Thermal Stability and Soft Magnetic Properties of (Fe, Co)–(Nd, Dy)–B Glassy Alloys with High Boron Concentrations

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1. Introduction

Since the finding of a melt-spun amorphous Fe–P–C alloy with ferromagnetism in 1967,¹ Fe- and Co-based magnetic amorphous alloys have 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)–B 8) alloys in the early 1980s. Among these, the melt-spun (Fe, Co)–B–Si amorphous alloys have been practically used as soft magnetic materials in electronic transformers. 9) However, those amorphous alloys did not exhibit high glass-formation ability (GFA) and could be produced only at high cooling rates of over 10⁵ K/s by melt spinning. As a result, the ribbon sample thickness has been limited to less than about 50 μm.

Glasses alloys with a large supercooled liquid region \( \Delta T_g \) and crystallization temperature \( T_c \) and/or high reduced glass transition temperature \( T_g/T_l \) (liquidus temperature) have high resistance against crystallization, leading to high GFA. ¹⁰,¹¹ 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. Recently, it has been reported that ferromagnetic Fe- and Co-based glassy alloys with a large supercooled liquid region above 50 K as well as a higher GFA in the Fe–(Al, Ga)–(P, C, B, Si) ¹² (Fe–(Co, Ni))–(Zr, Hf, Nb)–B ¹³ and Co–Fe–(Zr, Ta, Nb)–B ¹⁴ systems exhibit good soft magnetic properties. The critical thickness of these glassy alloys reaches 2 mm for (Al, Ga)–(P, C, B, Si) ¹² and Fe–(Co, Ni)–(Zr, Hf, Nb)–B systems, ¹⁰ and 1.5 mm for Co–Fe–(Zr, Ta, Nb)–B ¹⁷ system by the copper mold casting method. However, relatively low Fe and Co concentrations lead to a low saturation magnetization. We have searched for a new glassy alloy in (Fe, Co)–RE–B (RE = rare earth elements) system with a B content of 20 at% in which a supercooled liquid region is observed and high saturation magnetization and low coercive force are obtained. ¹⁸,¹⁹ The \( \Delta T_g \) and \( T_g/T_l \) for the Fe-based glassy alloys reported up to date are about 45 K and 0.55, respectively, and hence an extremely large GFA cannot be expected. ²⁰,²¹

Recently, we have reported that (Fe, Co)–RE–B glassy alloys with high B concentrations about 20 at% exhibit a large \( \Delta T_g \) above 55 K and good soft magnetic properties. ²² Subsequently, we have examined the effect of additional transition metals on the thermal stability, glass-formation ability and magnetic properties of those glassy alloys. This paper presents the thermal stability of the supercooled liquid, glass-formation ability and magnetic properties of the Fe⁶⁷–Co⁶²–Nd³–Dy⁰–B⁲⁵ glassy alloy rods produced in the diameter range up to 0.75 mm by copper mold casting. The substitution of 2 at% elements TM (TM = Nb, Ta, Mo and W) for Fe and Co remarkably increases the \( \Delta T_g \) and \( T_g/T_l \), leading to an increase in the glass-formation ability (GFA) for Fe⁹⁰–Co⁶–Nd³–Dy⁰–B⁲⁵ glassy alloy rods were produced in the diameter range up to 1.2 mm. The saturation magnetization \( I_s \) decreases slightly, while the coercive force \( H_c \) remains almost unchanged by the addition of 2 at% TM elements.

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2. Experimental Procedure

Allloy ingots of Fe–Co–Nd–Dy–B–TM (TM = V, Nb, Ta, Cr, Mo and W) were prepared by arc melting from 99.9 to 99.99 mass% purity elemental metals and boron (99.5 mass%) in an argon atmosphere. The ingots were crushed into small pieces, in order to place them into a quartz crucible for melt spinning. Ribbons were produced at a wheel speed of 35 m/s in an argon atmosphere. Bulk samples with length of about 50 mm and rod form with different diameters were produced by injection casting of the molten alloy.
The large $\Delta$s. As marked with the glass transition temperature ($T_g$) into copper molds. The structure of the samples was examined by X-ray diffraction (Cu Ka), 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 K/s, and a cooling rate 0.033 K/s, respectively. The saturation magnetization was measured at room temperature with a vibrating sample magnetometer (VSM) under a maximum applied magnetic field of 670 kA/m. The coercive force was measured with a $B$-$H$ loop tracer. The saturated magnetostriction was measured by a capacitance method in a maximum applied field of 240 kA/m.

