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ORIGINAL REPORT



Chemical variation induced nanoscale spatial heterogeneity in metallic glasses

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ABSTRACT

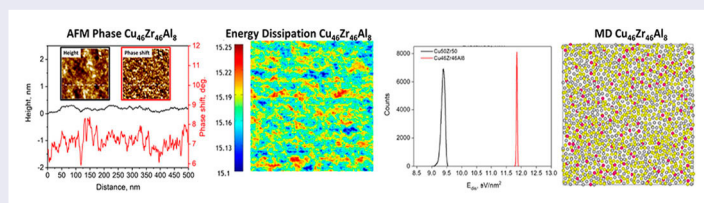
Metallic glasses possess amorphous structures with inherent heterogeneity at the nanoscale. A combined experimental and modeling investigation to elucidate the chemical effect on such nanoscale heterogeneity in a Cu-Zr-Al metallic glass system is conducted. By using the dynamic atomic force microscopy, we reveal a reduction of the nanoscale spatial heterogeneity in the local viscoelastic response after introducing Al into the Cu₅₀Zr₅₀ metallic glass. The change of such nanoscale heterogeneity can be contributed to the variation of local atomic structures. The addition of Al increases the population of the icosahedral short-range ordered clusters, thus reducing the structural heterogeneity at the nanoscale.

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KEYWORDS

Metallic glass; spatial heterogeneity; chemical variation; dynamic force microscopy; nanoscale



IMPACT STATEMENT

This paper provides a combination between the nanoscale experimental and theoretical understanding of the chemical variation induced spatial heterogeneity in CuZrAl metallic glass and their impacts on the mechanical properties.

1. Introduction

Metallic glasses' (MGs') response to external excitation can vary drastically with both alloy composition and processing conditions, implying the existence of complex small-scale structures in the deceptively homogeneous amorphous system. Extensive experiments and computational simulations have demonstrated that the monolithic MGs exhibit inherent heterogeneity, which can have strong correlations with the glass dynamics and mechanical properties. [1,2]

At the atomic scale, the structure of the MGs is inherently heterogeneous, possessing a statistical distribution of different atomic cluster configurations, such as icosahedral short-range order and other Kasper polyhedra.[3] Several theoretical models, such as free volume,[4] shear transformation zone, [5] atomic level stresses, [6] have been proposed to describe the heterogeneity in local

inelastic responses upon external stimulus as a consequence of structural heterogeneity. The experimental evidence of the nanoscale heterogeneity has also been detected by both advanced electron diffraction characterizations [7–9] and dynamic mechanical measurements. [2,9,10] Particularly, using amplitude modulation dynamic atomic force microscopy (AM-AFM), the phase shift and energy dissipation of Zr₅₅Cu₃₀Ni₅Al₁₀ MG thin film at the nanoscale have been recorded, resolving a characteristic correlation length of ~ 2.5 nm. [2] By applying dynamic modulus mapping on a nanoindentation platform, a complex elastic microstructure consisting of interpenetrating locally stiff and compliant regions in a Zr-based bulk metallic glass has been identified, which has the characteristic feature lengths on the order of 100 nm. [10] The diversity of the characteristic lengths associated with nanoscale heterogeneity, from atomic

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structures at several nanometers [2,3] to potential amorphous phase separation at several hundred nanometers, [10] suggests the complicated underlying mechanisms that could control the nanoscale heterogeneity in MGs.

On the other hand, the MG properties can be very sensitive to the minor change of chemical composition. [11] For instance, both yield stress [12] and the glass formability [13] of CuZr MGs can be dramatically improved with minor Al addition. Cheng *et al.* [11] employed the ab initio MD simulations to evaluate the effect of Al, discovering a large jump in the fraction of icosahedral clusters and enhanced fivefold symmetry upon Al alloying. The change of chemical composition can remarkably tune the local atomic structures of monolithic MGs. And yet the chemical effect on the nanoscale heterogeneity remains unexplored, which could link to the dramatic variation of MG performance at large scales.

In this work, we focus on providing an understanding of the chemical composition dependent nanoscale heterogeneity of MGs via a combined experimental and modeling approach. The AM-AFM has been employed to characterize the nanoscale mechanical heterogeneity of Cu₅₀Zr₅₀ and Cu₄₆Zr₄₆Al₈ (at. %) MG thin films; while the MD simulations are applied to elucidate the inherent chemical effect on such heterogeneity.

