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LETTER TO THE EDITOR

Pressure dependence of crystallization in $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ bulk metallic glass

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Abstract

The pressure dependence of crystallization in $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ bulk metallic glass has been studied by means of high-pressure annealing close to and beyond the glass transition temperature, using differential scanning calorimetry and x-ray diffraction. The results reveal that high pressure markedly decreases the crystallization temperature of the glass. It is deduced that high-pressure annealing can promote crystal nucleation by decreasing the work of formation of the critical nucleus, but it also restrains crystal growth by decreasing the diffusion velocity of atoms.

According to thermodynamics, amorphous metallic alloys like other amorphous solids are metastable and will be transformed into crystalline or more stable amorphous metastable phases under suitable conditions such as thermal annealing [1–4]. Investigations into these transitions are often limited because of the difficult accessibility to the metastable glass state and the exceptionally high stability against crystallization. The current generation of Zr-, Fe- and Nd-based bulk metallic glass (BMG) forming alloys has aroused considerable scientific and technological interest due to their wide supercooled liquid region and high thermal stability as well as excellent mechanical properties [5–9]. It has been found that pressure and electric field are also effective in influencing the relaxation and crystallization process of amorphous solids induced by thermal annealing [10–15]. In the experiments on enthalpic recovery, results show that the higher the hydrostatic pressure, the lower is the enthalpic state reached during relaxation in Zr- and Pd-based BMG [16, 17]. The ZrTiCuNiBe BMG can be directly transformed into a bulk nanostructural solid [12]. This means that pressure is another variable that can be used to control the structural relaxation and crystallization of BMGs. However, there is little information on the effect of pressure on the kinetics and thermodynamics of phase transition in bulk metallic glassy alloys. In this letter we report an investigation of the pressure dependence of crystallization in $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ BMG using differential scanning calorimetry (DSC) and x-ray diffraction (XRD). The results indicate that high pressure markedly promotes the nucleation of crystals but restrains further growth as the pressure increases further in the BMG.

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A $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk amorphous bar was prepared from a mixture of the (up to 99.9 at%) pure elements by induction melting in a water-cooled copper mould in a Ti gettered Ar atmosphere and then cooling the molten liquid alloy into the glassy state in a quartz container. The amorphous rod was cut into many discs of 1 mm thickness and 5 mm diameter. A resistance furnace with a vacuum of 5×10^{-3} Pa was used for heat treatment of the samples with a temperature stability of ± 1 K. The specimens and thermocouple were placed near the metal disc to ensure homogeneity of the temperature. The annealing at high pressure was conducted in a pressure device with six anvil tops. Pyrophyllite was used for the outside layer of the pressure transmitting media, and specimens were embedded in sodium chloride. A graphite tube heater was used in the high-pressure device. At room temperature the pressure on a given sample was first increased to a certain value and then kept constant, after which the specimen was heated to a given annealing temperature at a heating rate of about 50 K min^{-1} and then maintained at this temperature for 2 hrs. After this the specimen was cooled to room temperature at a cooling rate of about 50 K min^{-1} and then the pressure on it was decreased. The annealing temperatures were 623, 673 and 723 K and the applied pressures 0, 3, 4, 5 and 6 GPa. The DSC measurements were carried out under a purified argon atmosphere in a Perkin-Elmer DSC7 device at a heating rate of 10 K min^{-1} . The value of the glass transition temperature T_g , the onset temperature T_{x1} for the first crystallization peak, and the crystallization peak temperature T_{pi} were determined from DSC traces with an accuracy of ± 1 K.

When the annealing temperature was near calorimetric T_g in the presence of high pressure, distinct structural differences were revealed by XRD and DSC. Figure 1 is the XRD result for the samples annealed at 623 K under different pressures. It was found that crystallization occurred when the annealing pressure was increased to 3 GPa from vacuum. This indicates that the applied pressure markedly decreases the crystallization temperature of the BMG. The amplitude of the temperature decrease is at least $\sim 16 \text{ K GPa}^{-1}$. This annealing temperature is much lower than the onset temperature T_{x1} (697.6 K) of the first crystallization peak under ambient pressure. In the figure we can see, however, that the crystallization peaks becomes lower and lower with increasing annealing pressure, and almost completely disappear when the pressure reaches 5 GPa. Figure 2 shows the DSC traces of the specimens corresponding

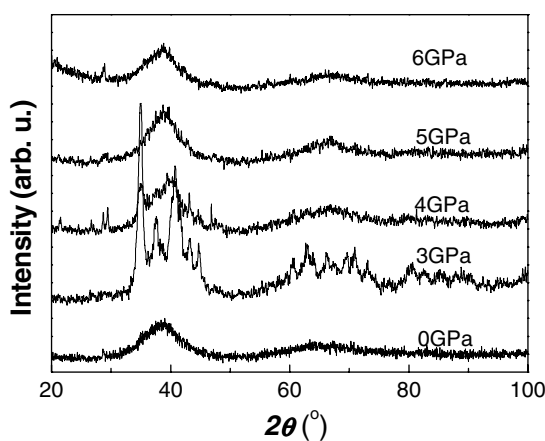


Figure 1. XRD results of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMGs annealed at 623 K under different pressures.

to those in figure 1. The traces of the specimens compressed under 3 and 4 GPa only exhibit a single crystallization peak near 818 K and 805 K, respectively. This further confirms the XRD result of figure 1. When the annealing pressure is up to 6 GPa, the first and second crystallization peaks reappear once again, but their width and height are decreased compared with those obtained under vacuum. Comparing the XRD and DSC results of the specimens annealed at 623 K, one can see that further increase of the applied pressure restrains the lowering of the crystallization temperature. Thus our results exhibit the effect of high pressure on the relaxation and phase transition of the BMG.

