Effects of high pressure on the nucleation of $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ bulk metallic glass

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Abstract

The effects of high pressure on nucleation of $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ bulk metallic glass (BMG) are studied by means of differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The activation energies of crystallization for the BMG at different pressures are determined by the Kissinger method. The experimental results demonstrate that applied pressure promotes nucleation. The effects of high pressure on nucleation are discussed in terms of the nucleation kinetics and thermodynamics.
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Keywords: Bulk metallic glass; Nucleation; High pressure

1. Introduction

Nucleation studies of bulk metallic glasses (BMGs) are of importance in understanding mechanisms of phase transformations far from equilibrium, evaluating the glass-forming ability (GFA) of the melts and producing controlled ultra-refined microstructure [1–3]. However, up to now, a proper understanding for the nucleation under high pressure of the BMGs is still lacking. Different investigators sometimes obtained alternative and even contradictory results about the effects of high pressure on crystallization, due to their different pressure annealing conditions and detecting methods applied [4–7]. Recently, some authors reported that the nucleation and growth of crystallization occur in different stages and have different kinetics [8,9]. This offers the possibility to investigate nucleation and growth in BMGs separately. Cu–Zr–Hf–Ti BMGs were developed in 2000, and they were found to have excellent mechanical properties, their fracture strength being above 2001 MPa [10]. In addition, they have high thermal stability against crystallization. Therefore, Cu-based BMGs have significant importance both in basic research and engineering aspects.

In this work, the effect of high pressure on the nucleation of the $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ BMG is investigated. The annealing temperature is 36 K lower than the glass temperature T_g. The crystallization activation energies of the samples preannealed under high pressure are obtained by the Kissinger method. The role of high pressure on the nucleation is discussed.

2. Experimental

$Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ BMG was prepared by melting a mixture of the elements (with purity of about 99.99 at.%) in a Ti-gettered arc furnace and then casting in a water-cooled copper mould to obtain rods with diameters of 3 and 1 mm. The amorphous nature, as well as the homogeneity of the rods, was ascertained with X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Slices with a thickness of 0.5 mm and a diameter of 1 mm were cut from rods for annealing under different pressure condition and for DSC measurements. The samples were annealed under ambient pressure in a furnace with a vacuum of 10^{-4} Pa. The annealing of the samples under high pressure was performed in an apparatus with six anvil tops. NaCl powder was used

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as the solid pressure-transmitting medium. A NiCr–NiAl thermocouple was brought into the pressurized zone through a graphite furnace and was near the sample. The accuracy to measure the temperature of the sample itself under high pressure was better than ± 2 K. The details of high-pressure experiment were described in ref. [11]. The samples were annealed at 698 K for 1 h under ambient pressure 2, 3.5, 5 GPa, respectively. The structure of the samples was investigated by XRD using a Rigaku Rapid-XRD diffractometer with Cu Kα radiation. The DSC measurements were carried out under a purified argon atmosphere in a Perkin-Elmer DSC7 at heating rates, ϕ ranging from 5 to 80 K/min. The calorimeter was calibrated for temperature and energy at various heating rates with high purity indium and zinc.

3. Results and discussions

The glass transition temperature T_g, onset crystallization temperature T_x and melting temperature T_m of the Cu-based BMG at ambient condition are 734, 782 and 1189 K, respectively [7]. Fig. 1 shows the XRD patterns of the $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ BMG, which annealed at 698 K under different pressures. No distinct crystalline peaks are found in the XRD patterns, indicating that the amorphous phase is retained without clear indication of crystallization after annealing for 1 h at 698 K under different pressures. Fig. 2 shows the DSC curves of the BMGs annealed at 698 K under different pressure. The onset temperature of the first crystallization peak T_{x1}, and the second peak of the samples T_{x2}, are 781 and 835 K for sample annealed under ambient pressure. With increasing pressure, the crystallization temperature of the sample decreases. The crystallization temperature shows obvious differences under different pressures, indicating that the applied pressure changes the microstructure of the BMG during annealing, although differences of the microstructure cannot be found from the XRD patterns.