2. Experimental methods

The 2 μm thick MG films are prepared by ion beam assisted deposition with Cu₅₀Zr₅₀ and Cu₄₆Zr₄₆Al₈ (at. %) as the target, respectively. The base pressure of the chamber is better than 2×10^{-4} Pa, the depositing argon pressure is 2.4×10^{-2} Pa. The X-ray diffraction is performed in a Bruker D8 Discover X-ray diffractometer with Co K α radiation ($\lambda = 1.78896$ Å). The thermal analysis is performed in a differential scanning calorimeter (Perkin-Elmer DSC 8000) at a heating rate of 20 K/min. The AM-AFM is conducted on a Park System (XE-70) in an ambient environment (i.e., N₂ protection to prevent surface oxidization). To achieve ultrahigh spatial resolution, a sharp diamond-like extra tip with a ~ 1 nm apex (MMHiRes-C15 coated with Cr/Au) was used for a high spatial resolution with the spring constant, k of 37 Nm⁻¹ and a resonance frequency of 300 kHz. [14] The associated energy dissipation, E_{dis} was calculated as [15]

$$E_{\text{dis}} = \frac{\pi k A_{\text{sp}} A_0}{Q} \left[\sin \left(\frac{\pi}{2} - \Delta\varphi \right) - \frac{A_{\text{sp}}}{A_0} \frac{\omega}{\omega_0} \right] \quad (1)$$

where k is the spring constant of the AFM cantilever; A_{sp} and A_0 represent, respectively, the set-point and free amplitude; Q is the quality factor; $\Delta\varphi$ is the local phase

shift measured by the AM-AFM, and ω and ω_0 represent the respective driving and resonant frequency. [16] To prevent the surface oxidization during the AFM measurement, we limited the film ambient exposure time with dry N₂ filled in the AFM enclosure and store the sample in high vacuum container before and after the measurement.

The MD simulations were employed to produce Cu₅₀Zr₅₀ and Cu₄₆Zr₄₆Al₈ MGs via the optimized embedded atom method (EAM) potential. [11,17,18]. Those samples with 31,250 atoms were equilibrated at 2000 K and then quenched to 300 K with the various cooling rates, including 10⁹, 10¹⁰ and 10¹¹ K/s, under Nose-Hoover thermostat. The size of the prepared Cu₅₀Zr₅₀ and Cu₄₆Zr₄₆Al₈ MG samples were around 8.18 nm $\times$ 8.18 nm $\times$ 8.18 nm and 8.15 nm $\times$ 8.15 nm $\times$ 8.15 nm, respectively. Periodic boundary condition was applied, and the external pressure was maintained around zero during the whole process of cooling. Geometrical analysis of the atomic configurations, using the Voronoi tessellation method, yields information about the short-range order polyhedra. An autocorrelation function was used to characterize the spatial distribution of icosahedral/non-icosahedral atoms in those MGs. [18]

3. Results and discussions

The amorphous state of Cu₅₀Zr₅₀ and Cu₄₆Zr₄₆Al₈ MG films has been confirmed by the X-ray diffraction spectra without crystalline peaks, as shown in Figure 1(a). Figure 1(b) illustrates that the glass transition temperature increases with additives of Al, suggesting that Cu₄₆Zr₄₆Al₈ has a more stable energy state when compared with Cu₅₀Zr₅₀. [13] The working principle of AM-AFM is shown in Figure 1(c), when the tip approaches the sample surface, the resonant frequency is shifted due to the repulsive force between the atoms of the tip and the atoms on the sample surface. Figure 1(d) shows the surface height and phase shift evolutions on the same horizontal path (the topography and phase images collected from Cu₅₀Zr₅₀ are shown in the inset of Figure 1(d)), demonstrating that our phase shift results are decoupled from the surface height fluctuation (less than 1 nm).