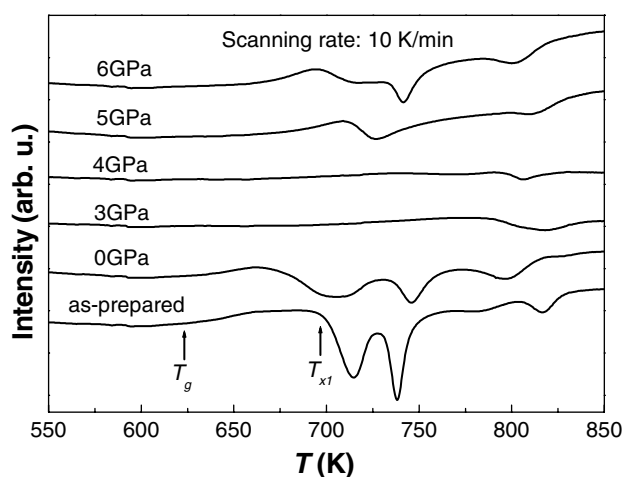


Figure 2. DSC traces of the specimens corresponding to those in figure 1.

Figure 3 shows the XRD patterns of the BMG specimens after processing under different pressures and at various temperatures. No crystalline diffraction peak in the specimen annealed up to 673 K and under vacuum is observed by XRD, but many peaks appear in the specimen annealed at 723 K and under vacuum. Although crystallization in the specimen annealed at 623 K occurs under an external pressure of 3 GPa, the number and position of the diffraction peaks are somewhat different from those in the specimen annealed at 723 K and under vacuum. Not only is the number of the peaks in the specimen annealed at 3 GPa less than that in the specimen annealed under vacuum, but also the intensities of the peaks are much lower and the widths are broader, indicating a reduction in the fraction and size of crystals in the BMG as the applied pressure increases. In figure 4, we can see that the average crystalline size, calculated from the full width at half maximum of the XRD peak according to Scherrer's formula [18], first increases and then decreases with increase of pressure for annealed specimens both at 673 K and at 723 K. As a first approximation, we have ignored the contribution of strains to the broadening of peaks. The higher pressure leads to a more apparent suppression of the growth of crystals when the annealing temperature increases. A comparison of the XRD curves in figure 3 shows that the formation of certain crystalline phases is inhibited by applied pressure during crystallization in the BMG. These phenomena illustrate that the effect of pressure on structural relaxation and crystallization of amorphous solids is complex.

The crystallization of BMGs is a diffusion-controlled process; the nucleation and growth of crystals need a long-range atomic diffusion due to a large composition difference between the amorphous phases and its crystallization products [19]. On the one hand, high pressure promotes a short-range atomic rearrangement in metallic glass by the reduction of the free

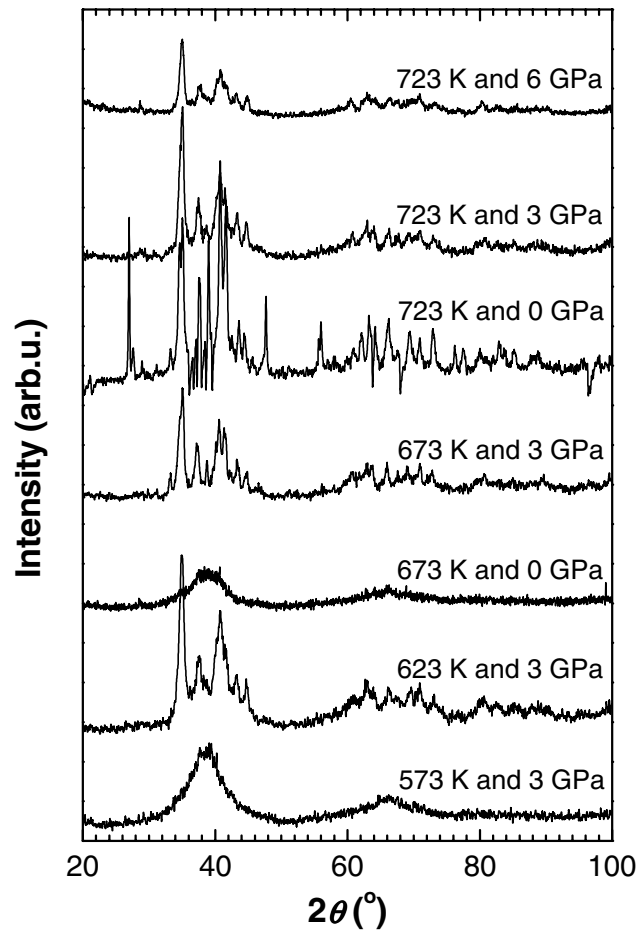


Figure 3. XRD patterns of the BMG specimens processed under different pressures and at various temperatures.

