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L L Sun[1,4], T Kikegawa[2], Q Wu[1], Z J Zhan[1], L M Cao[1], L M Wang[1], G J Shao[3], J Zhang[1] and W K Wang[1,3]

[1] Laboratory of Extreme Physics Conditions, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China
[2] Photon Factory, Institute for Materials Structure Science, High Energy Accelerator Organization, Tsukuba 355-0801, Japan
[3] College of Materials Science and Chemical Engineering, Yanshan University, Qinhuangdao 066004, People's Republic of China

E-mail: llsun@aphy.iphy.ac.cn

Abstract
Structural changes in bulk metallic $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ glass subjected to heat treatments under high pressure were investigated by means of synchrotron radiation x-ray diffraction (SRXRD). *In situ* SRXRD measurements showed that the crystallization process of this material is comprised of two stages. Subsequent heating at 10 GPa converts the sample from the amorphous (Am) phase into a metastable fcc phase and then leads to the fcc phase changing back to the Am phase, indicating that there is a kind of 'reversible' phase transition phenomenon occurring in the alloy. Such phenomenon is explained on the basis of free energy considerations.

1. Introduction

The bulk metallic glass (BMG) $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ which has exceptional glass-forming ability and reasonable thermodynamic stability against crystallization over a wide range of 100 K above the glass transition temperature has provided a means to extend our understanding of phase transition kinetics of glass-forming alloys in the supercooled liquid state [1, 2]. The complex constitution and relatively high stability against crystallization of this BMG lead to a different crystallization behaviour compared with conventional metallic glasses. During its transition from the amorphous (Am) to the crystalline phase, there is a decomposition event in the supercooled liquid prior to the crystallization and this decomposition appears to

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[4] Author to whom any correspondence should be addressed.
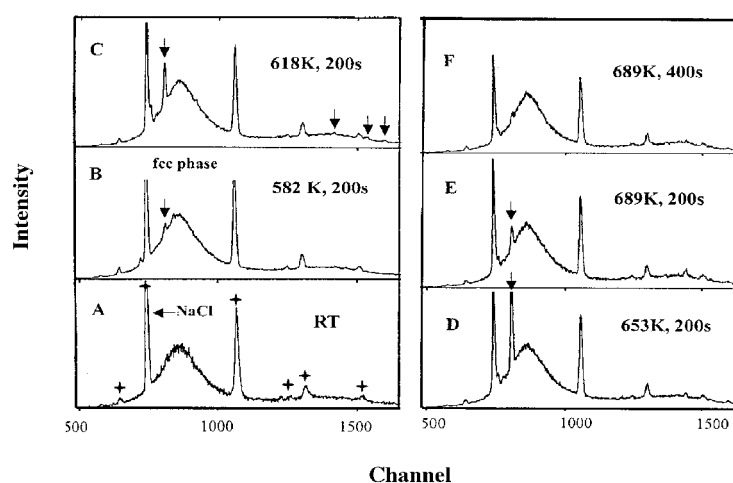
Figure 1. *In situ* synchrotron radiation XRD patterns of the first-stage crystallization in the BMG at temperatures between 298 and 689 K under a compression of 10 GPa.

be a necessary precursor for the nucleation of crystals [3]. The crystallization behaviours of this material at ambient pressure and high temperature have been intensively investigated [4–7]. Recently, several groups have studied its crystallization under conditions of very high pressure and room temperature [8, 9], as well as at high temperature and pressure below 3 GPa [10]. However, there has been little investigation on what the behaviours are like for this material under high-pressure and high-temperature (HPHT) conditions. In this paper, we report an unusual physical phenomenon detected by an *in situ* synchrotron radiation x-ray diffraction method (SRXRD) under HPHT. It was found that, on compressing the sample to 10 GPa, and then heating it, a reversible amorphous–crystalline–amorphous phase transition occurred. This unusual phase transition induced by heating at fixed high pressure gave us a fresh way to understand the natural characteristics of this BMG, which is an extremely interesting phenomenon and worth paying attention to.

