Structural homogeneity and mass density of bulk metallic glasses revealed by their rough surfaces and ultra-small angle neutron scattering (USANS)

Man-Ho Kim¹, Jin-Yoo Suh², Eric Fleury³, Su Gyeong Han¹ & Kyung Tae Hong⁴

The ultra-small angle neutron scattering (USANS) measures the microscale structure of heterogeneity and the scattering from rough surfaces with small scattering volumes can be neglected. But this is not true in amorphous alloys. The small angle scattering from such surfaces is not negligible, regardless of scattering volume. However, we demonstrate that the unwanted rough surfaces can be utilized to determine the homogeneity and mass density of amorphous metallic glasses using the USANS and surface neutron contrast matching technique. The power law scattering of the homogeneous Cu₅₀Zr₅₀ amorphous alloy disappeared under the surface contrast-matched environment, a mixture of hydrogenated/deuterated ethanol having low surface tension against the metallic alloys, indicating that the scattering originated not from its internal structure but from the rough surface. This confirms the structural homogeneity not only at the atomic level but also on a larger scale of micrometer. On the other hand, the crystallized Cu₅₀Zr₅₀ alloy showed strong power-law scattering under the matching environment due to the structural heterogeneity inside the alloy. This technique can apply to the bulk samples when the transmission is high enough not causing multiple scattering that is easily detected with USANS and when the surface roughness is dominant source of scattering.

Metallic alloys with robust glass forming ability, also known as metallic glasses, consist of amorphous structure that is free of heterogeneities like crystalline phase, grain boundaries, and dislocations. The structural homogeneity of metallic glasses is widely investigated at an atomic level using X-ray diffraction and transmission electron microscopy. In only a few cases, the small angle x-ray scatterings (SAXS) and small angle neutron scatterings (SANS) have been used to measure the heterogeneities at a nanometer level¹⁻¹⁰.

In addition to the well-known homogeneous nature of the amorphous metallic structure in the nanometer scale, spontaneous decomposition in larger scale, also known as phase separation, was also reported¹¹,¹². The molecular dynamics simulation showed density fluctuation (i.e., local structural fluctuation) on the atomic length scale in the quenched Cu₅₇Zr₄₃ alloy¹³. However, only limited information on the phase uniformity of metallic glasses is available in a wide range of length scales. In this context, we have questioned whether the homogeneity of metallic glasses confirmed at the atomic and nanometer levels can be sustained at a much larger scale, at least up to the micrometer scale. Ultra-small angle neutron scattering (USANS) enables us to measure the homogeneity and heterogeneity up to tens of micrometers. Due to the strong penetration power of neutrons into most alloys with the interaction of a neutron to nucleus, USANS and SANS are excellent tools to investigate the structure of thick samples over hundreds of micrometers or even thicker samples when the transmission is high enough not to cause multiple scattering, while SAXS may require the specimen to be thinned down to a few microns in materials...
with high atomic number due to the shallow penetration capability caused by the interaction of the electromagnetic waves with electrons that have a higher number density than nucleus.

Bulk metallic ribbons have inherent rough surface of which surface topology has been known to affect properties such as corrosion, friction, wear, and plastic deformation. For bulk samples in most alloys, the surface roughness can be less important in USANS and SANS measurements due to the smaller surface-to-volume ratio than SAXS. However, in amorphous materials like BMGs, scattering from the surface cannot be neglected even though the scattering volume is considerably less than that of bulk samples, since the internal homogeneous (i.e., no density and composition fluctuation) phase must not have any structures that cause scattering. In fact, Roth demonstrated that the Porod scattering (i.e., the scattering intensity decreases with a power of −4 against Q, representing a sharp interface of a structure) from SANS originated from the surface irregularities and oxide layers of pure polycrystalline metals. Rodmacq et al. showed the influence of surface conditions on the SANS profile of Pd₈₀Si₂₀ alloys by measuring specimens under different surface treatments: quenched, polished, and chemically etched. Therefore, it is likely that the rough surface causes the non-trivial surface scatterings which could lead to misinterpretation of SANS and USANS data as the homogeneous amorphous alloys have inner heterogeneity.

Thus, the surface roughness hinders us from determining the structural homogeneity of metallic glass structure. In addition, the evaluation of the mass density of an amorphous metallic glasses with the rough surface is another challenging task. For example, in the well-known Archimedes method, entrapped air bubbles can cause lower density when high surface tension liquids are used, or by the closed pores that liquids cannot be accessible. Also, if any internal heterogeneities are present, the measured density can be misunderstood as the density of the sample in a pure homogeneous state, unless homogeneities or heterogeneities are confirmed with other density measurement methods. In this study, however, we will show how the rough surface, which is not desired in most characterization methods, can be applied to determine the microscale homogeneity and the mass density of BMG alloys simultaneously using the unique contrast-matched USANS technique. For this purpose, USANS is more useful than SANS because only USANS can properly evaluate the typical micron-sized roughness. Also, USANS is less sensitive to incoherent backgrounds than SANS.

**Surface neutron contract-matching (SNCM) method**

Expected small angle scatterings from an amorphous alloy can be schematically shown in Fig. 1. Small angle scattering is registered on the detector when scattering materials have a contrast (∆SLD)² defined as the squared difference of the coherent scattering length densities (SLD) and/or volume fraction (1 − φ) between domains or elements, i and j:

\[
\frac{d^2S}{d\Omega} = P(Q) S(Q) \phi_i (1 - \phi_j) (\text{SLD}_i - \text{SLD}_j)^2
\]

where the macroscopic scattering cross-section (cross section per unit volume, cm⁻¹), \(d^2S(Q)/dQ\), is a function of the scattering vector, \(Q = (4\pi/\lambda)\sin(\theta/2)\), defined with the neutron wavelength \(\lambda\) and the scattering angle \(\theta\). \(P(Q)\) and \(S(Q)\) is a form factor that represents a shape of scattering object (i.e., scatterer) and a structure factor that does an inter-correlation distance, respectively.

