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2003 J. Phys.: Condens. Matter 15 L749

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LETTER TO THE EDITOR

Melting and crystallization of $\text{Nd}_{60}\text{Al}_{10}\text{Fe}_{20}\text{Co}_{10}$ bulk metallic glass under high pressure

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Received 11 August 2003

Published 3 December 2003

Online at stacks.iop.org/JPhysCM/15/L749

Abstract

Crystallization, melting and structural evolution upon crystallization in $\text{Nd}_{60}\text{Al}_{10}\text{Fe}_{20}\text{Co}_{10}$ bulk metallic glass (BMG) are *in situ* investigated by x-ray diffraction with synchrotron radiation under high pressure. It is found that the crystallization is pressure promoted, while the melting is inhibited. The crystallization and melting process are also changed under high pressure. The features of the crystallization and melting under high pressure are discussed.

Nd-based bulk metallic glasses (BMGs) with hard magnetic properties and the anomalous crystallization behaviour [1–5] have evoked intensive interest. Previous works show that the magnetic property of a BMG is very sensitive to the microstructure of the alloy, and crystallization can cause markedly changes of the thermal and magnetic properties [1–5]. In previous work, it has been found that an intermediate product involving the formation of metastable phases has been found in the crystallization process, the hard magnetic property of the BMG is related to the formed intermediate phases which are kinetically favourable in the supercooled melt prior to the crystallization [5]. It is also found that the Nd-based BMG can actually be regarded as a type of clustered amorphous material [2, 5]. The direct evidence is that the HRTEM image of as-cast BMG exhibits a large numbers of nano-scale ordered regions dispersed in the glassy matrix, and the volume fraction is as large as 50% [5]. Clustered BMG exhibits hard magnetism while a ribbon sample without clustered structure is magnetically soft [3, 5]. Furthermore, the BMG has no obvious glass transition in its differential scanning calorimetry (DSC) scans which is a common feature for other BMGs. High pressure (HP), which can cause a larger change of atom spacing, chemical bonding and Gibbs free energy, has been found to be a powerful tool for affecting and controlling the crystallization in the metallic

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glasses [6–8]. HP can possibly change the crystallization temperature, T_x , and crystallization process and type. It is most intriguing how the clustered amorphous alloy crystallizes under HP. The study of how HP affects and controls crystallization and melting of the Nd-based alloy is useful in understanding the glass formation as well as the origin of the hard magnetic property, exploring novel microstructures by controlled solidification, and examining the fundamentals of nucleation and growth processes.

In this letter, the crystallization and melting of the $\text{Nd}_{60}\text{Al}_{10}\text{Fe}_{20}\text{Co}_{10}$ BMG under high pressure and high temperature are investigated *in situ* using x-ray diffraction (XRD) with synchrotron radiation. The results are compared with those obtained at ambient conditions. Some interesting features in the crystallization and melting processes of the BMG are found and discussed.

The $\text{Nd}_{60}\text{Al}_{10}\text{Fe}_{20}\text{Co}_{10}$ BMG was prepared by a cast method [2, 3]. The phase evolution and melt of the alloy were investigated by an *in situ* XRD at Spring-8, a third-generation synchrotron radiation facility in Japan. HP and high-temperature conditions were generated using a cubic-type multi-anvil press (SMAP 180) installed on BL14B1 [9]. The sample assembly was similar to that used in [10]. The graphite furnace was surrounded by ZrO_2 as a thermal insulator. An NiCr–NiAl thermocouple was brought into the pressurized zone and near the sample. The temperature was increased in steps of 5 K, and the average heating rate in the temperature range of 300–1200 K was roughly estimated to be 0.167 K s^{-1} . NaCl powder was used as the pressure transmitting medium. The pressure was calibrated from the lattice constant of NaCl; the accuracy was better than $\pm 0.2 \text{ GPa}$. An energy dispersive method was utilized using white x-rays with energy of 20–160 keV. The diffracted x-rays were detected by a solid state Ge detector; the diffraction angle 2θ was fixed to 3.0° .

The XRD patterns of the BMG at various annealing temperatures at ambient pressure show that the BMG crystallizes at 633 K, and metastable phases are formed and transform into stable crystalline phases at higher temperature. The BMG is fully crystallized above 753 K and the melting temperature, T_m , is about 793 K [5]. Figure 1 shows the XRD patterns of the BMG *in situ* measured under 5.0 GPa at various temperatures. The XRD patterns were recorded every 5 K to determine the onset temperatures for crystallization and melting, and phase evolution upon temperature. So the onset T_x is the temperature where the XRD can detect the crystalline peaks. T_m is the temperature where all crystalline peaks (not including some crystalline peaks from the pressure medium) disappear from the XRD curve. The BMG starts to crystallize at about 593 K ($< T_x = 633 \text{ K}$, at ambient pressure), the crystalline phase fraction gradually grows and fully crystallizes at 713 K during the elevated heating (the average heating rate is about 0.167 K s^{-1}). The results indicate that T_x is decreased from 633 K at ambient pressure to about 593 K under 5.0 GPa.

