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Abnormal change of electrical resistivity in the $Cu_{46}Zr_{46}Al_8$ bulk metallic glass during crystallization

Binbin Liu, Ningning Zuo, Feng Ye*

State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, 30 Xueyuan Road, 100083 Beijing, China

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ABSTRACT

The crystallization of bulk metallic glass occurs with heat release, volume shrinkage, and electrical resistivity decrease because of the differences in properties between the glass and crystalline phases. A standard four-probe electrical resistivity measurement during the crystallization of the $Cu_{46}Zr_{46}Al_8$ bulk metallic glass shows an abnormal increase of resistivity at the initial stage before the normal declining stage. High-density nanocrystals emerged in the matrix, which enhanced electron scattering and resulted in increasing of resistivity. The subsequent normal declining of resistivity was dominated by the growth of the nanocrystals. This high-density site-saturated nucleation followed by slow growth crystallization kinetics was supported by microstructure analysis with SEM and TEM.

1. Introduction

Clarifying the crystallization behaviors of bulk metallic glasses (BMGs) can provide useful information to understand the origin of high thermal stability and good glass-forming ability [1,2]. Many efforts have been contributed to the crystallization kinetics of metallic glasses by thermal analysis. Electrical resistivity is always related to the electronic structure of alloys and sensitive to structural changes. Due to structural disorder, the electrical resistivity of metallic glasses is one or two orders of magnitude higher than that of the corresponding crystalline alloys. Variation of electrical resistivity during crystallization is governed by the residual glass matrix, crystalline nuclei formation and their growth up. Especially, the appearance of grain changes the disorder arrangement of atoms as well as the band structure of metallic glasses, which leads to sharp decline of resistivity [3–6]. However, there are fewer reports correlating resistivity variation with different types and path of crystallization, such as phase decomposition, formation of icosahedral phases, and formation of intermetallic compounds [7].

In present work, we report an abnormal variation of electrical resistivity of the $Cu_{46}Zr_{46}Al_8$ BMG during the crystallization and correlate it with the crystallization kinetics, which provide useful information to understand good glass-forming ability of this BMG. The result also indicates that electrical resistivity measurement is a more intuitive approach to investigate structure evolution of metallic glasses.

2. Experimental details

Master alloy ingot with composition of $Cu_{46}Zr_{46}Al_8$ (atomic%) was prepared by arc melting a mixture of Zr, Cu and Al. The ingot was suction cast into a cylindrical specimen with a diameter of 5 mm under Ar atmosphere. The amorphous nature was examined by X-ray diffraction using Cu Kα radiation in the Rigaku D/MAXDRB X-ray diffractometer. Samples with dimensions of about 1.5 mm × 1.0 mm × 0.2 mm were prepared for electrical resistivity measurements using a standard four-probe technique with a heating rate of 10 K/min. Thermal analysis was carried out using NETZSCH Differential Scanning Calorimetry (DSC-404f1). Microstructure analysis was investigated by means of scanning electron microscopes on Zeiss SUPRA™55 and transmission electron microscopes on Tecnai G2 F30.

3. Results and discussion

Variation of normalized resistivity ($\rho_T/\rho_{323\ K}$) with temperature of the $Cu_{46}Zr_{46}Al_8$ BMG at a heating rate of 10 K/min is shown in Fig. 1(a). Normalized resistivity of the $Cu_{36}Zr_{56}Al_8$ alloy is also shown for comparison. Both BMGs show negative temperature coefficient of resistance (TCR) below 500 K. The glass transition temperature (T_g) and the onset crystallization temperature (T_x) could be determined from the electrical resistivity curves. However, unlike with $Cu_{36}Zr_{56}Al_8$ alloy and other Zr- and Cu-based metallic glasses [3–6], which show continuous decrease of resistivity during crystallization, the resistivity of the $Cu_{46}Zr_{46}Al_8$

* Corresponding author.
E-mail address: yefeng@skl.ustb.edu.cn (F. Ye).

