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Tuning local structures in metallic glasses by cooling rate

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ABSTRACT

The $Zr_{48}Cu_{45}Al_7$ amorphous alloy samples quenched under cooling rates of about 2×10^6 K/s and 1×10^2 K/s were prepared by melt spinning and copper-mold suction casting, respectively. Synchrotron-radiation based experiments, combined with a series of calculations, were performed to study the microstructures in both samples. It was found that although the short-range orderings are similar in Zr-centered clusters for both samples, the atom arrangements and distributions in Cu- and Al-centered clusters are very different in terms of atomic-packing efficiencies and regularity of clusters in these two samples. A quantitative analysis revealed that the lower cooling rate leads to the higher packing efficiency and the higher regularity of clusters. This revealed how the cooling rate during quenching fine-tunes the atomic- and cluster-level microstructures in amorphous alloys with the same composition, which may be the structural basis to address the issue why macroscopic properties change with the cooling rate.

1. Introduction

As a class of amorphous materials, metallic glasses (MGs) have attracted intense interest since 1960 [1], because they have unique chemical, physical, and mechanical properties [2–6], as compared with their corresponding crystalline alloys. Great efforts have been devoted to study their microstructures to understand their unique properties and glass-forming mechanisms [7–11]. However, it is still a challenge to establish the explicit structural pictures of MGs. It has been realized that while some determined unit cells are regarded as the basic structural components in crystals, clusters (the convex polyhedra made up of one center atom and some shell atoms) should be the building blocks in microstructure of this class of glassy materials. Several structural models have been proposed according to this viewpoint [9,12,13]. These studies revealed an essential structural feature that the short-to-medium range orderings in MGs can be formed by packing atoms topologically and chemically within clusters and stacking or connecting clusters to fill space. The short-to-medium range orderings significantly contribute to the glass formation and unique properties in alloys.

In MGs with different compositions, different properties have been proven to originate from their different chemical and topological short-to-medium range orderings [14–16]. Therefore, the question arises, should the amorphous microstructure and the properties always be the same in one MG composition? So far, it has been reported that the cooling rate in vitrifying one alloy from the liquid affects its properties [17–21], i.e., the macroscopic properties vary with the cooling rate during quench. This indicates that the cooling rate might be able to influence the microstructure in the alloy. However, because the structure change caused by cooling rate is much slighter than that by composition, it is still unknown how to detect and analyze the subtle structure change induced by cooling rate [22–24].

In this work, we address this issue by using the state-of-the-art synchrotron-radiation based experiments coupled with a series of calculations. It was detected that their atomic arrangements and distributions around Cu and Al centers are different. Furthermore, a quantitative analysis revealed that the atomic-packing efficiencies and the regularity of clusters are different between these two samples quenched at different cooling rates. In particular, the lower cooling rate relates to the higher packing efficiency and the higher regularity. This study reveals how the cooling rate during quenching tunes the atomic-level microstructures in amorphous alloys with the same composition.

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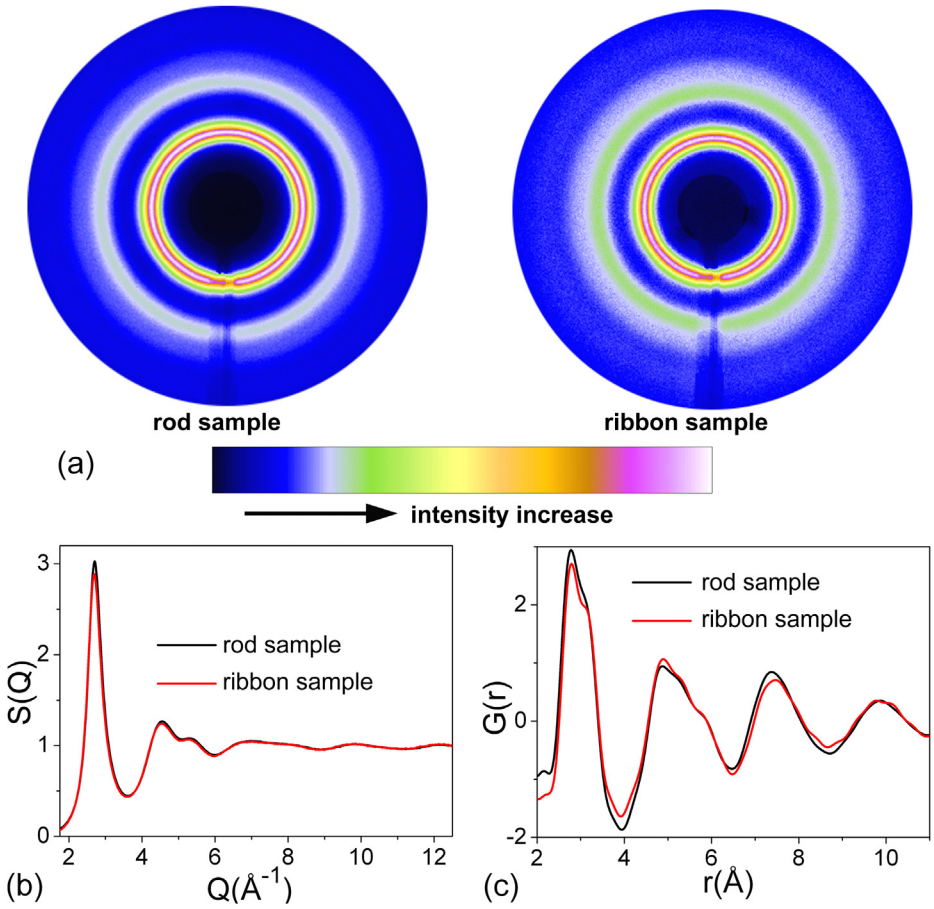