For the homogeneous phase (i.e., single phase) as shown in Fig. 1(a), no small angle scattering must be observed since Eq. (1) becomes equal to zero since there are no scatterers (i.e., \(\phi(1 - \phi) = 0\)) due to internal homogeneity and smooth surface even with a difference in SLD between surface and air. Unlike our expectation, the preliminary USANS and SANS results of Cu₅₀Zr₅₀ show strong power-law scattering under air environment, which may indicate significant heterogeneities in the metallic glasses. However, since the homogeneous BMG alloys have no scattering regardless of scattering volume (i.e., thin or bulk samples), the rough surface (Fig. 1(b)) could be a reason for the power law or fractal-like scattering. In this case, the origin of the power law scattering may be due to the contrast (SLDsurf − SLDair)² between the rough surface SLDsurf and the air environment SLDair (as shown in Fig. 1(ii)), even with the inner homogeneity of the metallic glass. When the rough surface is contrast-matched (CM) to the neutron SLD of the homogeneous phase to make SLDsurf = SLDair = SLD_CM (i.e., the air environment is replaced with a surface neutron contrast-matched (SNCM) environment by filling the surface furrows with a matching liquid which masks the rough surface from neutrons (Fig. 1(c))), the scattering from the rough surface should not be observed because of no contrast as shown schematically in Fig. 1(iii). It is shown that the scattering from the rough surface or open networked-pores can be suppressed by the neutron contrast-matching technique.

When the sample has heterogeneities, such as polycrystals with boundaries (Fig. 1(d)) and dispersion of particles or voids (Fig. 1(e)) in a matrix, USANS and SANS scatterings from such heterogeneities occur due to a contrast mismatching, i.e., \(\Delta\text{SLD}_\text{hetero} \neq \Delta\text{SLD}_\text{CM}\), with the CM liquid matched to the homogeneous phase (Fig. 1(iv)). In this case, the surface contrast may be selectively matched to only one of the phases in a system comprising multi heterogeneous domains (Fig. 1(d) and (e)), which may enable us to measure the other phases or pores.

In the process of finding the optimum liquid composition that matches the SLD of a constituent phase, the mass density of the constituent phase could be estimated. The procedure for density estimation will be presented in detail in the later part of this paper. Overall, the schematics in Fig. 1 will be demonstrated and used to determine the microscale homogeneity and the mass density of BMG alloys.

**Results and Discussion**

**Homogeneity in atomic level.** Before determining the homogeneity and the mass density using USANS, the structure of Cu₅₀Zr₅₀ metallic glass samples in the form of ribbons was checked by DSC thermal analysis and X-ray diffraction (Fig. 2).
The DSC thermal scan was carried out twice to confirm the complete crystallization after the first scan up to 550 °C; upon cooling and reheating of the same specimen for the second run, the heat flow curve (dotted green line in Fig. 2(A)) was almost constant suggesting complete crystallization of the amorphous phase during the first heating (orange solid line). For the XRD spectra (shown in Fig. 2(B)), the two broad amorphous halos and full width at half maxima (FWHM) of both the as-cast and sub-T_g annealed samples were identical within a lab-scale XRD error range indicating the same atomic number density and no noticeable change in correlation distances between atoms (i.e., identical amorphous structures in both the as-cast and sub-T_g annealed Cu_{50}Zr_{50}). Results of the X-ray and DSC analyses confirm that Cu and Zr elements in the as-cast and sub-T_g annealed Cu_{50}Zr_{50} are homogeneously mixed and do not form any crystallite at the atomic level (in the available range of lab-scale XRD). The USANS measurements were undertaken to investigate whether the homogeneity in the amorphous phase is limited at the atomic level or is extended to larger scale, i.e., micrometers.

**Determination of homogeneity and heterogeneity in the micron scale with SNCM technique.**

Before investigating the homogeneity at the micrometer level, the USANS profiles of the Cu\textsubscript{50}Zr\textsubscript{50} ribbons without surface polishing (open orange triangle) and with polishing (open green circle) by means of the sandpapers (600, 1000, and finally 2000 grade in order) were compared with air scattering (closed circle) in Fig. 3(a).

Scatterings from both samples are stronger than the window scattering from the empty sample container, indicating the presence of effective scatterers (i.e., heterogeneity in the structure) which must not be observed.

**Figure 1.** Schematics of ultra-small and small angle scatterings at various sample environments of amorphous alloy: (a) homogeneous BMGs with smooth surface, (b) homogeneous BMGs with rough surface, (c) homogeneous BMGs with rough surface at surface neutron contrast-matched (SNCM) environment, (d) crystallized (i.e., heterogeneous) BMGs with rough surface, and (e) BMGs with precipitates, pores, and/or rough surface. Corresponding SLD profiles with path length (i.e., sample thickness) are displayed in (i–iv). SLD_{hetero} indicates heterogeneity from precipitates, rough surfaces, or/and voids. The symbol \( \Delta \) represents the difference between the SLDs. No scatterings are expected in (a)-(i) condition because there are no scatterers (i.e. \( \phi(1-\phi)=0 \)) even with a difference in SLD between surface and air and in (c)-(iii) condition because of no contrast (i.e., \( \Delta=0 \)). Sample thickness and roughness are not scaled. The samples have two surfaces that contribute to the forward scatterings, but for clarity, note that the schematics show only one-sided surfaces. \( \vec{k}_i \) and \( \vec{k}_s \) are the incident and scattered wave vectors, respectively. \( \vec{Q} \) is the scattering vector.

|          | (a) | (b) | (c) | (d) and (e) |
|----------|-----|-----|-----|-------------|
| (\(\Delta \text{SLD})^2\) | >0  | >0  | 0 (contrast matched) | >0 |
| \(\phi(1-\phi)\) | 0 (no scatterers) | >0 | >0 | >0 |
| \(dQ/d\Omega\) | 0 (no scattering) | >0 | 0 (no scattering) | >0 |

**Table 1.** Summary of scattering origin based on Fig. 1 and Eq. (1).
in the homogeneous BMG as shown in Fig. 1(a) and Table 1. The polished sample (open circles in green color, Fig. 3(a)) shows higher intensity around Q ~ 2 × 10^{-4} ~ 3 × 10^{-3} Å^{-1} than the as-cast sample (open triangles in orange color, Fig. 3(a)), suggesting a greater number of scatterers in the surface-treated (polished) sample. Note also that the scattering intensities and shapes of the rocking curves in the Q-resolution limit with/without the Cu_{50}Zr_{50} samples are almost identical (i.e., no attenuation of intensity and no beam broadening at all as shown in inset), resulting in high transmission around 92% (+/−2%) and ensuring no multiple scattering (see Method section later regarding details of multiple scattering).

