Crystallization of Zr$_{41}$Ti$_{14}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$ bulk metallic glass under high pressure examined by *in situ* synchrotron radiation x-ray diffraction

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Crystallization of Zr$_{41}$Ti$_{14}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$ bulk metallic glass under high temperature and high pressure has been investigated by *in situ* synchrotron radiation x-ray diffraction. The onset temperature of crystallization was found to increase with pressure, but with a sudden drop at about 5.6 GPa. Though the primarily precipitated phase is the same at different pressures, the sequences of the following phase precipitation are different. © *2006 American Institute of Physics.*
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I. INTRODUCTION

Crystallization of metallic glass is a kinetic transformation process from nonequilibrium state to equilibrium state. In general, metallic glass transforms into equilibrium crystal phases while experiencing formation of certain intermediate metastable phases under heating.[1] Both the phase precipitation onset temperature and the precipitation sequences or routes, during crystallization may even be further influenced by pressure, because pressure can change the atomic configuration and atomic mobility in the metallic glass. Results[2] have shown that pressure can restrain crystallization, because the long-range atomic transport required for crystallization is retarded by pressure. Thus, increase of the crystallization temperature (T_x) is unavoidable. Pressure influence on crystallization sequence has also been proved experimentally.[3–5] Unfortunately, most of the effort in the past has been given to the binary metallic glasses (films and ribbons) that possess relatively simple crystallization processes. For the recently developed multicomponent bulk metallic glasses (BMGs), which are of great engineering application potential,[6,7] the crystallization processes are more complex.[2,8–10] Revealing of the crystallization processes under pressure is much more difficult and of great importance for studying the thermal stability and understanding the structure of the multicomponent glasses.[11]

In the present work, crystallization of Zr$_{41}$Ti$_{14}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$ BMG under high temperature and high pressure was examined by *in situ* synchrotron radiation x-ray diffraction. It is expected that it may provide insight into pressure effect on crystallization temperature and sequences of the BMG.

II. EXPERIMENTS

Ingots of Zr$_{41}$Ti$_{14}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$ alloy were prepared from mixture of pure elements in an arc-melting furnace under Ti-gettered argon atmosphere. The purities of Zr, Ti, Cu, Ni, and Be were 99.999%, 99.9%, 99.5%, 99%, and 99.5%, respectively. The ingots were then melted again in quartz tubes and quenched into water to obtain BMG rods, 18 mm in diameter and 50 mm in length. The amorphous nature of the samples from both ends of the rod was confirmed by D/max-2500/pc x-ray diffraction (XRD), NETSCH STA449C differential scanning calorimetry (DSC), and transmission electron microscopy (TEM).

In situ high-temperature and high-pressure energy-dispersive x-ray diffraction patterns (EDXRD) for the BMG were recorded using synchrotron radiation in HASYLAB in Hamburg, Germany, by a multianvil pressure apparatus with 8 mm^3 pressure cells at the MAX 80 station.[10] The sample assembly is shown in Fig. 1. A cylindrical boron nitride container with 1 mm in the inner diameter was used. The center of the container was filled with the sample, the powder filed from Zr$_{41}$Ti$_{14}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$ BMG, and the lower part was filled with NaCl powder for pressure calibration. Electric current was sent through a graphite heater via two appropriate anvils. The temperature was measured by means of ther-

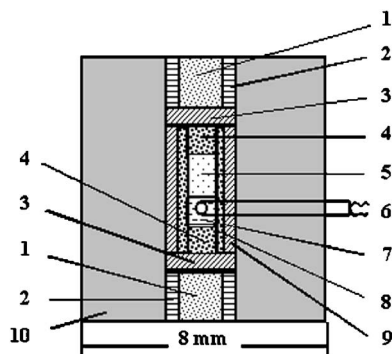[a)]Author to whom correspondence should be addressed; electronic mail: chaoyang666@hotmail.com

FIG. 1. Schematic map of the sample assembly for high-pressure and high-temperature x-ray powder diffraction studies [(1) pyrophyllite disk; (2) copper ring; (3) graphite disk; (4) boron nitride; (5) $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG powder; (6) thermocouple; (7) NaCl; (8) BN container; (9) graphite heater; (10) boron-epoxy cube].

mocouple close to the sample with a stability of ±1 K. The pressure of the sample was calculated from the lattice constant of NaCl using the Decker equation of state.[12] In each run of the experiment, the sample was firstly compressed to a certain pressure at room temperature and then isobarically heated up to 889 K in steps of 8 K with a recorded EDXRD pattern for every 4 min in order to observe the onset T_x in the pressure range up to 6.5 GPa. Pure Zr, Fe, and the BMG powders were used to examine the possible oxidation of samples during the heating treatments using the high-pressure sample assembly. It was found that only pure metallic phases in these three systems were detected after heating treatment at temperatures up to 889 K under pressure.

