Microstructural transformation in a $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass under high pressure

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The microstructure and its evolution of a $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass (BMG) annealed under high pressure and below glass transition temperature are investigated by using high resolution transmission electron microscope, differential scanning calorimeter, x-ray diffraction, ultrasonic study, and density measurements. It is found that high pressure annealing below T_g results in a microstructural transformation from short-range order to medium-range order in the BMG; the BMG with medium-range order structure exhibits different structural, thermal and acoustic properties.

Recently, a new family of multicomponent glass-forming alloys such as La-Al-Ni, Zr-Ni-Al-Cu, and Zr-Ti-Cu-Ni-Be has been discovered which exhibits extraordinary glass forming ability (GFA) and properties.[1,2] The alloys require no special processing treatments, and fully metallic glass in greater bulk can be obtained. When heated through the glass transition, the bulk metallic glasses (BMG's) yield a supercooled liquid state of unusual stability for metals. The stability of the supercooled liquid in large temperature region, and the larger geometric size of the BMG have permitted far more extensive structural and properties investigations upon temperature and pressure than possible previously. There seems to be general agreement in that the basic process induced by annealing below glass transition temperature, T_g is the structural relaxation,[3,4] but it is not clear to what extent this leads to structural units and what phenomena will happen when annealed under high pressure below T_g. The structural relaxation is found to have significant effects on the microstructure, thermal stability, physical properties and subsequent crystallization,[5,6] but the cause for the effects is still unknown. The detailed knowledge of the atomic structure is essential to understand the special properties of the BMG. In this report, the local microstructural change of a $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG induced by high pressure annealing below T_g is studied. The ultrasonic study, density measurement, high-resolution transmission electron microscope (HRTEM), differential scanning calorimeter (DSC), and x-ray diffraction (XRD) are used to monitor the microstructural and properties changes.

Ingots with a nominal composition of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ were prepared by melting a mixture of elements in Ti-gettered arc furnace, and remelted in a vacuum-sealed quartz tube, and then quenched in water to get rod with a diameter of 12 mm. The details of the experimental procedure can be seen in Ref. 7. The amorphous nature as well as the homogeneity of the rod was ascertained with XRD, transmission electron microscope (TEM), small angle neutron scattering and reduced density function analyses.[5–7] The rod was machined down to 8 mm in diameter, by grinding off the outer surface, any possible oxide materials from the quartz tube container were removed. The composition carefully checked by chemical analysis. XRD was performed using a MAC M03 XHF diffractometer with Cu K_α radiation. The rod was cut to a cylinder with a length of 7 mm for ultrasonic measurements before and after high pressure. The ends of the cylinder were carefully polished flat and parallel before ultrasonic measurement. The acoustic velocities were measured by using a pulse echo overlap method.[8] The excitation and detection of the ultrasonic pulses were provided by *X* or *Y* cut (for longitudinal and transverse waves, respectively) 10 MHz quartz transducers. The travel time of ultrasonic waves propagating through the sample with a 10 MHz carry frequency was measured using a MATEC 6600 ultrasonic system with a measuring sensitive of 0.5 ns. Density ρ was measured by the Archimedian principle and the accuracy was evaluated to be 0.005 g/cm^3. DSC measurements were carried out under a purified argon atmosphere in a Perkin Elmer DSC-7 at the heating rate of 0.33 K/s. High pressure (HP) was performed in an apparatus with six anvils tops. NaCl powder was used as solid pressure transmitting media. NiCr-NiAl thermocouple was brought into the pressurized zone through graphite furnace and near the sample. The samples were prepressured to a certain value to enhance the homogeneity of the pressurization. The pressure was calibrated by the known materials of Ba, Bi, and oxide glasses, the accuracy was better than ± 0.1 GPa. The accuracy to measure the temperature of the sample itself under applied pressure was better than ± 3 K. The details of the HP experiment were described in Ref. 9. HRTEM observation was performed at a Jeol-2010 operating at 200 kV. The as-prepared BMG samples (referred to as alloy *A*) was annealed at 573 K, 3.0 GPa for 2 h, and referred to as alloys *B*.