The SEM image shows sharper scratches with significantly higher number density for the surface-treated sample [image (c-1) and (c-2) of Fig. 3] than on the surface of the as-cast sample [image (b-1) and (b-2) of Fig. 3], suggesting that the surface scratches (i.e. rough surface) could be the origin of the USANS scattering. However, in the case of metallic glass ribbons having both macro-heterogeneity and rough surface, it would not be clear whether the power law scattering results from the large heterogeneity (i.e., much larger than atomic scale) inside the sample or from the rough surface [Fig. 1(d) and (e)]. To identify the origin of the scattering and to determine the homogeneity in much larger size scale than atomic level, the USANS measurements were performed at different sample environments corresponding to each schematic diagrams of Fig. 1 for the homogeneous Cu_{50}Zr_{50} alloy.

The sample was placed in several buffers from 100% hydrogenated ethanol (C{sub 2}H{sub 5}OH, ethanol-h, Fig. 4(a)), ethanol-h/ethanol-d of 60/40 vol./vol. (Fig. 4(b)), 29.8/79.2 vol./vol. (Fig. 4(c)), and 100% deuterated ethanol (C{sub 2}D{sub 5}OD, ethanol-d, Fig. 4(d). The samples (open circles) show different scattering intensities from the buffers (closed circles) due to a difference in contrast (i.e., ΔSLD) between the sample and liquid buffer as shown in Tables 2 and 3.

The sample immersed in the 100% hydrogenated ethanol-h (Fig. 4(a)), shows strong scattering due to the large contrast, while the same specimen immersed in the 100% deuterated ethanol-d shows weak scattering (Fig. 4(d)). In the mixture of ethanol-h/ethanol-d, 20.8/79.2 vol./vol. ratio (Fig. 4(c)), the scattering (open circles) from the sample almost superimposes to the scattering (closed circles) from the buffer liquid of 79.2% ethanol-d, confirming that the SLD of the buffer liquid is close to that of the homogeneous Cu_{50}Zr_{50} alloy. The estimated density of Cu_{50}Zr_{50} alloy from this ratio is approximately 8.23 g/cm{sup 3} that is about 11–14% higher than the known densities, 7.23 ~ 7.41 g/cm{sup 3}, in the literature {sup 25–28}. The exact matching ratio and density determination will be shown from a SLD matching plot later in the section of mass density estimation. Figure 4(c) indicates that the USANS scattering of the BMG is not from the internal heterogeneous structure but mostly from the rough surface (i.e., no scattering from the inside as shown in Fig. 1(c) and 1(iii)).

The USANS scattering phenomena measured with the ethanol-h/ethanol-d mixtures with low surface tension were cross-checked with the H_2O and D_2O mixtures with high surface tension in the same manner as that of the ethanol mixture. Figure 5(a) shows that the USANS scattering (open circles) of the Cu_{50}Zr_{50} immersed in the mixture of 30/70 H_2O/D_2O vol./vol. almost superimposes to the empty scattering (buffer liquid only, closed circles) within experimental error, confirming that the SLD of the mixture is close to that of the homogeneous Cu_{50}Zr_{50} alloy. However, when the USANS of the Cu_{50}Zr_{50} crystallized at 500 °C (see Fig. S2 for XRD) was measured with the same H_2O/D_2O mixture, strong power law scattering was observed (open circle in Fig. 5(b)) due to the large differences in the contrast (i.e., due to large mismatching in SLDs between crystalline domains of the crystallized Cu_{50}Zr_{50} alloy and 30/70 H_2O/D_2O vol./vol. mixture), indicating the existence of inner heterogeneity as schematically shown in Fig. 1(d) and 1(iv). Figures 4 and 5 demonstrate that the homogeneity and heterogeneity (schematically illustrated in Fig. 1) of the Cu_{50}Zr_{50} alloy in the large scale can be determined from the rough surface at the SNCM condition.
Mass density estimation. The rough surface can be further applied to determine the mass density of homogeneous metallic glasses together with the SNCM technique. Two methods were used in this study: the invariant method and the zero-angle scattering method. The invariant, $Q_{\text{inv}}$, defined as:

$$Q_{\text{inv}} = 2\pi^2 \phi (1 - \phi) (\Delta SLD)^2$$  \hspace{1cm} (2)

is used. In Eq. (2), the $Q_{\text{inv}}$ depends only on the contrast term, $(\Delta SLD)^2$, in a two-phase system that can be controlled by tuning the sample environment as shown in the CM experiments, since the volume fraction ($\phi$) of the empty space in the rough surface and the rest, $(1 - \phi)$, composed of the Cu$_{50}$Zr$_{50}$ materials are constant. $Q_{\text{inv}}$ is obtained from the area of the invariant plot, $(\Sigma \Omega \cdot dQ^2)$ vs. $Q$, in the desmeared scattering profile:

$$Q_{\text{inv}} = \int_{Q_{\text{min}}}^{Q_{\text{max}}} \frac{d \Sigma \Omega}{d \Omega} (Q) \cdot Q^2 dQ$$  \hspace{1cm} (3)

where $Q_{\text{min}}$ and $Q_{\text{max}}$ are the minimum and maximum $Q$, respectively.

