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Pressure effect on crystallization of metallic glass $\text{Fe}_{72}\text{P}_{11}\text{C}_6\text{Al}_5\text{B}_4\text{Ga}_2$ alloy with wide supercooled liquid region

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The effect of pressure on the crystallization behavior of metallic glass $\text{Fe}_{72}\text{P}_{11}\text{C}_6\text{Al}_5\text{B}_4\text{Ga}_2$ alloy with a wide supercooled liquid region has been investigated by *in situ* high-pressure and high-temperature x-ray diffraction measurements using synchrotron radiation. In the pressure range from 0 to 2.4 GPa, the crystallization temperature, T_x , increases with pressure, p , having a slope of 30 K/GPa while a minimum in T_x was detected in the range from 2.4 to 3.9 GPa. With a further increase of p , T_x is independent of p . The T_x vs p behavior can be qualitatively explained by the suppression of atomic mobility and changes of the Gibbs free energy of various phases with pressure. © 2000 American Institute of Physics. [S0021-8979(00)01902-2]

Recently, Inoue *et al.*¹ found that Fe–Al–P–C–B–Ga alloys have wide supercooled liquid regions and good soft magnetic properties. The large glass forming ability of this alloy system enables the formation of bulk glassy samples with diameters up to 1 mm by slow cooling. Such samples have a coercive force down to 12.7 A/m and a saturation magnetization up to 1.07 T, promising future use as a new soft magnetic material.² However, the magnetic properties of metallic glasses are highly sensitive to small amounts of crystalline material. Thus, the danger of using them without detailed knowledge of their crystallization process cannot be overstressed. In general, metallic glasses possess a few percent of free volume. The crystallization of metallic glasses is accompanied by a densification of about a few percent.³ Thus, one might expect that external pressure would accelerate the crystallization process since the metallic glass can be densified by the applied pressure. In this work we report the pressure effect on the crystallization for a Fe-based metallic glass alloy with a wide supercooled liquid region.

$\text{Fe}_{72}\text{P}_{11}\text{C}_6\text{Al}_5\text{B}_4\text{Ga}_2$ ribbons with a width of about 10 mm and a thickness of about 25 μm were prepared by the melt-spinning technique. Thermal analysis was performed in a Perkin-Elmer DSC 7 differential scanning calorimeter (DSC) at a heating rate of 40 K/min under a flow of purified argon. It was found that the glass transition temperature is $T_g = 743$ K, the crystallization temperature is $T_x = 798$ K and

$\Delta T = T_x - T_g = 55$ K. *In situ* high-pressure and high-temperature energy-dispersive x-ray diffraction (EDXRD) measurements were performed using synchrotron radiation by the MAX80 station at HASYLAB in Hamburg, Germany. Each run consists of isothermal room-temperature compression followed by isobaric heating to high temperature. The pressure, p , of the sample (<6 GPa) is calculated from the lattice constant of NaCl using the Decker equation of state.⁴ In addition, we have also carried out room-temperature compression EDXRD measurements up to 35 GPa using a diamond-anvil cell by the F3 station at HASYLAB. A pressure transmitting medium of 4:1 methanol:ethanol solution was used. The actual pressure was calculated from the wavelength shift of the ruby line using the nonlinear pressure scale of Mao *et al.*⁵ For crystalline phase identification standard x-ray powder diffraction using Cu $K\alpha$ radiation as well as Mössbauer spectroscopy measurements at ambient temperature and pressure were performed in the samples which were isochronally annealed in a vacuum of 3×10^{-5} Pa at various temperatures for 1 h.

A large number of EDXRD patterns of the metallic glass were recorded at pressures ranging from 0 to approximately 35 GPa at room temperature. Up to a pressure of approximately 35 GPa, no crystalline phase was observed. The position of the main peak was found to increase with pressure. This means that the corresponding d spacing decreases with pressure. If one assumes that the density of the amorphous alloy is proportional to $1/d^3$, one can estimate the ratio of the

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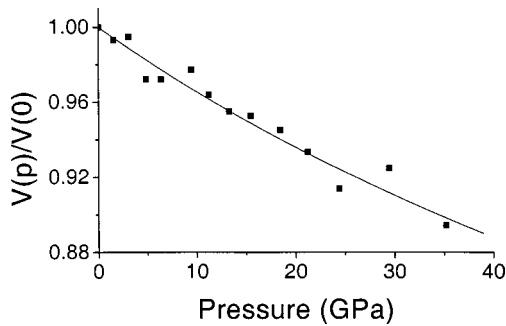


FIG. 1. Compression data of the $\text{Fe}_{72}\text{P}_{11}\text{C}_6\text{Al}_5\text{B}_4\text{Ga}_2$ metallic glass at room temperature. The solid curve is calculated from the Birch equation of state.