Figure 1 shows XRD patterns for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG in as-prepared state (alloy *A*) and isothermal annealed at 573 K under 3.0 GPa (alloy *B*). The annealing temperature is much lower than the T_g (623 K). The annealing time is 2 h. The XRD pattern for the BMG annealed under HP exhibits no difference comparing to that of the alloy *A*, this indicates that the crystalliza-

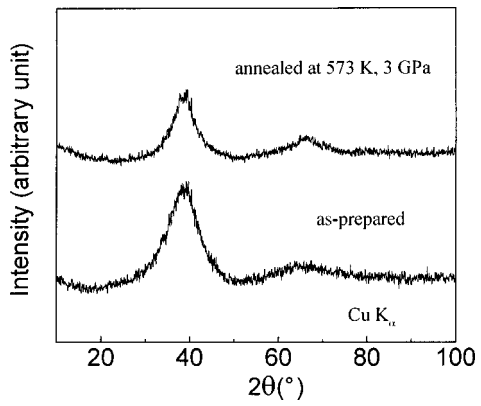

FIG. 1. XRD patterns for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$BMG in as-prepared state (alloy *A*) and isothermal annealed at 573 K under 3.0 GPa for 2 h (alloy *B*).

tion does not occur in the sample within the examining limit of XRD. Figure 2 presents continuous DSC traces of the alloy *A* and *B* at a heating rate of 0.33 K/s. Both of the DSC traces exhibit endothermic characteristic of a glass transition followed by exothermic crystallization reactions at higher temperature. However, the glass transition, crystallization and supercooled liquid region, $\Delta T = T_x - T_g$, are markedly different for the two alloys. The T_g, T_x, and ΔT for the alloy *A* are 629, 710, and 81 K, respectively. For the alloy *B*, the T_g, T_x, and ΔT are 687, 731, and 44 K, respectively. The first DSC crystallization peak disappears after HP annealing. Furthermore, the second peak of the BMG is broadened and shrunk, and its position shifts to high temperature after HP annealing. The T_g and T_x are markedly increased after HP annealing, indicating that the amorphous phase is more stable. However, the preannealing without applied pressure at the identical temperature does not have the same effect.[10] The marked effects of HP on the crystallization have also been found in the $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ BMG.[11]

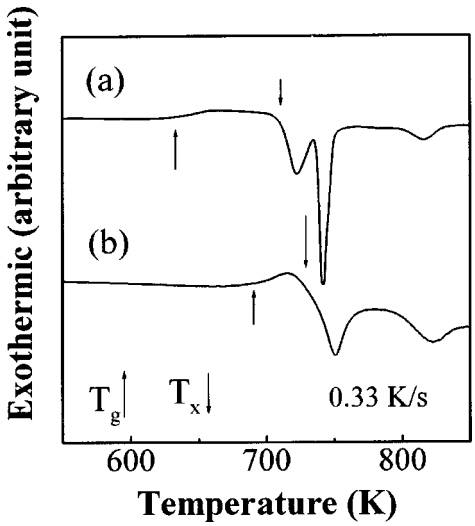

FIG. 2. DSC traces for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy at different annealing temperatures at the heating rate of 0.33 K/s: (a) as-prepared state (alloy *A*); (b) annealed at 573 K, 3.0 GPa for 2 h (alloy *B*).