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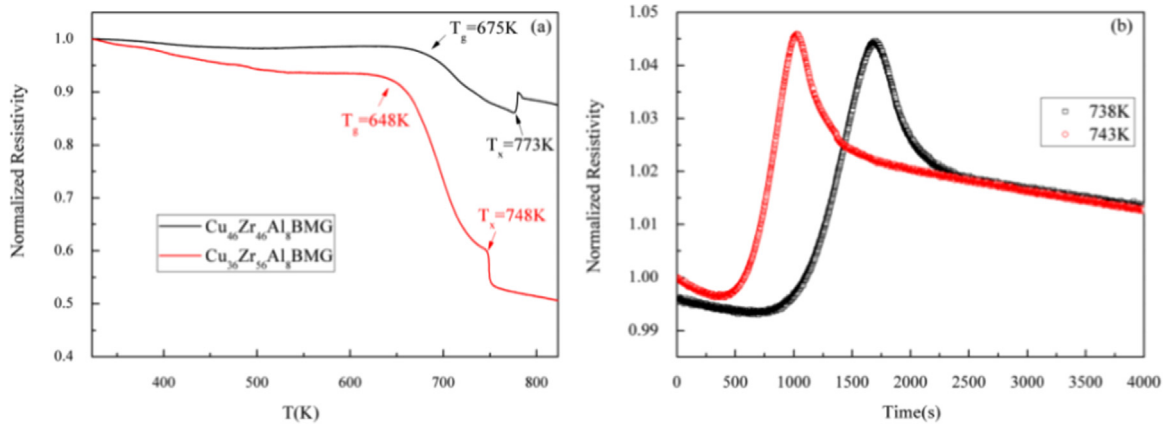

Fig. 1. (a) Variation of normalized resistivity ($\rho_T/\rho_{323\ K}$) with temperature of the $Cu_{46}Zr_{46}Al_8$ and $Cu_{36}Zr_{56}Al_8$ alloys at a heating rate of 10 K/min; (b) Variation of normalized resistivity ($\rho_t/\rho_{t=0}$) with time of the $Cu_{46}Zr_{46}Al_8$ alloy annealed at 738 and 743 K.

alloy exhibits an abnormal increase at the initial stage before the normal declining stage under both continuous heating and isothermal annealing.

DSC traces with two exothermic peaks of the $Cu_{46}Zr_{46}Al_8$ alloy under isothermal annealing at 738 K also implies a two-step crystallization process (Fig. 2(a)). The resistivity declines when the second peak appears. The phases evolution during the crystallization were obtained from the XRD patterns after the samples were isothermally annealed at 738 K for 1300, 1600, 1800, and 2100 s as displayed in Fig. 2(b). No obvious crystalline phases can be observed when annealing at 738 K for 1300 s and 1600 s. The glass matrix started to precipitate crystalline phases which were identified to be orthorhombic-Zr_7Cu_{10} via Search-Match to the ICDD Powder Diffraction File and an unknown phase. This is also confirmed by SEM images in Fig. 3. Many crystals emerged in the matrix after annealing for 1800 s (Fig. 3(a)). Crystals grew up with longer annealing time (Fig. 3(b)), and no new phase precipitated. Therefore, the second declining stage is mainly due to grain growth.

The microstructure for the $Cu_{46}Zr_{46}Al_8$ alloy at the initial rising stage was further investigated via TEM observation. Fig. 4(a) shows many black dots scattered in the glass matrix. The SAED pattern (inset) shows that some outer-diffraction rings. Lots of black dots indicate a high density of nucleation. Meanwhile, some medium range orders (MROs) existed in the matrix (the white ring in Fig. 4 (b)). Voyles and co-workers have performed systematic analysis of MRO in metallic glasses using fluctuation electron microscopy and revealed that MRO acted as precursor for nanocrystal [8,9]. The emerged MRO might finally lead to high-density nucleation. The nearby nanocrystallines could also overlap (Fig. 4c). More black dots appeared with longer annealing time (Fig. 4(d)), which represented higher-density nucleation. However, there were fewer large crystals distributed in the matrix (Fig. 4(e)), which were also identified to be Zr_7Cu_{10} (inset SAED pattern). This observation is corroborated by XRD patterns. Meanwhile, some smaller crystalline particles (about 2 nm) emerged in the residual matrix (Fig. 4 (f)). Therefore, the initial rising of resistivity is reconciled with high-density nucleation with slower growth.