volume at a given pressure to that at zero pressure, $V(p)/V(0)$, of the metallic glass, as shown in Fig. 1. The volume ratio decreases monotonically with pressure. At approximately 35 GPa, the metallic glass has contracted by approximately 10%. The pressure-volume data shown in Fig. 1 have subsequently been fitted to the Birch equation of state.⁶ The zero-pressure bulk modulus is found to be 265 ± 10 GPa, which is much larger than that for body-centered-cubic bcc iron, 170 ± 5 GPa.⁷

Figure 2 exemplifies EDXRD patterns recorded for crystallized samples at various pressures. The phases, A1, A2, and A3, will be explained below. Figure 3 shows the crystallization temperature, which was estimated from EDXRD patterns recorded by increasing temperature with a stepsize of about 10 K as a function of pressure. It is clearly seen that the applied pressure strongly affects the crystallization temperature of the Fe-based metallic glass, and that the behavior of T_x vs p differs in various pressure ranges. From 0 to 2.4 GPa, T_x increases with pressure, having a slope of 30 K/GPa. This value is larger than those reported for metallic glasses with no wide supercooled liquid range, where $dT_x/dp \sim 0-20$ K/GPa.⁸⁻¹⁴ In the range from 2.4 to 3.9 GPa, a minimum in T_x was detected at a pressure of 3.2 GPa. With a further increase of pressure, the T_x is independent of the external pressure. In order to understand these differences in the T_x vs p behavior, crystalline phase identification in crys-

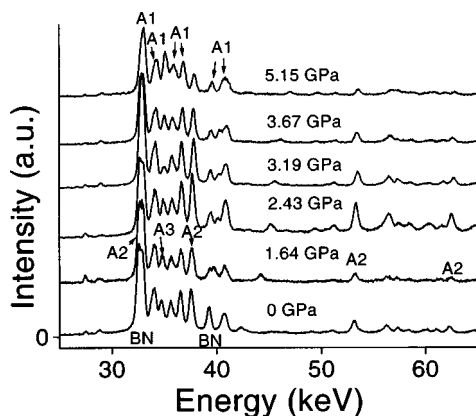


FIG. 2. Energy-dispersive x-ray diffraction patterns recorded for crystallized samples at various pressures. Notations A1, A2, and A3 refer to three crystalline phases. Some diffraction peaks of boron nitride originating from the sample holder are marked by BN.

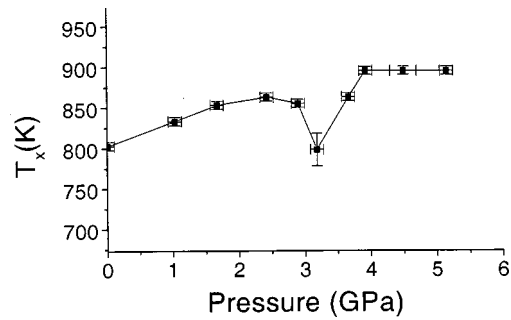


FIG. 3. Crystallization temperature of the $\text{Fe}_{72}\text{P}_{11}\text{C}_6\text{Al}_5\text{B}_4\text{Ga}_2$ metallic glass as a function of pressure. The solid line is a guide for the eye.

tallized samples at various pressures is essential. Due to the poor resolution in the EDXRD measurements and the fact that several phases exist in the crystallized samples, we first attempt to identify the crystalline phases in samples annealed in vacuum by using standard x-ray powder diffraction (XRD) and Mössbauer spectroscopy (MS) at ambient temperature and pressure. Figure 4 exemplifies an XRD pattern and a MS spectrum of a sample annealed at 823 K. Three crystalline phases were identified from the XRD and MS measurements in the annealed samples. They are (1) a phase (marked A1) with a Ni_3P -like tetragonal structure¹⁵ (space group: I4) having lattice constants of $a = 8.93 \text{ \AA}$ and $c = 4.41 \text{ \AA}$ and a composition close to $\text{Fe}_3(\text{M})$, where M stands for P, C, Al, B, and Ga elements; (2) a phase (marked A2) with a $\text{Fe}_3(\text{NiN})_2$ -like cubic structure¹⁵ (space group: $Pm\bar{3}m$) having a lattice constant of $a = 3.78 \text{ \AA}$ and a com-

