Formation and Magnetic Properties of Bulk Glassy Fe–Co–Nd–Dy–B Alloys with High Boron Concentrations

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New Fe-based glassy alloys in Fe–Co–Nd–Dy–B system with high boron concentrations were found to exhibit a wide supercooled liquid region exceeding 50 K. The high stability of the supercooled liquid enabled us to produce cylindrical bulk glassy alloys with diameters up to 0.75 mm by copper mold casting. The glass transition temperature (T_g), crystallization temperature (T_x), supercooled liquid region ΔT_x ($=T_x - T_g$) and heat of crystallization of the ϕ 0.75 mm rod of glassy Fe₆₂Co_{9.5}Nd₃Dy_{0.5}B₂₅ alloy are 844 K, 899 K, 55 K and 4.46 kJ/mol, respectively. No appreciable difference in the thermal stability is seen between the bulk rods and melt-spun ribbon. The saturation magnetization (I_s), coercive force (H_c), saturated magnetostriction (λ_s) and Curie temperature (T_c) of the melt-spun Fe₆₂Co_{9.5}Nd₃Dy_{0.5}B₂₅ ribbon are 1.37 T, 4.58 A/m, 17.9×10^{-6} and 663 K, respectively, and I_s and T_c are nearly the same as those for the bulk glass rods with diameters of 0.5 and 0.75 mm. The success of forming the Fe-based bulk glassy alloys exhibiting good soft magnetic properties is promising for future development as a new type of soft magnetic material.

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1. Introduction

Since the finding of the melt-spun amorphous ferromagnetic Fe–P–C alloy in 1967,¹⁾ Fe- and Co-based magnetic amorphous alloys attracted increasing interest. Subsequently, (Fe, Co)–P–B and (Fe, Co)–B–Si alloys were reported to exhibit good soft magnetic properties in 1974,^{2–4)} followed by (Fe, Co)–(Cr, Mo, W)–C,⁵⁾ (Fe, Co)–(Zr, Hf),^{6,7)} and then (Fe, Co)–(Zr, Hf, Nb)–B⁸⁾ alloys in early 1980s. Among these, the melt-spun (Fe, Co)–B–Si amorphous alloys have been used as practical soft magnetic materials in electronic transformers.⁹⁾ However, those amorphous alloys does not exhibit high glass-formation ability (GFA) and can be produced only at high cooling rates of over 10^5 K/s by melt spinning. As a result, the thickness of ribbons has been limited to less than 50 μ m. Thin amorphous ribbons are difficult to handle and thus the transformers cannot be built by the traditional methods used for conventional 0.3 mm thick crystalline Fe–Si laminas. In addition, thin ribbons causes a decrease in the core packing density since air gaps are left between large number of thin ribbons needed to build the core, and this decreases the efficiency of the transformer. Therefore, the advent of thicker glassy ferromagnetic ribbons would be of benefit. More recently, it has been reported that ferromagnetic Fe- and Co-based glassy alloys with a large supercooled liquid region over 50 K as well as a higher GFA in the Fe–(Al, Ga)–(P, C, B, Si),¹⁰⁾ Fe–(Co, Ni)–(Zr, Hf, Nb)–B¹¹⁾ and Co–Fe–(Zr, Ta, Nb)–B¹²⁾ systems exhibit good soft magnetic properties. The critical thickness of these glassy alloys reaches 2 mm for (Al, Ga)–(P, C, B, Si)¹³⁾ and Fe–(Co, Ni)–(Zr, Hf, Nb)–B,¹⁴⁾ and 1 mm for Co–Fe–(Zr, Ta, Nb)–B¹⁵⁾ systems by the copper mold casting method. However, relatively low Fe and Co concentrations in those alloys lead to a low saturation magnetization value less than

1.2 T. We have searched for a new glassy alloy in the (Fe, Co)–RE–B system with a B content of 20 at%, in which a supercooled liquid region and a high saturation magnetization and low coercive force are obtained.^{16,17)} The supercooled liquid region, ΔT_x , and reduced glass transition temperature, T_g/T_m , for the Fe-based glassy alloys reported up to date are about 40 K and 0.56, respectively.^{18,19)} In this paper, we examined effects of addition of B element on the thermal stability of the supercooled liquid, glass-formation ability and magnetic properties of the Fe_{87–x}Co_{9.5}Nd₃Dy_{0.5}B_x ($x \geq 20$ at%) glassy alloys, and report results of the formation behaviors and properties of a bulk glassy Fe₆₂Co_{9.5}Nd₃Dy_{0.5}B₂₅ alloy.

