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The structure and magnetic property for bulk Fe–Zr–Nd–Y–B alloys

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Abstract

The structure and magnetic property for bulk $Fe_{73-x}Zr_2Nd_xY_4B_{21}$ ($x = 0, 2, 5, 7$) alloys prepared by suction casting had been investigated. It was found that the bulk amorphous alloys of $Fe_{73}Zr_2Y_4B_{21}$ and $Fe_{68}Zr_2Y_4B_{21}Nd_5$ were obtained. It is noted that the as-cast $Fe_{68}Zr_2Nd_5Y_4B_{21}$ alloy presented soft magnetic behavior, while showed hard magnetic behavior after annealing at temperatures above the crystalline temperature. A bulk permanent magnet was obtained after annealing at 963 K for 30 min, which could provide one promising way for the bulk magnet produced by the simple process of copper mold casting and subsequent heat treatment.

Keywords: Amorphous materials; Permanent magnets; Microstructure

1. Introduction

Bulk metallic glasses (BMGs) have progressively attracted the interest of the scientific community as a promising new class of materials for engineering and technological applications. Among this, the preparation of hard magnetic amorphous alloys and the study of their magnetic properties have provided the greatest stimulus for research of permanent magnets. Such fully dense magnets have the advantage that can be cast in precise dimensions and potentially cheaper than conventionally manufactured magnet obtained by consolidation of alloy powders produced by melt spinning or mechanical alloying. A number of recent studies have demonstrated that Nd (Pr)–(Fe,Co)–Al bulk amorphous alloys can be produced in the as-cast state exhibiting hard magnetic properties at room temperature [1–5]. However, the low remanence, low maximum energy product at room temperature and high cost resulting from more than 50 at.% of rare earth (RE) elements, limit its applications.

In 2000, on the basis of investigations for $Nd_4Fe_{78}B_{18}$ alloy [6] and having adjusted the composition, Zhang and Inoue reported that the $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ glassy alloy in a rod form with a diameter of 0.5 mm could be produced by copper mold casting [7]. From his work, fully dense hard magnet having nanocomposite structure can be derived by suitable annealing. Some other researches on the preparation, thermal and magnetic properties of bulk Fe–Co–RE–B (RE = Nd, Pr, Dy) magnets have been done in Refs. [8–12]. However, bulk amorphous alloys with more size could not be obtained due to limited glass-forming ability (GFA).

In recent years, Fe-based BMGs with Y element have received great attentions due to high GFA and unique physical mechanical properties [13–16]. Li et al. [15] reported that the ternary Fe–Y–B alloy system has wide glass forming region and a fully amorphous rod with diameter of 1 mm for Fe–Y–B alloy could be obtained prepared by low pressure casting. Lin et al. [16] also found that bulk amorphous $Fe_{100-x-y}M_xB_y$ (M = Sc, Y, Dy, Ho, Er) ($x = 3$–10 at.%, $y = 18$–27 at.%) alloys with 1–2 mm in rod diameter existing excellent soft magnetic properties could be prepared by injection casting into a copper mold. It has been reported that Zr element could enhance the GFA for BMGs [17–19]. In this paper, the structure and magnetic property for bulk Fe–Zr–Nd–Y–B alloys are investigated. Nd was selected as candidate element for the Fe–Zr–Y–B system because it satisfies the empirical rules for the achievement of Fe-based BMGs with high GFA [20,21]. That is, in the Fe–Zr–Y–B system, the addition of Nd element causes the more change in atomic size in the order of $Nd > Y > Zr > Fe \gg B$, as well as the generation of atomic pairs with relatively large negative heats of mixing. Furthermore, by adding Nd to the Fe–Zr–Y–B system, $Nd_2Fe_{14}B$ phase might be formed and expected to improve magnetic prop-

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erties. The present study focused especially on the achievement of a new bulk glassy system with high GFA and good ferromagnetic magnetic property.

