Structural Study of Zr-Cu-Ag Bulk Metallic Glasses Using the Anomalous X-ray Scattering Method

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Abstract. The structures of Zr_{45}Cu_{45}Ag_{10} and Zr_{40}Cu_{40}Ag_{20} bulk metallic glasses (BMGs) were investigated using the anomalous x-ray scattering and reverse Monte Carlo simulation (AXS-RMC) method. The fundamental structural features of Zr_{45}Cu_{45}Ag_{10} and Zr_{40}Cu_{40}Ag_{20} can be properly demonstrated through the common dense random packing of the hard spheres, and the addition of Ag appeared to result in no prominent formation of the particular chemical ordering units. A Voronoi analysis indicated that the fraction of the icosahedron-like coordination was the largest around the Cu in Zr_{45}Cu_{45}Ag_{10} BMG, where the best glass-forming ability was realized. The improvement in the glass-forming ability in a Zr-Cu-Ag system appears to be associated with the icosahedron-like local coordination.

1. Introduction
An encouraging multi-component alloy system for the formation of BMGs at a very low cooling rate was recently found [1]. The atomic origin of such an interesting BMG formation has been studied from the viewpoint of chemical and topological ordering in the atomic arrangement. Nevertheless, the essential structural features providing superior BMG properties have yet to be elucidated. Zr-Cu-Ag is interesting for a BMG system, and its chemical short-range ordering and corresponding heterogeneity were suggested through a molecular-dynamics simulation [2]. The anomalous X-ray scattering (AXS) method utilizing the anomalous dispersion effect near the absorption edge provides environmental structural information on the atoms of interest. Additionally, an analysis using a reverse Monte Carlo (RMC) simulation coupled with AXS measurements subsequently allows us to obtain a three-dimensional (3D) atomic arrangement under the necessary conditions [3, 4]. The main purpose of this paper is to report the structural features of Zr-Cu-Ag BMGs as demonstrated using the advanced AXS-RMC method.

2. Experimental
Alloy ingots with nominal compositions of Zr_{45}Cu_{45}Ag_{10} and Zr_{40}Cu_{40}Ag_{20} were prepared through the conventional arc melting of the pure-metal mixtures (99.99 wt. % Zr, 99.99 wt. % Cu, and 99.99 wt. % Ag). To minimize the oxygen concentration in the sample, a high purity Zr crystal rod (less than 0.05 wt. % oxygen) was used. The tilt-casting technique was applied in a purified Ar atmosphere to avoid the formation of cold spots, which is an inherent source of unfavorable crystallization during the solidification of a melt. A platy-shaped mold with a thickness of 1.0 mm and a length of about 30 mm was employed for the casting, and the surface of each sample alloy was polished for X-ray diffraction.
measurements of the reflection geometry. The density of the sample was measured using the Archimedes method with n-tridecane (7.72 and 8.02 g/cm$^3$ for Zr$_{45}$Cu$_{45}$Ag$_{10}$ and Zr$_{40}$Cu$_{40}$Ag$_{20}$, respectively). Ordinary X-ray diffraction and AXS measurements of the Cu, Zr, and Ag K absorption edges were carried out at BL-7C and NW10A of the Photon Factory at the Institute of Material Structure Science (IMSS), High Energy Accelerator Research Organization, Tsukuba, Japan. A pair of incident energies, corresponding to 25 eV and 300 eV below each K absorption edge (Cu, 8.980 keV; Zr, 17.037 keV; Ag, 25.517 keV), was used. Environmental interference functions, $\Delta Q_{i\text{Cu}}(Q)$, $\Delta Q_{i\text{Zr}}(Q)$, and $\Delta Q_{i\text{Ag}}(Q)$ for each sample were obtained from the measured scattering intensities. Environmental radial distribution functions (RDFs) were obtained based on the Fourier transformation of the interference functions. In the AXS-RMC analysis, four independent interference functions were employed for modeling the structure of each sample. A model consisting of 25,000 atoms placed within a cubic hyper-cell with a classical dense random packing (DRP) of the hard spheres [5] was employed as the initial model. The number of atoms and the unit hyper-cell size were set corresponding to the chemical composition and experimental density value of the sample. It should be noted that the closest distance between two atoms were determined in order to prevent atoms coming un-physically close to one another.