2. Experimental Procedure

Alloy ingots with different compositions of the Fe–Co–Nd–Dy–B system were prepared by arc melting the mixture of pure metals and B crystal in an argon atmosphere. The ingots were crushed into small pieces in order to place them into a quartz crucible for melt spinning. The nozzle size of the crucible is about 0.5 mm in diameter. Ribbons were produced with a wheel speed of 35 m/s in an argon atmosphere. Bulk samples of rod shape and plate form with different diameters and thicknesses were produced by injection casting of the molten alloy into copper molds. The structure of the samples was examined by X-ray diffraction (Cu K α), transmission electron microscopy (TEM) and optical microscopy (MO). Thermal stability was examined by differential scanning calorimetry (DSC) and differential thermal analysis (DTA) under an argon atmosphere at a heating rate of 0.67 and 0.033 K/s, respectively. The saturation magnetization was measured at room temperature by a vibrating sample magnetometer (VSM) with a maximum applied magnetic field of 670 kA/m. The coercive force was measured with a B–H loop tracer. The saturated magnetostriction was mea-

sured by a capacitance method in a maximum applied field of 240 kA/m.

3. Results and Discussion

The X-ray diffraction patterns indicated that the melt-spun ribbons in the composition range of 20 to 30 at%B were of a glassy single phase. Figure 1 shows the DSC curves of the $\text{Fe}_{87-x}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_x$ ($x = 20$ to 30 at%) glassy alloys. As marked with the 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 seen for those of the B concentration range of 20 to 30 at%. Based on the DSC curves, T_x , T_g and ΔT_x values are plotted as a function of the B content in Fig. 2. The T_g and T_x values increase from 801 to 888 K and 846 to 933 K, respectively, with increasing the B content from 20 to 30 at%. And the ΔT_x increases from 45 to 57 K with increasing the B content from 20 to 27.5 at% and then decreases to 45 K with further increasing the B content to 30 at%. The larger ΔT_x values of 56 and 57 K are obtained at 25 and 27.5 at%B, respectively. We further measured the melting point (T_m) by DTA. The reduced glass transition temperature (T_g/T_m) is determined to be 0.57–0.58 for the $\text{Fe}_{87-x}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_x$ ($x = 22.5$ to 30 at%) glassy alloys. The wide ΔT_x and higher T_g/T_m indicate the possibility that the high glass-forming ability is obtained for the alloys containing 25 to 27.5 at%B.^{18,19)}

Figure 3 shows the saturation magnetization (I_s), coercive force (H_c), saturated magnetostriction (λ_s) and Curie temperature (T_c) as a function of the B content for the melt-spun $\text{Fe}_{87-x}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_x$ ($x = 20$ to 30 at%) glassy alloys. The I_s , H_c and T_c values decrease gradually from 1.53 to 1.26 T, 10.4 to 3.76 A/m and 678 to 638 K, respectively, with increasing the B content from 20 to 30 at%. The λ_s value

Fig. 1 DSC curves of melt-spun $\text{Fe}_{87-x}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_x$ ($x = 20$ to 30 at%) glassy alloys.

Fig. 2 T_g , T_x and $\Delta T_x (=T_x - T_g)$ as functions of the B content for melt-spun $\text{Fe}_{87-x}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_x$ ($x = 20$ to 30 at%) glassy alloys.

also decreases gradually from 21.6×10^{-6} to 15.7×10^{-6} with increasing the B content from 20 to 27.5 at%. From the compositional dependence of ΔT_x , T_g/T_m , H_c , I_s and λ_s , it is concluded that the $\text{Fe}_{87-x}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_x$ ($x = 25$ and 27.5 at%) glassy alloys have a good combination of higher thermal stability of the supercooled liquid and better soft magnetic properties with high T_c . Consequently, the production of a bulk glassy alloy by copper mold casting was tried for the $\text{Fe}_{62}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_{25}$ composition.

The cast $\text{Fe}_{62}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_{25}$ alloy of cylinder form with diameters of 0.5 and 0.75 mm and length of 20 mm, and plate form with thicknesses of 0.5 and 0.75 mm were produced. Figure 4 shows the X-ray diffraction patterns of the cast $\text{Fe}_{62}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_{25}$ alloy plates with thicknesses of 0.5 and 0.75 mm, together with that of the melt-spun glassy ribbon. The diffraction patterns consist only of one broad peak and no diffraction peak corresponding to a crystalline phase is seen, indicating that glassy single phase alloys were formed. Figure 5 shows the DSC curves of glassy $\text{Fe}_{62}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_{25}$ cylinders with diameters of 0.5 and 0.75 mm, together with that of the melt-spun glassy ribbon. The supercooled liquid region (ΔT_x), heat of crystallization (ΔH_x) and T_c for the $\phi 0.5$ mm sample were 56 K, 4.57 kJ/mol and 663 K, respectively, and those for the $\phi 0.75$ mm sample were 55 K, 4.46 kJ/mol and 665 K, respectively. No appreciable difference in T_g , T_x , ΔT_x , ΔH_x and T_c are seen between these samples. This result is consistent with the results obtained by X-ray diffraction. The larger GFA of the present Fe-based alloy is concluded to be due to the high thermal stability of the supercooled liquid against crystallization. The reason for the larger ΔT_x for the Fe–Co–Nd–Dy–B glassy