2. Experimental procedure

The $Fe_{73-x}Zr_2Nd_xY_4B_{21}$ ($x = 0, 2, 5, 7$) ingots were prepared by arc melting the mixture of pure metals Fe, Zr, Nd, Y, and Fe–B alloy in an argon atmosphere. Bulk sheet specimens (0.8 mm × 10 mm × 50 mm) were prepared by suction casting of the molten alloy into a copper mold under argon atmosphere. The annealing processes were performed in vacuum furnace with 2×10^{-3} Pa at temperatures ranging from 913 to 1033 K for 30 min. Structural investigations were monitored by X-ray diffraction (XRD) using Cu Kα radiation. The thermal stability was measured using differential thermal analysis (DTA) under argon atmosphere at a heating rate of 0.33 K/s. Magnetic measurements were performed with a vibrating sample magnetometer (VSM) using a maximum applied field of 1.8 T.

3. Results and discussion

The hysteresis loops for as-cast $Fe_{73-x}Zr_2Nd_xY_4B_{21}$ ($x = 0$, 2, 5, 7) alloys are shown in Fig. 1. When $x \leq 5$ at.%, the as-cast samples present the obvious soft magnetic behavior. When $x = 7$ at.%, that is for the $Fe_{66}Zr_2Nd_7Y_4B_{21}$ alloy, the sample exhibit hard magnetic behavior. However, the saturation magnetization (M_s) decreased drastically.

Fig. 2 shows the XRD patterns for as-cast $Fe_{73-x}Zr_2Nd_xY_4B_{21}$ ($x = 0$, 2, 5, 7) alloys. It can be seen that only main halo for the $Fe_{73}Zr_2Y_4B_{21}$ ($x = 0$) alloy is observed, indicating the alloy contains amorphous phase. For the sample of $Fe_{71}Zr_2Nd_2Y_4B_{21}$ ($x = 2$), besides unknown phase, α-Fe phase is present together with the amorphous phase. For the alloy with 5 at.% Nd, that is the $Fe_{68}Zr_2Nd_5Y_4B_{21}$ alloy, a broad scattering peak is exhibited suggesting that the alloy consists of mainly amorphous structure. However, with the further increase of Nd addition up to 7 at.%, more formation of crystalline phases corresponding to α-Fe, $Nd_2Fe_{14}B$ and $NdFe_4B_4$ phases, which deteriorate the GFA. The existence of the $Nd_2Fe_{14}B$ phase is the main reason for exhibiting hard magnetic behavior for the $Fe_{66}Zr_2Nd_7Y_4B_{21}$ alloy (see Fig. 1).

Based on XRD results, we choose the $Fe_{68}Zr_2Nd_5Y_4B_{21}$ alloy to study in detail. For comparison, the as-cast $Fe_{73}Zr_2Y_4B_{21}$ sample is also included. Fig. 3 illustrates the DTA scans for both alloys recorded at a heating rate of 0.33 K/s. It can be seen that the exothermal peak related to crystallization is clearly found in both DTA curves, indicating that these samples are composed of amorphous phase, which is in agreement with the results of XRD. Three exothermic reactions are observed for the $Fe_{73}Zr_2Y_4B_{21}$ alloy, while only one exothermic peak for the $Fe_{68}Zr_2Nd_5Y_4B_{21}$ alloy. It is suggested that the formal alloy exists three-step crystallization processes and the latter alloy has only one stage crystallization process. The first crystallization temperature T_x (marked with arrows) are 903 K for the $Fe_{73}Zr_2Y_4B_{21}$ alloy and 951 K for the $Fe_{68}Zr_2Nd_5Y_4B_{21}$ alloy, respectively.

