Glass-Forming Ability, Crystallized Structure and Magnetic Properties of Fe$_{67}$Co$_{9.5}$Nd$_3$Dy$_{0.5}$B$_{20}$ Glassy Alloy with Large Supercooled Liquid Region

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The glass-forming ability, thermal stability and magnetic properties have been investigated for a Fe$_{67}$Co$_{9.5}$Nd$_3$Dy$_{0.5}$B$_{20}$ glassy alloy with a large supercooled liquid region of 48 K prepared by the melt-spinning technique. The glassy phase is formed in the wide sheet thickness range from 20 to 250 µm. The glass transition temperature ($T_g$), crystallization temperature ($T_x$), supercooled liquid region ($\Delta T_x = T_x - T_g$) and heat of crystallization ($\Delta H_c$) remain almost unchanged in the thickness range below 250 µm, and then the $\Delta H_c$ gradually decreases with further increasing sheet thickness. The crystallized nanocomposite structure consists of Fe$_3$B, α-Fe, Nd$_2$Fe$_{14}$B and remaining glassy phase, and their average grain sizes are about 25 nm annealed at 903 K for 420 s. The remanence ($B_r$), coercivity ($H_c$), and maximum energy product ($BH_{\text{max}}$) are 1.26 T, 235 kA/m, and 104 kJ/m$^3$, respectively, for the sheet of 250 µm in thickness annealed at 903 K for 420 s. The hard magnetic properties remain almost unchanged in the thickness range below 250 µm, and decrease gradually in the sheets with thicknesses above 250 µm.

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1. Introduction

In the Nd$_2$Fe$_{14}$B-type nanocomposite permanent magnets, two type of composites, Nd$_2$Fe$_{14}$B/Fe$_3$B and Nd$_2$Fe$_{14}$B/α-Fe have been widely studied. 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 including an amorphous phase are crystallized to obtain optimal hard magnetic properties. However, the ordinary Fe–Nd–B alloys do not have a sufficiently large glass-forming ability (GFA) which is enough to obtain nanocomposite permanent magnets in the melt-spun sheet with large thickness. The nanocomposite magnets have been prepared directly without subsequent heat treatment after melt spinning with controlled roll surface velocity. However, the structure of the resulting thick sheet is not homogeneous and the magnetic properties have significant scattering. If a finer nanocomposite structure is obtained in the crystallized state of the glassy alloys with large GFA, a nanocomposite permanent magnet in a bulk or a thick sheet form is expected to be synthesized by the process of the formation of the glassy alloy followed by crystallizing treatment.

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 $T_g/T_1$ ($T_1$: liquid point) have a high resistance against crystallization leading to high GFA. In addition, the large deformation and easy working due to its low viscosity and ideal Newtonian flow have been reported to be obtained in the supercooled liquid region. More recently, we have searched for a new glassy alloy in (Fe, Co)–(Nd, Dy)–B system where a large $\Delta T_x$ exceeding 45 K and high $T_g/T_1$ above 0.57 are obtained.

The appearance of large $\Delta T_x$ and high $T_g/T_1$ indicates the possibility that the high GFA is obtained for the alloy system. And furthermore, good hard magnetic properties are obtained after an optimum heat treatment. This may be regarded as a new type nanocomposite permanent magnet consisting of exchange-coupled hard Nd$_2$Fe$_{14}$B and soft Fe$_3$B, α-Fe and remaining amorphous phases. This paper intends to present the glass-forming ability, thermal stability of the supercooled liquid, nanocrystallized structure and magnetic properties of the glassy Fe$_{67}$Co$_{9.5}$Nd$_3$Dy$_{0.5}$B$_{20}$ alloy prepared by the melt-spinning technique.