3. Results

The X-ray diffraction patterns indicated that the melt-spun ribbons in the composition range of 0 to 80 at%Co, 0 to 3.5 at%Nd, and 0 to 27.5 at%B were composed of an amorphous single phase. Figure 1 shows the DSC curves of the melt-spun Fe$_{87-x}$Co$_9$Nd$_{5}$Dy$_{0.5}$B$_x$ ribbons in the composition range of 0 to 35 at%Co, 0 to 35 at%Nd, and 25 to 35 at%B, respectively. We further measured the liquidus temperature ($T_l$), transition temperature ($T_g$), and crystallization temperature ($T_c$) at 1 kHz are 1.41 T, 2.6 A/m, 23.7 × 10$^{-6}$ and 12000, respectively. From the compositional dependence of thermal stability and magnetic properties, it is concluded that the Fe$_{62}$Co$_9$Nd$_5$Dy$_{0.5}$B$_{25}$ glassy alloy has a good combination of higher GFA and better soft magnetic properties. Consequently, subsequent trials on the production of a bulk glassy rod by copper mold casting were made for the Fe$_{62}$Co$_9$Nd$_5$Dy$_{0.5}$B$_{25}$ alloy.

The cast Fe$_{62}$Co$_9$Nd$_5$Dy$_{0.5}$B$_{25}$ rods with diameters of 0.5 and 0.75 mm were produced. The X-ray diffraction patterns of the bulk alloys consist only of broad peak and no diffraction peak corresponding to a crystalline phase is observed, indicating that a single glassy phase is formed. The hysteresis $B$-$H$ loops of the cast glassy Fe$_{62}$Co$_9$Nd$_5$Dy$_{0.5}$B$_{25}$ rods with diameters of 0.50 and 0.75 mm were measured by VSM. No distinct difference in the hysteresis $B$-$H$ loops is observed between the bulk samples and the melt-spun glassy ribbon. The high GFA of the melt-spun Fe$_{62}$Co$_9$Nd$_5$Dy$_{0.5}$B$_{25}$ alloy also exhibits high saturation magnetization $I_s$, e.g., 1.33 T for the Fe$_{62}$Co$_9$Nd$_5$Dy$_{0.5}$B$_{25}$ alloy, indicating that the glassy alloy rods have nearly the same soft magnetic properties as those for the melt-spun ribbon.

In order to improve further the GFA of the (Fe, Co)–(Nd, Dy)–B glassy alloys. 1975

![Figure 1](image1.png)  
**Fig. 1** DSC curves of melt-spun Fe$_{87-x}$Co$_9$Nd$_{5}$Dy$_{0.5}$B$_x$ ($x = 17.5$ to $35$ at%) glassy alloys.