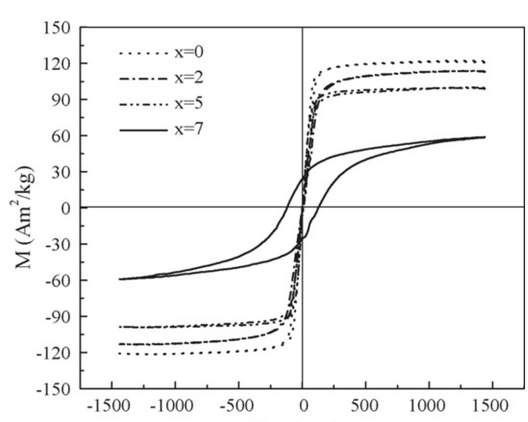

Fig. 1. Hysteresis loops for as-cast bulk $Fe_{73-x}Zr_2Nd_xY_4B_{21}$ ($x = 0, 2, 5, 7$) alloys.

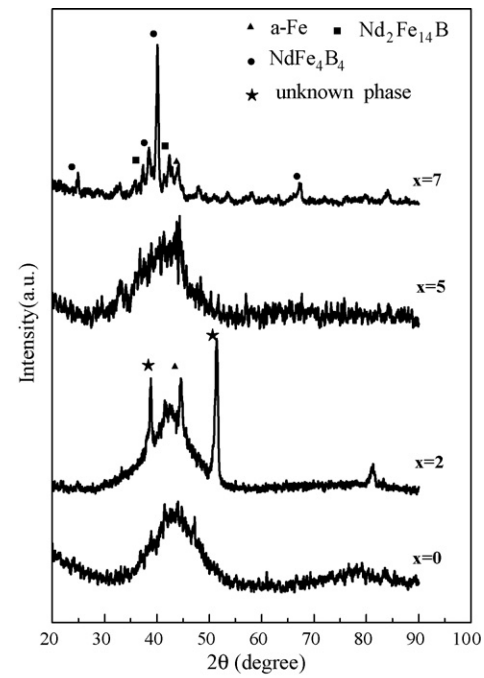

Fig. 2. X-ray diffraction patterns for as-cast $Fe_{73-x}Zr_2Nd_xY_4B_{21}$ ($x = 0, 2, 5, 7$) alloys.

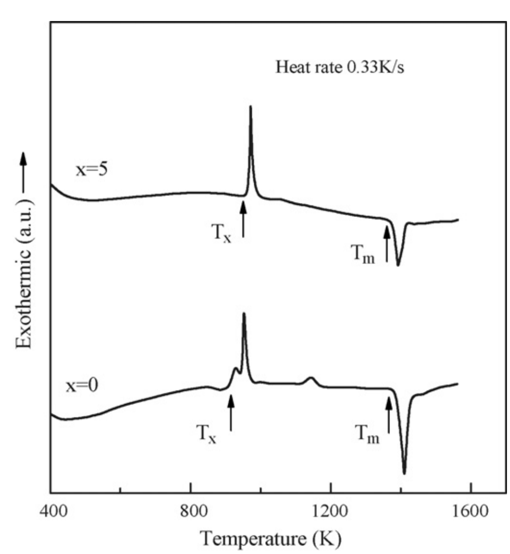

Fig. 3. DTA curves for as-cast $Fe_{73-x}Zr_2Nd_xY_4B_{21}$ ($x = 0, 5$) alloys.

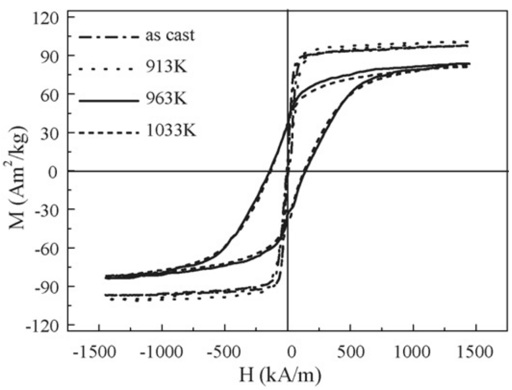

Fig. 4. Hysteresis loops for the $Fe_{68}Zr_2Nd_5Y_4B_{21}$ alloy annealed at different temperatures for 30 min.