Surface topography and phase shift are simultaneously recorded during the AM-AFM scanning, and the energy dissipation is calculated based on the obtained phase shift and the instrumental parameters according to **Equation 1**. The atomic force microscopy topography images are presented in Figure 2(a,b). The surface root-mean-square (RMS) roughness for the Cu₅₀Zr₅₀ and Cu₄₆Zr₄₆Al₈ is 0.94 and 0.79 nm, respectively, confirming an atomically smooth surface. Figure 2(c) shows the height profiles of Cu₅₀Zr₅₀ and Cu₄₆Zr₄₆Al₈ MGs,

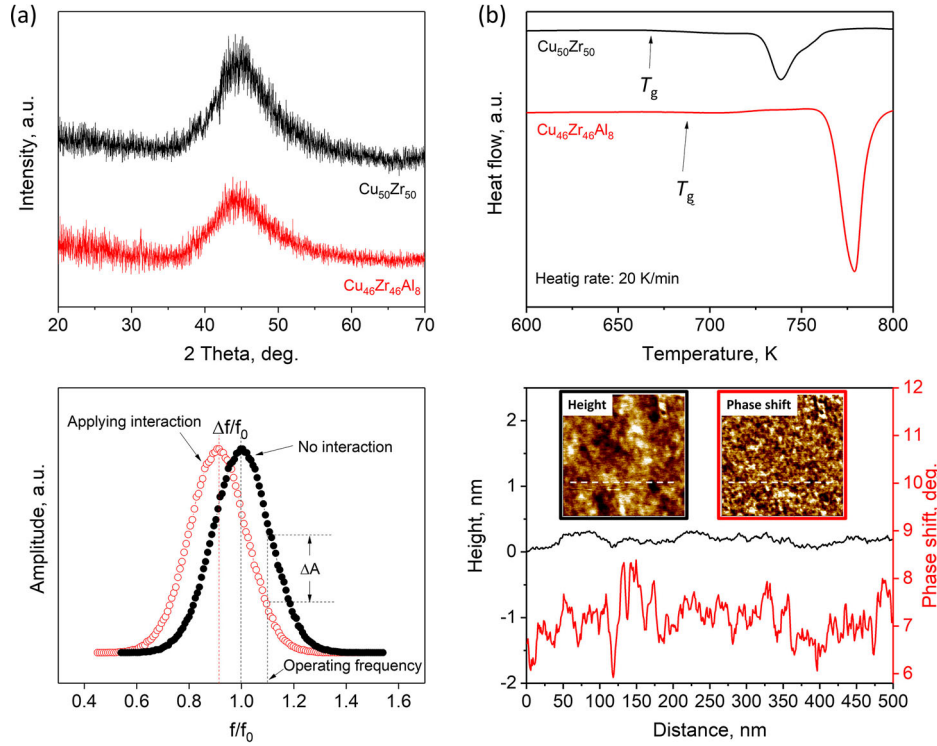


Figure 1. (a) XRD spectra, (b) DSC curves of MG films with the indication of the glass transition temperature. (c) AM-AFM working principle, and (d) the height and phase shift profiles taken from the same region of the $\text{Cu}_{50}\text{Zr}_{50}$ MG thin film shown in the inset of the height and phase shift AM-AFM images with indexed by the white dashed line.

indicating a height variation is less than 0.5 nm, around 1–2 atomic layers on average. Figure 2(d,e) show the images of the phase shift of $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ MGs, respectively. The ‘isolated island’ of large (in red) and small (in blue) phase shift regions capture the nanoscale spatial heterogeneity in viscoelastic responses. Figure 2(f) shows the representative phase shift line profiles plotted from $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ MGs, respectively. The peak distances of $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ are larger than those of $\text{Cu}_{50}\text{Zr}_{50}$, indicating that $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ MG has a finer aggregation size than that of $\text{Cu}_{50}\text{Zr}_{50}$, and the addition of Al has reduced the phase spatial heterogeneity (quantitative analysis of the spatial correlation of the phase shift will be present later). No apparent correlation between the topography and phase shift are observed when comparing Figure 2(c) and Figure 2(f), indicating the influence of the topography can be ruled out from the phase shift images.

