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Phase transition of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk amorphous below glass transition temperature under high pressure

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The effect of high pressure annealing on phase transition of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass (BMG) is studied on compressed specimens by x-ray diffraction and differential scanning calorimetry (DSC) after annealing treatments at 573 K and under pressures up to 6 GPa. The results of DSC and transmission electron microscope show that the high pressure annealing cannot only promote structural relaxation, but also induce the occurrence of a phase transition at a temperature below the glass transition temperature in the BMG. The role of pressure on structural relaxation and phase transition is discussed. © *2001 American Institute of Physics.*
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It is known that metallic glasses exhibit excellent mechanical and physical properties. Within the amorphous structure, structural relaxation under the influence of an elevated temperature occurs and this leads to significant changes in physical properties. Recently, new families of multicomponent glass formers have been discovered which exhibit a much higher glass forming ability than previously known alloys.[1–4] So far many reports have been presented concerning their crystallization process,[5,6] glass structure,[7] mechanical properties,[8] and thermal stability.[9] Most of these studies have been carried out at ambient pressure and in the absence of constraints such as applied stress and external fields. It has been noticed that pressure[10] and electric field are also effective in influencing the crystallization process induced by thermal annealing.[11] The pressure, similarly to temperature, can induce structural relaxation and crystallization of metallic glasses. But there are very few experimental studies of the effect of pressure on these processes. It is found that nanocrystallization is pressure assisted in the $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ BMG.[10] The primary nanocrystallization temperature decreases as the applied pressure increases. The BMG could be crystallized to a very fine grained nanostructural material under high pressure. Thus, crystallization of BMGs under high pressure is also a promising way for synthesizing bulk nanocrystalline alloys. It is expected that the study of pressure-controlled relaxation and crystallization behavior may provide insight into the mechanism of phase transition processes in BMGs.[12,13] In this letter, we present a high pressure annealing study on the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG. The aim of this work is to understand the effect of high pressure on the relaxation behavior and crystallization of the BMG.

The $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk amorphous bar was prepared from a mixture of the pure (up to 99.9 at. %) elements by induction melting on a water-cooled copper mold under Ti gettered Ar atmosphere. The formed ingot was remelted in a quartz tube with an inner diameter of 12 mm, and then quenched in water. This particular alloy was chosen because many thermal properties and excellent mechanical properties have been reported by other authors in contrast to other alloys of the ZrTiCuNiBe family. The amorphous nature of the as-quenched bar was confirmed by D/Max-2400 x-ray diffraction (XRD), differential scanning calorimetry, and transmission electron microscopy (TEM). The amorphous rod was cut into many disks with a thickness of 1 mm and a diameter of 5 mm. A resistance furnace with a vacuum of 5×10^{-3} Pa was used for the heat treatment of specimens. The stability of temperature was controlled in the range of ±1 K. The annealing of specimens at high pressure was done in a pressure device with six anvil tops. Each sample was kept under a given pressure and temperature for 2 h. The pyrophyllite was used for the outside layer of pressure transmitting media, and samples were embedded into sodium chloride. The powdered sodium chloride can satisfy our experimental need because of its high chemical stability and excellent pressure transmitting behavior. The heating furnace in the high pressure device is a graphite tube heater. We did not correct the thermocouple potential for the effect of pressure because it is very low. At room temperature, increasing pressure on the specimen to a given value and keeping it constant, we heated the specimen to a given annealing temperature at a heating rate of about 50 K/min, and then kept it at this temperature for 2 h. After this the specimen was cooled to room temperature with a cooling rate of about 50 K/min and then the pressure on the specimen was decreased. Differential scanning calorimetry (DSC) measurements were carried out under a purified argon atmosphere in a Perkin-Elmer DSC7 at a heating rate of 10 K/min. The value of the glass transition temperature T_g and the onset temperature for the first crystallization peak T_x were determined from DSC traces with an accuracy of ±1 K. The annealing temperature was at 573 K which is far lower than the glass transition T_g.

The XRD pattern of specimens annealed at 573 K under different pressures are shown in Fig. 1. Within the resolution of our x-ray intensity, no observable distinctness in phase structure was found between these specimens.