Fig. 3 shows the DSC curves of representative samples annealed under 5 GPa at various heating rates of 5, 10, 20, 40 and
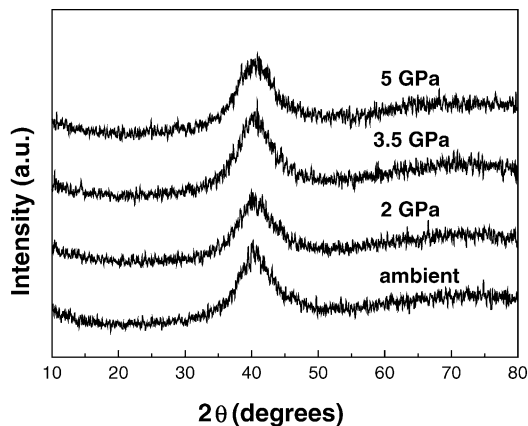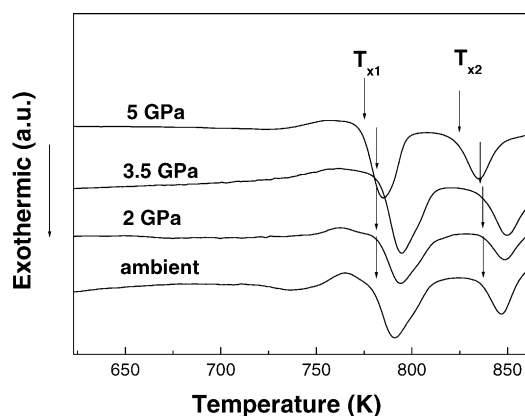

Fig. 2. The DSC curves for the samples which annealed at 698 K for 1 h under different pressures. The heating rate is 40 K/min.

80 K/min. The T_{xi} and T_{pi} (crystallization peak temperature) of the sample are shifted to higher temperature with increasing heating rate, indicating that the crystallization behaves markedly different. The activation energy E_{xi} for the crystallization reaction is determined by the Kissinger's equation [12]

$$\ln \frac{T^2}{\phi} = \frac{E}{k_B T} + C, \qquad (1)$$

where k_B is the Boltzmann constant. The Kissinger plots of the crystallization for the sample are shown in Fig. 4. The E_{x1} and E_{x2} values are determined to be 312.5 and 326.6 kJ/mol, respectively.

Fig. 5 shows the crystallization activation energy E_{xi} as a function of the applied pressure. The kinetics studies confirm that preannealing under high pressure has a large effect on the subsequent crystallization. With increasing applied pressure, the corresponding crystallization activation energy E_{xi} decreases linearly, as shown in Fig. 5. The activation energy decrease with pressure has a rate of 8.21 kJ/mol·GPa for the first crystallization peak and 7.40 kJ/mol·GPa for the second crystallization peak.

Fig. 1. The XRD patterns of the samples which annealed at 698 K for 1 h under different pressures.
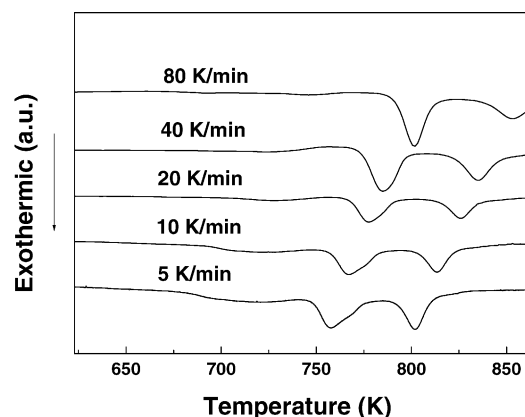