III. RESULTS AND DISCUSSION

The primarily precipitated phase is Zr_2Be_{17} under the pressure from 0.5 to 6.5 GPa. It is found that the applied pressure strongly affects T_x, as shown in Fig. 2. T_x increases largely with the pressure, except a sudden drop around 5.6 GPa. In addition, the pressure effect on the phase precipitation is very complicated as shown in Figs. 3 and 4. Figure 3 exemplifies the EDXRD patterns recorded for the sample at 0.5 GPa and at various temperatures. A broad amorphous peak, located at about $E=45$ keV, together with Bragg peaks from BN and fluorescence peaks in the energy range of
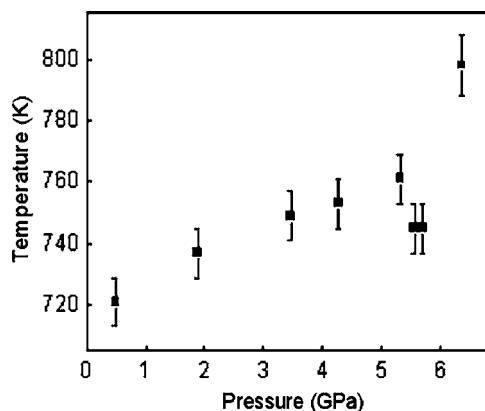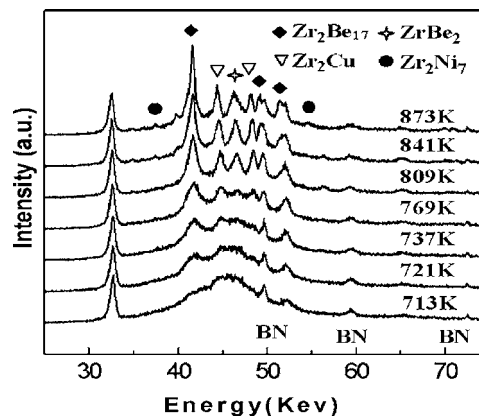

FIG. 3. *In situ* energy-dispersive x-ray powder diffraction patterns recorded at various temperatures for $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG at 0.5 GPa (Ed =108.34 keV Å). The step of 8 K was used for the temperature range. The fluorescence peaks, located in the energy range of 31–34 keV, and a few Bragg peaks from BN were detected.

31–34 keV, is observed in the patterns recorded at each temperature. A new tiny crystalline peak ($E=41.7$ keV) from Zr_2Be_{17} phase appears at 721 K. At 737 K, another new crystalline peak ($E=44.7$ keV) from Zr_2Cu crystals is detected. The peak from $ZrBe_2$ phases, located at E =46.3 keV, is recorded at 769 K. With the increase of temperature, the intensities of the peaks from these three phases increase gradually. Up to 873 K, the peak, at $E=37.5$ keV, of Zr_2Ni_7 phase is detected. Figure 4 shows the EDXRD patterns recorded at 5.6 GPa and at various temperatures. It is found that the primary phase is also Zr_2Be_{17}, but the peak, at $E=42.2$ keV, appears at 745 K, lower than that of 761 K at 5.3 GPa. The peaks, at $E=45.1$ and 47.7 keV, respectively, from the Zr_2Cu phase, and other peaks from the Zr_2Be_{17} phase, are recorded at 777 K. At 793 K, a new peak at E =43.5 keV from Zr_2Ni phase, another two new peaks from Zr_2Ni_7 at $E=38.8$ and 55.2 keV, respectively, and some other peaks from the Zr_2Be_{17} and Zr_2Cu phases, are observed. With the further increase of temperature, the intensities of these peaks continue to increase. Up to 849 K, a new peak from the $ZrBe_2$ phase at $E=47.0$ keV begins to appear.
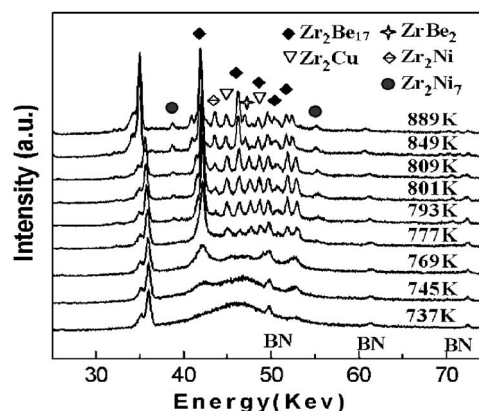

FIG. 2. Pressure dependence of crystallization temperature for $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG.

FIG. 4. *In situ* energy-dispersive x-ray powder diffraction patterns recorded at various temperatures for $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG at 5.6 GPa (Ed =108.24 keV Å). The step of 8 K was used for the temperature range. The fluorescence peaks, located in the energy range of 34–37 keV, and a few Bragg peaks from BN were detected.
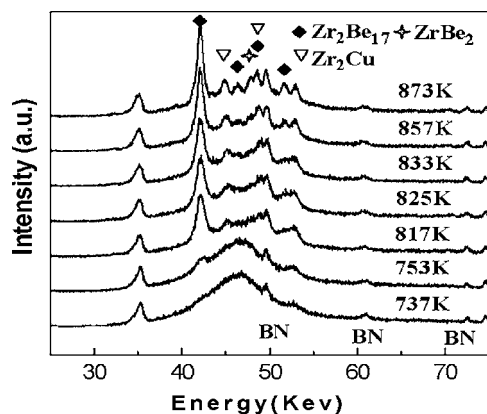
FIG. 5. *In situ* energy-dispersive x-ray powder diffraction patterns recorded at various temperatures for $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG at 4.3 GPa ($Ed = 108.24$ keV Å). The step of 8 K was used for the temperature range. The fluorescence peaks, located in the energy range of 33–37 keV, and a few Bragg peaks from BN were detected.

