Unveiling the Formation Mechanism of Medium Range Ordering in Zr-based Bulk Metallic Glasses Using Angular Correlation Analysis of 4D-STEM

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Bulk metallic glasses (BMGs) have a unique set of exceptional properties, such as extremely high strength, elastic energy, and fracture toughness, which have been progressively more utilized in various applications. However, the fundamental understanding of the varying mechanical properties exhibited by different compositions is still largely missing. Investigating the structure of BMGs in terms of structural heterogeneity, or medium-range ordering (MRO), and correlating it to the deformation behavior has been very challenging. Recently, 4D-STEM has evolved the way we perform what had previously been known as fluctuation microscopy [1], and we have been able to successfully employ it to extract the hidden MRO symmetry information by means of angular correlation (AC) analysis conducted on 4D-STEM nanodiffraction patterns (Fig. 1a) [2, 3]. This enables us to acquire vital insights into the origin of the structural heterogeneity of amorphous materials and its relationship to the observed properties.

Our current experimental approach involves the Fourier transformation (FT) analysis of the AC data from 4D-STEM and real mapping of the power spectrum (FT^2) of the AC to reveal the type, size, and distribution of MRO and how it constitutes nanoscale heterogeneity in BMGs. AC examines the correlation among the intensity of pixels along the azimuthal angle (φ) in each nanodiffraction pattern (Fig. 1a). Next, the FT analysis from AC data uncovers a sinusoidal function characterized by a frequency of n, which represents the rotational symmetry of the MRO (i.e., n-fold symmetry). After that, the reconstructed images using the n-fold peaks in real space reveal how the structural heterogeneity is present (with the distribution of MRO) at the nanometer scale. The hotspots in the reconstructed images, which indicate the regions where the strongly diffracted electrons from MRO are concentrated, provide information on MRO, including its size, distribution, and volume fraction. Therefore, the results can provide new, in-depth details about the nanoscale heterogeneity, how they change over different compositions, and correlate with important properties.

We present the results of three Zr-based compositions: $Zr_{50}Cu_{50}$, $Zr_{50}Cu_{40}Al_{10}$, and $Zr_{65}Cu_{25}Al_{10}$ (Fig. 1b). These 3 compositions have shown substantial changes in properties, such as ductility (Fig. 1c), but the origin of such dramatic change has been unknown. The AC analysis reveals noticeable changes in structural symmetry depending on the composition (Figs. 2a, 2e, and 2i). $Zr_{50}Cu_{50}$ shows Cu FCC (111) like MRO, involving a relatively high population with sizes of 1 to 3 nm (Figs. 2b and 2c). This indicates that, when quenched from the liquid, this composition forms Cu-rich clusters in the glassy matrix (Fig. 2d). On the other hand, $Zr_{50}Cu_{40}Al_{10}$ shows a similar type of MRO but with bigger sizes, leading to fewer MROs (Figs. 2e to 2h). The strong affinity between Zr and Al dictated by the negative heat of mixing [4] leads to the formation of bigger Cu clusters in the matrix than a binary composition. However, these clusters disappear upon annealing, indicating that they are not nanocrystal nuclei. At an even higher Zr content, $Zr_{65}Cu_{25}Al_{10}$, a different type of MRO similar to HCP Zr (Figs. 2i to 2l), emerges. In this case, the population of the MRO is high, but their sizes are smaller since the Zr atoms are already big and the clusters cannot occupy a larger volume. Overall, there is a noticeable correlation between the observed MRO structure and compression test results (Fig. 1c). A very fine distribution of MRO in the structure appears to lead to more ductile behavior, which we can correlate to our previous results from the mesoscale deformation simulation [3] that revealed how the size and distribution of MRO affect the overall distribution of shear bands and eventually dictate the ductility of the BMGs [5].