Fig. 3 Saturation magnetization (I_s), coercive force (H_c), Curie temperature (T_c) and saturated magnetostriction (λ_s) as functions of the B content for the melt-spun $\text{Fe}_{87-x}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_x$ ($x = 20$ to 30 at%) glassy alloys.

Fig. 4 X-ray diffraction pattern of cast glassy $\text{Fe}_{62}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_{25}$ alloy plates with thicknesses of 0.5 and 0.75 mm. The data of the melt-spun glassy ribbon are also shown for comparison.

Fig. 5 DSC curves of cast glassy $\text{Fe}_{62}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_{25}$ alloy cylinders with diameters of 0.5 and 0.75 mm. The data of the melt-spun glassy ribbon are also shown for comparison.

alloy is discussed in the framework of the three empirical rules^{18,19} for the achievement of large GFA. The three empirical rules are (1) multicomponent systems consisting of more than three elements, (2) significant difference in atomic size above about 12% among the main three constituent elements, and (3) large negative heats of mixing among the elements. 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 improves 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 $\text{Nd} > \text{Dy} \gg \text{Fe} > \text{Co} \gg \text{B}$, 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 dense random packed structure with low diffusivity, which is the case of the present Fe–Co–Nd–Dy–B glassy alloys. The larger supercooled liquid region for the Fe–Co–Nd–Dy–B glassy alloy containing 25–27.5 at%B is presumed to results of the formation of a higher degree of dense random packed structure at these B concentrations in the present the glassy alloy series.²⁰⁾

The hysteresis B–H loops of the cast glassy $\text{Fe}_{62}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_{25}$ cylinders with diameters of 0.5 and 0.75 mm are shown in Fig. 6, where the data of the melt-spun glassy ribbon are also shown for comparison. No distinct difference in the hysteresis B–H loops is seen between the bulk samples and the melt-spun glassy ribbon. The bulk glassy $\text{Fe}_{62}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_{25}$ alloy also exhibits high saturation magnetization I_s , e.g., 1.33 T for $\phi 0.5$ mm cylinder and

Fig. 6 The hysteresis B-H loops of the cast glassy $\text{Fe}_{62}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_{25}$ alloy cylinders with diameters of 0.5 and 0.75 mm. The data of the melt-spun glassy ribbon are also shown for comparison.

1.31 T for $\phi 0.75$ mm cylinder. Here, it is reasonable to conclude that the cast bulk glassy sample also have nearly the same soft magnetic properties as the melt-spun ribbon based on the observation of the similarity in the B-H loops measured by VSM.

Finally, the combination of high glass-forming ability and good soft magnetic properties for the Fe-Co-Nd-Dy-B glassy alloys are encouraging for the future application of Fe-based bulk glassy alloys as bulk soft magnetic material.

4. Summary

For new Fe-based glassy alloys exhibiting a large supercooled liquid region above 50 K, we examined the thermal stability of the supercooled liquid, magnetic properties and the formation of a bulk glassy alloy by copper mold casting. The results obtained are summarized as follows.

(1) The supercooled liquid region (ΔT_x) exceeds 50 K in the range 22.5 to 27.5 at%B for $\text{Fe}_{87-x}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_x$ glassy alloys. The ΔT_x and T_g/T_m values are 56 K and 0.58,

respectively, for the $\text{Fe}_{62}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_{25}$ glassy alloy.

(2) The I_s , H_c , λ_s and T_c values are 1.37 T, 4.58 A/m, 17.9×10^{-6} and 663 K, respectively, for the melt-spun $\text{Fe}_{62}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_{25}$ glassy alloy.

(3) The bulk glassy alloys were produced in the diameter range up to 0.75 mm by copper mold casting of the $\text{Fe}_{62}\text{Co}_{9.5}\text{Nd}_3\text{Dy}_{0.5}\text{B}_{25}$ alloy. The bulk glassy alloys also exhibit a high I_s of 1.31 T and T_c of 665 K. Those properties are nearly the same as those for the melt-spun glassy ribbons.

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