Figure 1 also shows the phase evolution from amorphous to crystalline and then to liquid state of the Nd-based alloy. The first precipitated crystalline phase during HP annealing can be well identified as hexagonal Nd as indicated in figure 1. This is in agreement with that of the BMG crystallized at ambient pressure [5]. At higher temperature, the intensities of the crystalline reflections change. A remarkable phenomenon is that the relative intensity of the first precipitated crystalline Nd phase is reduced and disappears first during melting as indicated in figure 1. Nd phase disappears completely at 973 K which is much lower than the melting temperature of Nd at ambient pressure (1394 K). Meanwhile, more crystalline phases appear, and their intensities increase during the whole crystallization process; the main crystalline peak intensity even increases at the beginning of the melting process as marked in figure 1. This implies that during the crystallization and melting process under HP the precipitated crystalline Nd, like unstable intermediate product, reacts with other phases or elements and transforms into another crystalline phase; the mechanism for the phenomenon,

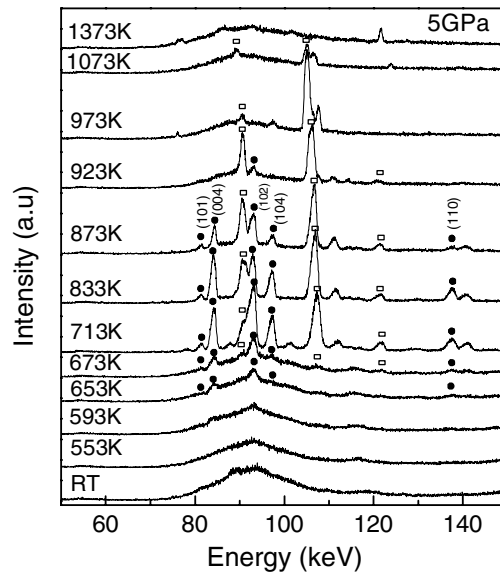


Figure 1. *In situ* XRD patterns of the $\text{Nd}_{60}\text{Al}_{10}\text{Fe}_{20}\text{Co}_{10}$ BMG at elevating temperature under 5.0 GPa. The precipitated h-Nd phase is indicated by ●, and other crystalline compounds by □.

which has not been observed in the BMG at ambient pressure and other BMGs, is unclear. The identification of the crystallized phases is also difficult due to the multicomponent alloy, and the crystalline peaks in the diffraction pattern do not exactly match any previously known phases. However, from comparison with crystallization results at ambient pressure [4, 5], these intermetallic crystalline compounds may correspond to a paramagnetic $\text{Nd}(\text{Fe}, \text{Co}, \text{Al})_2$ with a MgCu_2 -type structure [4]. The Nd-based alloy starts to melt at 873 K, and is completely melted at 1173 K. Some sharp crystalline peaks in the XRD pattern of the melt result from the merging of ZrO_2 powder in the melt.

Figure 2 exhibits XRD patterns of the BMG measured *in situ* at various temperatures under 8.0 GPa (the average heating rate is about 0.167 K s^{-1}). The BMG onset crystallizes at about 473 K which is much lower than T_x at ambient pressure. When the BMG is isothermally annealed at 633 K, the BMG is fully crystallized for 30 min annealing at this temperature, which is much lower than that at ambient pressure. HP strongly affects the T_x of the BMG. The phase evolution is similar to that under 5.0 GPa. The first precipitated crystalline phase during 8.0 GPa annealing is also hexagonal Nd as indicated in figure 2. At higher temperatures, the relative intensity of the first precipitated crystalline Nd phase is reduced and disappears completely at 1173 K which is much higher than that at 5.0 GPa. Meanwhile, the main crystalline peak intensity also increases at the beginning of the melting process. At 8 GPa, the alloy starts to melt at about 923 K, and is completely melted at 1173 K. T_m increases with increasing pressure. Table 1 lists the thermal parameters of the BMG under different pressures. The observation is in agreement with what happens in most alloys under HP.

The above results indicate features of crystallization under HP.