The quadratic contrast term can be linearized by taking $\sqrt{Q_{\text{inv}}} (\approx \Delta SLD)$ and by reflecting one side of $\sqrt{Q_{\text{inv}}}$ values about the abscissa in the plot of $\sqrt{Q_{\text{inv}}}$ versus deuterated liquid amount in the H/D mixture$^{22,29}$. The positive values (open circles) of $\sqrt{Q_{\text{inv}}}$ for 75.0, 79.2, and 100% ethanol-d were reflected to the negative side (closed circles) with respect to the x-axis as shown in Fig. 6(a). The error bars in vertical direction calculated using Eq. (B5) are not shown because they are screened by the symbols. The propagation of uncertainty is derived in
the Appendix]. If the system is a two-phase alloy (i.e., consisting of the homogeneous phase of metallic glass and the empty space in rough surface), the data must align linearly and the exact surface neutron CM ratio is determined from the x-intercept that represents $\Delta \text{SLD} = 0$.

Figure 6(a) shows the linearity of $Q^{-1}$ with the deuterated ethanol, which means that the Cu50Zr50 phase is homogeneous at the micron scale. The results confirm that the well-known homogeneity at the atomic level is extended to the micron size in scale. From the matching ratio, 29.1/70.9 vol./vol., of ethanol-h/ethanol-d, the mass density $\rho_{\text{CM}} = 0.860(2) \text{g/cm}^3$ of the matching mixture is obtained from $\rho_{\phi} = \rho_{\text{H}} \rho_{\phi}^{\text{H}} + \rho_{\text{D}} \rho_{\phi}^{\text{D}}$, where the subscripts H and D represent the hydrogenated and the deuterated liquid, respectively. Using the values of known densities and SLDs given from Tables 2 and 3, the SLD of the contrast-matched ethanol mixture is $\text{SLD}_{\text{CM}} = 4.2296 \times 10^{-10} \text{cm}^{-2}$. Figure 1(c) and 1(iii) show schematic representations of the contrast-matched environment and Fig. 6 shows the corresponding experimental results with the SLD of the ethanol mixture.

Table 2. Neutron bound coherent scattering lengths, b, of elements for calculating SLD of ethanol mixture and Cu50Zr50. *reference 30 Read the numbers in the column as $-3.739 \times 10^{-13}$, $6.671 \times 10^{-13}$, and so on.

| elements | $b \times 10^{13}$ (cm)$^b$ |
|----------|-------------------------------|
| H        | $-3.739$                     |
| D        | $6.671$                      |
| C        | $6.646$                      |
| O        | $5.803$                      |
| Cu       | $7.718$                      |
| Zr       | $7.160$                      |
| Cu50Zr50 | $7.439$                      |

Figure 4. Ultra-small angle neutron scatterings of the polished Cu50Zr50 (open) immersed in different buffers: (a) pure ethanol-h, (b) mixture of ethanol-h/ethanol-d, 60/40 vol./vol., (c) mixture of ethanol-h/ethanol-d, 20.8/79.2 vol./vol., and (d) pure ethanol-d. Scatterings from the buffers are shown as closed symbols.
Since the SLD of Cu$_{50}$Zr$_{50}$ must be the same as that of the matched mixture at the SNCM condition (i.e., $SLD_{Cu_{50}Zr_{50}} = SLD_{CM}$), the mass density of homogeneous BMG is determined using the following relation:

$$\rho_{BMG} = \frac{SLD_{CM}(\sum_i n_i M_i)_{BMG}}{N_A(\sum_i n_i b_i)_{BMG}}$$

(4)

where $\sum_i n_i M_i$ and $\sum_i n_i b_i$ are the molecular weight and the scattering length of BMG consisting of atomic species $i$ with the number ($n_i$) of atoms $i$, atomic weight ($M_i$) and scattering length ($b_i$), and $N_A$ is Avogadro number. The mass density of Cu$_{50}$Zr$_{50}$ using Eq. (4) and the values listed in Tables 2 and 3 is estimated as $\rho_{Cu_{50}Zr_{50}} = 7.2(4) \pm 0.2(3)$ g/cm$^3$ (see main text for details). From the matching ratio, 70.9(9) vol. % of ethanol-d from SNCM plot of squared root invariants.

**Table 3.** Density and SLD of Cu$_{50}$Zr$_{50}$, water, ethanol, and contrast matched ratio at 25 °C. *Read the numbers in the column as $-0.55993 \times 10^{10}$, 6.3988 $\times 10^{-10}$ and so on. **Read the numbers in the column as 23.0508 $\times 10^{20}$, 17.9878 $\times 10^{20}$ and so on. *Estimated from this study using the squared invariant. Also, from the squared zero-angle scattering method, we obtained the density of $PCu_{50}Zr_{50} = 7.2(4) \pm 0.2(3)$ (see main text for details) from the matching ratio, 70.9(9) vol. % of ethanol-d from SNCM plot of squared root invariants.

**Conclusion**

The results demonstrate that the rough surface of amorphous metallic materials, which is a result of manufacturing process or intended purpose, can be used to determine the homogeneity and mass density of the bulk metallic glasses when the surfaces are sufficiently rough. The power-law scattering of amorphous Cu$_{50}$Zr$_{50}$ melt-spun ribbons with rough surface in the USANS measurements disappeared at the SNCM (surface neutron contrast-matched) condition which can be optimized by finding a proper composition of ethanol-h/ethanol-d mixture as well as H$_2$O/D$_2$O mixture within the experimental error. However, the crystallized ribbons showed strong power-law scattering with the matching mixture suggesting that the inside of the alloy is heterogeneous. This confirms that the small angle scattering originates from the rough surface and that, at the same time, the

![Figure 5.](image-url)
BMG consists of the homogeneous single phase. The compositional homogeneity of the amorphous metals down to the atomic level turned out to hold over an even a wider range of scale: nanometer to micrometer, over 4 orders. It was also demonstrated that the rough surface can be used to determine the mass density of a homogeneous amorphous metallic ribbon, Cu$_{50}$Zr$_{50}$.

Therefore, by utilizing USANS, which has much higher Q resolution and is less sensitive in incoherent scattering than the typical SANS, the SNCM technique can be an alternative characterization method for determining homogeneity of BMG in a larger scale (i.e., micron level) than the atomic level and can be used for estimating the mass density of homogeneous BMG with a rough surface. Our method can also be applied to much thicker BMG alloys due to their high transparency to neutrons.