The nucleation and growth process are related to atomic diffusion. The main crystalline phase was identified to be Zr_7Cu_{10}. Therefore, the diffusion of Zr and Cu is the dominant factor during the crystallization. The mixing enthalpy between Zr and Al is -44 kJ/mol while the value between Zr and Cu is -23 kJ/mol, but the value between Cu and Al is only -1 kJ/mol. The Al atoms have preference to form strong bonds with Zr atoms, which means a stronger binding tendency between Zr and Al atoms. Such bonds could enhance the medium-range order in the system and cause a denser packing as well as a lower mobility of Zr atoms, which indicates a much slower dynamical behavior [10,11]. Zhang and Eckert [12] also suggested that the $(Cu_{0.5}Zr_{0.5})_{100-x}Al_x$ ($x \leq 10$) with x=7 or 8 has higher viscosity and lower diffusivity. The poor ordered Zr_7Cu_{10} also indicated slower diffusion in the $Cu_{46}Zr_{46}Al_8$ BMG. The slower diffusion in the $Cu_{46}Zr_{46}Al_8$ alloy leads to slower growth of the nucleated crystalline particles. Tang and Harrowell have revealed that the crystal growth rates for a good glass former are much slower than that in a poor glass former using molecular

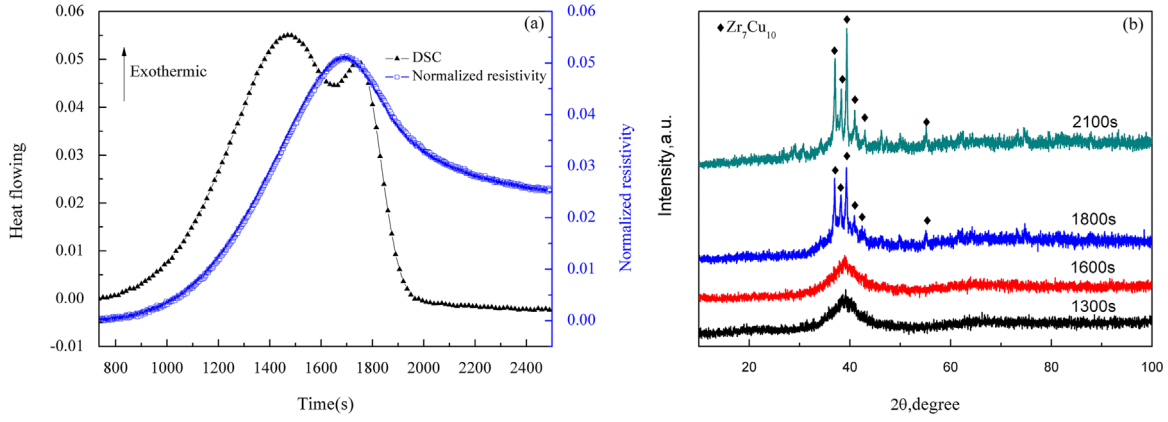

Fig. 2. (a) The DSC and normalized resistivity ($\rho_t/\rho_{t=735\ s}$) with time traces of the $Cu_{46}Zr_{46}Al_8$ alloy annealed at 738 K. (b) XRD patterns of the $Cu_{46}Zr_{46}Al_8$ alloy annealed at 738 K for 1300 s, 1600 s, 1800 s and 2100 s, respectively.