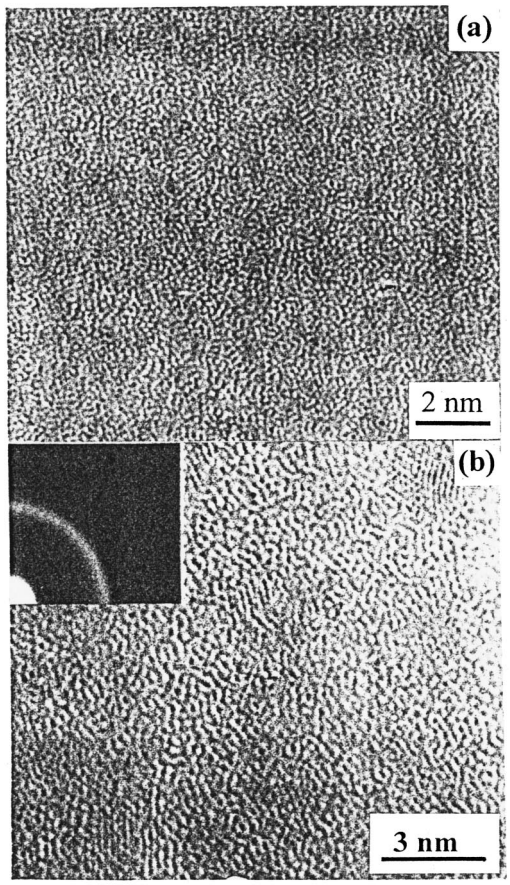

FIG. 3. (a) HRTEM picture of the bulk amorphous alloy in as-prepared state (alloy *A*); (b) HRTEM picture of the amorphous alloy after HP annealing at 573 K, 3.0 GPa for 2 h (alloy *B*). The small nuclei with the size of 1–2 nm can be clearly seen. It confirms that a microstructural transformation from the SRO to the MRO occurs in the HP annealed BMG.

These results indicate that pressure annealing cause significant structural relaxation, which affects markedly on the subsequent glass transition and crystallization behaviors. Previous work[5] shows that the BMG obtained in a very low cooling rate (~5 K/s) has highly random packed microstructure, it might be tempted to expect little structural relaxation during the pressure annealing due to a low cooling rate for formation and a highly random packed microstructure. Above results indicate significant microstructural change is induced by HP annealing, the conclusion has also been confirmed by volume-pressure relation measurements,[12] which shows the BMG has larger volume change upon HP compared with crystalline metals or alloys, because the structural change induced by pressure. The structural change induced by pressure annealing affects the subsequent glass transition and crystallization behaviors through the annihilation of the free volume and the atomic relaxation.

Figure 3(a) exhibits HRTEM picture of the homogeneous microstructure of the as-prepared BMG. The homogeneous microstructure as well as the character of a short-range order (SRO) has also been confirmed by transmission electron microscope, SANS,[6,7] and reduced density function analysis.[5] HRTEM picture presented in Fig. 3(b) shows the microstructure in the HP annealed BMG (alloy *B*). The small clusters with the size of 1–2 nm are frequently seen locally in spite

TABLE I. The properties of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG in as-prepared glassy state (alloy *A*) (density, $\rho_0 = 6.125\ g/cm^3$, acoustic velocities, v_l^0, v_s^0, elastic constant G_0, Debye temperature θ_{D0}) and HP annealing state at 573 K and 3.0 GPa for 2 h (alloy *B*). For comparison, the relative changes of the density, acoustic velocities of the BMG annealed at 573 K in vacuum for 2 h (alloy *C*) are also listed.

Sample	$\frac{\Delta\rho}{\rho_0}$ (%)	v_l (km/s)	$\frac{\Delta v_l}{v_l^0}$ (%)	v_s (km/s)	$\frac{\Delta v_s}{v_s^0}$ (%)	G (GPa)	$\frac{\Delta G}{G_0}$ (%)	θ_D (K)	$\frac{\Delta\theta_D}{\theta_{D0}}$ (%)
Alloy *A*		5.17		2.47		37.4		326.8	
Alloy *B*	0.35	5.30	2.4	2.65	7.2	43.4	16.0	350.7	7.3
Alloy *C*	0.1	5.21	0.7	2.52	2.0	39.0	4.3	333.3	2.0