The DSC trace analysis shows that there are distinct dif-

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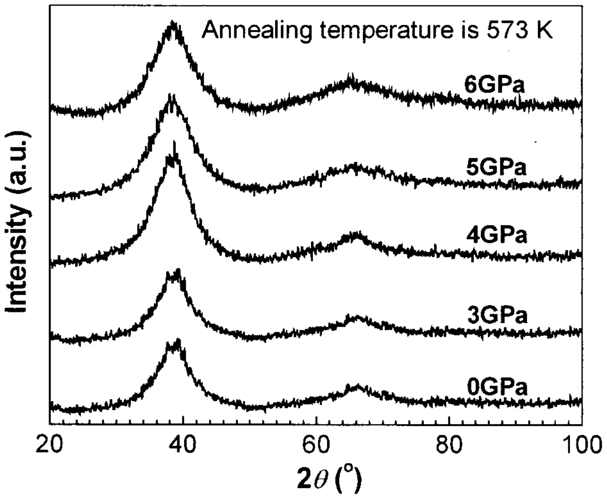

FIG. 1. XRD patterns of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glasses annealed at 573 K and under different pressures for 2 h.

ferences between these samples (Fig. 2). There is only a difference of peak height between the as-prepared specimen and the one annealed under vacuum, which is a result of thermal relaxation. The most interesting results are the disappearance and reappearance of the first crystallization peak when high external pressures are applied to specimens during annealing as compared with the as-quenched specimen. From these curves we can see that there are glass transitions for all specimens, but glass transition temperatures were obviously changed. This means that some processes must occur during annealing under high pressure, although the XRD does not reflect the structural change from these compressed specimens. When the external pressure is increased to 3 GPa, the first crystallization peak (which corresponds to the peak at 716 K for the as-quenched specimen) could hardly be observed, and disappears when the pressure is up to 4 GPa. The second crystallization peak (at 738 K) decreases, and its position also moves to higher temperature. The shapes of DSC curves for the specimens processed with 3 and 4 GPa are similar to that of Schneider's result of the same alloy, but their annealing temperature was 623 K which was near T_g, and the annealing time was very long (600 min). Schneider observed that the crystallization peak decreases and disappears as annealing duration increases. The XRD pattern of specimens isothermally annealed at 623 K for a duration longer than 100 min reveals the formation of a metastable simple fcc Cu–Ti phase.[14] This difference indicates that a microstructural change such as phase transition or a medium range order process perhaps occurs in our specimens.

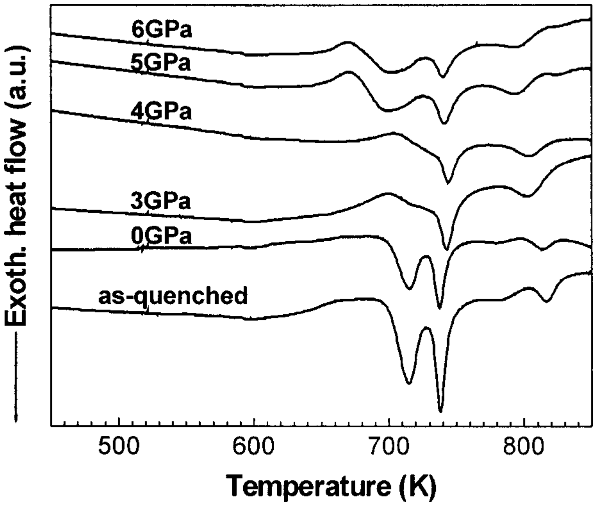

FIG. 2. DSC curves of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glasses annealed at 573 K and under different pressures for 2 h, scanning rate is 10 K/min.

When the external pressure is increased to 5 GPa, the first crystallization peak reappears, but its position moves to lower temperature, and the peak broadens, and its height also decreases. There is no change in the position of the second crystallization peak, but its height decreases continuously. These phenomena show that the effect of pressure on structural relaxation and crystallization of the amorphous phase is complex.

In order to confirm the occurrence of structural change during high pressure annealing, we carried out TEM observations on the specimens compressed with 3 and 6 GPa. The results show that a phase separation occurred for the specimen compressed with 3 GPa. The electron diffraction pattern exhibits two close diffusion rings which come from two amorphous phases. The observation on the specimen compressed with 6 GPa indicates the formation of nanocrystals. Schneider also observed the existence of phase separation preceding crystallization and an incubation time for crystallization when they annealed specimens at 623 K for different times under ambient pressure.[14] However, high pressure cannot only cause the phase transition at a temperature below T_g, but also change the sequence of the transition, where the phase separation occurs when annealing pressure is 3–4 GPa, and the nanocrystals are formed when annealing pressure is higher than 4 GPa. Further study on these specimens by TEM is still going on, and the detailed results will be reported elsewhere.

