Bulk nanocomposite permanent magnets produced by crystallization of (Fe,Co)–(Nd,Dy)–B bulk glassy alloy

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The glass-forming ability, thermal stability, and magnetic properties have been investigated for an $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ glassy alloy with a large supercooled liquid of 48 K before crystallization prepared by copper mold casting. The glassy phase is formed in a rod form with a diameter of 0.5 mm. The crystallized nanocomposite structure consists of Fe_3B, α-Fe, and $Nd_2Fe_{14}B$ phases, and the remanence (B_r), coercivity $({}_iH_c)$ and maximum energy product $(BH)_{\max}$ are 1.19 T, 244 kA/m, and 92.7 kJ/m^3, respectively, for the rod of 0.5 mm in diameter annealed at 913 K for 600 s. [DOI: 10.1063/1.1456259]

In the $Nd_2Fe_{14}B$-type nanocomposite permanent magnets, two types of composites, $Nd_2Fe_{14}B/Fe_3B$ and $Nd_2Fe_{14}B/\alpha$-Fe have been widely studied.[1–4] These composite materials consist of exchange-coupled nanoscale hard and soft magnetic phases. The methods for preparing the permanent magnet materials include melt spinning or mechanical alloying. Generally, the melt-spun sheets consisting mainly of an amorphous phase are crystallized to obtain optimal hard magnetic properties. However, the ordinary Fe–Nd–B alloys do not have a sufficiently high glass-forming ability (GFA) which is enough to obtain nanocomposite permanent magnets in a bulk form. If a similar nanocomposite structure is obtained in a crystallized state of glassy alloys with high GFA, a nanocomposite permanent magnet in a bulk form is expected to be synthesized by the process of the formation of a bulk glassy alloy followed by crystallization.

Glassy alloys with a large supercooled liquid region $\Delta T_x(=T_x-T_g)$ defined by the difference between glass transition temperature (T_g) and crystallization temperature (T_x) and/or high reduced glass transition temperature T_g/T_1 (T_1: liquidus temperature) have a high resistance against crystallization leading to high GFA.[5,6] More recently, we have searched for a glassy alloy in a B-rich (Fe, Co)–Nd(Pr)–B system where a large ΔT_x and high T_g/T_1 are obtained.[7,8] The B-rich Fe–Re–B amorphous alloys have some advantage points as compared with the rare earth (RE) rich Fe-RE-B amorphous alloys.[1,7–11] These include (1) lower RE contents, (2) the appearance of glass transition and supercooled liquid region prior to crystallization, (3) lower melting points, and (4) higher glass-forming ability. Good hard magnetic properties magnet in a bulk form are expected to be obtained after heat treatment for such glassy alloys, when a nanocomposite structure consisting of hard magnetic $Nd_2Fe_{14}B$ and soft magnetic Fe_3B and α-Fe phases is obtained.[9,10] This letter intends to present the GFA, thermal stability of the supercooled liquid, crystallized structure and magnetic properties of a glassy $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ alloy prepared by copper mold casting.

The alloy ingot was prepared by arc melting the mixture of pure metals and boron in an argon atmosphere. The ingot was crushed into small pieces to accommodate the size of a quartz crucible for copper mold casting. The nozzle of the crucible is about 0.5 mm in diameter. Bulk rod samples with a length of about 12 mm and different diameters of 0.5 to 1.0 mm were produced by injection casting of the molten alloy into copper molds in an argon atmosphere. The injection pressure was about 200 kPa higher relative to the chamber pressure. These rods were sealed in a quartz tube with an evacuated state of 4×10^{-3} Pa and then isothermally annealed at 913 K for 600 s. The structure of the rod samples was examined by x-ray diffraction (Cu K_α) using their powder obtained by crushing the rod samples. The microstructure of samples was examined by transmission electron microscopy (TEM). The thermal stability was investigated under an Ar atmosphere at a heating rate of 0.67 K/s by differential scanning calorimetry (DSC). Magnetic properties were measured by a vibrating sample magnetometer (VSM) with a maximum applied magnetic field of 1274 kA/m. The density of the cast $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ alloy rod was determined as 7.60 Mg/m^3 by the Archimedean method using toluene.

Figure 1 shows an outer surface appearance of the bulk $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ alloy rod with a diameter of 0.5 mm prepared by copper mold casting. The Bright-field transmission electron micrograph and selected-area electron diffraction pattern from center of the rod sample are shown in Fig. 2(a). The x-ray diffraction pattern of the cast $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ alloy rod with a diameter of 0.5 mm is shown in Fig. 2(b). The bright-field TEM reveals only a featureless contrast and no appreciable contrast corresponding to a crystalline phase is seen. The electron and x-ray diffraction patterns consist only of halo rings and a broad peak, respectively. These results indicate that a single glassy phase was formed. The further increase in the rods diameter to 1.0 mm causes the formation of crystalline phases. It is therefore concluded that the critical rod diameter for