![Figure 2](image2.png)  
**Fig. 2** Saturation magnetization ($I_s$), coercive force ($H_c$) and saturated magnetostriction ($\lambda_s$) as a function of B content for the melt-spun Fe$_{87-x}$Co$_9$Nd$_{5}$Dy$_{0.5}$B$_x$ ($x = 17.5$ to $35$ at%) glassy alloys.
(Nd, Dy)–B glassy alloys with high boron concentrations, we have investigated the effects of addition of transition metals TM (TM = V, Nb, Ta, Cr, Mo and W) on the thermal stability, glass-formation ability and magnetic properties of the Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}TM\textsubscript{2} glassy alloy. Figure 3 shows DSC curves of the glassy Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}TM\textsubscript{2} alloys. As seen in Fig. 3, the \(T_g\) remains almost unchanged and the \(T_x\) shifts towards higher temperature by the addition of the TM elements, and all the glassy alloys crystallize through a single stage. The \(\Delta T_x\) exceeds 56 K, and the largest \(\Delta T_x\) is 87 K for the Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}Nb\textsubscript{2} alloy. In addition, we also measured the \(T_g\) of the Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}TM\textsubscript{2} alloys by DTA. Table 1 lists the thermal stability \((T_g, T_x, \Delta T_x, T_l, T_g/T_l)\) of the Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}TM\textsubscript{2} glassy alloys. From Table 1, it is seen that \(\Delta T_x\) increases significantly from 56 to 87 K, and the largest \(\Delta T_x\) is 87 K for the Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}Nb\textsubscript{2} alloy. In addition, we also measured the \(T_l\) of the Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}TM\textsubscript{2} alloys by DTA. Table 1 lists the thermal stability \((T_g, T_x, \Delta T_x, T_l, T_g/T_l)\) of the Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}TM\textsubscript{2} glassy alloys. From Table 1, it is seen that \(\Delta T_x\) increases significantly from 56 to 87 K, and the \(T_l\) decreases from 1522 to 1494 K with the replacement of 2 at\% Fe and Co by elements of Nb, Ta, Cr, Mo and W, leading to an increase of \(T_g/T_l\) from 0.56 to 0.57. The larger \(\Delta T_x\) and \(T_g/T_l\) for the Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}TM\textsubscript{2} alloys (TM = Nb, W, Mo and Ta) indicate that the glass-formation ability of the TM-containing alloys is higher than that of the alloy without TM. The largest \(\Delta T_x\) of 87 K and high \(T_g/T_l\) of 0.57 were obtained for the Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}Nb\textsubscript{2} alloy. Figure 4 shows the \(I_s\) and \(H_c\) of the melt-spun Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}TM\textsubscript{2} glassy alloys. The \(I_s\) values are lower than that of the alloy without TM because of the replacement of ferromagnetic elements by the non-ferromagnetic elements of TM.

A cast Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}Nb\textsubscript{2} alloy rod with a diameter of 1.2 mm.

![Fig. 3 DSC curves of melt-spun Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}TM\textsubscript{2} alloys.](image)

<table>
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<th>Composition</th>
<th>(T_g) (K)</th>
<th>(T_x) (K)</th>
<th>(\Delta T_x) (K)</th>
<th>(T_l) (K)</th>
<th>(T_g/T_l)</th>
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<tr>
<td>TM = none</td>
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<td>899</td>
<td>56</td>
<td>1522</td>
<td>0.56</td>
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<tr>
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<td>56</td>
<td>1541</td>
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<tr>
<td>TM = V</td>
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<td>907</td>
<td>60</td>
<td>1544</td>
<td>0.55</td>
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<tr>
<td>TM = Nb</td>
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<td>937</td>
<td>87</td>
<td>1497</td>
<td>0.57</td>
</tr>
<tr>
<td>TM = Ta</td>
<td>850</td>
<td>924</td>
<td>74</td>
<td>1494</td>
<td>0.57</td>
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</tbody>
</table>

![Fig. 4 Saturation magnetization \(I_s\) and coercive force \(H_c\) as a function of the transition element TM for the glassy Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}TM\textsubscript{2} alloys.](image)

![Fig. 5 Outer shape of the cast Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}Nb\textsubscript{2} rod with a diameter of 1.2 mm.](image)

![Fig. 6 X-ray diffraction pattern of the cast Fe\textsubscript{60}Co\textsubscript{9.2}Nd\textsubscript{3}Dy\textsubscript{0.5}B\textsubscript{25}Nb\textsubscript{2} rod with a diameter of 1.2 mm. The data of the melt-spun glassy ribbon with the same composition are also shown for comparison.](image)
eter of 1.2 mm was also produced. Figure 5 shows the outer surface of the cast Fe$_{60}$Co$_{9}$Nd$_{3}$Dy$_{0.5}$B$_{25}$Nb$_{2}$ rod. The rod sample has a smooth surface with good metallic luster and no distinct ruggedness due to the precipitation of a crystalline phase is seen on the outer surface. Figure 6 shows an X-ray diffraction pattern of the cast alloy rod, together with the result of the melt-spun glassy alloy ribbon. The X-ray diffraction pattern of the rod sample consists only of a broad peak and no distinct difference is seen between the rod and the melt-spun glassy ribbon samples, indicating the formation of a single glassy phase in the cast rod. The further increase in the rod diameter to 2.0 mm causes the precipitation of crystalline phases. It is therefore concluded that the critical rod diameter for formation of the glassy phase lies between 1.2 and 2.0 mm.

