Phase Transition of Shock-Loaded ZrTiCuNiBe Bulk Metallic Glass under Continuous Heating

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Phase transition of Zr₄₁.₅Ti₁₄.₇Cu₁₃.₁Ni₁₀.₁Be₂₀.₂ bulk metallic glasses (BMGs) treated by shock loading (transition from a solid state to a solid state) and prepared by shock-wave quenching (transition from a solid state to a liquid state to a solid state) are investigated by in situ X-ray diffraction measurements under continuous heating conditions. The thermal properties, precipitation phases and phase transitions of the shock-loaded and shock-wave-quenched BMGs are found to be different from those of water-quenched BMGs. The differences are probably due to different structures between the BMGs induced by complex effects of shock loading.

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1. Introduction

The structure of materials is profoundly altered under high pressure through large changes in atomic spacing, chemical bonding, and Gibbs free energy.¹¹) The structural transition, or phase transition, varies under dynamic high pressure²²) or shock loading. A new family of materials, ZrTiCuNiBe bulk metallic glass (BMG),³³) are of high thermal stability and have a high potential in engineering applications.⁴⁴) Consequently, the phase transition of these materials, or crystallization process under ambient conditions, has been widely investigated.⁵–¹²) Because Zr-based BMGs have potential applications in resisting high speed impact,⁴⁵) high strain rate response of the BMGs also has attracted much attention over the past five years.¹³–²¹) Under these circumstances, the BMGs can follow two transition routes, i.e., from a solid state to a solid state or from a solid state to a liquid state to a solid state, depending on the temperature provided by shock loading.

For Zr₄₁.₅Ti₁₄.₇Cu₁₃.₁Ni₁₀.₁Be₂₀.₂ BMG, the transition from a solid state to a solid state occurs if the temperature provided by shock loading is below the melting point of the alloy.¹³,¹₆,¹₈–₂₀) In this case, a BMG under planar shock loading may crystallize partially.¹₈) The main features of the damage include cracking and the occurrence of microvoids.¹³,¹₆,¹₈,¹⁹) Because re-melting does not occur, the recovered sample is referred to as shock-loading-treated BMG. If the temperature provided by shock loading is above the melting point of the alloy, the transition from a solid state to a liquid state takes place spontaneously.¹₂,¹₅) In such cases, the sample can be quenched again into a glassy state under the complex effect of shock loading, which is referred to as shock-wave quenching.¹₅) Furthermore, it has been reported that the crystallization sequence differs between shock-wave-quenched BMG at 100 GPa and water-quenched BMG under continuous heating.¹²) However, the effect of varying pressure on the crystallization sequence is unknown. It is, therefore, of great interest to comparatively study in detail the crystallization for the BMGs prepared by shock-wave quenching, treated by shock-loading and prepared by water-quenching.

In the present work, phase transitions of Zr₄₁.₅Ti₁₄.₇Cu₁₃.₁Ni₁₀.₁Be₂₀.₂ BMGs prepared under different conditions of shock loading are investigated under continuous heating using in situ X-ray diffraction measurements. It is expected that the results will provide further insight into physical processes that underlie the effect of shock loading on microstructure and phase transition.

2. Experimental Procedure

Firstly, the Zr₄₁.₅Ti₁₄.₇Cu₁₃.₁Ni₁₀.₁Be₂₀.₂ BMGs were fashioned into φ18 × 55 mm rods by water-quenching. The rods were treated by shock loading¹⁶,¹₈) and by shock-wave quenching.¹₅) respectively. In order to guarantee uniform composition, the quartz tube was repeatedly inverted before water quenching.²²) The composition of the two ends of the rod was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) methods, and no apparent difference was found within experimental uncertainty. Small cylindrical samples with a dimension of φ17.5 × 10 mm were cut from the as-cast rods. Some of the samples then were treated by shock loading under planar shock compression using a φ24 × 2 mm aluminum flyer plate, launched at a speed of 3.0 km/s by a two-stage light gas gun.¹₆,¹₈) The peak shock pressure in the samples was calculated to be about 45 GPa by the impedance-match method.²³) Another part of the water-quenched samples were quenched again into the glass state by shock-wave quenching at a peak shock pressure of 120 GPa,¹₅) generated by φ24 × 2 mm copper flyers at the speed of 3.4 km/s. The compositions of the shock-loading-treated and shock-wave-quenched samples were determined by ICP-AES methods to be identical to the water-quenched sample within the limits of the experimental procedures.
The samples before and after the treatment by shock loading or by shock-wave quenching were examined by X-ray diffraction (XRD) with a diffractometer Rigaku D/max 2500/pc and by differential scanning calorimetry (DSC) with a calorimeter NETSCH STA449C. Rectangular samples with a dimension of $13 \times 5 \times 0.8\, \text{mm}$ were cut from the shock-loading-treated or shock-wave-quenched samples and were ground and polished for in situ XRD analyses. In situ high-temperature XRD measurements were performed by the diffractometer D/max-2500/pc XRD (Cu $K_{\alpha}$) in a high-temperature oven under a pressure less than $10^{-3}\, \text{Pa}$. The temperature, with an uncertainty of $\pm 1\, \text{K}$, was measured by a type R thermocouple. To save time for collecting X-ray diffraction data, each run consisted of heating to 653 K from room temperature at 15 K/min followed by continuous heating to 789 K at 5 K/min and then heating to 923 K at 15 K/min. From 653 K to 923 K, an in situ XRD pattern was recorded every 8 K at constant temperature in order to observe the phase transition process.