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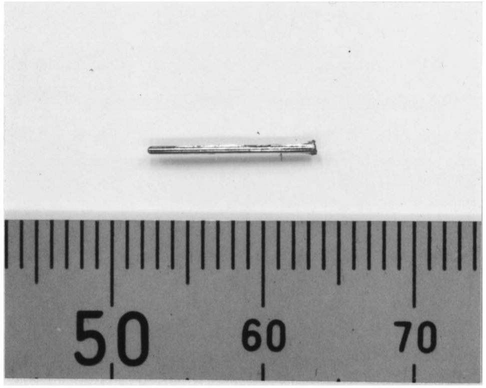

FIG. 1. Outer shape and surface appearance of a cast $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ rod with a diameter of 0.5 mm.

the formation of the glassy phase lies between 0.5 and 1.0 mm. Figure 3 shows DSC curve of a glassy $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ alloy rod with a diameter of 0.5 mm, together with that of the melt-spun glassy ribbon. The Curie temperature (T_C), T_g, T_x, ΔT_x and heat of crystallization (ΔH_c) were 673 K, 814 K, 862 K, 48 K, and 4.27 kJ/mol, respectively, for the rod sample and 676 K, 816 K, 865, 49 K and 4.42 kJ/mol, respectively, for the ribbon sample. No appreciable difference in T_C, T_g, T_x, ΔT_x, and ΔH_x are seen between these samples, being consistent with the result obtained by x-ray diffraction and TEM.

It has been reported that conventional $Fe_{77}Nd_{4.5}B_{18.5}$ and $Fe_{86}Nd_8B_6$ amorphous alloys are formed in the maximum sheet thickness (t_{max}) range below about 60 and 30 μm, respectively, by the melt spinning technique.[2,12–14] Consequently, it is said that the $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ alloy has a higher GFA which largely exceeds those of the $Fe_{77}Nd_{4.5}B_{18.5}$ and $Fe_{86}Nd_8B_6$ alloys. The higher GFA for the present Fe-based alloy is concluded to originated from the higher thermal stability of the supercooled liquid against crystallization. The reason for the larger ΔT_x for the (Fe,Co)–(Nd,Dy)–B glassy alloy is discussed in the framework of the three empirical rules[5,6] for the achievement of high GFA. The three empirical rules are (1) multicomponent consisting of more than three elements, (2) significant atomic size mismatches above 12%, and (3) suitable negative heats of mixing. The base composition in the present alloys is an Fe–Nd–B system which satisfies the three empirical rules. The addition of Co and Dy elements is effective for an increase in the degree of the satisfaction of the empirical rules. That is, the addition of these elements causes the more sequential change in atomic size in the order of Nd$>$Dy$\gg$Fe$>$Co$\gg$B, as well as the generation of atomic pairs with relatively large negative heats of mixing. In the supercooled liquid in which the three empirical rules are satisfied at a high level, the topological and chemical short-range orderings are enhanced, leading to the formation of a highly dense random packed structure with higher thermal stability of the supercooled liquid against crystallization.

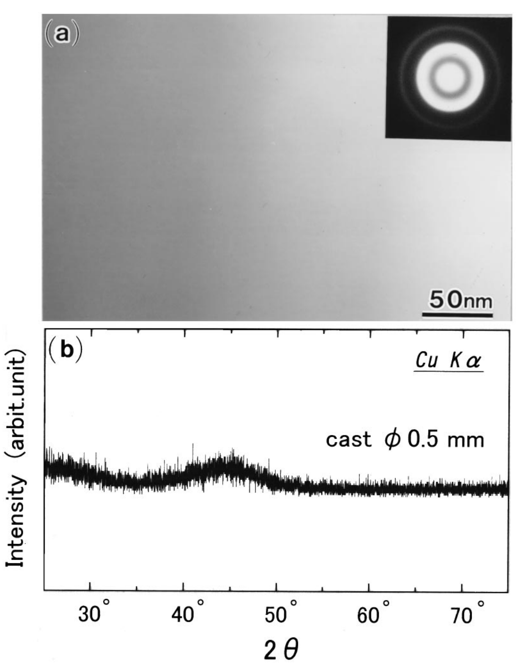

FIG. 2. Bright-field TEM and selected-area electron diffraction pattern (a) and x-ray diffraction pattern (b) of a cast $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ alloy rod with a diameter of 0.5 mm.

