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Quantitatively defining interconnecting-zone in metallic glasses

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ABSTRACT

The interconnecting-zone(I-zone) concept is important for understanding the nature of metallic glasses, especially the thermal-physical property change around the glass transition. The analyses of the pair-distribution function measured at 15 K using high intensity neutron source on the as-cast amorphous state and its crystallized counterpart of a Zr–Cu–Al alloy provided solid evidence on the I-zone concept. Together with the *ab*-initio molecular-dynamics simulations, it enables us to quantitatively describe this I-zone concept. The nearest atom pairs in the I-zone were also analyzed.

1. Introduction

Since the amorphous alloy was synthesized in the late 1950s [1], the unique physical, chemical and mechanical properties have been greatly attracting the interest of scientists [2–5]. The dense random packing of hard spheres model, which is the first model to be widely applied to metallic glasses, was initiated by Bernal in the late 1950s to try to elucidate the geometrical nature of the liquid state [6–8]. The basic concept in this model has been in the dominated position on the follow-up studies for several decades. It helped scientists to understand the amorphous structure in the early and preliminary stage. Entering 21st century, the overlapping face-centered cubic (f.c.c) packing model was proposed [9], and furthermore, the quasi-equivalent cluster model was introduced based on short to medium range order studies [10]. These geometric studies have made improvements for further understanding atomic packing, especially in clusters for metallic glasses.

Most recently, from different approach of atomic bonding length perspective, the authors have proposed an atomic structural model, the interconnected tight-bond containing cluster model, for metallic glasses with introducing the interconnecting zone (I-zone) concept [11,12]. This model essentially consists of three concepts: clusters, free-volume regions and I-zones, and the model is capable of qualitatively explaining thermal-physical and mechanical-property changes of metallic glasses around the T_g. Such as what happens on the glass transition, why the small amount of the heat release leads to the solid to supercooled liquid transition, and corresponded mechanical property changes, including the dramatic decrease in strength and essentially increase in plasticity – from limited plastic deformation to super plastic deformation. Similar to the case where a lack of quantitative specification for the medium-range-order concept, as compared with the short-range-order and long-range-order concepts, the I-zone concept is also a fuzzy one, even though it has been defined as the bonding length between the cluster – tight-bonded atoms, and the free volume – loose-bonded atoms. Then, we have to ask how to quantitatively understand the I-zone? How tight is the cluster-type bond, and how loose is the free volume type bond? Through the use of the pair distribution function (PDF) analyses and *ab*-inito molecular dynamics (*ab-inito MD*) simulations, we intend to answer these questions in the current study.

2. Experiment

$Zr_{55}Cu_{35}Al_{10}$ (at. %) bulk metallic glass (BMG) samples with 3 mm in diameter and more than 75 mm long were produced by arc melting in a pre-vacuumedand argon-gas refilled protection environment and subsequently suction casting into a copper mold. The

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as-cast and fully crystallized (annealed for 1.8 ks at 1000 K) specimens were prepared for neutron-diffraction PDF measurements. The $CuZr_2$ structure was identified as the primary phase in the crystallized sample by X-ray diffraction analysis.

Neutron scattering data for the PDF analyses was collected on the Neutron Powder Diffractometer (NPDF), a high-resolution, total-scattering, powder diffractometer at the Manuel J. Lujan Neutron Scattering Center at the Los Alamos National Laboratory, USA. The powder diffraction data, $I(Q)$, were collected over a wide range of Q (up to 51.1 $Å^{-1}$, $Q = 4\pi^*\sin(\theta)/\lambda$, λ is the neutron wavelength) at cryogenic temperature of 15 K. Subsequently, the PDF, $G(r)$, was computed using the program PDFGETN [13] via the Fourier transform of $Q[S(Q)-1]$, PDFs, $G(r)$ vs r, where r is the distance between pairs in the as-cast BMG and its crystallized $Zr_{55}Cu_{35}Al_{10}$.

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

The simulations were performed using the Vienna ab-initio MD simulation [14] package (VASP). The input structure contains 128 atoms in a cubic box with the composition of the $Zr_{55}Cu_{35}Al_{10}$.

3. Results and discussion

Fig. 1(a) shows the PDF $g(r)$ converted from the high intensity neutron scattering data measured at 15 K for as-cast $Zr_{60}Cu_{35}Al_{10}$ samples. Fig. 1(b) presents the $S(Q)$ vs. Q curve to show the confirmation of the amorphous state. The investigation on the nearest atom pairs is the focus of this analysis, and their PDF trace is shown in Fig. 1(c). It is clear to see that the broad peak covering the range $r = 2.2$–3.8 Å and it separates itself into at least two broad peaks.

The measurements were conducted at a cryogenic temperature of 15 K for the neutron-diffraction data collecting because this temperature minimizes the thermal induced atom vibration effect and atomic distance in the PDF can be better measured. The results obtained from the cryogenic temperature would not be affected by the increase of temperature from 15 K to room temperature.