2. Experimental Procedure

The alloy ingots were prepared by arc melting the mixtures of pure metals and boron in an argon atmosphere. Ingots were crushed into small pieces to accommodate the size of a quartz crucible for melt spinning. The crucible was about 0.7 mm in diameter. Sheet samples were prepared by using a single-roll melt spinning equipment with copper wheel in an argon atmosphere. The injection pressure was kept to be a value of 30 kPa relative to the chamber pressure. The circumferential velocity ($V_c$) of the wheel was changed in a range from 1.5 to 40 m/s. These sheets were sealed in a quartz tube of an evacuated state of $4 \times 10^{-3}$ Pa and then isothermally annealed at 903 K for 420 s. The structure of the sheets was examined by X-ray diffraction (CuKα) and the thermal stability was investigated under an Ar atmosphere at a heating rate of 0.67 K/s by differential scanning calorimetry (DSC). The microstructure was examined by a transmission electron microscopy (TEM) JEM-3000F, operated at 200 kV. The diameter of electron beam was focused to 0.5 and 2.4 nm in the nano-beam diffraction. Magnetic properties were measured by a vibrating sample magnetometer (VSM) with a maximum applied magnetic field of 1274 kA/m. The density of the sheet...
was determined as 7.58 Mg/m$^3$ for Fe$_{67}$Co$_{28.5}$Nd$_3$Dy$_{0.5}$B$_{20}$ glassy alloy by the Archimedean method with toluene.

3. Results and Discussion

3.1 Glass-forming ability and thermal stability

Figure 1 shows X-ray diffraction patterns taken from the freely solidified surface of the melt-spun Fe$_{67}$Co$_{28.5}$Nd$_3$Dy$_{0.5}$B$_{20}$ sheets with thicknesses ranging from 20 to 340 $\mu$m prepared by changing the surface velocity ($V_s$) of the roll in the range of 1.5 to 40 m/s. The sheet samples with thickness below about 250 $\mu$m show a broad halo peak and no distinct crystalline peak is observed. However, the further increase in the sheet thickness over about 250 $\mu$m causes the formation of crystalline phases. Therefore, it is concluded that the critical sheet thickness for formation of glassy phase lies around 250 $\mu$m.

Figure 2 shows DSC curves of the melt-spun Fe$_{67}$Co$_{28.5}$Nd$_3$Dy$_{0.5}$B$_{20}$ sheets with thicknesses ranging from 80 to 340 $\mu$m. As marked with glass transition temperature ($T_g$) and crystallization temperature ($T_x$), it is noticed that the glass transition and supercooled liquid region ($\Delta T_x = T_x - T_g$) are observed in the sheets with a thickness range below 290 $\mu$m, and the two stage exothermic peak behavior is seen in thickness range up to 340 $\mu$m, indicating that the glassy phase still exists in the sheet sample with a thickness of 340 $\mu$m. Based on the DSC curves, the $T_g$, $T_x$, $\Delta T_x$ and heat of crystallization ($\Delta H_x$) are plotted as a function of sheet thickness in Fig. 3. The $T_g$, $T_x$, and $\Delta T_x$ remain almost constant in the sheet sample with a thickness range below about 290 $\mu$m. On the other hand, the $\Delta H_x$ keeps a constant value in the thickness range up to about 250 $\mu$m, and then gradually decreases with increasing sample thickness in the range above 250 $\mu$m. It is interpreted that a glassy phase is formed in the sheet with a thickness range below 250 $\mu$m, and the volume fraction of glassy phase in the sheet samples gradually decreases above 250 $\mu$m, being consistent with that obtained by X-ray diffraction.

It has been reported that conventional Fe$_{77}$Nd$_{4.5}$B$_{18.5}$ and
Fe$_{86}$Nd$_8$B$_6$ amorphous alloys are formed in the maximum sheet thickness ($t_{\text{max}}$) range below about 60 and 30 μm, respectively, by the melt spinning technique. Consequently, it is said that the Fe$_{57}$Co$_{43}$Nd$_3$Dy$_{0.5}$B$_{30}$ alloy has a large glass-forming ability and exceeds largely those of the Fe$_{77}$Nd$_{14}$B$_{18.5}$ and Fe$_{86}$Nd$_8$B$_6$ alloys. The larger GFA for the present Fe-based alloy is concluded to originate from the high thermal stability of the supercooled liquid against crystallization. The reason for the larger $\Delta T_c$ and $t_{\text{max}}$ for the (Fe, Co)-(Nd, Dy)-B glassy alloy is discussed in the framework of the three empirical rules$^{4,5}$ for the achievement of large GFA. 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 >> Fe > Co >> B, as well as the generation of new 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.

