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Report:

In the last two decades, bulk metallic glasses (BMG) with distinct glass transitions have been discovered in various multi-component metallic alloys. They show extremely excellent glass-forming abilities (GFA), where even a very slow cooling rate such as ∼1 K/s can avoid crystallization. Among these BMGs, the Zr-Cu alloys strongly improve their GFA by adding a small amount of Al atoms, having a critical cooling rate of some K/s and allowing to form a massive BMG with a diameter of about 10 mm [1]. Since Al has small values of the scattering cross-sections for x-ray and neutron and its $K$ x-ray absorption edge energy is too low, however, knowledges on the partial structure around the Al atoms can hardly be obtained experimentally by diffraction and XAFS experiments for the Zr-Cu-Al BMG alloys [2].

Zhang et al. [3] reported that by adding Ag atoms to ZrCu alloy, their GFA greatly improves as Al atoms, and the critical diameter increases up to 6 mm at 10 at.% Ag. In this study, we have performed anomalous x-ray scattering (AXS) on $Zr_{45}Cu_{45}Ag_{10}$ BMG close to the Zr, Cu, and Ag $K$ absorption edges. The obtained differential structure factors $\Delta_k S(Q)$ were analyzed together with a complementary neutron diffraction result $S_{\rm N}(Q)$ using reverse Monte Carlo (RMC) modeling to evaluate the partial structure factors $S_{ij}(Q)$ and the corresponding partial pair distribution functions $g_{ij}(r)$ [4].

A $Zr_{45}Cu_{45}Ag_{10}$ alloy ingot with nominal compositions was prepared by arc-melting of mixtures in a high-purity Ar atmosphere. From this, a cylindrical rod of ∼ 3 mm in diameter and ∼ 10 mm in length was manufactured by tilt casting with a Cu mold. The AXS experiments near the Zr (17.998 keV) and Cu (8.979 keV) $K$ edges were carried out at BM02/ESRF, and that near the Ag $K$ edge (25.514 keV) at BL13XU/SPring-8. For obtaining $\Delta_k S(Q)$s, scattering experiments were performed at two different incident x-ray energies of 30 and 200 eV below the the Zr and Ag $K$ edges, and 20 and 200 eV below the Cu $K$ edge, using standard $\omega - 2\theta$ diffractometers installed at the beamlines.

The left panel of the figure shows $\Delta_k S(Q)$s close to the Zr, Cu, and Ag $K$ edges, total x-ray structure factor $S_\mathrm{X}(Q)$, and $S_\mathrm{N}(Q)$ from top to bottom. The circles indicate the experimental data and the solid curves denote the best fits of the RMC modeling. As clearly seen in the figure, the coincidences between the experiments and the RMC fits are excellent. The middle panel of the figure shows $S_{ij}(Q)$s obtained from the RMC fits. $S_\mathrm{ZrAg}(Q)$ shows a large shoulder at the small $Q$ side of the first peak, indicating the existence of Zr-Ag intermediate-range correlations. On the other hand, enhancements are observed at the low $Q$ region in $S_\mathrm{CuCu}(Q)$, $S_\mathrm{CuAg}(Q)$, and $S_\mathrm{AgAg}(Q)$, indicating phase separation tendencies of Cu and Ag atoms. These findings may be related to an atomic-scale heterogeneity predicted by theoretical simulation [5] .

The right panel of the figure shows $g_{ij}(r)$s obtained from the RMC fits. From those, the partial interatomic distances were obtained, and are slightly smaller than the Goldschmidt values [6]. For the further discussion, Voronoi analyses using the obtained atomic configurations are now in progress.


[1] J. Saida et al., Ann. Chim. Sci. Mater. **27**, 77 (2002).
[2] S. Hosokawa et al., J. Phys.: Conf. Ser. **502**, 012023 (2014).
[3] W. Zhang et al., Mater. Sci. Eng. A **459**, 330 (2007).
[4] S. Hosokawa et al., JPS Conf. Proc., in press.
[5] T. Fujita et al., Phys. Rev. Lett. **103**, 075502 (2009).
[6] A. E. Brandes and G. B. Brook (ed.), Smithells Metals Reference Book, 7th ed. (Butterworth-Heinemann, Oxford, 1992).