Figure 2(g) and 2(h) plot the calculated energy dissipation maps for $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ MGs, respectively. The high energy dissipation (red) regions result from the more pronounced inelastic response upon tip stimulation, reflecting local loose-packing glassy phases; whereas the low energy dissipation (blue) regions possess more instantaneous elastic response, implying local condensed-packing glassy phases. The stress exerted by the AFM tip on the surface can be proved within the

elastic deformation regime of the MGs. The estimated value of the exerted force F is close to 0.3 mN according to the tip loading geometry. [14] Figure 2(i) reveals that the energy dissipations of $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ thin films MGs exhibit a Gaussian-type distribution with the average values of 9.37 eV/nm² and 11.85 eV/nm², respectively; and standard deviation of 0.065 eV for $\text{Cu}_{50}\text{Zr}_{50}$, and 0.016 eV for $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$. The increased energy dissipation with the additive of Al implies an enhancement of the viscoelastic response and thus deformability of the MGs.

To quantitatively study the nanoscale spatial heterogeneity, the spatial correlation length, ξ , of the phase shift images are computed based on a spatial auto-correlation function [19] given as:

$$P(r) = \sum_{r_0, r_0+r} (\Delta\varphi_{r_0} - \Delta\varphi_{r_0+r})^2 \quad (2)$$

where $\Delta\varphi_{r_0}$ is the phase shift of a reference position r_0 ; $\Delta\varphi_{r_0+r}$ is the phase shift at the position which has a distance of r from the reference. The calculated auto-correlation function can be fitted into an exponential function with respect to distance,

$$P(r) = 2\sigma^2[1 - \exp(-(r/\xi)^{2\alpha})] \quad (3)$$

where σ is the standard deviation of phase shift values, α is the phase shift exponent, and ξ is the correlation