3.2 Nanocrystallized structure and magnetic properties

The hysteresis loops of the melt-spun Fe$_{57}$Co$_{43}$Nd$_3$Dy$_{0.5}$B$_{30}$ sheets are shown in Fig. 4(a). The soft magnetic behaviors are recognized in the sheets with thicknesses ranging from 20 to 250 μm. The thicker sheets show very low coercivity and do not indicate hard magnetic behavior. It is known that the melt-spun Fe$_{86}$Nd$_8$B$_6$ and Fe$_{77}$Nd$_{14}$B$_{18.5}$ ribbons show good hard magnetic properties in the as-spun state,$^2,5$ namely the Nd$_2$Fe$_{14}$B/α-Fe and Nd$_2$Fe$_{14}$B/Fe$_3$B nanocomposite permanent magnets are obtained by the melt-spinning technique with an optimal roll speeds. In contrast, the melt-spun Fe$_{57}$Co$_{43}$Nd$_3$Dy$_{0.5}$B$_{30}$ sheets do not exhibit good hard magnetic properties. This is because the Fe$_{57}$Co$_{43}$Nd$_3$Dy$_{0.5}$B$_{30}$ alloy has large glass-forming ability and high resistance against crystallization, leading to the Nd$_2$Fe$_{14}$B(Fe$_3$B, α-Fe) nanocomposite structure which cannot be formed in the melt-spun state. Hysteresis loops of the melt-spun sheets annealed at 903 K for 420 s are shown in Fig. 4(b). The loops are similar to those for the sheets with thicknesses below 250 μm, exhibiting good hard magnetic properties. However, the remanence ($B_r$), coercivity ($H_c$) and hysteresis squareness decrease gradually for the sheets with thicknesses above 250 μm. Based on the Hysteresis loops, the $B_r$, $H_c$ and $(BH)_{\text{max}}$ of the melt-spun sheets are plotted as a function of sheet thickness in Fig. 5. The $B_r$, $H_c$ and $(BH)_{\text{max}}$ are nearly constant in the thickness range below 250 μm, and decreases gradually in the sheets with thickness range above about 250 μm. The $B_r$, $H_c$ and $(BH)_{\text{max}}$ are 1.36 T, 228 kA/m and 110 kJ/m$^3$, respectively, for the sheet of 20 μm in thickness, and 1.26 T, 235 kA/m and 104 kJ/m$^3$, respectively, for the sheet of 250 μm in thickness. These materials are magnetically isotropic. It is noticed that the changes in the magnetic properties and $\Delta H_c$ (Fig. 3) with sheet thickness are extremely analogous, indicating that the hard magnetic properties are dependent on the volume fraction of glassy phase in the melt-spun sheets. This is because the nanocomposite structure was obtained from the glassy phase in the melt-spun sheets by heat treatment.
The X-ray diffraction patterns of the melt-spun \( \text{Fe}_{67}\text{Co}_{23}\text{Nd}_{3}\text{Dy}_{0.5}\text{B}_{30} \) alloy sheets with thicknesses of 20 and 250\( \mu \)m annealed at 903 K for 420 s are shown in Fig. 6, and identified as \( \alpha\)-Fe, \( \alpha\)-Fe and \( \text{Nd}_2\text{Fe}_{14}\text{B} \) phases for both samples. Figure 7 shows bright-field TEM images and the selected-area electron diffraction pattern of the \( \text{Fe}_{67}\text{Co}_{23}\text{Nd}_{3}\text{Dy}_{0.5}\text{B}_{30} \) alloy sheets with thicknesses of 20 and 250\( \mu \)m annealed at 903 K for 420 s. From the TEM images, the nanocomposite structure was obtained in both samples and the average grain sizes are about 25 nm. However, the microstructure of the sheet with thickness of 20\( \mu \)m is more homogeneous. The selected-area electron diffraction patterns indicate that the microstructures are crystallographically isotropic. Moreover, the microstructures of the sheet with thickness of 20\( \mu \)m after optimal heat treatment were examined by high-resolution TEM. The TEM image and nanobeam electron diffraction pattern are shown in Fig. 8. The nanobeam diffraction pattern taken from the region A consists of a diffuse halo ring typical for a glassy phase. Consequently, the structure is concluded to consist of \( \text{Fe}_3\text{B} \), \( \alpha\)-Fe, \( \text{Nd}_2\text{Fe}_{14}\text{B} \) and remaining glassy phase. The grain size is measured to be about 20 nm for \( \text{Fe}_3\text{B} \), 10 nm for \( \text{Nd}_2\text{Fe}_{14}\text{B} \), 30 nm for \( \alpha\)-Fe and 5 nm for remaining glassy phase. The interparticle spacing is about 10 nm between \( \text{Fe}_3\text{B} \) and \( \text{Nd}_2\text{Fe}_{14}\text{B} \) phases and about 40 nm between two \( \text{Nd}_2\text{Fe}_{14}\text{B} \) phases. These interparticle spacings are short enough to enable the exchanging magnetic coupling interaction among these ferromagnetic phases.\(^{13,14}\) The good hard magnetic properties are interpreted to result from the exchange magnetic coupling in-