Figure 5 further testifies that the phase precipitation sequence at 4.3 GPa is different from that around 5.6 GPa. The primary crystalline peak from the Zr_2Be_{17} phase appears at 753 K, followed by the appearance of the peak of the Zr_2Cu phase at 817 K. At 833 K, the peak from the $ZrBe_2$ phase begins to appear.

In our present experiments, the primary phase, determined from the EDXRD patterns, is Zr_2Be_{17} at all the applied pressures. But the subsequent phase precipitation sequences are different as presented above.

Prior to crystallization, the BMG decomposes into Zr-rich and Be-rich regions with different short-range orders, which exhibit higher nucleation probability for the formation of intermetallic compounds compared with the initial homogeneous liquid state.[13,14] The decomposition in this state is a diffusion-controlled process.[13] Because Be atoms have the biggest diffusivity among the constitutive elements of the BMG under high pressure,[15] the primary crystal phase will possibly shift to Be-richer side in the Zr–Be binary phase diagram under high pressure. Thus, compared with the primarily precipitated phase $ZrBe_2$ under ambient pressure and annealing conditions,[16,17] the primary crystal phase is Zr_2Be_{17} for the BMG under high pressure. This is similar to the primary crystal phase which is Fe under ambient pressure, yet Fe_3B for $Fe_{83}B_{17}$, and Fe_3C and Fe_3P for $Fe_{13}P_7C_{80}$ metallic glasses under high pressure,[1,2] respectively.

In the present result, the primarily precipitated phase is Zr_2Be_{17}. This is different from that in Ref. 18, which reported that a Zr_2Ni-like phase was first precipitated from $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG under 10 GPa with continuous increase of temperature. Although the same technique, water quenching, was used to prepare BMG samples in our case and in other experiments,[11,18] differences in cooling rate, overheating temperature, and atomic transport in the melt during water quenching may exist, which can cause slight differences in the short-range orders and local compositions in the sample.[19,20] In fact, it has already been reported that pressure and preparation conditions did lead to formation of different atomic configurations and physical properties for BMGs with the same alloy composition.[21,22] The

slight difference in atomic configuration may possibly lead to dramatic changes in the primarily precipitated phases and the subsequent crystallization process under ambient pressure[16,17,23,24] and high pressure[11,18,25] for the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG.

Additionally, the drop of T_x is also not in agreement with the previous results on $Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$ BMG.[9,10] It was well accepted that pressure could cause increase of T_x,[2,8–10,25] because pressure could reduce atomic mobility and then retard crystallization. However, Sun *et al.* also reported that pressure could lead to a collapse of the initial atomic configuration of the amorphous structure for $Fe_{60}Co_{10}Zr_8Mo_5Nb_2B_{15}$ metallic glass.[26] Likewise, $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG may also correspond to different atomic configurations under different pressures, which in turn causes unusual transition phenomenon in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG at 10 GPa (Ref. 11) and the drop of T_x at about 5.6 GPa in the present experiment. As for $Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$ BMG,[9,10] no drop of T_x was found, possibly because the applied pressure did not change its initial atomic configuration, or simply because the appropriate pressure was not found. In a word, pressure effect on BMG is very complicated.

Due to many related factors, such as sample size, experimental method, cooling rate, overheating temperature, condition of the mold, and so on, one can obtain unexpected, discriminating or different experimental results for the same alloy system. Lots of controversies have been reported, for instance unexpected transition phenomenon in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG,[11] discriminating data points about crystallization temperature in $Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$ BMG,[9,10] and different primarily precipitated phase for $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG in the present case and in Refs. 18 and 25. In some cases, it is even difficult to repeat the same results. Perhaps, there is something secret about the glass structure that is greatly influenced by the preparation methods and their parameters. Though wide research on these interesting phenomena has been given, the problem of the structure of the metallic glass remains unsolved even though several empirical models were proposed. A detailed and comprehensive explanation of the present results is difficult to approach, due to the limitation of knowledge about pressure effect on atomic movement in the complex alloy system. Further research work about this aspect will be done in the future.

IV. CONCLUSION

The effect of high pressure on crystallization temperature and processes of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG was presented. The same primary phase but different phase precipitation sequence is reported for different pressures. At about 5.6 GPa, a sudden drop of the onset crystallization temperature is examined. Both the different phase precipitation sequence and the sudden drop of the onset crystallization temperature may be attributed to the differences in atomic configurations at different pressures.

ACKNOWLEDGMENTS

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