The lack of the unit cell in metallic glasses results an overall random atomic distribution, trending to form a normal distributed PDF peak; the existence of the local atomic clusters inclines to split it to multi-peaks for the nearest atom pairs. The atomic radius is 1.62 for Zr, 1.28 for Cu and 1.43 Å for Al. The characteristic atom pair distances based on their atomic radius in Zr–Cu–Al system are shown in Fig. 1(c). They are in the order of the Cu–Cu, Cu–Al, Al–Al, Zr–Cu, Zr–Al and Zr–Zr pairs. The atom pair distances are quite close to each other. As a result, as shown in Fig. 1, the nearest atom pairs in clusters, I-zones and free volumes generate an overlapped smooth experimental PDF curve with no gaps or steps for the inclined separation in the glassy state. This leads to the I-zone to be a fuzzy concept and no any specific boundaries among the clusters, interconnecting pairs and free volumes can be simply identified in the experimental PDF curve.

For crystal structures, they have unit cells with their theoretical lattice constants, which determine the peaks in their PDF curves. Since thermal effect makes atoms vibrating around their ideal position and broadens the atomic pair peaks in their PDF curves, the peak widths thus contain thermal, zero-point motion of atoms and any static displacement of the atoms away from ideal lattice sites (i.e., the atom-pair probability distribution) [15]. The thermal effect can be seen clearly in Fig. 2(a), in which it shows the PDFs measured at 298 K and 15 K. The influences of the thermal vibration on PDFs should be not significant at 15 K, in comparison to that at room

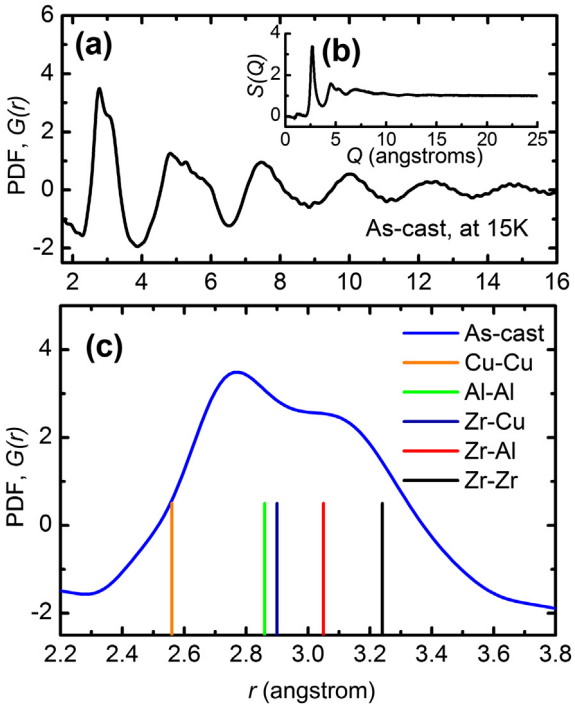

Fig. 1. (a) $G(r)$. vs. r and (b) $S(Q)$ vs. Q for the $Zr_{55}Cu_{35}Al$ as-cast rods, data collected from high intensity neutron course at 15 K. (c) PDF plot enlarged from (a) for nearest atom pairs (smooth curve in blue color); The vertical strait lines indicate the atom pair position based on their atomic radius. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

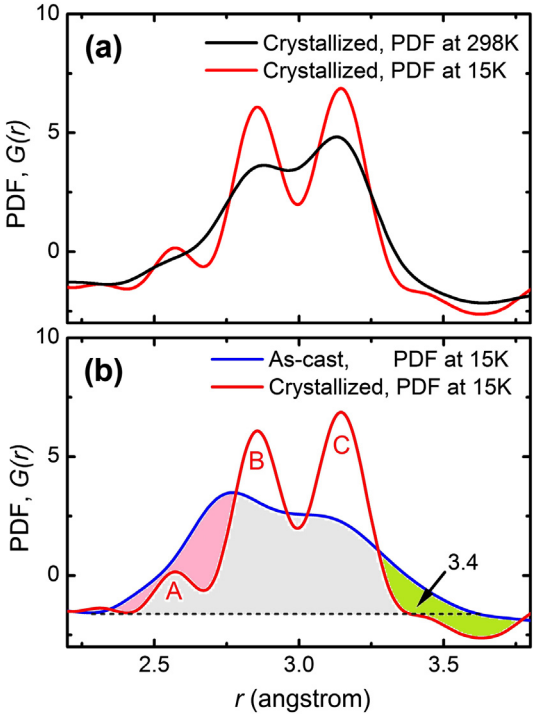

Fig. 2. (a) Comparison of PDFs measured at 298 and 15 K on NPDF (high intensity neutron scattering) for crystallized (for 1.8 ks at 1000 K) $Zr_{55}Cu_{35}Al_{10}$ BMG rods. (b) The PDFs measured at 15 K on NPDF for as-cast and the crystallized BMG. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).