3. Results and Discussion

Figure 1 shows the XRD patterns of the Zr$_{41.9}$Ti$_{14.7}$-Cu$_{13.1}$Ni$_{10.1}$Be$_{20.2}$ samples treated by shock loading and prepared by shock-wave quenching. Apparently, the water-quenched sample [Fig. 1(a)] was partially crystallized after treatment by shock loading [Fig. 1(b)]. After shock-wave quenching at 120 GPa, the recovered sample was fully amorphous [Fig. 1(d)]. For comparison, the XRD pattern of a sample prepared by shock-wave quenching at 100 GPa was also characterized [Fig. 1(c)].

Figure 2 shows the DSC traces of Zr$_{41.9}$Ti$_{14.7}$-Cu$_{13.1}$Ni$_{10.1}$Be$_{20.2}$ samples treated by shock loading and prepared by shock-wave quenching at 120 GPa by a heating rate of 10 K/min under a flow of purified argon. For comparison, the DSC trace of a sample prepared by shock-wave quenching at 120 GPa [Fig. 2(c)], and for the samples prepared by shock-wave quenching at 100 GPa [Fig. 2(d)] and 120 GPa [Fig. 2(b)], respectively. Thus, $T_x$ increased with the pressure of shock loading, regardless of the transition routes during treatment by shock loading and shock-wave quenching. The peak height differed between the samples treated differently. The third weak exothermic crystallization peak, indicated by the dashed arrows on the DSC curves [Figs. 2(a), (b) and (c)], disappeared for the sample prepared by shock-wave quenching at 120 GPa [Fig. 2(d)]. Using the Kissinger method, the effective activation energy of the glass transition ($E_g$), crystallization ($E_x$) and crystallization peak ($E_{p1}$ and $E_{p2}$) for the shock-loading-treated sample (Fig. 3) and the shock-wave-quenched sample at 120 GPa (Fig. 4) were obtained from DSC results at different heating rates ($\phi$) (Table 1). For comparison, the $E_g$, $E_x$, $E_{p1}$ and $E_{p2}$ for the water-quenched sample and the shock-wave-quenched sample at 100 GPa are also presented, which were reproduced from Ref. 12. Higher $T_x$, $E_g$, $E_x$, $E_{p1}$, $E_{p2}$ and the disappearance of the third exothermic crystallization peak suggest that the shock-loading-treated and shock-wave-quenched samples had better thermal stability and different structures relative to the water-quenched one.

The phase transition sequence during crystallization of the shock-loading-treated sample studied by in situ XRD was evaluated (Fig. 5(a)). A metastable phase marked by the arrows precipitated from the water-quenched sample after treatment of shock loading at 45 GPa [Figs. 5 and 1(b)].
diffraction peaks from the phase suggested that it was Be$_{21}$Ni$_5$. With increased temperature, the intensity of the diffraction peaks from the metastable phase decreased; the metastable phase disappeared at 923 K. Several new crystalline phases began to precipitate at 717 K. The indexing of the peaks from these phases suggested that there were mainly six phases, i.e., the metastable icosahedral quasicrystalline (I phase),$^9$ the ZrBe$_2$ phase (hex, $a = 0.38$ nm, $c = 0.32$ nm), the Zr$_2$Cu phase (tetragonal, $a = 0.32$ nm, $c = 1.14$ nm), the BeNi phase, the ZrNi phase and the Ti$_2$Ni phase. With the continuously increased temperature, together with the increases in the intensities of the precipitated phases, the Zr$_2$Ni phase started to appear at 765 K, followed by the precipitation of the CuTi$_2$ and BeTi phases at 781 K. With the further increases in temperature, the intensity of the diffraction peaks from the metastable I phase, the metastable Be$_{21}$Ni$_5$ phase and the ZrBe$_2$ phase, decreased continuously. Up to 873 K, the I phase had disappeared completely. After that, the metastable Be$_{21}$Ni$_5$ phase disappeared at 923 K, accompanying the decrease of the intensities of the ZrBe$_2$ phase and the precipitation of the ZrCu and Zr$_2$Ni$_7$ phases.