Fig. 1. The synchrotron radiation-based XRD data for both samples, including: (a) The two-dimensional diffraction patterns, (b) The normalized structure factor, $S(Q)$, and (c) The total pair distribution function, $G(r)$.

2. Experimental and simulation methods

2.1. Sample preparation

The alloy ingots were prepared by arc melting the mixture of Zr (99.9 wt.%), Cu (99.9 wt.%), and Al (99.99 wt.%) elements in Ti-gettered high-purity argon atmosphere. The ingots were melted at least 5 times in order to ensure their compositional homogeneity. The $Zr_{48}Cu_{45}Al_7$ ribbons with a cross section of 0.04 × 2 mm and the $Zr_{48}Cu_{45}Al_7$ rods with a diameter of 6 mm were prepared by melt spinning and copper-mold suction casting, respectively [25]. The cooling rates (R) for ribbon and rod samples are about 2×10^6 K/s and 1×10^2 K/s respectively, which were estimated from the size of the minimum dimension of these samples, according to:

$$R = \frac{A}{t^2} \tag{1}$$

where t is thickness of the casting in mm and A is 3840 mm^2 K/s [26].

2.2. Synchrotron radiation-based experiments

The synchrotron-radiation based high-energy (about 100 keV) X-ray diffraction measurements were performed for both samples at the beam line, BW5, of Hasylab in Germany. To achieve the proper penetrating depth in the diffraction measurement, the rod was cut into a slice having a thickness of 1 mm. Subsequently, the Zr and Cu K-edge extended X-ray absorption fine structure (EXAFS) spectra were measured for both samples using the transmission mode at the beam lines, BL14W1, in the Shanghai Synchrotron Radiation Facility (SSRF) of China, and A1, in the Hasylab of Germany. Because the EXAFS measurement also requires a proper transmission thickness, slices cut from the rod were polished manually till their thickness is 30–40 microns. Subsequently, the diffraction patterns and EXAFS spectra were normalized via a standard data-reduced procedure [27], employing the PDFgetX [28] and Visual Processing in EXAFS Researches (VIPER) [29] softwares, respectively.

2.3. Reverse Monte-Carlo (RMC) simulation

The RMC-simulation technique is an iterative method extensively used for building the possible structural models to probe the detailed structural information in disordered systems that agree quantitatively with the available experimental data (such as the synchrotron radiation-based X-ray diffraction, EXAFS, and neutron-diffraction data). In particular, it is available for glassy alloys [30]. In this work, the synchrotron radiation-based diffraction and EXAFS data were adopted and simulated simultaneously in the RMC frame, using the software RMCA [31]. The initial cubic boxes for the rod and the ribbon samples were built, which contain 40,000 random-distributed Cu, Zr, and Al atoms, matching the $Zr_{48}Cu_{45}Al_7$ ternary composition. During the RMC simulation, when all the atoms move randomly within a determined time interval, the experimental diffraction and EXAFS data are compared with the simulation spectra using the iterative calculation expression [32]: