

Nanocrystallization of ZrTiCuNiBeC bulk metallic glass under high pressure

Wei Hua Wang,^{a)} D. W. He, D. Q. Zhao, and Y. S. Yao
Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

M. He
Department of Materials Engineering, Dalian University of Technology, Dalian, 116024, China

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Nanocrystallization of $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ bulk metallic glass (BMG) under high pressure is investigated. It is found that the nanocrystallization is pressure assisted, and the primary nanocrystallization temperature decreases as the applied pressure increases. Pressure annealing of the BMG in the supercooled liquid region produces a composite with dispersion of very fine nanocrystallites in the amorphous matrix. A fully nanocrystallization is obtained by pressure annealing under 6 GPa at 723 K. The pressure also controls the phase selection during the crystallization. The mechanism for the pressure-assisted nanocrystallization is discussed. © 1999 American Institute of Physics. [S0003-6951(99)04444-7]

The recent discovery of complex multicomponent bulk metallic glasses (BMGs) with excellent glass forming ability (GFA) and physical properties is exciting for both fundamental and practical reasons.¹⁻⁴ $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ glass forming system represents one such group of BMGs, which shows excellent GFA.² Little dissolution of carbon and silicon (about 1 at. %) into the Zr-based BMGs can further enhance the thermal stability and mechanical properties of the BMGs.^{5,6} The BMGs contain more than three constituents with significantly different atomic sizes, and a long-range diffusion in the alloys is extremely difficult. However, since these BMGs crystallize to crystalline phases with composition different from the metallic glassy state, a redistribution by long-range diffusion is required for the crystallization in the BMGs.⁴ These characteristics make the crystallization very difficult in the supercooled liquid region of the BMG.⁴ The slow crystallization kinetics, similar to silicate glasses, makes it possible to control a partially or a fully crystallization of the metallic glass better. High pressure (HP) is powerful tool which might be applied to control the nucleation and growth in the BMGs,⁷ the BMG could be crystallized to very fine-grained nanostructural material under HP. The contamination and grain growth occurring during consolidation of nanoparticles could be avoided in the crystallized nanostructural material that is produced in the already-consolidated state. Thus, crystallization of the BMGs under HP is a promising way for synthesizing bulk nanocrystalline alloys. The synthesis of bulk nanocrystalline alloy from the BMGs could enable the application of the nanocrystalline alloy as engineering materials. On the other hand, it is expected that the study of the pressure-controlled crystallization behavior may provide a way for insight into the mechanism of the nucleation and growth process in the BMGs. Nanocrystalline alloys with useful characteristics have been obtained by the partial crystallization of an amorphous phase

in a number of melt-spun metallic glasses.⁸⁻¹⁰ However, little work has been done on the crystallization of the BMGs under high pressure even at ambient pressure owing to the complexity of the alloys, the crystallization process is poorly understood. In this letter, the nanocrystallization of the Zr-Ti-Cu-Ni-Be-C BMG under HP is investigated by using x-ray diffraction (XRD), high-resolution transition electron microscope (HRTEM). The effects of the pressure on the crystallization are discussed.

Ni-C lump was prepared by sintering 99.999 pure Ni and 99.99 pure C powders at 1500 °C. 99.99% pure Ti, 99.9% pure Zr, 99.999 pure Cu, 99.97 pure Be elements and the NiC lump were induction melted together under a pure argon atmosphere to form homogeneous ingots with desired composition. The ingots were remelted together in a silica tube and subsequently quenched in water resulting a cylindrical rod with a diameter of 12 mm. XRD was performed using a MAC M03 XHF diffractometer with $Cu K_{\alpha}$ radiation. HRTEM observation was performed at a Jeol-2010 operating at 200 kV. The HP was performed in an apparatus with six anvil tops. NaCl powder was used as solid pressure transmitting media. NiCr-NiAl thermocouple was brought into the pressurized zone through graphite furnace and was near the sample. The samples were prepressured to a certain value to enhance the homogeneity of the pressurization. The accuracy to measure the temperature of the sample itself under applied pressure was about ± 1.5 K. The details of the HP experiment were described at length in Ref. 11.

