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The evolution of Cu-rich domains in the $Cu_{60}Zr_{30}Ti_{10}$ metallic glass by ASAXS

Cheng Weidong [a], Sun Minhua [a,*], Liu Fang [a], Liu Xiongjun [b], Sun Yongli [a]

[a] Department of Physics, Harbin Normal University, Harbin, 150025, P.R. China
[b] State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing, 100083, P.R. China

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Abstract

The structure of the melt-spun $Cu_{60}Zr_{30}Ti_{10}$ metallic glass is investigated by anomalous small angle X-ray scattering (ASAXS). It is confirmed that the compositional segregation in the diameter range of 30–50 nm exists in the as-quenched state. ASAXS results have convincingly shown the aggregation of Cu atoms and the formation of Cu-rich domains in the amorphous matrix. The Cu-rich domains grow slightly with low growth rate below the glass transition temperature, while the sizes of these domains drastically increase with high growth rate in the supercooled liquid temperature region. The Cu-rich domains are presumed to be associated with nucleation for the primary crystallization process.

Keywords: Bulk metallic glass (BMG); Crystallization; Anomalous small angle X-ray scattering

1. Introduction

In the past decades, Cu-based bulk metallic glasses have been largely investigated due to their unique physical, chemical and mechanical properties and have attracted increasing attention for a wide range of potential applications [1–4]. Inoue et al., recently, have developed a new family of Cu-based BMGs in Cu–Zr–Ti, Cu–Hf–Ti [5–7] and Cu–Ni–P [8] systems. Many Cu-based bulk glassy alloys exhibit excellent glass-forming ability with a large supercooled liquid region [9,10], better corrosion resistance [11], and so on.

The precipitation of nanocrystals in the amorphous matrix may be induced by partial crystallization during casting or by primary crystallization during heat treatment. Sometimes, the precipitation may strongly degrade the toughness and the plasticity of the material [2,12]. Crystallization in the supercooled liquid region has attracted intensive interest [5,6,13–15]. While bulk amorphous alloys are rather resistant to nucleation during quenching, many metallic glasses transform into the nanocrystalline state upon annealing in the supercooled liquid region.

M. Kasai and J. Saida demonstrated that the Cu-rich nanocrystalline cubic phases were directly formed during the melt-quenching process in the $Cu_{60}Zr_{30}Ti_{10}$ and the high stability of the Cu-rich nanocrystalline cubic phase led to the coexistence with the glassy phase in the nanometer scale. The nano-bcc CuZr phase was precipitated with the remaining Cu-rich nanocrystalline phases in the primary devitrification process in the $Cu_{60}Zr_{30}Ti_{10}$ alloy [5,6]. The present work aims at investigating the evolution of Cu-rich domains in the relaxation and supercooled region by ASAXS technique.

2. Theory and experimental

The size range of particles between 1 nm and several hundreds of nm can be well detected by small angle X-ray scattering (SAXS) [16]. Anomalous small angle X-ray scattering (ASAXS) [17–20] is an excellent method to overcome the problem of separating the small angle scattering of the concerning element from that of the whole system. If the SAXS measurements are carried out at different X-ray energies which are close to the X-ray absorption edge of the resonant atom, the scattering factor of the

* Corresponding author.
E-mail address: smhuaa@gmail.com (S. Minhua).

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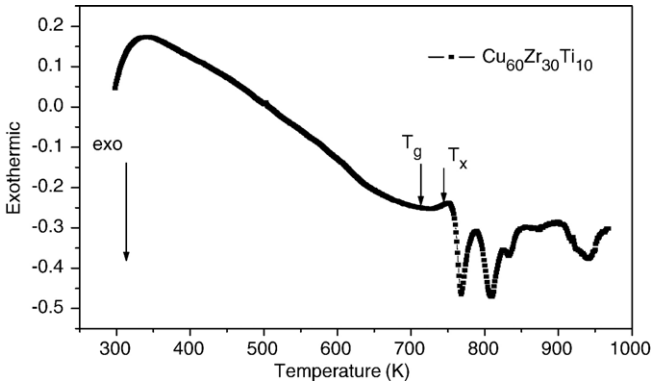

Fig. 1. DSC curve of the melt-spun $Cu_{60}Zr_{30}Ti_{10}$ metallic glass scanned at a heating rate of 20 K/min.

resonant atom can be sharply varied. Therefore, by using the ASAXS method not only the size distribution of the concerning particles is calculated, but also their shapes are determined.

An alloy ingot of $Cu_{60}Zr_{30}Ti_{10}$ ternary amorphous alloy was produced by arc melting high-purity raw materials of 99.99 mass% Cu, 99.9 mass% Zr, 99.9 mass% Ti in a purified argon atmosphere. Amorphous ribbons were prepared by rapidly solidifying the alloy by the single roller melt-spinning technique. Thermal analysis was performed by differential scanning calorimeter (DSC) at a heating rate of 20 K/min.

ASAXS measurement was performed at the 4B9A beam line at different temperatures (from 303 K to 833 K) at Beijing Synchrotron Radiation Laboratory (BSRF), using five different energies (8976, 8972, 8964, 8930 and 8780 eV) below the Cu K-absorption edge at 8980 eV. The thickness of the specimen used for ASAXS experiments was 20 μm. Intensities were normalized to the primary beam intensity.