Figure 6. SNCM (Surface neutron contrast-matching) plot of (a) squared root invariants and (b) squared root of extrapolated zero angle scattering against ethanol-d content in the mixture of ethanol-h/ethanol-d. For (a), open circles are the squared root of extrapolated zero angle scattering against ethanol-d content in the mixture of ethanol-h/ethanol-d. For (a), open circles are the squared root invariants measured with five ethanol-d contents (0, 40.0, 75.0, 79.2, and 100%). The negative values (closed circle) for 75.0, 79.2, and 100% were used to find the ethanol mixing ratio at which the contrast is zero by linearly fitting the squared root invariants as a function of ethanol-d content. Surface contrast matching point is in the range of 68.9% ~ 73.2% (indicated as error bar on x axis) and a corresponding mass density is approximately 7.3(1) ± 0.2(4) g/cm$^3$ from the matching ratio 70.9(9) ± 2.1(3) vol. % of ethanol-d (indicated as an orange arrow). The errors in vertical direction is within the symbols [see Appendix]. (b) Surface contrast matching point from the zero angle scattering is in the range of 68.1(9) % ~ 72.4(1) % and a corresponding mass density is approximately 7.2(4) ± 0.2(3) g/cm$^3$ from the matching point 70.2(9) ± 2.1 vol. % of ethanol-d (indicated as an arrow). The vertical error bar was estimated from the count statistics [see Appendix]. The horizontal error bars are assumed to be 3% in both (a) and (b) methods.
Methods

Sample preparation. Cu₅₀Zr₅₀ ribbons of ~80 μm in thickness and ~75 mm in width were produced by the melt-spinning method at Eco-FM Company, Incheon, Korea. The ribbons were isothermally annealed under a vacuum environment at a temperature of 400 °C for 1 hour to homogenize the as-cast structure by equilibrating at a temperature slightly under the glass transition point (Tᵣ ~ 404 °C). The metallic glass ribbons were also crystal-lized at 500 °C above a crystallization temperature (Tₓ ~ 456 °C; see Fig. 2(A)) under a vacuum environment. To remove oxide layers that can evolve on the sample surface during heat treatment, the samples were polished using 600, 1000, and 2000 grade sandpapers.

Thermal Analysis and X-ray Diffraction. Thermal analysis was carried out using a differential scanning calorimeter (Perkin Elmer Diamond DSC) with a heating rate of 10 °C/min under flowing nitrogen condition. The wide-angle X-ray diffraction (WAXD) (model: PAN analytical, EMPYREAN) was measured with a Cu Kα radiation generated at 40 kV and 45 mA.

Ultra-small angle scattering (USANS) measurement. Pieces about 20 × 20 mm² in size cut from the Cu₅₀Zr₅₀ ribbons (approximately, 80 μm thickness), stacked in three layers to increase the scattering intensity, were attached on a Gadolinium (Gd) diaphragm with a 5/8 inch aperture. The metallic glass ribbons were placed in a SANS environment, i.e., degassed hydrogenated ethanol (C₆H₁₂OH)/deuterated ethanol (C₆D₁₂OD) mixtures, in the 1 mm path length quartz cell for SNCM experiments. Ethanol was selected due to the low surface tension on the Cu₅₀Zr₅₀. The H₂O/D₂O mixtures with high surface tension were also used to cross-check the results from the ethanol mixtures. The entrapped air bubbles were removed under vacuum.

Ultra-small angle neutron scattering (USANS) was measured with the recently commissioned KIST-USANS at the HANARO cold neutron guide, CG4B, Daejeon, Korea. The KIST-USANS instrument uses a pair of modified Bonse-Hart-Agamalian channel-cut crystals¹⁰,₃¹ as a monochromator and an analyzer, with a wavelength of 4 Å. The minimum Q-resolution can reach down to ~2 × 10⁻⁵ Å⁻¹. The transmission of Cu₅₀Zr₅₀ was more than 92%, which assures no multiple scatterings from the metallic samples. Details of multiple scattering is described in the next section. The data reduction was performed with the NIST data reduction package²² modified for the KIST-USANS instrument. The USANS intensities are expressed in intensity, I(Q), (unit: counts/sec/ Monx₁₀⁶) corrected only with instrumental parameters for the comparison of the scatterings from the sample with a sample environment, or expressed in smeared macroscopic nuclear scattering cross-section, dΣₑₑ(Q)/dQ₀, (unit: cm⁻¹sr⁻¹) in absolute unit with additional corrections for sample thickness, transmission, and background. The USANS cross-section dΣₑₑ(Q)/dQ₀ in absolute scale were converted to the pin-hole SANS cross-sections dΣ(Q)/dQ by multiplying a Δqᵥ/Q, where Δqᵥ is the vertical divergence of the one-dimensional detector²⁵ to estimate the invariant quantity.

Multiple scattering measurement. Multiple scattering is proportional to the size of heterogeneity of the scatterer (D) as well as the sample thickness (t), the volume fraction of scatterers (ω), the square of neutron wavelength (λ²), and the contrast (i.e., ~dΔΛ²(ΔSLD)²). Since the USANS measures the microscale heterogeneity, multiple scattering is more concerning than in SANS, which measures on the nano scale. In order to assure that a neutron scatter only once (i.e., no multiple scattering) in the BMG alloys with the large rough surfaces, multiple scattering was estimated by comparing the sample transmissions measured with two independent detectors, a transmission detector and a detector bank (see Fig. 7), in the following manner: after aligning both monochroma-
tor and analyzer crystals to satisfy Bragg’s law, the peak intensity of rocking curve is measured at Q = 0 with the detector bank by rotating the analyzer step-by-step through the rocking peak of the main beam. The ratio, Trock = I₀(sample)/I₀( empyrene), of the rocking peak intensity with and without sample is the sample transmission attenuated by absorption, incoherent scattering, and coherent small angle scattering. A second transmission is measured from the transmission detector at non-Bragg condition. The detector located behind the first analyzer reflector captures all transmitted neutrons not to satisfy the Bragg’s law for the analyzer, which was achieved by rotating the analyzer to a relatively wide angle (Q → ∞, a few degree) from the aligned rocking peak position (Q = 0). The transmission detector measures both the direct beam and forward coherent small angle scattering. The neutron counts collected by the transmission detector are decreased due to absorption and incoherent scattering. Thus, the ratio, Twide = <I(∞)sample>/<I(∞) empyrene>, of averaged count rate on the transmission detector with and without the sample represents the sample transmission attenuated by absorption and incoherent scattering.