Fig. 4 exhibits the hysteresis loops for as-cast and $Fe_{68}Zr_2Nd_5Y_4B_{21}$ alloy annealed at different temperatures for 30 min. The as-cast alloy and sample annealed below 913 K show soft magnetic property. When it is annealed at temperatures above its crystallization temperature, the magnetic behavior is changed from soft magnetic to hard magnetic behavior. The coercivity increases substantially, gets high values at the annealing temperature at 963 K, and then decreases slightly with further increasing annealing temperature. The obtaining maximum values of M_s, M_r, ${}_iH_c$ and $(BH)_{max}$ for the $Fe_{68}Zr_2Nd_5Y_4B_{21}$ alloy annealed at 963 K is 83.59A m^2/kg, 33.94A m^2/kg, 143kA/m and 10 kJ/m^3, respectively.

The XRD patterns for the $Fe_{68}Zr_2Nd_5Y_4B_{21}$ alloy annealed at different temperature for 30 min are shown in Fig. 5. For comparison, the XRD pattern of as-cast sample is also included. It can be seen that the $Fe_{68}Zr_2Nd_5Y_4B_{21}$ alloy is mainly consisted of amorphous phase annealing below 913 K. When annealed at 963 K, α-Fe, $Nd_2Fe_{14}B$, Fe_3B, B_3Fe_3Nd and $NdFe_4B_4$ phases are observed. One can know that B_3Fe_3Nd and $NdFe_4B_4$ phases are non-ferromagnetic phases. The α-Fe and Fe_3B phases are soft magnetic phases, while $Nd_2Fe_{14}B$ phase is hard magnetic phase. From Fig. 4, it is worthy of note that the smooth hysteresis loop without any steps is obtained, which is typical of the exchange spring magnet. It is indicated that the hard magnetic properties are due to the exchange magnetic interaction between soft and hard phases. That is, a nanocomposite permanent magnet could be obtained by the simple process of copper mold casting and subsequent heat treatment. With further increasing of annealing temperature, the same crystalline phases are observed. However, the relative intensities of α-Fe, $Nd_2Fe_{14}B$, Fe_3B, B_3Fe_3Nd and $NdFe_4B_4$ phases changed slightly, implying that the volume fractions of the crystalline phases were changed slightly with increasing temperature.

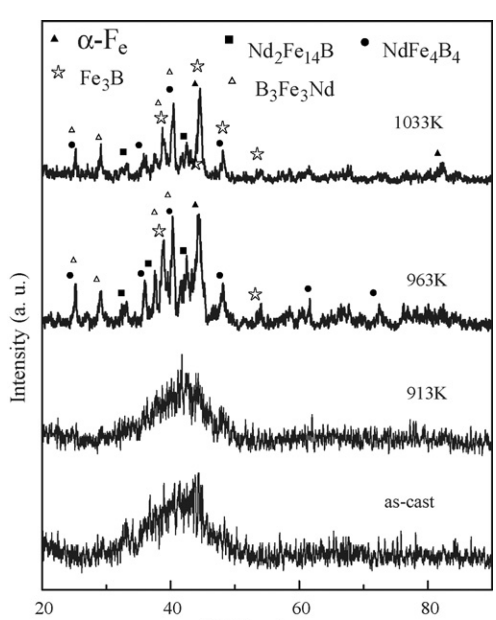

Fig. 5. XRD patterns for the $Fe_{73}Zr_2Nd_5Y_4B_{21}$ alloy annealed at different temperatures for 30 min.