2. Experimental details

The high-pressure and high-temperature experiments were performed at the Photon Factory in Japan. The structural changes were probed and identified by the SRXRD method. The energy-dispersive diffraction investigation was performed on the MAX80 high-pressure facility using an intrinsic Ge detector set at a diffraction angle of 3°. The temperature was measured with a pair of thermocouples. The starting BMG was embedded in the pressure-transmitting medium NaCl, loaded into cubic-type high-pressure apparatus up to 10 GPa and then heated at a rate of 10 K min^{-1}.

3. Results and discussion

From SRXRD measurements of the BMG at 10 GPa, it was found that there exist two stages of distinct phase transitions with temperature increase. Figure 1 shows XRD profiles of the first-stage phase transition. The strong peaks of pattern A in figure 1 were the signals originating from the pressure-transmitting medium NaCl. We found that the full Am structure is lost at 582 K; a crystalline peak is superimposed on the Am halo (figure 1(B)) and begins
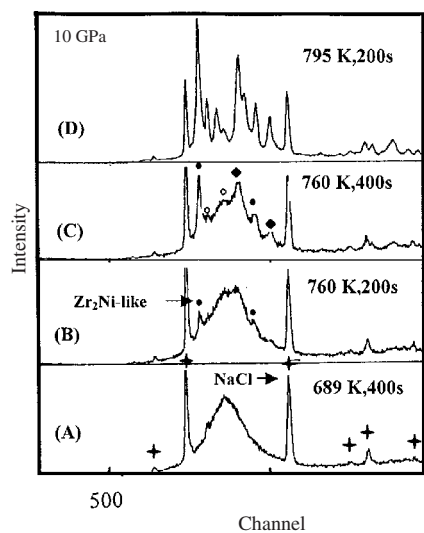
Figure 2. *In situ* XRD patterns of the second-stage crystallization for the BMG at temperatures between 689 and 795 K; the open circle represents Zr_2Cu-like phase and the solid square the Be_2Zr-like phase.

to grow with increasing temperature (figures 1(C) and (D)). When the temperature reaches 618 K, new peaks appear following the first response. These crystalline peaks are centred at $C = 787.9$, 1413.0, 1528.8 and 1586.4 respectively, where C denotes the channel number ($C = E - 1.2934/0.058\,86$) and E denotes the energy. According to the relation between the energy E and d-spacing ($d = hc/2E \sin\theta$, where h is Planck's constant, c the light velocity, θ the angle of incidence of the x-rays, $\theta = 3°$), we obtained corresponding d-values of 0.245, 0.138, 0.128 and 0.123 nm respectively. Indexed results confirm that the primary crystalline phase takes the face-centred cubic (fcc) structure. On increasing the temperature to 689 K, the intensity of the XRD peak centred at $C = 787.9$ becomes weaker (figure 1(E)) and it disappears at this temperature for durations of about 400 s or a temperature of 698 K. The loss of the XRD peaks on compression to about 10 GPa and at a temperature of 698 K demonstrates that the first crystalline phase reverts back to the Am state.

The 'reversible' phase transition phenomenon upon heating below 698 K in this BMG prompts us to consider what will happen with further heating steps. To answer this question, higher temperature (>750 K) was applied in the experiments. Figure 2 presents XRD patterns of the BMG subjected to temperatures between 760 and 795 K at 10 GPa. *In situ* XRD measurements indicated that, as temperature reaches 760 K, a crystalline Zr_2Ni-like phase was first precipitated from the Am matrix instead of an fcc phase (figure 2(B)). Further annealing leads to Zr_2Cu-like and Be_2Zr-like crystallized phases (figures 2(C) and (D)), and these phases can be preserved up to the melting point. This clearly reveals that the first-stage transition of the amorphous–crystalline–amorphous phase did not reappear at higher temperature, i.e. the second-stage phase transition for the BMG is irreversible.