The ratio Tₛₛ = Trock/Twide( = exp(−Σ · t)) of these two separate transmissions is used to estimate the amount of multiple scattering. If the USANS measurements are free of multiple scattering, Trock ∝ Twide. Thus, (1 − Tₛₛ) is the measured scattering probability including multiple scattering. As a rule of thumb, multiple scattering can be neglected when Tₛₛ ≥ 90% or Σ · t ≤ 0.1 where Σ is the macroscopic scattering cross section (i.e., cross section per unit volume) that estimate the attenuation due to small angle scattering and t is the sample thickness. If any significant multiple scattering occurs, it can also be shown as a broadening (i.e., flattening) of the sample rocking curve, which can cause an artificial Guinier-like scattering shape. In this study, two independent transmissions were more than 92% for all measurements, Tₛₛ ≥ 0.95, and only power law scattering was observed, which confirms that multiple scattering is negligible and the USANS measurements are reliable. Based on this argument, USANS can be measured for homogeneous Cu₅₀Zr₅₀ alloy samples with a thickness (t = 0.1/Σ) of up to 1.5 mm. If only power law scattering is observed, USANS can also be measured for thicker samples.
Appendix: Propagation of Uncertainty in the Contrast Matching Plot

The propagation of uncertainty in the two contrast matching methods, the squared root zero angle scattering method and the squared root invariant method, was treated in the following manner:

A1. Propagation of Uncertainty (vertical error bar) in the zero-angle scattering (or near zero-angle) plot.

The measured USANS count \( I_{SAM} \) of the sample is corrected in absolute scale (unit \( \text{cm}^{-1} \text{sr}^{-1} \)), \( I_{cor}(Q) \), with empty count (or, buffer scattering), \( I_{EMP} \), sample transmission \( T_{trans} \), sample thickness \( t \), detector solid angle \( d\Omega \) and a constant background \( I_{BKG} \) in the following manner;

\[
I_{cor}(Q) = \frac{d\Sigma_{sam}(Q)}{dQ} = sf \cdot \left( I_{SAM} - T_{trans}I_{EMP} - (1 - T_{trans})I_{BKG} \right)
\]  

(A1)

where \( sf \) is an absolute scale factor containing sample transmission \( T_{wide} \) measured in a background region, and a rocking curve peak count of the empty run \( pk_{EMP} \).

\[
sf = \frac{1}{t \cdot d\Omega \cdot T_{wide} \cdot pk_{EMP}}
\]  

(A2)

The last term, \( (1 - T_{trans})I_{BKG} \) in Eq. (A1) is a negligibly small constant. Equation (A1) has the following general form

\[
f(x) = c(ax \pm bx \pm \cdots)
\]  

(A3)

where \( a, b, \) and \( c \) are constants. The propagation of uncertainty \( \sigma_f \) of Eq. (S3) is generally expressed as

\[
\sigma_f = \sqrt{(\frac{\partial f}{\partial x})^2 \sigma_x^2 + (\frac{\partial f}{\partial y})^2 \sigma_y^2 + \cdots}
\]  

(A4)

Thus, the propagation of uncertainty of Eq. (S1) is
\[
\sigma_{\text{COR}} = \sqrt{\left(\frac{\partial I_{\text{COR}}(Q)}{\partial I_{\text{SAM}}}\right)^2 \sigma_{\text{SAM}}^2 + \left(\frac{\partial I_{\text{COR}}(Q)}{\partial I_{\text{EMP}}}\right)^2 \sigma_{\text{EMP}}^2}
\]  
(A5)

and

\[
\sigma_{\text{COR}} = sf \cdot \sqrt{\sigma_{\text{SAM}}^2 + T_{\text{trans}} \sigma_{\text{EMP}}^2}
\]  
(A6)

Equations (A1) and (A6) were used in the USANS data reduction. The measured USANS scattering including the errors is expressed as \( I_{\text{USANS}}(Q) \pm \sigma_{\text{COR}} \).

The USANS total cross-section, \( \Sigma_{\text{USANS}}(Q) \pm \Sigma_{\text{COR}} \), is the smeared total cross-section due to the one dimensional-detector geometry that has a high resolution only in the horizontal direction. The \( I_{\text{USANS}}(Q) \pm \sigma_{\text{COR}} \) is demesured with the detector resolution and normalized with \( Q \).

\[
d\Sigma(Q) / d\Omega = (I_{\text{USANS}}(Q) \pm \sigma_{\text{COR}}) \cdot \Delta q_v / Q
\]  
(A7)

which has a standard form of

\[
f(x) = ax \pm b,
\]

(where \( a = \Delta q_v / Q \), and \( b = \sigma_{\text{COR}} \))

(A8)

and because of \( \partial f(x) / \partial x = a \), the uncertainty is given as

\[
\sigma_{d\Sigma(Q) / d\Omega} = \sqrt{\left(\frac{\Delta q_v}{Q}\right)^2 \sigma_{\Sigma(0) / d\Omega}^2}
\]  
(A9)

which is simply a scaling of the smeared total cross-section, \( d\Sigma_{\text{us}}(Q) / dQ \), by \( \Delta q_v / Q \), \( \Delta q_v \), and \( Q \) are the detector divergence and scattering vector, respectively. In the contrast matching plot, where \( y \) axis is represented by the squared root of the extrapolated zero angle scattering, \( \sqrt{I(Q \rightarrow 0)} \), the general form for the uncertainty calculation is given by

\[
f(x) = ax^m
\]  
(A10)

and the error is described as Eq. (A4)

\[
\sigma_f = \sqrt{m^2a^2x^{2(m-1)}\sigma_x^2} = m \cdot a \cdot x^{(m-1)} \sigma_x
\]  
(A11)