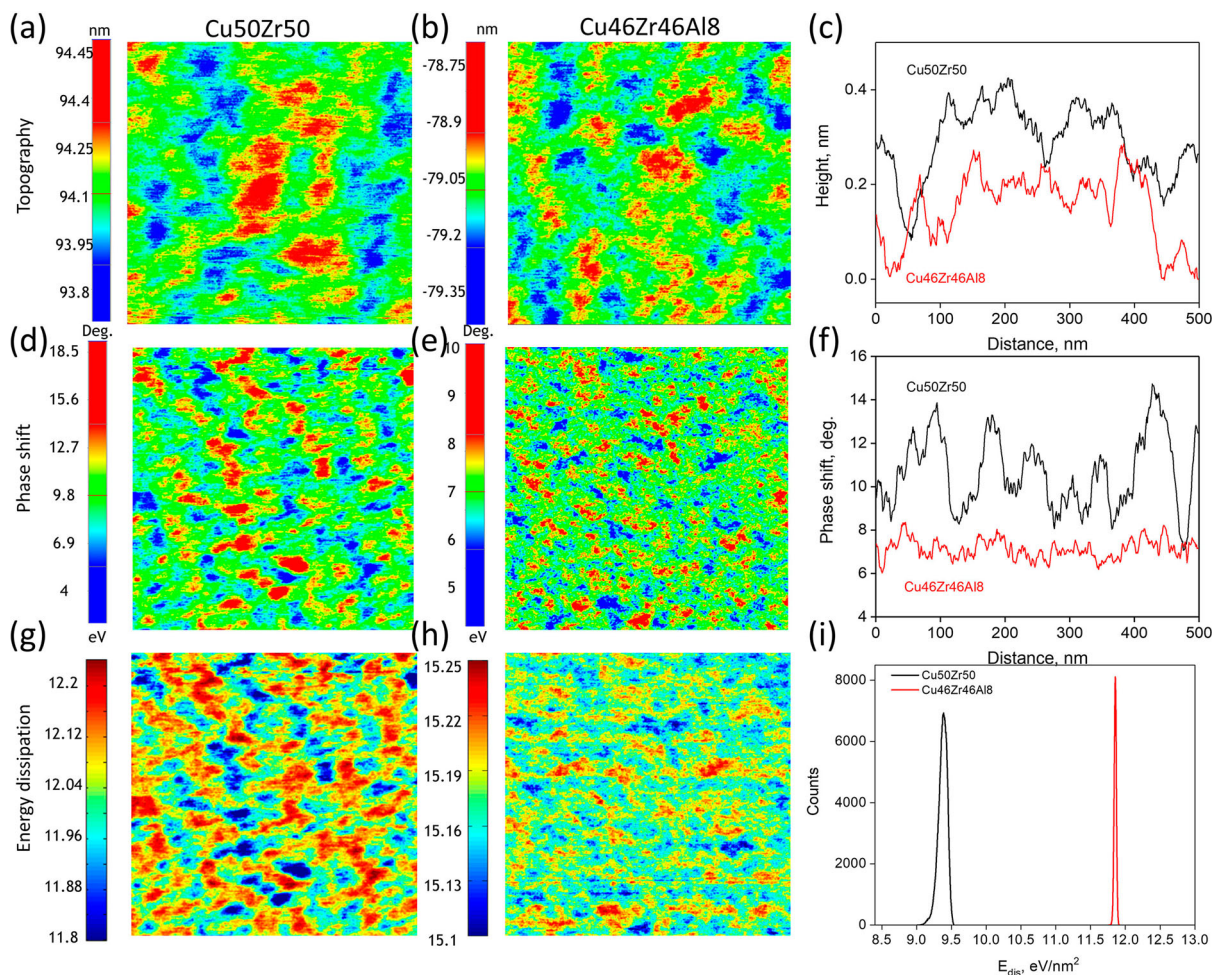


Figure 2. (a)–(b) the height image, (c) height profile, (d)–(e) the phase shift images and (f) phase shift profiles taken from Cu₅₀Zr₅₀ and Cu₄₆Zr₄₆Al₈ MGs, respectively, (g)–(h) energy dissipation images and (i) the Gaussian distribution of energy dissipation in Cu₅₀Zr₅₀ and Cu₄₆Zr₄₆Al₈ MGs, respectively. The AFM scanning dimension is 500 nm × 500 nm.

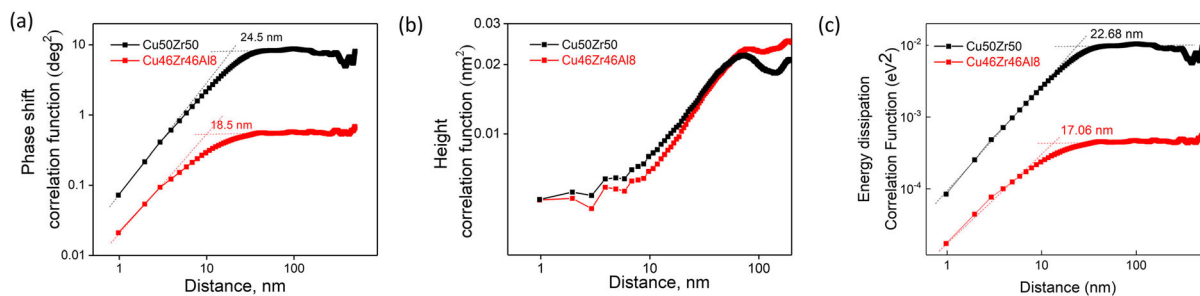


Figure 3. Autocorrelation functions of phase shift (a), surface topography (b), and energy dissipation (c) of the Cu₅₀Zr₅₀ and Cu₄₆Zr₄₆Al₈, calculated based on the phase shift, height, and energy dissipation images according to Equation 2.

length. As shown in Figure 3(a), the calculated correlation length of the phase shift is 24 nm for Cu₅₀Zr₅₀ and 18.5 nm for Cu₄₆Zr₄₆Al₈, respectively. Figure 3(b) displays the calculated spatial autocorrelation function of the height according to Equation (2) for the two films by using the height values at various AFM scanning locations. Both specimens exhibit atomic smooth surface, and no clear difference of the height correlation lengths

can be identified, confirming that the spatial heterogeneity of the phase shift measured by AM-AFM stems from the intrinsic inelastic material responses rather than topographic variation. Consistent with the trend of the phase shift, Cu₄₆Zr₄₆Al₈ exhibits a smaller correlation length (17.06 nm) than that of Cu₅₀Zr₅₀ (22.68 nm) in energy dissipation, as shown in Figure 3(c). The energy dissipation is directly related with the local