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**Fig. 6** XRD patterns of melt-spun \( \text{Fe}_{67}\text{Co}_{23}\text{Nd}_{3}\text{Dy}_{0.5}\text{B}_{30} \) glassy sheets with various thicknesses of 20 and 250\( \mu \)m annealed at 903 K for 420 s. (a) 20\( \mu \)m (b) 250\( \mu \)m.

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**Fig. 7** Bright-field transmission electron micrographs and selected-area electron diffraction patterns of melt-spun \( \text{Fe}_{67}\text{Co}_{23}\text{Nd}_{3}\text{Dy}_{0.5}\text{B}_{30} \) glassy sheets with thicknesses of 20 and 250\( \mu \)m annealed at 903 K for 420 s. (a) 20\( \mu \)m (b) 250\( \mu \)m.
Fig. 8 High-resolution TEM image and nanobeam electron diffraction pattern of the melt-spun Fe_{0.5}Co_{0.5}Nd_{2}Dy_{0.5}B_{20} glassy sheet with thickness of 20 μm annealed at 903 K for 420 s.

interaction among the four ferromagnetic phases of Nd_{2}Fe_{14}B, Fe_{2}B, α-Fe and remaining glass owing to their small interparticle spacings.

4. Conclusions

With the aim of producing a thick nanocomposite permanent magnet sheet in a new Fe-based (Fe,Co)–(Nd, Dy)–B system, we examined the glass-forming ability, thermal stability of the supercooled liquid, crystallized structure and magnetic properties for the melt-spun Fe_{0.5}Co_{0.5}Nd_{2}Dy_{0.5}B_{20} alloy sheets with different thickness. The results obtained are summarized as follows.

(1) The glassy alloys were formed in the wide sheet thickness range up to about 250 μm, and the further increase in the sheet thickness to above 250 μm causes the formation of the crystalline phases.

(2) The glass transition temperature (Tg), crystallization temperature (Tc) and supercooled liquid region (ΔTc = Tc − Tg) remain almost constant in the sheet sample with a thickness range below 290 μm. The Tg, Tc, and ΔTc of the glassy sheet with a thickness of 290 μm are 806 K, 853 K and 47 K respectively. The heat of crystallization (ΔHc) keeps a constant value in the thickness range up to about 250 μm, and then gradually decreases with further increasing sheet thickness.

(3) The crystallized structure consists of Nd_{2}Fe_{14}B, Fe_{2}B, α-Fe and remaining glassy phase, and their average grain sizes are about 25 nm for the Fe_{0.5}Co_{0.5}Nd_{2}Dy_{0.5}B_{20} glassy sheets annealed at 903 K for 420 s.

(4) The remanence (Br), coercivity (Hc) and maximum energy product (BH)max are 1.26 T, 235 kA/m and 104 kJ/m³, respectively, for the sample of 250 μm in thickness. The hard magnetic properties remain almost unchanged in the thickness range below 250 μm and decrease gradually in the sheets with thickness above 250 μm. The hard magnetic properties are dominated by the volume fraction of glassy phase in the melt-spun sheets.

REFERENCES