3. Result and discussion

Fig. 1 shows the DSC curve of the melt-spun $Cu_{60}Zr_{30}Ti_{10}$ amorphous alloy. It shows that the onset temperatures of glass transition, T_g and crystallization, T_x are 711 K and 745 K, respectively.

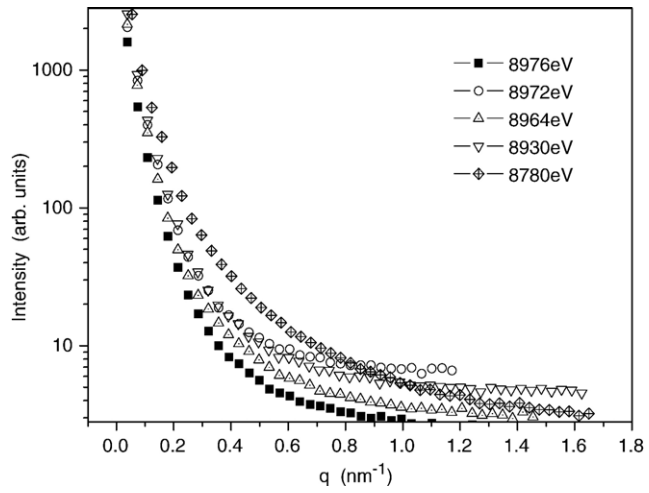

Fig. 2. ASAXS scattering intensities near the Cu K-edge for the sample at 673 K.

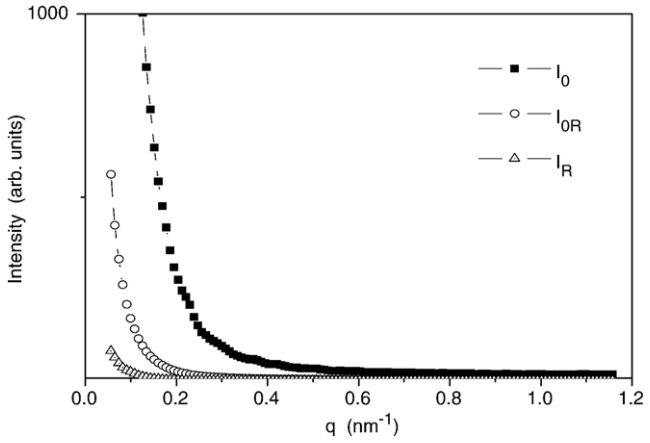

Fig. 3. Result of the dispersion analysis according to Eq. (1), Cu partial scattering function (I_R) extracted from ASAXS curve.

The exothermic reactions with four peaks appear after the glass transition in the crystallization process. The first exothermic peak is due to the primary devitrification process as follows: glass + nanocrystal (cubic)→nano-CuZr + nanocrystal (cubic) in the $Cu_{60}Zr_{30}Ti_{10}$ alloy [5,6].

Fig. 2 shows an example of the ASAXS pattern near the Cu absorption edge energy in the $Cu_{60}Zr_{30}Ti_{10}$ amorphous alloy heated at 673 K. From Fig. 2 we can find that the closer the energy applied to the Cu absorption edge, the smaller the SAXS intensity. The contribution of Cu element to the scattering intensity can be separated from the total scattering intensity by the following method. The scattering intensities $I(q,E_i)$ recorded at different energies E_i close to but below the absorption edge of the resonant atoms can be divided into partial scattering functions [17,21]:

$$I(q,E_i) = I_0(q) + 2f'(E_i)I_{0R}(q) + [f'^2(E_i) + f''^2(E_i)]I_R(q). \quad (1)$$

Where $q = 4\pi \sin(\theta/2)/\lambda$ is the magnitude of the scattering vector, λ is the wavelength and θ is the scattering angle. The term f' is proportional to the absorption coefficient and can be obtained directly from the XANES spectrum of the specimen. The correction f'' is calculated from f' according to the Kramers–Kronig relation. The nonresonant scattering term $I_0(q)$ is the Fourier transform of the excess electron

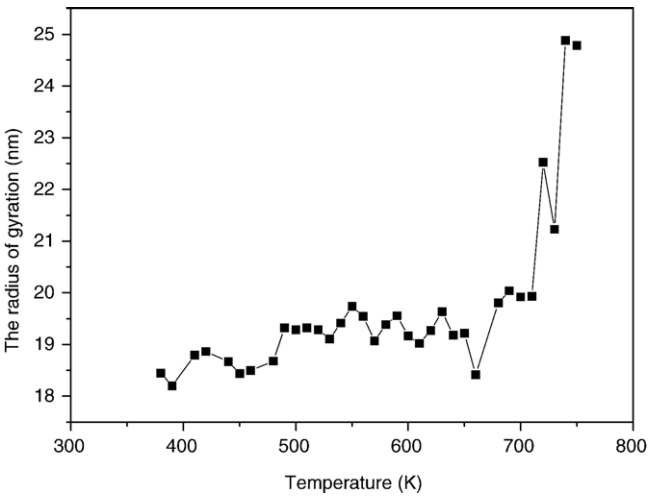

Fig. 4. The radius of gyration as a function of temperature.