cluster: natural communities consist of strongly
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24 connected atoms, in which the bond distances of the nearest atoms equal to or shorter
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26 than those within the crystal grains in the crystallized counterpart. Clusters may not
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28 have crystal unit cell structures, can be called as MRO (medium range order); (2)
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30 i-zone: areas consists of weak bonded atoms that have the bond lengths of the nearest
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32 atoms compared to those in the crystal boundaries in its crystallized counterpart. It is
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34 similar to the crystal (grain) boundary in crystals. There are no crystals/grains, but
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36 clusters in metallic glasses, it is the reason why we use the concept of i-zone to
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38 describe the boundary-like area. The bond lengths in i-zone grow larger to form free
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40 volume network at glass transition temperature. The atoms weakly connected i-zone
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42 should be one of the most dominated factors on mechanical properties in metallic
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44 glasses. The initiating atom pair distance for i-zone can be defined as that they are at
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46 least 2.8% greater than that calculated from their characteristic atomic radius based on
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48 our data showed above; (3) free volume: areas consists of the weakest bonded atoms
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50 that have the bond distances of the nearest atoms longer than those existed in its
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5 crystallized counterpart. Free-volumes do not exist in its crystallized counterpart, it
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7 can be considered as supercooled-liquid-like area. It is also one of the most important
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9 factor in metallic glasses. The initiating distance of the nearest neighbor atoms for
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11 free volumes can be defined as that they are at least 9.6 % greater than that the
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13 calculated one from their characteristic atomic radius as we investigated above.
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17 Based on the definitions and previous studies, we draw a diagram of the model for
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19 metallic glasses as shown in Fig. 3. The black solid circles A, B and C, as well as the blue solid A1,
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21 B1 and C1 represent tight-bonded clusters, and the i-zones are shown as the blue solid lines.
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23 Among these clusters, the longer bond forms free volumes, as indicated by the red dash lines. The
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25 bond lengths of atoms between the clusters becomes significantly dilated as they gain energy,
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27 resulting in the formation of additional free volumes when temperature is above T_g . The glass
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29 enters the supercooled liquid state when the clusters are surrounded by a network of free volumes
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31 as shown in Fig. 3(b). From this illustration, we can have an inference that the i-zones and
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33 free-volumes play a key role in the strength and deformation mechanisms above and below T_g .
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35 The i-zones keep the clusters connected to each other at $T < T_g$, resulting in a high yield strength.
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37 The i-zones are “dissolved” into free-volume network at $T > T_g$, and the solid-like clusters move
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39 or rotate easily in the liquid-like free-volume matrix, resulting in homogeneous deformation at low
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41 applied stresses. Since only transitional bonds i-zones break up into free volume, only small
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43 energy absorption is involved during the glass transition at T_g .
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54 With these definitions and calculations based on PDFs and RDFs obtained
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56 from neutron scattering at 15K, the quantitative information for clusters, i-zones and
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5 free volumes can be calculated. The free volumes are estimated to be ~7%, the i-zones
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7 are ~15%, and the rest is the atomic cluster region in the as-cast $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ BMG.
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10 In conclusion, the high intensity neutron scattering technology enable us to
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12 quantitatively determine the interconnecting-zone concept based on atom bonding
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14 lengths from the PDF studies of a metallic glass and its crystallized counterparts.
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16 These definitions can helps us to qualitatively analyze local atomic packing in
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18 amorphous alloys.
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Fig. 1. The PDFs of $G(r)$ vs. r for the nearest atom pairs measured at 15 K on HRNS for the as-cast and crystallized $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ BMG. The vertical straight lines indicate the atom pair position based on their atomic radius.

Fig. 2. The RDFs of $R(r)$ vs. r for the nearest atom pairs measured at 15 K on HRNS for the as-cast and crystallized $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ BMG.

Fig. 3. (a) and (b), a schematic showing atomic clusters, i-zones and free volumes below and above T_g .

—●— *I*-zone connection
- - - *FV* connection