Since \( \sqrt{d\Sigma(0) / d\Omega} \) is the case of \( m=1/2 \) and \( a=1 \) in Eq. (A11), the error propagation in \( \sqrt{d\Sigma(0) / d\Omega} \) is expressed as

\[
\sigma_{\sqrt{d\Sigma(0) / d\Omega}} = \frac{1}{2} \cdot \frac{\sqrt{d\Sigma(0) / d\Omega}}{d\Sigma(0) / d\Omega} \sigma_{d\Sigma(0) / d\Omega}
\]  
(A12)

which is shown in the vertical error bar in Fig. 6(b). Note that in the power law scattering, the \( \sqrt{d\Sigma(0) / d\Omega} \) is replaced with a low \( Q \) limit, \( \sqrt{I(Q \rightarrow 0)} \), for practical purposes. As long as the scattering follows a single power law, a choice of a low \( Q \) limit does not affect the matching point.

**Appendix B: Propagation of Uncertainty (vertical error bar) in the squared root invariant plot.** The invariant was numerically calculated with the following trapezoidal summation from the measured total scattering section \( I(Q) \):

\[
Q_{\text{INV}} = \sum_{i=1}^{n} \left( I_i Q_i^2 + I_{i+1} Q_{i+1}^2 \right) \Delta Q_i
\]  
(B1)

where \( \Delta Q_i \) is defined as \( \Delta Q_i = Q_{i+1} - Q_i \). instead of \( \Delta Q_i = (Q_{i+1} - Q_i) / m \), since the USANS intensity was measured with different intervals of \( Q \) for each angular region. For simplicity in the notation \( I_i \) is used for representing \( I(Q)_i \) (\( \approx d\Sigma(Q) / d\Omega \)). In order to separate out the \( 1^{st} \) \((i=0)\), the last \((i=n)\) term, and the rest term \((i=1 \sim n - 1)\) for numerical calculation, Eq. (B1) was expanded and rearranged as

\[
Q_{\text{INV}} = \frac{1}{2} I_0 Q_0^2(Q_1 - Q_0) + \frac{1}{2} \sum_{i=1}^{n-1} I_i Q_i^2(Q_{i+1} - Q_i) + \frac{1}{2} I_n Q_n^2(Q_n - Q_{n-1})
\]  
(B2)

Each of the partial derivatives of Eq. (B2) are

\[
\frac{\partial Q_{\text{INV}}}{\partial I_0} = \frac{1}{2} I_0^2(Q_1 - Q_0), \quad \frac{\partial Q_{\text{INV}}}{\partial I_n} = \frac{1}{2} I_n^2(Q_n - Q_{n-1}) \quad \frac{\partial Q_{\text{INV}}}{\partial I_i} = \frac{1}{2} I_i Q_i^2(Q_{i+1} - Q_i)
\]  
(B3)

By inserting Eq. (B3) into Eq. (A4), we obtain the following expression for the propagation of uncertainty in invariant
\[ \sigma_{\text{Qinv}} = \sqrt{\left( \frac{1}{2} Q_0^2 (Q_1 - Q_0) \sigma_{\text{Q}} \right)^2 + \frac{1}{2} \sum_{i=1}^{n-1} Q_i^2 (Q_{i+1} - Q_{i-1}) \sigma_{\text{Q}}^2 + \left( \frac{1}{2} Q_n^2 (Q_n - Q_{n-1}) \sigma_{\text{Q}} \right)^2} \]  

(B4)

The invariant including the error propagation is expressed as \( Q_{\text{inv}} \). In contrast matching plot where the y axis is \( \sqrt{Q_{\text{inv}}} \), the vertical error bar is given by

\[ \sigma_{\sqrt{Q_{\text{inv}}}} = \frac{1}{2} \cdot \frac{\sqrt{Q_{\text{inv}}}}{Q_{\text{inv}}} \sigma_{Q_{\text{inv}}} \]  

(B5)

Note that in Fig. 6(a) (in the main text), the vertical error bars within the symbols. Apparently, the squared root method shows smaller error bars than the squared root of the extrapolated zero angle scattering, \( \sqrt{dF(0)/d\Omega} \) method. However, regardless of the method, the densities estimated from both methods are identical within experimental error.