The in situ XRD patterns of the shock-wave-quenched sample at 120 GPa at various temperatures were characterized (Fig. 6). The sample remained in an amorphous state below 709 K. At 709 K, some broad peaks began to emerge
on the diffuse peak of the amorphous structure. When the temperature increased to 717 K, the I phase, the Ti$_2$Ni phase, and the metastable CuTi phase began to precipitate. The metastable CuTi phase disappeared at 781 K, which is consistent with Schneider’s result. With the continuous increase in temperature, the BeNi phase, the ZrNi phase and the Zr$_2$Cu phase precipitated at 725 K, followed by the appearance of ZrBe$_2$ and CuTi$_2$ phases at 765 K. The CuTi$_2$ phase disappeared at 923 K, which does not take place in the water-quenched sample. A remarkable result is that the disappearance of ZrBe$_2$ phase from 789 to 873 K was replaced by a large number of Zr$_2$Cu$_{10}$ precipitates, yet together with some residual I phase until 923 K, compared with the disappearance of the I phase and the coexistence of the ZrBe$_2$ phase until 923 K for the water-quenched sample, as seen in Fig. 6(b) and Ref. 12). At 873 K, the BeTi phase began to emerge.

The phase transitions of the shock-loading-treated sample and the shock-wave-quenched sample at 120 GPa are different from each other (Figs. 5 and 6). They are also different from the phase transition of the water-quenched BMG reported in Ref. 12). The phase transitions observed under continuous heating is summarized below. Note that precipitated phases and residual amorphous phase are not listed in the phase transition sequences.

Water-quenched BMG: Amorphous $\rightarrow$ (693 K) I phase + ZrBe$_2$ + BeNi + Ti$_2$Ni $\rightarrow$ (781 K) Zr$_2$Cu $\rightarrow$ (789 K) BeTi + Zr$_2$Ni $\rightarrow$ (873 K) disappearance of I phase + ZrNi $\rightarrow$ (923 K) ZrCu + unidentified phases,

Shock-loading-treated BMG at 45 GPa: Amorphous $\rightarrow$ (693 K) II phase + ZrBe$_2$ + BeNi + Ti$_2$Ni + Zr$_2$Cu + ZrNi $\rightarrow$ (765 K) Zr$_2$Ni $\rightarrow$ (781 K) CuTi$_2$ + BeTi $\rightarrow$ (873 K) disappearance of I phase $\rightarrow$ (923 K) disappearance of Be$_{21}$Ni$_5$ phase + Zr$_2$Ni$_7$ + ZrCu + unidentified Phases (Fig. 5).

Shock-wave-quenched BMG at 100 GPa: Amorphous $\rightarrow$ (693 K) I phase + ZrBe$_2$ + BeNi + Ti$_2$Ni $\rightarrow$ (717 K) Zr$_2$Cu $\rightarrow$ (737 K) Zr$_2$Ni $\rightarrow$ (773 K) BeTi + Zr$_2$Ni$_7$ $\rightarrow$ (789 K) ZrNi $\rightarrow$ (873 K) disappearance of I phase + CuTi$_2$ $\rightarrow$ (923 K) ZrCu + unidentified phases,

Shock-wave-quenched BMG at 120 GPa: Amorphous $\rightarrow$ (717 K) I phase + CuTi + Ti$_2$Ni $\rightarrow$ (725 K) BeNi + ZrNi + Zr$_2$Cu $\rightarrow$ (765 K) CuTi$_2$ + ZrBe$_2$ $\rightarrow$ (781 K) disappearance of CuTi $\rightarrow$ (873 K) disappearance of ZrBe$_2$ + BeTi + Zr$_2$Cu$_{10}$ $\rightarrow$ (923 K) disappearance of CuTi$_2$ + unidentified phases (Fig. 6).

Evidently, the differences in $T_g$, $T_x$, $E_g$, $E_x$, $E_{p1}$, $E_{p2}$, and phase transition sequences were distinct for the samples treated by shock loading and prepared by shock-wave quenching relative to the water-quenched one. Because the composition of the samples was identical, these differences could have originated from the structural differences, i.e., the BMGs could have had different atomic configurations. Actually, the shock loading can exert significant effects on atomic mobility and on the creation and annihilation of free volume. Because the precipitation of the metastable Be$_{21}$Ni$_5$ phase induced by shock loading, the composition and microstructure of the residual amorphous phase for the shock-loading-treated and the water-quenched samples differed. In shock-wave quenching, metallic alloys were influenced by dynamic high pressure in an extremely short time, superheated to melting by extremely high heating rate, overheated by extremely high temperature, and then solidified into a glass state. Different short range orders were obtained for the BMGs prepared by shock-wave quenching and water quenching. Shock loading, water quenching and shock-wave quenching lead to different phase transition sequences.

Using a computer program for multi-peak fitting with the Gaussian function, the center of the diffuse maxima was determined (Fig. 1). Apparently, the center of the first diffuse maximum was located at 37.5, 38.0, 38.1, and 38.4° for the water-quenched [Fig. 1(a)] and shock-loading-treated samples [Fig. 1(b)], and for the shock-wave-quenched samples at 100 GPa [Fig. 1(c)] and 120 GPa [Fig. 1(d)], respectively. Hence, the first maximum shifted toward higher angles for the shock-loading-treated samples may indicate that the BMGs subjected to shock loading at a higher pressure have a more densely packed structure and larger short-range order.
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