To clarify the pressure contribution for the structural change in this investigation, parallel experiments were carried out at ambient pressure. Each sample exposed to temperature treatments in a vacuum was examined by the powder XRD method. Figure 3 shows the XRD measurements of the BMG at ambient pressure. It can be seen that no crystalline phase exists in the Am matrix for samples that are annealed at 582 and 650 K for durations longer than 200 s, suggesting that the high pressure plays an important role in the formation of the fcc phase. With further increase of temperature to 689 K, a Zr_2Ni-like phase appeared from the Am matrix, then Zr_2Cu-like and Be_2Zr-like phases precipitated in turn, as temperature
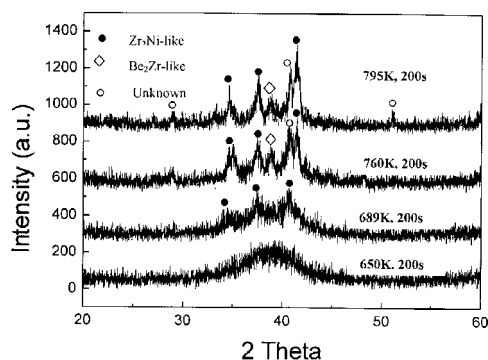
Figure 3. XRD patterns of BMG at ambient pressure and various temperatures.
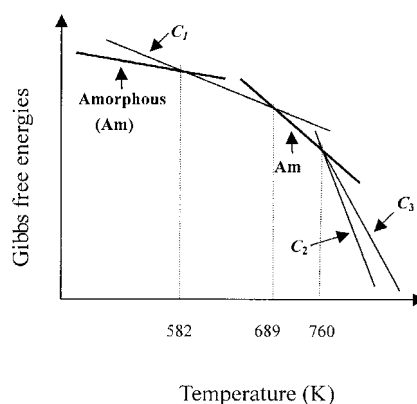
Figure 4. A schematic diagram of the Gibbs free energy as a function of temperature for phase transitions in BMG.

increased. This indicates that, like for conventional glass, the basic path of crystallization for this BMG follows the same irreversible route on heating at ambient pressure.

The two-stage phase transitions in this BMG upon heating under high pressure can be explained from the thermodynamic point of view. Despite no experimental data being available on the energy level of the fcc phase in the present study so far, the 'reversible' transition described here suggested that the free energy in this supersaturated solid solution should be higher than that in the Am phase. Figure 4 illustrates a schematic Gibbs free energy curve for the starting Am phase, the fcc phase (C_1), the Zr_2Ni-like phase (C_2) and the Zr_2Cu-like phase (C_3) as a function of temperature at 10 GPa. It can be seen that three points of intersection among the energies of these phases exist at the temperature adopted, at which the free energies of the crystalline phase and the Am phase are identical.

Below 582 K, the Am phase is highly stable due to its lower energy. When the temperature exceeds 582 K, there exists a driving force for a transition from the Am to the fcc phase; as a result, the fcc phase crystallized from the starting BMG as detected by means of the XRD. In the temperature range of 582–653 K, the fcc phase becomes more stable with increasing temperature, and its volume fraction rises, as shown in figures 1(C) and (D). At 653 K, the Gibbs free energy should drop to the lowest value as the intensity of its XRD peak reaches a maximum. With further increase of temperature from 653 to 689 K, the structural stability of the fcc phase becomes weaker because its solutes supersaturate. Beyond 689 K, the fcc phase is no longer stable and the distortion of its lattice gives a free energy higher than that of the Am phase; therefore, the fcc phase itself transformed back into the Am form. On heating the sample continuously to a higher temperature, the crystalline products C_2 and C_3 have lower free energies compared with their counterparts; hence they did not revert back to the original Am state.

4. Conclusions

The two-stage crystallization behaviour of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG was discovered through a process of heating under high pressure. *In situ* SRXRD measurements reveal that a reversible amorphous–crystalline–amorphous phase transition occurred at temperatures below 698 K. Under a compression of 10 GPa, heating the sample up to 582 K promotes the formation

of metastable fcc phase from the starting BMG and a further heating step at this pressure leads to the fcc phase reverting back to the Am phase. With further increase of temperature, the Am solid, which has undergone first-stage crystallization, experiences an irreversible phase transition. At 760 K, a Zr_2Ni-like phase appeared from the Am matrix; Zr_2Cu-like and Be_2Zr-like phases then precipitated in turn. The high-pressure behaviours of BMG are governed by thermodynamic factors.

Acknowledgments

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