![Figure 1. Ordinary and environmental RDFs around Cu, Zr, and Ag of Zr$_{45}$Cu$_{45}$Ag$_{10}$. Ordinary RDF was obtained from the intensity profile measured at 15.0 keV.](image1)

![Figure 2. Ordinary and environmental interference functions. The solid and dotted lines correspond to the experimental data and the data obtained using the AXS-RMC method, respectively.](image2)

3. Results and discussion

As an example, the environmental RDFs obtained from the AXS measurements of Zr$_{45}$Cu$_{45}$Ag$_{10}$ are shown in Figure 1. The dashed lines indicate the interatomic distances estimated based on the Goldschmidt radii [6] (Zr, 0.160 nm; Cu, 0.128 nm; Ag, 0.144 nm). The correlation peak for the Zr-Zr pair was not observed in the environmental RDF for Cu and Ag, which indicates the excellent performance of the AXS analysis. A similar description is possible in the environmental RDF around Zr, where only the pair correlations associated with Zr are pronounced. Figure 2 shows four experimental interference functions, $Q_i(Q)$, $\Delta Q_{i\text{Cu}}(Q)$, $\Delta Q_{i\text{Zr}}(Q)$, and $\Delta Q_{i\text{Ag}}(Q)$, together with those obtained through the AXS-RMC simulation. A pre-peak signal at the lower $Q$-region, which implies the presence of a strong chemical ordering unit, could not be observed for each function. This suggests that
the fundamental atomic arrangement of Zr$_{45}$Cu$_{45}$Ag$_{10}$ can be approximated through the dense random packing (DRP) model. We therefore started the AXS-RMC simulation using the initial model based on the DRP, and the successive AXS-RMC simulation converged to represent the experimental interference functions, as shown in Figure 2. The atomic arrangement, such as an icosahedral structure, has been frequently suggested to contribute to the development of the glass-forming ability (GFA), and Voronoi tessellation [7] is one of the most convenient methods for discriminating the coordination topology in the local atomic arrangement. A Voronoi polyhedron can be described using a set of Voronoi index numbers, (n$_i$) = (n$_3$, n$_4$, n$_5$, n$_6$, n$_7$...), where n$_i$ is the number of i-edged faces of a Voronoi polyhedron.

The structural parameters of the nearest-neighbor region of two BMG samples are summarized in Table 1. The averaged coordination numbers increase in the order of atomic size, suggesting that the coordination number around Cu is the smallest, corresponding to that of a icosahedron. On the other hand, the coordination number around Zr is the largest, which is closely attributable to a body-centered cubic structure. The values obtained through the AXS-RMC simulation are nearly equal those by the DRP model, implying that the fundamental structures of the two BMG samples are described well based on the classical DRP structure. Additionally, the first peak position of each partial pair distribution functions in Zr$_{45}$Cu$_{45}$Ag$_{10}$ and Zr$_{40}$Cu$_{40}$Ag$_{20}$ corresponds to the sum of the Gold Schmidt radii. These features are similar to those found in Zr$_{50}$Cu$_{50}$ amorphous alloy [4], and the unique local atomic arrangement based on the strong chemical ordering was not developed through the addition of Ag. Figure 3 shows the relationship between $R^*$ and the fraction of icosahedron-like ordering units. The value of $R^*$ is closely associated with the fraction of icosahedron-like units, and the most efficient icosahedral packing is realized at approximately $R^*$=0.90 of the ideal icosahedral unit. At the same time, the significant development of icosahedron-like units is readily suggested in the BMGs. These results imply that the structural features of the BMGs cannot be fully demonstrated through the common DRP model, where only the effects of the bulk chemical composition and the hard sphere sizes of the individual constituents are considered. The chemical affinity for the paired atoms, which corresponds to the chemical effect arising from the interatomic interactions, is one of the possible reasons for realizing such topological characteristics of the nearest-neighbor region of the BMGs.