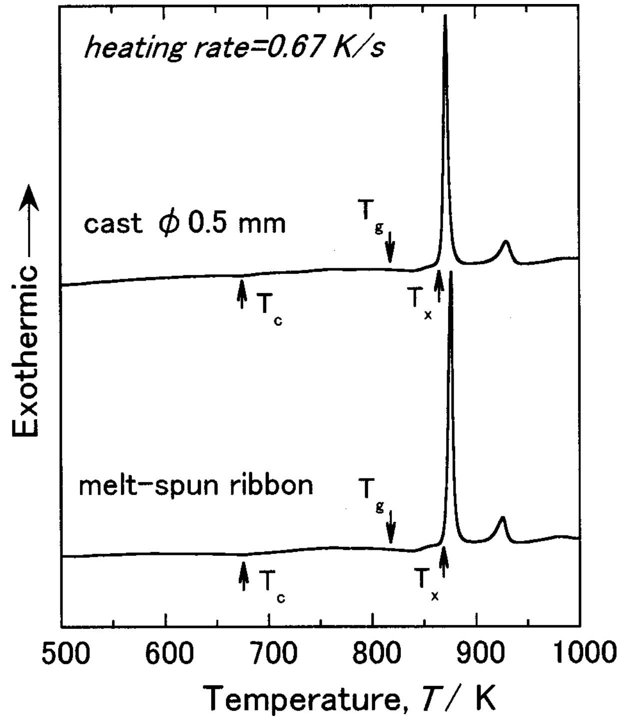

FIG. 3. DSC curves of a cast $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ glassy rod with diameter of 0.5 mm. The data of the melt-spun glassy ribbon are also shown for comparison.

The hysteresis B–H loop of the as-cast glassy $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ rod with a diameter of 0.5 mm is shown in Fig. 4(a). The soft magnetic feature is recognized for the rod sample, and no distinct difference in the hysteresis loops is observed between the bulk sample and the melt-spun ribbon. A hysteresis loop of the cast $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ glassy rod annealed for 600 s at 913 K is shown in Fig. 4(b). The loop is exhibiting the achievement of good hard magnetic properties. The remanence (B_r), reduced remanence (M_r/M_s), coercivity (iH_c), and maximum energy product $(BH)_{max}$ are 1.19 T, 0.82, 244 kA/m, and 92.7 kJ/m^3, respectively. This material is magnetically isotropic. The x-ray diffraction patterns of the cast glassy $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ rod with a diameter of 0.5 mm an-

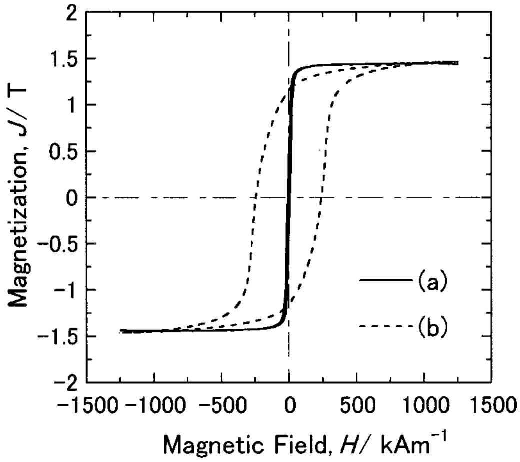

FIG. 4. Hysteresis loops of the cast $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ glassy rod with a diameter of 0.5 mm. (a) cast state and (b) annealed state for 600 s at 913 K.

nealed for 600 s at 913 K are shown in Fig. 5. The diffraction pattern is identified as Fe_3B, α-Fe, and $Nd_2Fe_{14}B$ phases for the sample, but the width of their diffraction peaks is relatively broad, indicating that the annealed sample material consist of nanometer-sized crystallites. No distinct difference in the diffraction patterns is observed between the glassy rod and the melt-spun ribbons in the annealed state.[9,10] In addition, although the alloy consists of three magnetic components, the smooth hysteresis loop typical of a single component system is seen accompanying high remanence value [Fig. 4(b)]. The high reduced remanence ($M_r/M_s > 0.8$) and reversible demagnetization curves in the isotropic alloy indicates the behavior of the exchange-coupled type magnets.[15]

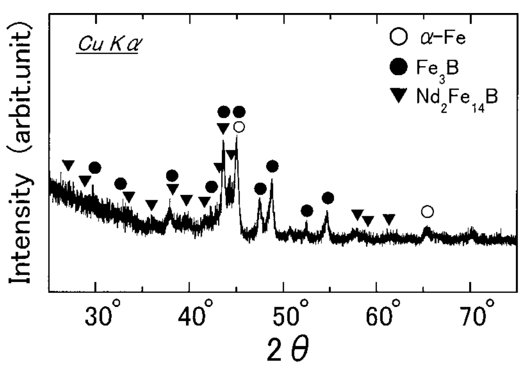

FIG. 5. X-ray diffraction patterns of the cast $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ glassy rod with a diameter of 0.5 mm annealed for 600 s at 913 K.

In conclusion, the bulk glassy $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B_{20}$ alloy was produced in the diameter range up to 0.5 mm by copper mold casting. The $Nd_2Fe_{14}B$/(Fe_3B and α-Fe) nanocomposite structure was obtained by crystallization of the bulk glassy alloy. The B_r, iH_c, and $(BH)_{max}$ are 1.19 T, 244 kA/m, and 92.7 kJ/m^3, respectively, for the rod alloy annealed at 913 K for 600 s. The bulk $Nd_2Fe_{14}B$/(Fe_3B and α-Fe) nanocomposite permanent magnet in the rod form of 0.5 mm in diameter is promising for the bulk magnet produced by the simple process of copper mold casting and then heat treatment.

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