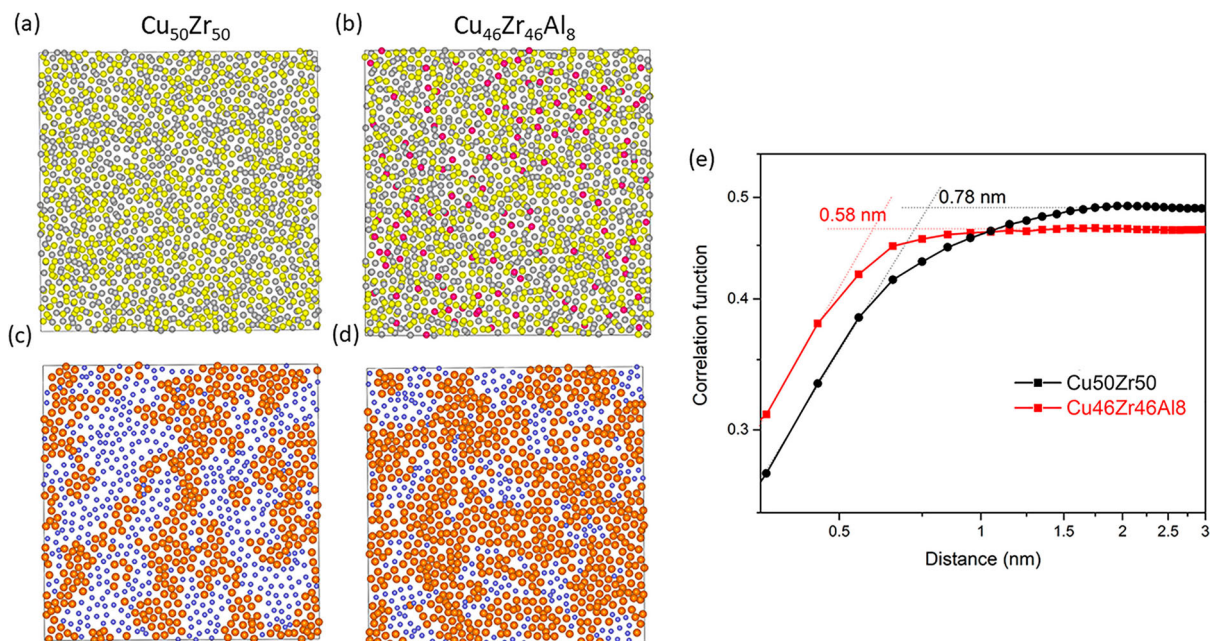


Figure 4. (a)-(b) Atomic configuration of the MD simulated $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ MGs, respectively; Zr atoms in grey, Cu atoms in yellow and Al atoms in pink (c-d) Atomic configurations of the icosahedral (in orange) and non-icosahedral atoms (in violet) in $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ MGs, respectively; (e) The calculated autocorrelation function of the heterogeneity of icosahedral order in the $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ the model MGs (the simulation method and interatomic potential used is detailed in [11]).

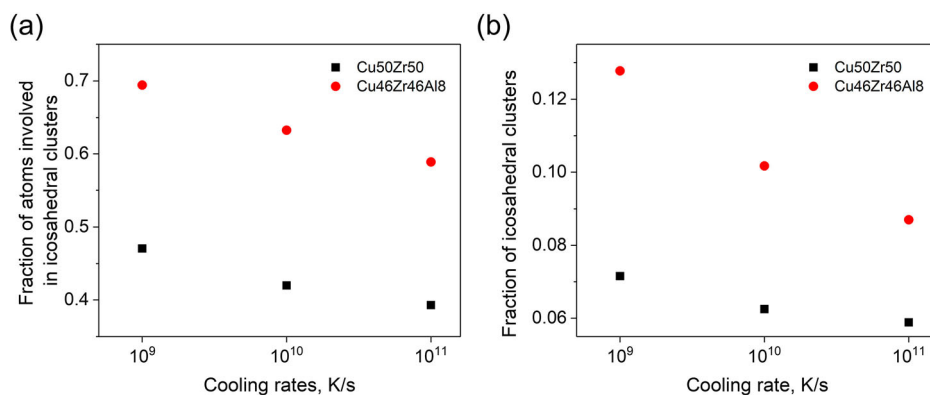


Figure 5. (a) Fraction of atoms involved in icosahedral and (b) fraction of icosahedral clusters in $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ MG thin films under various cooling rate.

viscoelastic response of the sample surface subject to dynamic loading imposed by the AFM tip, [20] reflecting the propensity of inelastic rearrangement of atomic clusters in response to excitations (e.g., STZ activities).

