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A Trial on Detecting Fluctuations in Bulk Metallic Glass Beams by Strain Contrast Variation Method–Use of High Energy Small-Angle Scattering

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Heterogeneity in annealed Zr-Cu-Al alloys with high ductility has been examined by high-energy small-angle scattering with strain variation method. Although the statistics is still poor for detailed analysis, it was found that the heterogeneity in the sample showed clear enhancement by applied tensile strain, and the characteristic size of the heterogeneity was of the same order of magnitude as the one observed by high resolution electron microscopy. With surface insensitivity of the present method, anomalous small-angle scattering results at Cu K absorption edge for the same sample was briefly discussed. [doi:10.2320/matertrans.M2015020]

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1. Introduction

Heterogeneities in bulk metallic glasses have been of keen interest in the past decades to inquire into the origin of stability of bulk metallic glasses.[1–4] Such heterogeneity has been examined by electron microscopy,[5] XAFS,[6] small-angle scattering,[7–9] diffraction[8] and inelastic scattering.[10] Recent works using fluctuation microscopy[11] are quite powerful for its sensitivity to the local heterogeneity in atomic structures. Yet, it is desirable to seek an approach which detects chemical and mechanical/volumetric heterogeneity as an ensemble average, because bridging atomistic short-range order as observed by electron high resolution microscopy or XAFS and nanoscopic fluctuations in composition/structure is not easy.

Small-angle X-ray scattering (SAXS) is a powerful tool to evaluate heterogeneity of contrast of electron density in nanoscopic scales and as macroscopic statistical average, and has been used to examine either precipitates in glass[12,13] or weak and diffuse concentration fluctuations.[7,9] However, in case of bulk metallic glasses without crystalline/quasicrystalline precipitates, small amplitude of electron density fluctuation has made it hard to obtain reliable scattering profile by conventional small-angle scattering. Sometimes reported fluctuations was even pointed out to be originated from crystalline precipitates, not fluctuations by later investigations.[14] From inelastic scattering approach, Ichitsubo *et al.*[10] reported that nanoscopic heterogeneities of elastic modulus exist in Zr-based and Pd-based metallic glasses. However, conventional small-angle scattering measurements found difficulty in obtaining well-defined scattering profiles with good reproducibility having a characteristic and universal length scale, though such nanoscopic heterogeneities without crystallization are clearly observed under several conditions for some materials.[7,12] For example, ZrCuPt alloy system gives a well defined nano-quasicrystal precipitations,[12,15] but the fluctuation before formation of nanoquasicrystals is still not well determined yet.

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2. Experimental Procedure

One of the important question for examining heterogeneity in the metallic glasses by small angle scattering is the origin of the contrast, i.e., whether it is atomic density fluctuations or composition fluctuations. Since they are naturally coupled for multinary alloy systems, they can be mixed, either with the same structure (strongly coupled) or nearly independent fluctuations (weak coupling). Our previous works using anomalous small-angle scattering (ASAXS) suggested[7,9,12] that an essential difficulty arises for ASAXS analysis in separating bulk and surface heterogeneities when the sample surfaces also give surface scattering from compositional modulation, i.e., anomalous effect applies both for surface and bulk heterogeneities. To solve this problem, we introduced strain variation method with higher energy X-rays, and compared with anomalous SAXS at the Cu K absorption edge. High energy small and large angle scattering/diffraction were measured at BL04B2 with mixed harmonics of 37.8 keV, 113 keV and 151 keV photon energies. High energy SAXS intensities were measured with Image Plates and 5.7 m of camera length with a 2 mm of Cu attenuator to filter out 37.8 keV X-rays. Anomalous small-angle scattering were measured at BL13XU and BL40B2 of Spring8.

3. Results and Discussions

Figure 1 gives change in the radial and tangential strains by bending and a photograph of bent-beam measurements. A beam with the size of 2.0 mm × 2.0 mm × 15 mm was cut from Charpy test peices of $Zr_{59}Cu_{31}Al_{10}$ after annealed at 623 K and Charpy test,[16] and placed in a bending jig with three points in contact. The preceding works by Yokoyama suggest toughening of the materials due to internal heterogeneity by HREM. The curvature of the bending within elastic deformation was evaluated from the peak shift of the first halo with the displacement in radial (x) directions. When the heterogeneity in the sample is given as a Fourier transform of electron density distributions, $\Delta\rho(r)$ as:

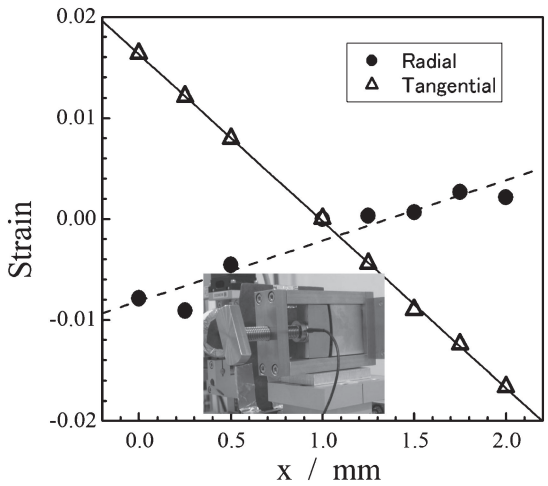

Fig. 1 Change in the strain observed by peak shift of halo in the line-cuts in radial and tangential directions of bending. The bending jig with a load cell used in the present work is shown in the inset.