References

1. Lamparter, P., Steeb, S., Kroeger, D. M. & Spooner, S. Neutron and X-ray small angle scattering with Fe-based metallic glasses. *Materials Science and Engineering* **B** 97, 227–230 (1988).
2. Lamparter, P. & Steeb, S. Small angle X-ray and neutron scattering for the investigation of the medium-range structure of metallic glasses. *Journal of Non-Crystalline Solids* **106**, 137–146 (1988).
3. Wang, X.-L. *Acta Materialia* **60**, 493–500 (2012).
4. Mattern, N. *Surface roughness effect on the friction and wear of bulk metallic glasses*. *Advances in Materials and Processing Technologies* 12, 93–102 (2014).
5. Mattern, N., Shariq, A., Schwarz, B., Vainio, U. & Eckert, J. Structural and magnetic nanoclusters in Cu_{50}Zr_{50} metallic glasses. *Journal of Non-Crystalline Solids* **350**, 179–191 (2005).
6. Mattern, N., Shariq, A., Schwarz, B., Vainio, U. & Eckert, J. Structural and magnetic nanoclusters in Cu_{50}Zr_{50} metallic glasses. *Acta Materialia* **60**, 1946–1956 (2012).
7. Han, J. H. et al. Phase separation in Zr_{54-x}Al_{x}Co_{28}Al_{16} metallic glasses (0 \( \leq x \leq 20 \)). *Acta Materialia* **2014**, 262–272 (2014).
8. Mattern, N. et al. Spinodal decomposition of Ni–Nb–Y metallic glasses. *Acta Materialia* **57**, 903–908 (2009).
9. Fadonougbo, J. O. et al. Hydrogen-induced decomposition of Cu_{72}Zr_{28} binary amorphous metallic alloys. *Met. Mat. Comp* **660**, 456–460 (2016).
10. Agamalian, M., Wignall, G. D. & Triolo, R. Optimization of a bone-hart ultra-small-angle neutron scattering facility by elimination of the rocking-curve wings. *J. Appl. Cryst.* **30**, 345–352 (1997).
11. Hays, C. C., Kim, C. P. & Johnson, W. L. Large supercooled liquid region and phase separation in the Zr–Ti–Ni–Cu–Be bulk metallic glasses. *Advanced Physics* **75**, 1089–1091 (1999).
12. Liu, Y. et al. Super plastic bulk metallic glasses at high temperature. *Science* **315**, 1385–1388 (2007).
13. Lee, J.-C. et al. Origin of the plasticity in bulk amorphous alloys. *J. Mater. Res.* **22**, 3087–3097 (2007).
14. Jahanmir, S. & Buh, N. P. Surface topography and integrity effects on sliding wear. *Wear* **323–323**, 1231–1237, https://doi.org/10.1016/j.wear.2014.11.030 (2015).
15. KOSTORZ, G. Neutron scattering. Vol. 15 (ACADEMIC PRESS, 1979).
16. Roth, M. The small-angle scattering of neutrons by surface imperfections. *J. Appl. Cryst.* **10**, 172–176 (1977).
17. Rodmacq, B., Mangin, P. & Chamberod, A. Small-angle neutron scattering by surface imperfections in amorphous alloys. *Physical Review B* **30**, 6188–6190 (1984).
18. Rodmacq, B., Mangin, P. & Chamberod, A. Contribution to s.a.n.s. of the surface state of pd80si20 amorphous alloys. *J. Phys. Colloques* **46**, C8–499–C499–503 (1985).
19. Spierings, A. B., Schneider, M. & Eggenberger, R. Comparison of density measurement techniques for additive manufactured metallic parts. *Rapid Prototyping Journal* **17**, 380–386 (2011).
20. Mazur, M. et al. Mechanical properties of Ti6Al4V and AlSi12Mg lattice structures manufactured by Selective Laser Melting (SLM). *Wear* **323–323**, 1231–1237, https://doi.org/10.1016/j.wear.2014.11.030 (2015).
21. Kim, M.-H. & Glinka, C. J. Ultra small angle neutron scattering study of the nanometer to micrometer structure of porous Vycor. *Microporous and Mesoporous Materials* **91**, 305–310 (2006).
22. Gatter, O. & Kratky, O. Small angle X-ray scattering. (Academic Press, 1982).
23. Melnichenko, Y. B. et al. Accessibility of pores in coal to methane and carbon dioxide. *Fuel* **91**, 200–208 (2012).
24. Alouinnizi, Z. & Strøm-Olsen, J. O. Superconductivity and spin fluctuations in M-Zr metallic glasses (M = Cu, Ni, Co, and Fe). *Physical Review B* **27**, 4149–4156 (1983).
25. Li, Y., Guo, Q., Kalb, J. A. & Thompson, C. V. Matching glass-forming ability with the density of the amorphous phase. *Science* **322**, 1816–1819 (2008).
26. Calvayrac, Y., Chevalier, J.-P., Harmelin, M. & Quivy, A. On the stability and structure of Cu–Zr based glasses. *Philosophical Magazine B* **48**, 323–332 (1983).
27. Ma, D., Stöica, A. D. & Wang, X.-L. Power-lawsing and fractal nature of medium-range order in metallic glasses. *Nature Materials* **8**, 30–34 (2009).
28. Stuhlmann, H. B. et al. High resolution model for SOS subunit of Escherichia coli ribosomes. *Proceedings of the National Academy of Science* USA **73**, 2379–2383 (1976).
29. Sears, V. F. Neutron scattering lengths and cross sections. *Neutron News* **3**, 26–37 (1992).
30. Barker, J. G. et al. Design and performance of a thermal-neutron double-crystal diffractometer for USANS at NIST. *J. Appl. Crystallography* **38**, 1004–1011 (2005).
31. Kline, S. R. Reduction and analysis of SANS and USANS data using IGOR Pro. *J. Appl. Crystallogr.* **39**, 895–900 (2006).
32. Kim, S. H., Han, S., Ha, H., Byun, J. Y. & Kim, M.-H. Support-shape dependent catalytic activity in Pt/alumina systems using ultra-small (USANS) and small angle neutron scattering (SANS). *Catalysis Today* **260**, 46–54 (2016).
33. Staron, P. & Bellmann, D. Analysis of neutron double-crystal diffractometer scattering curves including multiple scattering. *Journal of Applied Crystallography* **35**, 75–81 (2001).
34. Schelten, J. & Schmaltz, W. Multiple-Scattering Treatment for Small-Angle Scattering Problems. *J. Appl. Crystallogr.* **13**, 385–390 (1980).
35. Bevington, P. R. & Robinson, D. K. Data reduction and error analysis for the physical sciences. (McGraw-Hill, 2003).
Acknowledgements
We would like to thank Charlie J. Glinka and Boualem Hammouda for critical reading and comments. Specifically, CJG advised MHK to discuss the uncertainty in the contrast matching plot and to show how to handle the propagation of uncertainty. The preliminary SANS results obtained from the ORNL GP SANS with the help of Ken Littrell and from the HANARO 18 m and 40 m SANS were useful to initiate this study. We acknowledge partial financial support from KAERI and KIST (KIST funding number: 2G10480, 2V06030) and from the National Research Foundation of Korea (NRF) grant funded by the Korea government (NRF-2012M2B2A4030220).

Author Contributions
M.H.K. raised the issue, conceived the idea, performed the USANS experiments, and characterized the scattering data. S.G.H. prepared the solutions. J.Y.S., E.F. and K.T.H. designed the materials. J.Y.S., E.F. and S.G.H. performed the measurements of DSC and XRD, and SEM.s. M.H.K. wrote the manuscript with inputs from the all other authors. All authors discussed the results and reviewed the manuscripts.

Additional Information
Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-018-30333-9.

Competing Interests: The authors declare no competing interests.

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2018