Fig. 3. The DSC curves for the samples annealed under 5 GPa at different heating rates.
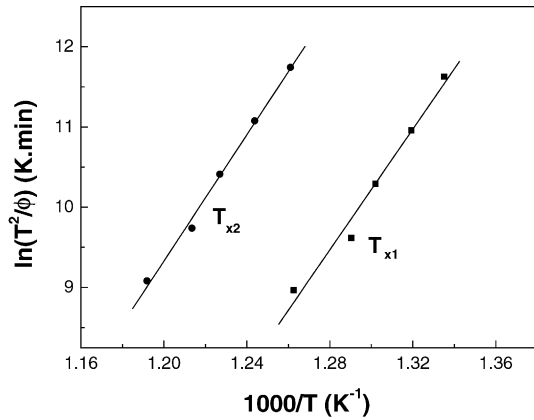
Fig. 4. Kissinger plots of the crystallization temperature obtained from the DSC measurements for the sample annealed under 5 GPa.

The processes of reheating to crystallization of the samples in DSC are the same. The difference of the activation energy is the effect of high pressure on the nucleation of the sample during preannealing. It is important to recognize that atomic diffusion in BMGs proceed via two parallel processes, single-atomic hopping and collective motions of groups of atoms [13,14]. The former dominates below T_g, whereas the latter dominates above T_g [14]. High pressure is an obstacle to the long-range atomic diffusion [15,16], when annealing at temperatures below T_g under high pressure, the atoms perform short-range motion, but long-range diffusion is very difficult. Therefore, the changing of the activation energy under different pressures is not dominantly the effect of high pressure on the growth, but on the nucleation. By assuming that there is only homogeneous nucleation during the crystallization process in the BMG, the effect of the pressure on the nucleation activation energy, $\Delta G*$ can be described as [17]

$$\left(\frac{\partial \Delta G*}{\partial P}\right) = -\frac{32\pi\sigma^3}{3}\frac{\Delta V}{(\Delta G)^3} \quad (2)$$
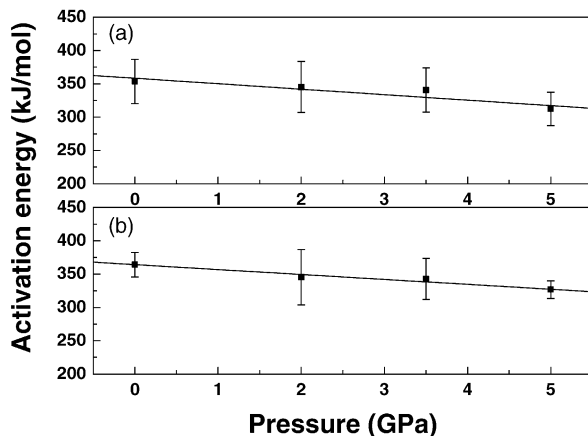

Fig. 5. Activation energy of the samples as a function of applied pressure. The data were linearly fitted as a solid line. (a) The activation energy of the first crystallization peak, and (b) the activation energy of the second crystallization peak.

where σ is the interfacial energy, which is not sensitive to the pressure, ΔG is the energy difference between the amorphous state and the crystallized state, ΔV is the difference of the molar volumes between the amorphous state and the crystallized state. The molar volume of the crystallized state is smaller than that of the amorphous state for $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ BMG [18]. The amorphous state is metastable with respect to the crystalline state, meaning that $\Delta G > 0$. Because ΔG and ΔV are both positive, the applied pressure should lead to a decrease for activation energy of the nucleation, which is in agreement with our experimental results. High pressure causes an annihilation of the free volume and reduces voids through compressing the glassy structure and reconstructing the atomic configuration, and these effects are related to the short-range rearrangement of atoms. The rearrangement favors a homogeneous formation of small clusters.

4. Conclusions

The nucleation of crystallization of the $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ BMG is studied by annealing under different pressure conditions. The experimental results have shown that the crystallization activation energies decrease with increasing applied pressure. The activation energy decreases with a rate of 8.21 kJ/mol·GPa for the first crystallization peak and 7.40 kJ/mol·GPa for the second crystallization peak. The differences in activation energy are due to the fact that high pressure promotes nucleation. The effects of high pressure on nucleation have been discussed in terms of the nucleation kinetics and thermodynamics.

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