The amorphous nature as well as the homogeneity of the water quenched $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ alloy was ascertained by using XRD, differential scanning calorimeter (DSC), transmission electron microscope (TEM), and small angle neutron scattering.^{5,12} The DSC trace exhibit a broad endothermic peak characteristic of the glass transition followed by four exothermic heat release peaks indicating a multistage crystallization process. The glass transition temperature T_g , the onset temperature of the first crystallization event T_{x1} , and $\Delta T = T_{x1} - T_g$, referred to as the supercooled liquid region are 623, 712, and 90 K, respectively.⁵

^{a)}Author to whom correspondence should be addressed; electronic mail: whw@aphy.iphy.ac.cn

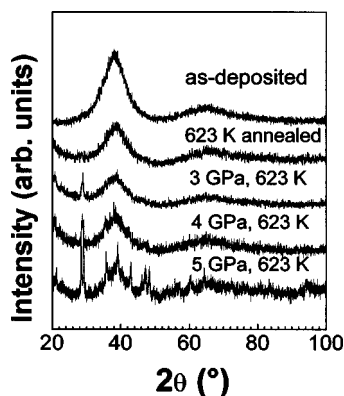


FIG. 1. The XRD patterns for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ BMG annealed at 623 K under different pressures for 4 h.

Figure 1 shows the XRD patterns for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ BMG isothermal annealed at 623 K under various pressures. The annealing temperature is much lower than the T_{x1} (712 K). All the XRD patterns for the BMG annealed under HP were obtained after releasing pressure in this work. The XRD pattern exhibits no change for the sample annealed at 623 K in vacuum for 20 h, indicating that the crystallization does not occur in the sample within the examining limit of the XRD. The sample has also been annealed in the sample assembly of the high pressure apparatus (after prepressurized) at 623 K for several hours without applied pressure. XRD results indicate that no crystallization of any kind was observed. This means that the possibility of the heterogeneous nucleation caused by contact pressuring transmitting medium can be excluded. However, when the BMG annealed at same temperature under HP for 4 h, the partial crystallization occurs progressively, starting at 3 GPa. More crystalline peaks appear and the intensity of the peaks increases with increasing pressure, meaning that the crystalline fraction in the BMG increases as the applied pressure increases. This result indicates that the HP favors the crystallization in the BMG. The crystallized phase can not be identified at present because of the complexity of the multi-component alloy and the undetectable Be element by using XRD. The partial crystallized BMG has broad XRD crystalline peaks resulting mainly from the fine grain size in the alloy. The average grain size for the sample annealed at 4 GPa calculated from the full width at half maximum of the diffraction peak according to Scherrer formula¹³ is about 4 nm, indicating the BMG crystallize to a composite material containing very fine nanometer-scale crystallites. Figure 2 presents the HRTEM micrograph of the BMG annealed at 623 K under 4 GPa. It can be clearly seen that the nanometer-scale crystallites (less than 5 nm) distribute in the remaining amorphous matrix. The average crystallite size is agreement well with that estimated from Scherrer formula. The volume fraction of the nanocrystalline particles is estimated to be 15%. The key features of the HRTEM image are uniform dispersion and random crystallographic orientations of the nanoparticles, indicating the independent nucleation events in the crystallization process under HP. The results also confirm that no obviously heterogeneous nucleation induced by contact medium occurs in the crystallization process. The ultrafine nanometer-scale dispersion of crystallites

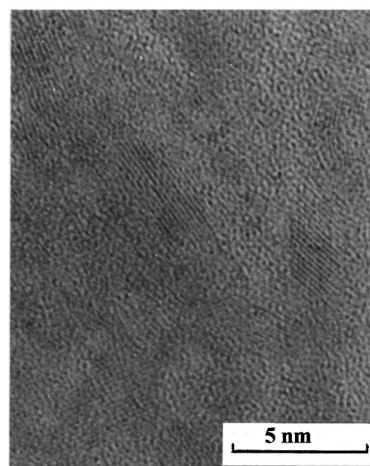


FIG. 2. The HRTEM micrograph of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ BMG annealed at 623 K under 4 GPa for 4 h.

in the amorphous matrix is a highly unusual microstructure, appearing to represent a action of copious nucleation and slow growth velocity in the BMG under HP.¹⁴ The pressure annealing temperature (623 K) is much lower than T_{x1} (712 K), the observed partial nanocrystallization demonstrates that the primary crystallization temperature of the BMG under HP is decreased. Figure 3 shows the dependence of the T_{x1} on the pressure for the BMG. The T_{x1} decreases from 683 K at ambient pressure to 588 K at 6 GPa. This phenomenon was also observed in amorphous semiconductors silicon and germanium.^{15,16} The results indicate that the T_{x1} decreases as the applied pressure increases in the BMG. Figure 4 presents the XRD patterns for the crystallization of the BMG at various processing conditions. A fully nanocrystallization of the BMG is obtained by pressure annealing under 6 GPa at 723 K, the crystallized BMG shows several broad XRD crystalline peaks [Fig. 4(b)], while the specimen crystallized at vacuum exhibits more and sharper crystalline diffraction peaks [Fig. 4(a)]. A comparison of the XRD patterns for the two crystallized specimens shows that some crystalline phases are inhibited by HP during the crystallization in the BMG. Meanwhile, the average crystallite size for the two crystallized specimens are markedly different. The average size of the crystallites evaluated according to Scherrer's formula for the sample crystallized under 6 GPa at 723 K is about 10 nm, and much smaller than that of the crystallization in vacuum (about 30 nm). The fully nanocrystallization has been confirmed by DSC results, no heat release peaks