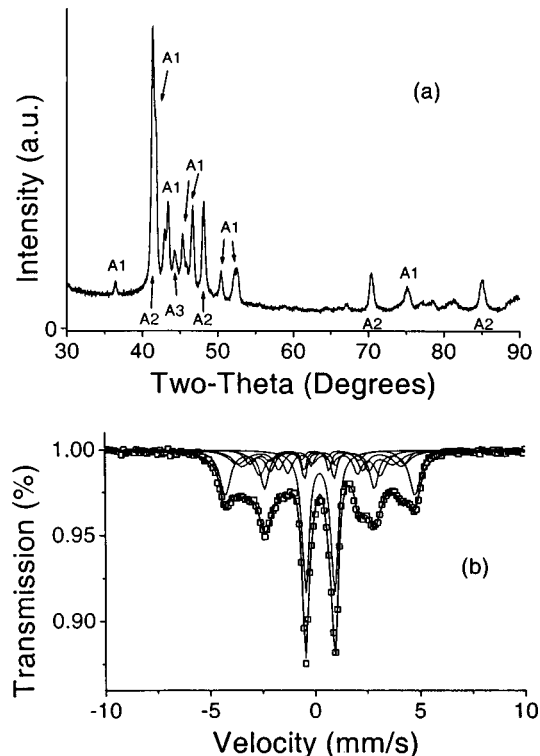


FIG. 4. (a) X-ray powder diffraction pattern and (b) Mössbauer spectrum recorded at 295 K for the sample annealed at 823 K in a vacuum of 3×10^{-5} Pa for 1 h. Notations A1, A2, and A3 refer to three crystalline phases. The solid lines in (b) are fitting curves.

position close to $\text{Fe}_3(\text{M})_2$; and (3) a phase (marked A3) with a $\text{Fe}_{23}(\text{CB})_6$ -like cubic structure¹⁵ (space group: $Fm\bar{3}m$) having a lattice constant of $a = 10.6 \text{ \AA}$ and a composition close to $\text{Fe}_{23}(\text{M})_6$. From the XRD and MS investigations of samples annealed at various temperatures, it is found that the crystallization process of the metallic glass Fe-based alloy in vacuum is characteristic of a three-phase eutectic reaction. Second, we compared the d spacings of the three phases with the EDXRD data and found that the diffraction peaks in the EDXRD patterns recorded from the crystallized samples under various pressures can be attributed to the three crystalline phases. The relative amounts of the three phases could be different in crystallized samples at various pressures.

In general, applied pressure on metallic glasses might have three effects. The first effect is densification, which reduces the free volume in the glass by pressure. This effect could favor the crystallization process because crystallization of metallic glasses involves densification. The second effect is suppression of atomic mobility at high pressures, which reduces the atomic diffusion in metallic glasses. At least for eutectic or primary crystallization processes this effect retards crystallization since atomic diffusion is required for these crystallization processes. The third effect is due to changes in relative Gibbs free energies of the glassy phase and crystalline phases by pressure, and in the energy barrier for crystallization. This effect could alter the relative amounts of the crystalline phases in the crystallized samples, and could be of either sign with regard to dT_x/dp .

Figure 1 reveals that no crystallization occurs at 295 K in the sample upon a volume reduction of approximately 10% which is much larger than the free volumes (of usually a few percent) reported for metallic glasses.³ For the bulk glass forming MgYCu system the amorphous state still remains in the sample for approximately 30% contraction in volume.¹⁶ These results suggest that densification induced by external pressure does not have any important influence on the crystallization temperature of these metallic glass systems with a wide supercooled liquid region. The crystallization process in the pressure range from 0 to 1.6 GPa is found to be similar, generating three phases (A1, A2, and A3). For the eutectic reaction, a redistribution of atoms (or atomic diffusion) is necessary. Due to the second effect mentioned above, pressure prevents crystallization so that a higher crystallization temperature is expected. This explains the observed increase in T_x with pressure in the range from 0 to 1.6 GPa in Fig. 3. At 3.2 GPa, the minimum in T_x could be linked with the fact that the relative amount of A3 phase is very small in the crystallized sample. The pressure here affects the relative amounts of three crystalline phases in the crystallized samples. It is not unreasonable to expect less difficulty to crystallize the glass into mainly two phases than into three phases. This implies that the third effect mentioned above may accelerate the crystallization. Further work is still required to understand the mechanism for the minimum in

T_x . With increasing pressure, the amount of A3 phase increases so that the crystallization process of the sample again involves a three-phase eutectic reaction. T_x increases accordingly with pressure in the range from 3.2 to 3.9 GPa. At still higher pressures (>3.9 GPa), a remarkable enhancement of the A3 phase is found in the crystallized samples while the relative amount of A2 phase decreases and the A1 phase remains almost unchanged. Hence, two competing effects (the second and third pressure effects) yield a saturated crystallization temperature within the pressure range from 3.9 to 5.2 GPa.

In conclusion, the effect of pressure on the crystallization processes of the metallic glass $\text{Fe}_{72}\text{P}_{11}\text{C}_6\text{Al}_5\text{B}_4\text{Ga}_2$ alloy with a wide supercooled liquid region has been investigated by *in situ* high-pressure and high-temperature x-ray diffraction measurements using synchrotron radiation. It was found that the external pressure can strongly influence the crystallization temperature of the metallic glass. The behavior of T_x vs p is mainly governed by the suppression of atomic mobility and changes in relative Gibbs free energy of various phases with pressure. The densification effect induced by pressure only plays a minor role in the crystallization behavior of this alloy.

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