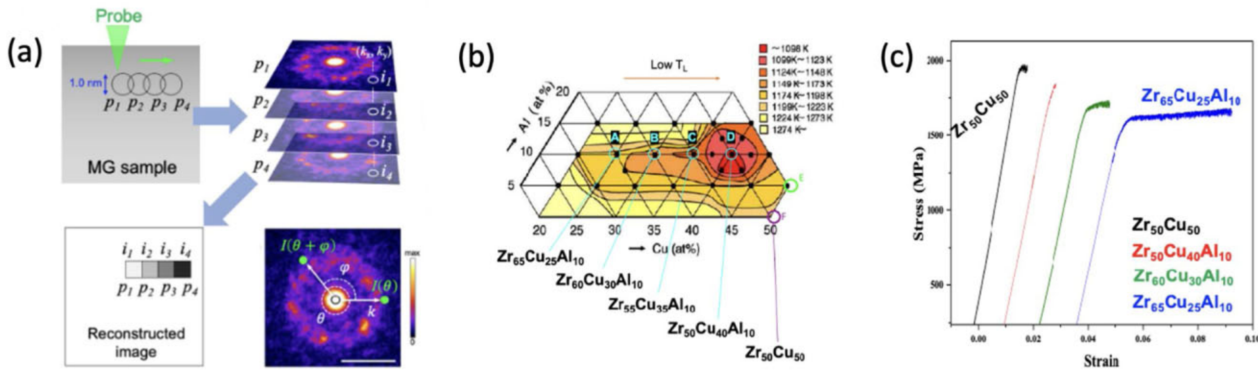

Fig. 1. (a) Schematic of 4D-STEM data acquisition and AC analysis. (b) Phase diagram indicating the compositions of BMGs. (c) Compression test results for BMGs under study.

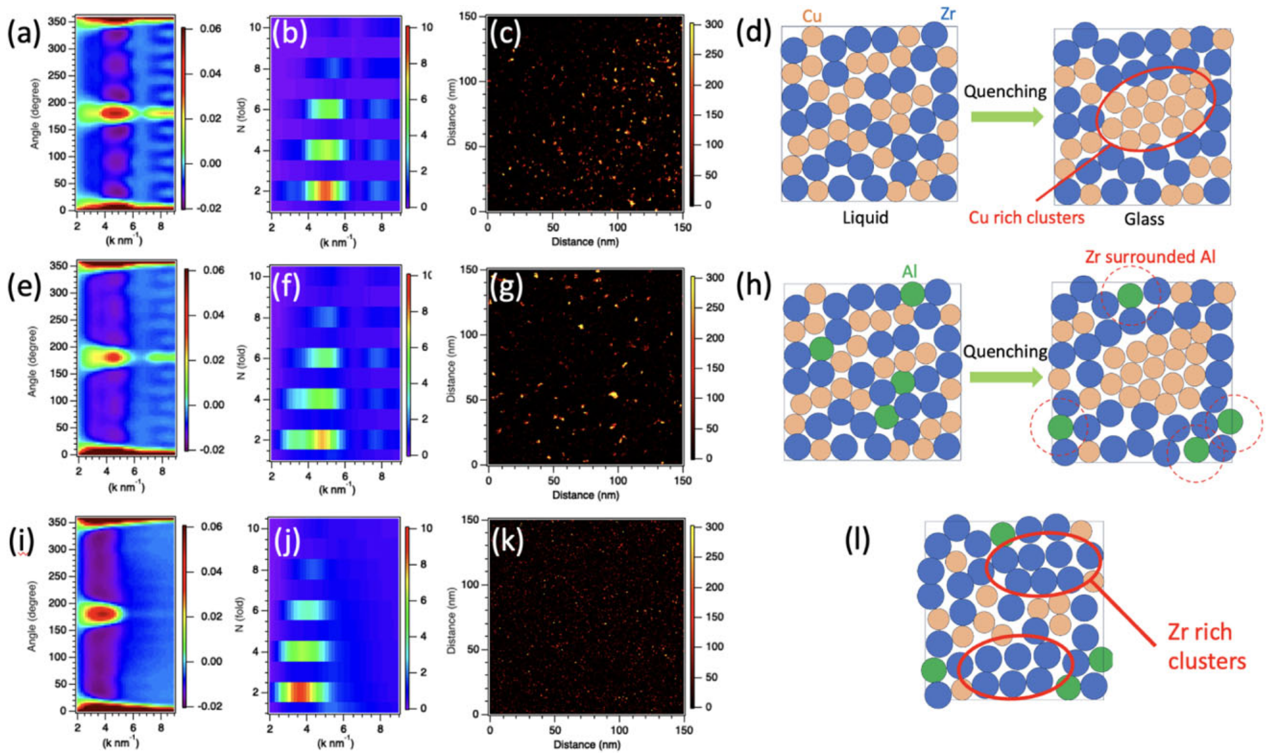

Fig. 2. (a) Averaged AC, (b) Power spectrum, (c) Real space MRO map of n = 2, and (d) Schematic depicting the MRO formation mechanism for $Zr_{50}Cu_{50}$. (e-h) Same for $Zr_{50}Cu_{40}Al_{10}$. (i-l) Same for $Zr_{65}Cu_{25}Al_{10}$.

References

1. P Voyles and J Hwang, *Characterization of Materials* (2012), p. 1.
2. S Im *et al.*, *Ultramicroscopy* **195** (2018), p. 189.
3. S Im *et al.*, *Physical Review Materials* **5** (2021).
4. A Takeuchi *et al.*, *MATERIALS TRANSACTIONS* **46**, (2005), p. 2817.

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