To ascertain whether the underlying mechanism of the reduced the spatial heterogeneity in $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ MG results from the change of the inherent local atomic packing, MD simulations have been performed in the model MGs with the same chemical compositions as experiments (their atomic configurations are as illustrated in Figure 4(a,b)). Figure 4(c,d) illustrate a 2D slice of the spatial distribution of the icosahedral order in $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ MGs. The adding of Al

atoms to the CuZr MG significantly increases the population of icosahedral clusters as shown in Figure 4(d). The icosahedral atoms (orange) tend to aggregate into larger clusters; while the non-icosahedral atoms (violet) get shrunk, making the $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ sample more homogeneous with a reduced correlation length of icosahedral clusters when compared to $\text{Cu}_{50}\text{Zr}_{50}$, as shown in Figure 4(e). The computed correlation lengths of the icosahedral atoms from MD samples are ~ 0.8 nm for $\text{Cu}_{50}\text{Zr}_{50}$ and 0.6 nm for $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$, respectively, much smaller than those measured in the AM-AFM experiments. This discrepancy is not surprising, and may be understood in the following aspects. The nanoscale

heterogeneity resolved by AFM is a dynamic response of the local stimulated regions, which can change upon the variation in the external loading conditions (e.g., the AFM tapping frequency). While the heterogeneity revealed from MD samples stems from inherent atomic packing configurations without dynamic information. In addition, the processing conditions in the MD simulations and the experiments are different. Notably, the MD samples are prepared by quenching from the liquid state under the cooling rates ranging from 10^9 to 10^{12} K/s. In contrast, the experimental MG thin films are fabricated by the sputtering process from the vapor phase depositing at a sputtering rate of 10^9 K/s. [21,22]. Furthermore, the correlation length measured from AFM reflects the surface dynamics of the MG thin films, which could differ from the film interior and the corresponding bulk state with the same chemical composition. [23,24]. Nevertheless, the effect of alloying Al on modulating the nanoscale heterogeneity remains unchanged, i.e., reducing the correlation length. And such effect is highly likely correlated with the inherent enhancement of icosahedral network after Al addition, promoting a uniform nanoscale amorphous structure.

To further confirm the effect of Al on the development of the icosahedral network, the population of the icosahedral clusters and the atoms involved in icosahedral clusters at different cooling rates are calculated from the MD samples. As shown in Figure 5(a,b), both the atoms involved in icosahedral clusters and the population of the icosahedral cluster are larger after adding Al for all the three cooling rates, implying a more homogeneous amorphous structure. It is noteworthy that for the same MG system, the spatial heterogeneity (i.e., correlation lengths) are different between experimental measurements and MD simulations. This could be due to the limitations of the MD simulations, such as the very small sample size and the uniform cooling condition, compared to the realist MG sample preparation. And yet we can clearly see that the intrinsic Al alloying effect on the structural heterogeneity by MD simulation, that exhibits the good consistency with our experimental observation. For instance, with the cooling rate decreasing, the fraction of icosahedral clusters increases for both MGs; but the icosahedral population of $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ MG increases much faster than that of $\text{Cu}_{50}\text{Zr}_{50}$, promoting a homogeneous network. Such inherent structural heterogeneity identified by MD has been indicated to relate with dynamical arrest upon glass transition, linking to the dynamic heterogeneity of glass response on nanoscale [25]. The structural origin of dynamical slowdown in the supercooled metallic liquids [26] and dynamic heterogeneity in the metallic glasses remain an open question, requiring further investigation.

4. Conclusions

In summary, we study the nanoscale heterogeneity in the Cu-Zr-Al MG system with a variation of chemical composition using both experiments and MD simulations. The AM-AFM provides direct evidence that the chemical composition can significantly affect the spatial heterogeneity in nanoscale inelastic response. The results of MD simulations support the experimental observation with the fact that the Al introduction into the Cu-Zr MGs can reduce the inherent structural heterogeneity due to the increased population of the icosahedral clusters and their connectivity. Such mechanisms that relate local atomic structures and their inelastic rearrangements due to the chemical variations may provide an understanding of the remarkable performance difference in the uniform monolithic MGs.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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