volume because of the compression and restructuring of the atomic configuration. This process favours the homogenous formation of crystal nuclei in the BMG matrix. On the other hand, high pressure limits the long distance atomic diffusion because of increasing viscosity and reduction of the free volume. The crystallization temperature of amorphous solids depends on the work required to form the critical nucleus and on the activation energy of diffusion [10, 20]. Assuming that only homogenous nucleation occurs in alloys, the variation of the work ΔG^* with pressure P may be expressed by

$$\left(\frac{\partial \Delta G^*}{\partial P}\right)_T = \Delta G^* \left[\frac{3}{\sigma} \left(\frac{\partial \sigma}{\partial P}\right)_T - \frac{2}{\Delta G^{a-c}} \left(\frac{\partial \Delta G^{a-c}}{\partial P}\right)_T \right].$$

Here σ is the nucleus–matrix specific interface free energy, ΔG^{a-c} is the difference in Gibbs free energy per unit volume between nucleus and matrix, and $\Delta G^{a-c} < 0$ when the system is in nonequilibrium below the melting point. We take $(\partial \sigma / \partial P)_T \approx 0$ (equivalent to assuming that σ is independent of pressure) [21]. When the pressure is lower than 10 GPa, the second term in the equation is $(\partial \Delta G^{a-c} / \partial P)_T = V^c - V^a = -0.12 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ for the alloy.

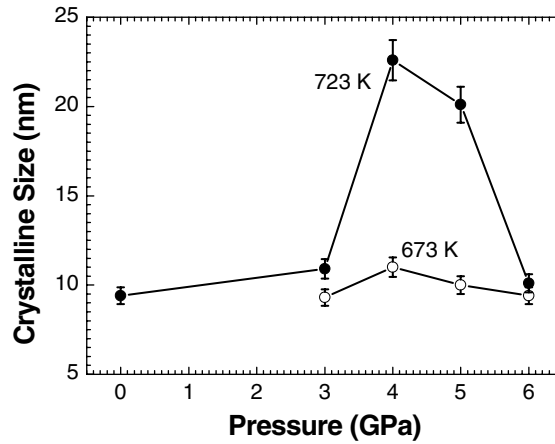


Figure 4. Relation between average crystalline size and applied pressure for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMGs annealed at different temperatures and pressures for two hours.

For ΔG^{a-c} , we take the first three terms of the expansion in the Maclaurin series, and obtain

$$\Delta G^{a-c} = (G^c - G^a) + (V^c - V^a)P - 0.5(\beta^c V^c - \beta^a V^a)P^2.$$

According to Bush's result for the Gibbs free energy of the undercooled liquid with respect to the crystal [22], we can estimate that $(2/\Delta G^{a-c})(\partial\Delta G^{a-c}/\partial P)_T$ varies approximately from $-0.13 \Delta G^* \text{ GPa}^{-1}$ to $-0.1 \Delta G^* \text{ GPa}^{-1}$ when the annealing temperature is 723 K, and from $-0.1 \Delta G^* \text{ GPa}^{-1}$ to $-0.08 \Delta G^* \text{ GPa}^{-1}$ at 560 K, i.e., the Kauzmann temperature, if the applied pressure changes from 1 GPa to 6 GPa. This represents a rapid decrease of ΔG^* with pressure, and indicates that, subject to the approximations employed, the rate of crystal nucleation should be markedly increased by pressure.

For the formation and growth of nuclei with diffusion phase transition, the diffusion coefficient D and the activation volume ΔV^* can be related by $[\partial(\ln D)/\partial P]_T = -\Delta V^*/kT$ [23]. As an estimate for our discussion, the activation volume of atomic diffusion is taken to be an atomic volume [24]. Since the average volume of the atoms in the BMG is 0.024 nm^3 , $D(P)$ varies from $-3D \text{ GPa}^{-1}$ to $-2.4D \text{ GPa}^{-1}$ when the annealing temperature increases to 723 K from 560 K. From this estimate, the larger the pressure is, the more difficult the diffusion of atoms. That is, pressure does not favour the diffusion of atoms. This explains why higher pressure can promote the nucleation of a crystal but also restrains its growth, thus the average size of the crystal first increases and then decreases with increasing annealing pressure in the BMG.

In summary, the crystallization of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG occurs near the calorimetric glass transition temperature when the specimen experiences high-pressure annealing, which suggests that the applied high pressure markedly decreases the crystallization temperature of the BMG. The average crystalline size first increases and then decreases with increase of pressure for annealed specimens both at 673 K and at 723 K. It is deduced that high-pressure annealing can promote crystal nucleation by decreasing the work of formation of the critical nucleus, but suppresses crystal growth by decreasing the diffusion velocity of atoms in the BMG.

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