The annealing process at a temperature below T_g is generally regarded as a structural relaxation process, and the excess volume in the structure will be removed with a sufficient annealing time. This process involves the movement (over a short) of atoms and is a thermally activated process. The pressure effect is thought to be a combined result of thermal and compressive influences to the activation process.[15] Since the local structures, which may be a decisive controlling factor to the atomic mobility in amorphous alloys, are multifarious and the correlated activation energies would be spectrally distributed over a wide range, it is also expected that the pressure effect would most likely be diversified. From Schneider's result,[14] it is shown that phase separation is a low activation energy process and crystallization is a high activation energy process in $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk amorphous alloys. Zhangyi found that high pressure (1.5–2.5 GPa) promotes the low activation energy processes (activation energy $E_a < 1.27\,\mathrm{eV}$ at room temperature) in metal glasses, but high activation energy processes are strongly restrained by such an external compression.[15] Our result is a confirmation of Schneider's and Zhongyi's one. However, in our results, it is also shown that the effect of higher pressure (>4 GPa) gradually reverses to promote high-energy activated processes, and restrain the low activation energy processes. Since the struc-

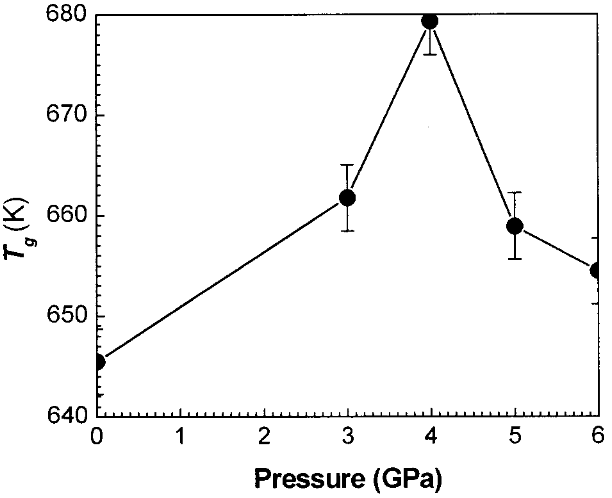

FIG. 3. Relationship between glass transition temperature and applied pressure of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glasses annealed at 573 K for 2 h.

tural relaxation and crystallization of metallic glass involves a densification, high pressures might be expected to accelerate the processes. The results of density measurement on the specimens processed by relaxation and crystallization show that the density of the amorphous alloy relaxed at 573 K is about 6.133 g/cm^3, an increase of only about 0.2% as compared with that of the as-quenched amorphous alloy.[16] However, if the full crystallization occurs, the increase of density is up to 1.1%. The relative volume compression ratio of the specimen at 573 K under 5 GP is conservatively estimated over 2%, as revealed by the study of the equation of state.[17,18] From this point, this large compression should favor the crystallization of the BMG, although the specimen is heavily overcompressed. At the same time the crystallization sequence is changed to favor the crystalline phases which have maximum density. On the other hand, according to the calculation of the equation of state, the strain energy density stored in BMG material caused by hydrostatic deformation with pressure up to 3–6 GPa is estimated at about $10^{-2}-10^{-4}$ eV per atom. Compared with bond energies which are of the order of 2–4 eV,[19] and activation energy of diffusion which is of the order of 1 eV in BMGs,[20] it is seen that the strain energy stored is extremely small on an atomic scale.

The effect of pressure on the glass transition T_g displays a nonmonotonic increasing function of pressure. First, the glass transition temperature T_g increases to a maximum with increasing applied pressure from 0 to 4 GPa, and then decreases with the continuous increasing of exerted pressure (Fig. 3). The nonmonotonic change of T_g with applied pressure can be understood for our result. The pressure is not only to promote the structural relaxation, but also to cause the phase transition in this metallic glass. Samwer, Busch, and Johnson reported an increase of glass transition temperature T_g with applied pressure ($<$2 GPa) when annealing temperature was fixed at 593 K (just below calorimetrically observed T_g) in another alloy of the ZrTiCuNiBe family.[13] They determined the shift of T_g with pressure by measuring the enthalpy change due to the various pressures from 0.0001 to 1.4 GPa, where the increase of T_g with rising pressure is approximately 3.6 K/GPa. Here the increase of T_g is about 5.3 K/GPa from 0 to 3 GPa; it reaches 17.6 K/GPa from 3 to 4 GPa. The phenomenon occurs at an annealing temperature which is much lower than $T_g(624\,\mathrm{K})$. A detailed mechanism or rigorous explanation of these processes is difficult to approach at present, since we know very little about the mechanism of atomic movement at ambient pressure as well as the exact correlation between T_g and the structure.

In conclusion, we show the effect of high pressure annealing below the glass transition temperature on the phase transition of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG. The high pressure annealing cannot only promote structural relaxation, but also induce the occurrence of phase separation, and a change of phase transition at a temperature below T_g in the BMG.

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