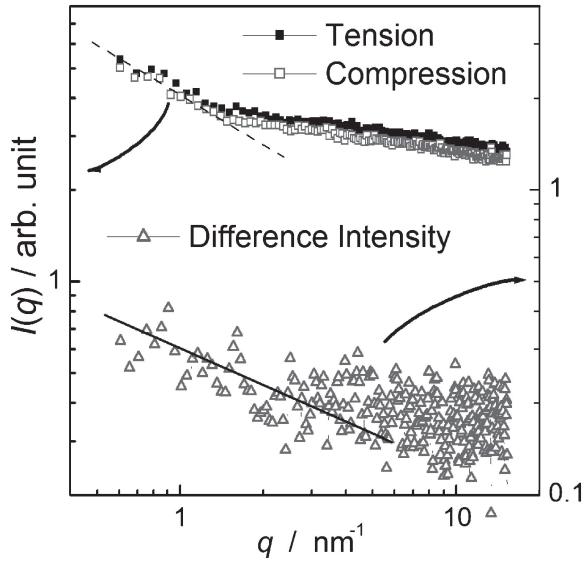

Fig. 2 High energy small-angle scattering profile and the difference intensity between the tensile and the compression sides. The scattering vector is calculated for 113 keV.

$$I(q) = \int \Delta\rho(r)\Delta\rho(r+r')dr \exp(iqr')dr'$$

where $\Delta\rho$ is the contrast from average electron density. When the contrast is described in terms of composition, it is written as

$$\Delta\rho(r) = \Delta c_{\mathrm{Zr,Al}}(r)(f_{\mathrm{Zr}} - f_{\mathrm{Al}}) + \Delta c_{\mathrm{Cu,Al}}(r)(f_{\mathrm{Cu}} - f_{\mathrm{Al}}) \quad (1)$$

where $\Delta c_{\mathrm{A,B}}(r)$ denotes the difference in the concentration between elements A and B at position r. Then the contrast may change with a use of resonant scattering near the absorption edge. This is a useful approach to detect weak chemical contrast.[13] On the other hand, when we change the strain of the sample for the same wavelength of X-rays, the contrast is written as[9]

$$\rho(r) = \bar{f}\Delta\rho_{\mathrm{num}}(r) \quad (2)$$

where $\bar{f}$ is the average scattering factor, and $\Delta\rho_{\mathrm{num}}(r)$ is the local atomic number density. Since the beam is bent with a radius r_0, the scattering intensities from the same beam but different position, x, reflect those from the same composition and thickness but under different strain. We may obtain the SAXS intensity originated from strain contrast by taking the difference of the intensities between compression and tension sides. The SAXS intensities obtained for $Zr_{59}Cu_{31}Al_{10}$ sample with $r_0 = 50$ mm is shown in Fig. 2. Although the scattering intensities are weak and do not show profile representing typical shape like spherical regions, contrast enhancement in the tension side was observed. When the contrast is purely that of elastic properties and density, the contrast enhancement is evaluated by the ratio of bulk modulus when softer regions with less dense regions surround the harder one. Although the statistics of the difference intensity shown in Fig. 2 is not good enough to discuss the form factor, i.e., the shape of the heterogeneity in detail, Guinier analysis gave the radius of 0.8 nm +/− 0.2 nm as a strain-sensitive heterogeneity in the sample. This size is the same order of magnitude as the heterogeneity observed in HRTEM micrograph in Ref. 16), about 1.4 nm in diameter, for the material showing high Charpy absorption

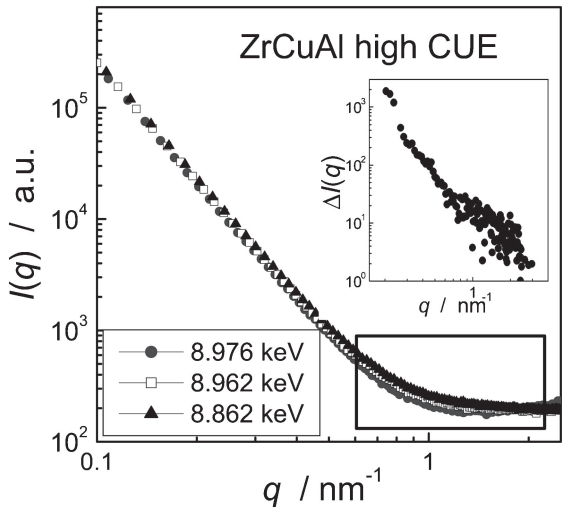

Fig. 3 Anomalous small-angle scattering profiles for the foil cut from the same sample shown in Fig. 2. Inset: the difference $\Delta I(q)$ between the intensity at 8.962 keV and 8.862 keV.

energy of 385 kJ/m^2. The anomalous SAS intensities at the Cu K absorption edge showed similar profiles that deceased monotonically with the scattering vector as shown in Fig. 3. Since the scattering intensity is smaller for the photon energies closer to the K absorption edge, it is concluded that the heterogeneity of the glass contain chemical heterogeneity, where the Cu rich region is denser in electron density. The power-law region at lower q in the ASAXS pattern also shows anomalous effect similar to the one analyzing here, suggesting that scattering from another scattering object, possibly at the surface, overlap for the ASAXS profile. The difference between the scattering intensity for 8.962 keV and 8.862 keV, $\Delta I(q)$ shown in the inset of Fig. 3, gives larger gyration radius of 1.2 nm. This difference may come from the power-law scattering component that still remains in the difference scattering intensity for the ASAXS. Present results suggest usefulness of strain contrast variation method to

examine weak heterogeneity with modulation of elastic properties.

4. Conclusion

Contrast change by strain variation approach was demonstrated for the first time, with qualitatively good agreement with preceding works. Coupled with resonant scattering results, the heterogeneity observed by inelastic scattering[10] and TEM[16] should contain both chemical and elastic heterogeneities. The merit of the strain contrast approach over anomalous SAXS is in removing surface effects. For more quantitative examination with strain variation approach, we still need to wait for developments of photon counting area detector for high energy photons over 100 keV, which is not available at present.

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