| Table 1. Structural parameters for the nearest-neighbor region simulated using the AXS-RMC method: $r_{ij}$, averaged distance; $Z_{ij}$, averaged coordination number; and $R^*$, atomic size ratio between the central atom and its ligands. Values given in parentheses are those for the initial DRP model. |
|---------------------------------|---------------------------------|
|                                | $\text{Zr}_{45}\text{Cu}_{45}\text{Ag}_{10}$ | $\text{Zr}_{40}\text{Cu}_{40}\text{Ag}_{20}$ |
| $r_{ij}$ (nm)                  | $Z_{ij}$                         | $r_{ij}$ (nm)                  | $Z_{ij}$                         |
| Zr-Zr                          | 0.320 (0.324)                    | 0.322 (0.324)                  | 6.4 (6.2)                       |
|                               | 7.0 (7.0)                        | 5.2 (5.1)                      | 1.100                           |
| Zr-Cu                          | 0.294 (0.298)                    | 0.296 (0.298)                  | 0.315 (0.313)                   |
|                               | 5.8 (5.7)                        | 5.1 (5.1)                      | 3.0 (2.9)                       |
| Zr-Ag                          | 0.313 (0.312)                    | 0.315 (0.313)                  | 0.315 (0.313)                   |
|                               | 1.4 (1.4)                        | 1.3 (1.3)                      | 2.6 (2.6)                       |
|                               | 14.2 (14.1)                      | 14.5 (14.2)                    |                                |
| Cu-Zr                          | 0.294 (0.298)                    | 0.296 (0.298)                  | 0.269 (0.267)                   |
|                               | 5.8 (5.7)                        | 5.1 (5.1)                      | 4.1 (4.0)                       |
| Cu-Cu                          | 0.271 (0.266)                    | 0.269 (0.267)                  | 0.278 (0.282)                   |
|                               | 4.7 (4.5)                        | 4.1 (4.0)                      | 2.3 (2.3)                       |
|                               | 0.880 (0.878)                    | 0.880 (0.880)                  |                                |
|                               | 11.6 (11.3)                      | 11.5 (11.4)                    |                                |
| Cu-Ag                          | 0.279 (0.282)                    | 0.278 (0.282)                  | 0.298 (0.297)                   |
|                               | 1.1 (1.1)                        | 2.3 (2.3)                      | 2.6 (2.6)                       |
|                               | 11.6 (11.3)                      |                                |                                |
| Ag-Zr                          | 0.313 (0.312)                    | 0.315 (0.313)                  | 0.315 (0.313)                   |
|                               | 6.4 (6.4)                        | 5.9 (5.7)                      | 5.9 (5.7)                       |
| Ag-Cu                          | 0.279 (0.282)                    | 0.278 (0.282)                  | 0.278 (0.282)                   |
|                               | 5.1 (5.2)                        | 4.5 (4.6)                      | 4.5 (4.6)                       |
| Ag-Ag                          | 0.301 (0.298)                    | 0.298 (0.297)                  | 0.298 (0.297)                   |
|                               | 1.3 (1.3)                        | 2.6 (2.6)                      | 2.6 (2.6)                       |
|                               | 12.8 (12.9)                      |                                |                                |
|                               | 13.0 (12.9)                      |                                |                                |
Figure 3. Relationship between $R^*$ and the fraction of icosahedron-like ordering units. The solid and open symbols indicate the results of AXS-RMC and DRP simulations, respectively. An atom with a set of Voronoi index numbers: (0 0 12 0 0), (0 2 8 1 0 0), (0 2 8 2 0), or (0 1 10 2 0) was ranked as that with an icosahedron-like ordering. The results for $Zr_{50}Cu_{50}$ were obtained using the experimental data from a previous study [4].

4. Conclusion

The structural features of ternary $Zr_{45}Cu_{45}Ag_{10}$ and $Zr_{40}Cu_{40}Ag_{20}$ BMGs were investigated through an AXS-RMC analysis. The 3D structural models obtained reproduced the environmental interference functions well. The structural change caused by the addition of Ag to $Zr_{50}Cu_{50}$ was discussed by comparing the structural models with the classical DRP models. The fundamental structural features of the BMGs studied in this work are well represented based on the classical DRP model, and the addition of Ag indicates no formation of the particular chemical ordering units. A Voronoi analysis indicates that the fraction of icosahedron-like coordination was largest around Cu in the $Zr_{45}Cu_{45}Ag_{10}$ BMG, where the best glass-forming ability was reported in the Zr-Cu-Ag system [8]. The improvement of the glass forming ability in a Zr-Cu-Ag system appears to be associated with the icosahedron-like local coordination.

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