- (1) T_x is decreased with the increase of applied pressure. That is, the crystallization is promoted under HP. In most amorphous alloys, however, it was found that HP suppresses the crystallization manifested by an evident increase in T_x [11–15], and the enhanced thermal stability was attributed to the pressure inhibition of long-range atomic diffusion

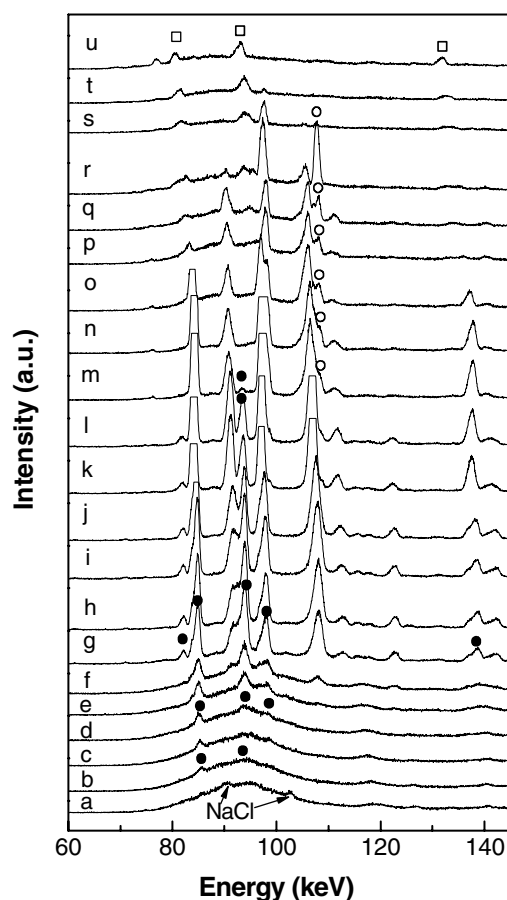


Figure 2. *In situ* XRD patterns of the $\text{Nd}_{60}\text{Al}_{10}\text{Fe}_{20}\text{Co}_{10}$ BMG at elevating temperature under 8.0 GPa. The precipitated h-Nd phase is indicated by the symbol ●, other crystalline compounds by ○, and ZrO_2 by □. (a) RT, (b) 473 K, (c) 553 K, (d) 573 K, (e) 633 K @ 0 min, (f) 633 K @ 10 min, (g) 633 K @ 30 min, (h) 673 K, (i) 713 K, (j) 753 K, (k) 793 K, (l) 813 K, (m) 853 K, (n) 873 K, (o) 923 K, (p) 973 K, (q) 1013 K, (r) 1123 K, (s) 1173 K, (t) 1223 K, (u) 1323 K.

Table 1. The thermal parameters of the BMG under different pressures.

P (GPa)	T_x (K)	T_m (K)
0.0	633	793
5.0	593	873
8.0	473	923

during crystallization [15]. HP suppresses the long-range diffusion (involving large energy fluctuation) and favours the atomic mobility over a short range (small energy fluctuation) in the BMG. Thus, HP can effectively suppress the crystallization through inhibiting the long-range diffusion in metallic glasses [10–15], because the primary crystallization product in metallic glasses is normally intermetallic crystalline compounds; this is a diffusion-controlled process and the crystalline growth needs a long-range atomic diffusion which is suppressed by HP. The precipitation of crystalline Nd in Nd-rich glass, however, depends

mainly on HP-favoured local atomic mobility. Therefore, the precipitation of crystalline Nd is a favourable phase at an early stage of crystallization and is promoted by HP.

The HP-promoted precipitation of fine nanocrystalline Nd observed in Fe-rich Nd-based alloys may also be related to phase separation in the glass which is a common phenomenon in multicomponent bulk glass forming alloys [16]. The origin of phase separation in the Nd–Fe–Al system is attributed to the heat of mixing of the two main components Nd and Fe [17], which is positive (+1 kJ mol⁻¹) [18]. This will lead to separation; HP like temperature can induce phase separation in the Fe- and Nd-rich alloy by promoted their mutually repulsive interaction [19].

- (2) There is no metastable phase formed during the HP crystallization, indicating different crystallization processes under HP compared to that at ambient pressure. Instead, the precipitated crystalline Nd acts as an intermediate product during the crystallization and melting process. The HP increases the viscosity of the supercooled liquid state and precipitation of Nd affects the formation of the metastable phase.

In conclusion, the *in situ* investigations of XRD with synchrotron radiation under high pressure and high temperature found that the crystallization in Nd₆₀Al₁₀Fe₂₀Co₁₀ bulk metallic glass is pressure promoted, and the T_x is decreased with the increase of applied pressure; the crystallization process is also changed under high pressure. The T_m increases with increasing pressure. The features are attributed to the slow atomic diffusion in the alloy and phase separation induced by high pressure.

The authors are grateful for the financial support of the National Natural Science Foundation of China (grant numbers 59925101 and 50031010) and the Japanese Sciences Promotion Society (JSPS) and the Chinesisch–Deutsches Zentrum Fuer Wissenschaftsfoerderung (grant number GZ032/7). The authors thank Spring8 in Japan for the financial support (2002B0242-ND2-np) and for use of the synchrotron radiation facilities.

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