of the halo electron diffraction pattern. The key feather of the HRTEM image is uniform dispersion and random crystallographic orientation of the clusters. The formation of the clusters with size of 1–2 nm is considered as a medium-range order (MRO) microstructure in contrast to the SRO in the as-prepared BMG. The so-called MRO is considered as an ordered configuration in amorphous phase in a size of 0.5–2 nm, which is larger than the critical nuclei but does not yield a characteristic crystalline reflecting in XRD and other diffraction patterns.[13,14] The transformation from the SRO to the MRO is induced by HP annealing below T_g as shown in above experiments. The MRO microstructure has also been observed in other BMG's and conventional metallic glasses.[15] The MRO structure of the alloy *B* exhibits similar XRD and electron diffraction patterns with the alloy *A*, however, the two alloys show different crystallization behaviors. The BMG with the MRO microstructure is thermodynamically more stable.

The primary crystallization of the BMG is known to be controlled by diffusion, it requires long-range atomic diffusion due to a large composition difference between the amorphous phases and its corresponding crystallization products.[1,5] HP is an obstacle to the long-range atomic diffusion during the growth process.[16,17] However, experimental studies and numerical modeling demonstrate that HP promotes a short-range atomic rearrangement in metallic glasses by the annihilation of the free volume through compression and reconstruction of the atomic configuration.[16,17] The short-range atomic rearrangement favors the homogenous formation of small nuclei. The formed nuclei distribute uniformly and randomly in the glassy matrix, which act as nucleation sites. Owing to the intrinsic extremely low atomic mobility in the BMG,[18] and the increased activation energy barrier under pressure for diffusion, the redistribution of atoms on a large-range scale is extremely difficult. The subsequent growth of the nucleation sites is inhabited, and this results in the formation of the uniformly and randomly distributed clusters with small size, the large population of small clusters and the inhibited atomic mobility in the amorphous phase result in the transformation from the SRO to the MRO. The change of the crystallization behavior of the as-prepared BMG is supposed to be related to the structural transformation. To verify the transformation from the SRO to the MRO induced by HP, the density ρ and the acoustic velocities, which are particularly sensitive to the microstructural change, were measured for the alloy *A* and *B*, the results are listed in Table I. The relative density change due to the HP annealing is 0.4%. The relative change of longitudinal velocity v_l, and transverse velocity v_s, are 2.4% and 7.2% respectively, the relative changes are much larger than that of the BMG annealed at 573 K without applying pressure as shown in Table I. The previous acoustic studies[18] have demonstrated that the increase of the acoustic velocities, especially v_s, indicates the increase in the degree of the SRO, it has widely been supposed that the increased SRO to some extent implied the formation of the MRO.[14] The acoustic and density results confirm the transformation from the SRO to the MRO induced by HP annealing.

Previous work[2,5,7] shows that the BMG separates into two different amorphous phases when annealed in the SLR (from 629 to 710 K). The reduced distribution function profiles suggest that the decomposition have also a great effect on the chemical and topological configuration of the BMG, and the decomposed amorphous phases are with different short-range orders and compositions.[5] The decomposed two amorphous phase networks in the order of nanometers intertwine with each other.[19] The phase separation is controlled by atomic mobility, the HP promotes local atomic motion and makes the long-range atomic diffusion much more difficult. Therefore, the HP annealing below T_g may induce very small decomposition wavelengths of the networks in the BMG and possibly result in the transformation from the SRO to the MRO. The BMG with the SRO has similar microstructure with that of a liquid,[5] it may be called liquidlike BMG, and the BMG with the MRO cluster could be regarded as a glass with latticelike microstructure. A phase transition may exist between the SRO and the MRO BMG's, because the SRO to the MRO transformation is related to the distinct property change and heat release (as indicated in DSC results). The phase transition between liquids, or between amorphous phases has been found in an amount of liquids and amorphous systems.[20–24]

In conclusion, high pressure annealing below T_g results in the microstructural transformation from short-range order to medium-range order in the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$BMG, the BMG with the MRO structure may be regarded as a glass exhibiting different structural, thermal and acoustic properties.

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