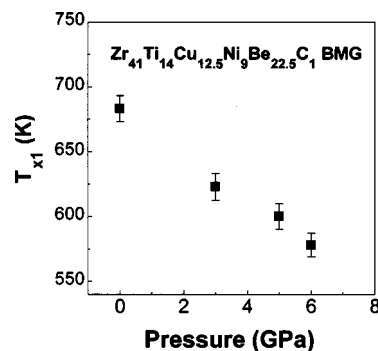


FIG. 3. The dependence of the T_{x1} on the pressure for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ BMG.

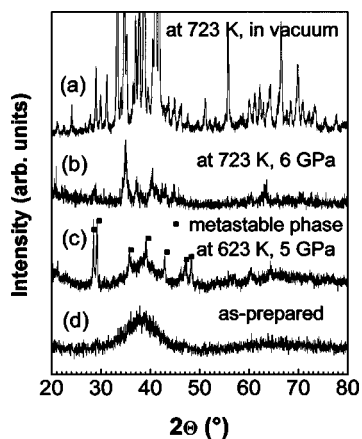


FIG. 4. The XRD patterns for the crystallization of the BMG at various processing conditions. (a) Annealed at 723 K in vacuum; (b) annealed at 723 K under 6 GPa for 4 h; (c) annealed at 623 K under 5 GPa for 4 h; and (d) the as-prepared BMG.

which indicating the crystallization of remaining amorphous phases have been observed. The XRD pattern of the BMG under 5 GPa at 623 K [Fig. 4(c)] shows some crystalline peaks which have not corresponding ones in that of the sample annealed in vacuum [Fig. 4(a)]. These crystalline peaks as indicated in Fig. 4(c), in our opinion, belong to a metastable phase which can only be obtained by pressure annealing induced crystallization. The different crystallization products at different applied annealing pressure indicate that the pressure has great effect on the phase selection during the crystallization process in the BMG.

Experimental studies and numerical modeling demonstrate that HP promotes a short-range rearrangement of the atoms (i.e., the structural relaxation) in the supercooled liquid region of the metallic glasses,^{17,18} because pressure can causes the annihilation of the free volume and reduces voids through compressing the glassy structure and reconstruct the atomic configuration, and these effects are related to the short-range rearrangement of atoms. The rearrangement favors the homogeneous formation of small clusters. The clusters distribute uniformly in the amorphous matrix which act as nucleation sites. On the other hand, owing to the highly dense random packed microstructure and extremely low atomic mobility in the BMG,¹⁹ the redistribution of atoms on a large-range scale is difficult, the HP makes the long-range atomic diffusion more difficult in the BMG, and the subsequent growth of the nucleation sites is inhabited by the extremely slow atomic mobility. Meanwhile, DSC results show that the residual amorphous phase around the crystalline particles has relatively higher thermal stability.²⁰ The crystallization of the BMG is a multistage process, its DSC trace exhibits four exothermic heat release peaks from 712 to 850 K, the partial crystallization induced by HP causes the change of the composition of the remaining amorphous phases and results in high thermal stability. The large population of small clusters and the inhibited atomic mobility as well as the higher thermal stability of the remaining amor-

phous phase result in the formation of high density of nanocrystallites that uniformly and randomly disperse in the amorphous matrix under HP. Shen *et al.*^{17,21} found that the activation energy of crystallization (ΔE_x) of binary metallic glass was pressure dependent, and an appropriate pressure could lower the ΔE_x for a crystallization. The crystallization of the BMG is multistage process, the effect of the pressure on the different crystallization stage is different, the crystallization stage with relatively lower value of ΔE_x under pressure is pressure promoted. It appears that for this reason we observe the pressure-controlled phase selection in the pressure annealing induced crystallization.

In conclusion, the partially nanocrystallization assisted by HP is observed in $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ BMG. The crystallization produces the composite consisting of a dispersion of fine nanometer-scale crystallite, less than 5 nm in size, in the amorphous matrix. The isothermal annealing under HP larger than 3 GPa results in the markedly decrease of the nanocrystallization temperature. The nanocrystallization products are pressure dependent. A fully nanocrystallization can be obtained by an appropriate HP annealing. The origin of the nanocrystallization phenomenon is attributed to the copious nucleation and slow growth velocity induced by HP annealing. The nanocrystallization under HP is expected to enable the formation of bulk nanocrystalline alloys with functional and engineering characteristics in the future.

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