It is worthy of point that the hard magnetic properties is exhibited even in the coexistent state with $NdFe_4B_4$ and B_3Fe_3Nd phases for the $Fe_{68}Zr_2Nd_5Y_4B_{21}$ alloy annealed at 963 K. However, the non-ferromagnetic $NdFe_4B_4$ and B_3Fe_3Nd phases may weaken the exchange magnetic interaction between soft and hard phases, resulting in deteriorating the hard magnetic property for the $Fe_{68}Zr_2Nd_5Y_4B_{21}$ alloy. Hence, it can be concluded that the magnetic property of $Fe_{68}Zr_2Nd_5Y_4B_{21}$ alloy could be further improved if the minor addition is proper chosen and controlled. Further studies of influence of annealing treatment and minor addition on the magnetic properties will be investigated.

4. Conclusions

In the present study, the bulk amorphous alloys of $Fe_{73}Zr_2Y_4B_{21}$ and $Fe_{68}Zr_2Y_4B_{21}Nd_5$ were obtained. Especially, the as-cast $Fe_{68}Zr_2Nd_5Y_4B_{21}$ alloy presented soft magnetic behavior, while showed the hard magnetic behavior after annealing at temperatures above the crystalline temperature. A bulk permanent magnet was obtained after annealing at 963 K for 30 min, which could provide one promising way for the bulk magnet produced by the simple process of copper mold casting and subsequent heat treatment.

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References

[1] A. Inoue, Mater. Sci. Eng. A 226–228 (1997) 357.
[2] X.Z. Wang, Y. Li, J. Ding, L. Si, H.Z. Kong, J. Alloy Comp. 290 (1999) 209.
[3] Y. Li, J. Ding, S.C. NG, X.Z. Wang, J. Magn. Magn. Mater. 187 (1998) L273.
[4] G.J. Fan, J. Eckert, W. Loser, S. Roth, L. Schultz, Mater. Sci. Forum 343–346 (2000) 97.
[5] G.J. Fan, W. Loser, S. Roth, J. Eckert, L. Schultz, J. Mater. Res. 15 (2000) 1556.
[6] R. Coehoorn, D.B. De Mooij, C. De Waard, J. Magn. Magn. Mater. 80 (1989) 101.
[7] W. Zhang, A. Inoue, Appl. Phys. Lett. 80 (2002) 1610.

[8] P. Pawlik, H.A. Davies, W. Kaszuwara, J.J. Wyslochi, J. Magn. Magn. Mater. 290-291 (2005) 1243.
[9] M. Marinescu, H. Chiriac, M. Grigoras, J. Magn. Magn. Mater. 290-291 (2005) 1267.
[10] P. Pawlik, H.A. Davies, Scripta. Mater. 49 (2003) 755.
[11] Y. Long, W. Zhang, X. Wang, Akihisa Inoue, J. Appl. Phys. 91 (2002) 5227.
[12] P. Pawlik, H.A. Davies, M.R.J. Gibbs, Appl. Phys. Lett. 83 (2003) 2775.
[13] V. Ponnambalam, S.J. Poon, D.J. Shiflet, J. Mater. Res. 19 (2004) 1320.
[14] Z.P. Lu, C.T. Liu, J.R. Thompson, W.T. Porter, Phys. Rev. Lett. 92 (2004) 245503.
[15] J. Zhang, H. Tan, Y.P. Feng, Y. Li, Scr. Mater. 53 (2005) 183–187.
[16] C.Y. Lin, H.Y. Tien, T.S. Chin, Appl. Phys. Lett. 86 (2005) 162501.
[17] J.M. Park, J.S. Park, D.H. Kim, J.-H. Kim, E. Fleury, J. Mater. Res. 21 (2006) 1019.
[18] H. Choi-Yim, R. Busch, W.L. Johnson, J. Appl. Phys. 83 (1998) 7993.
[19] T. Itoi, A. Inoue, Mater. Trans. JIM 41 (2000) 1256.
[20] A. Inoue, Mater. Sci. Eng. A 226 (1997) 357.
[21] T.D. Shen, R.B. Schwarz, Appl. Phys. Lett. 75 (1999) 5.