Figure 7 shows the DSC curves of the Fe$_{60}$Co$_{9}$Nd$_{3}$Dy$_{0.5}$B$_{25}$Nb$_{2}$ alloy rod with a diameter of 1.2 mm. The data of the melt-spun glassy ribbon are also shown for comparison. The hysteresis $B$-$H$ loops of the cast glassy Fe$_{60}$Co$_{9}$Nd$_{3}$Dy$_{0.5}$B$_{25}$Nb$_{2}$ rod with a diameter 1.2 mm. The data of the melt-spun glassy ribbon are also shown for comparison.

### 4. Discussion

The large supercooled liquid region for the Fe-based (Fe, Co)–(Nd, Dy)–B glassy alloys containing high boron concentrations (20–30 at%) seems to have a strong relation to local atomic structure. The essential structure feature of the (Fe, Co)–RE–B glassy alloys with large $\Delta T_x$ was characterized as the formation of the distorted dense random network of trigonal prism-like local units around boron connected with inserted RE. The significant difference in atomic sizes among the constituents and the strong chemical affinities of RE–B, RE–Co and RE–Fe pairs contribute to the strengthening of network of the prism, leading to the suppression of the rearrangement of the constituent elements on a long-range scale. Although the prism-like structure was also identified for the amorphous alloys with lower boron contents (18 at% < B), no supercooled liquid region was observed in these alloys. This implies that the network of the prisms is not strong enough to maintain during heating. As for the alloys with higher boron contents (B > 30 at%), the coordination numbers of first nearest neighboring B-(Fe, Co) pairs (N$_{B(Fe,Co)}$) are much smaller than those in the glassy alloys containing 20–30 at% B, the trigonal prism-like local structure is no longer dominant. This makes the rearrangements of the prisms during crystallization easy.

The substitution of TM (= Nb, Ta, Mo and W) for Fe and Co in the Fe$_{62}$Co$_{9.5}$Nd$_{3}$Dy$_{0.5}$B$_{25}$ glassy alloy increases significantly $\Delta T_x$, however, little change in $\Delta T_x$ is seen for the substitution of Cr and V (Fig. 3). This result has relation to the local atomic structures of the glassy alloys. The local atomic structures in the Fe$_{70}$TM$_{10}$B$_{20}$ glassy alloys (TM = Cr, Zr, Nb, Hf and W) with difference $\Delta T_x$ were studied. The essential features of the atomic structures resemble in these glassy alloys, but differ in the local atomic structure which is a distorted shape of the trigonal prism-like. In the glassy alloys containing TM elements larger than Fe atoms, the prisms show distorted shapes due to a size difference be-
between TM and Fe. A linear relation between the size difference and $\Delta T_c$, suggests that the difference of $\Delta T_c$ is closely related with the difficulty of rearrangements of the prisms during crystallization.\(^{27,28}\) Similarly, the substitution of larger atomic size TM ($= \text{Nb, Ta, Mo and W}$) for Fe and Co in the Fe$_{60}$Co$_{9}$Nd$_3$DY$_{0.5}$B$_{25}$ glassy alloy, the difference in atomic sizes between the constituents and the strong chemical affinities of TM–B, TM–Co and TM–Fe pairs contribute to the strengthening of network of the prism, leads to suppression of the rearrangements of the constituent elements on a long-range scale in the present Fe-based glassy alloys.\(^{26–28}\) On the other hand, the $\Delta T_c$ changes little with the substitution of Cr or V element because the atomic sizes of Cr and V are close to those of Fe and Co.

The large GFA of the present Fe-based (Fe, Co)–(Nd, Dy)–B–TM (TM = Nb, Mo, Ta, W) alloy with high boron concentrations is concluded to originate from the high thermal stability of the supercooled liquid against crystallization. The reason for the large $\Delta T_c$ and high $T_g/T_c$ for the (Fe, Co)–(Nd, Dy)–B–TM glassy alloy is discussed in the framework of the three component empirical rules.\(^{10,11}\) for the achievement of large GFA. The three component 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 component rules. The addition of Co, Dy and TM elements is effective for an increase in the degree of the satisfaction of the component rules. That is, the addition of these elements causes the more sequential change of the satisfaction of the component rules. That is, the addition in the present alloys is an Fe–Nd–B system which satisfies the same as those for the melt-spinning glassy ribbon.

5. Summary

We examined the thermal stability of the supercooled liquid, glass-forming ability and magnetic properties of the Fe$_{87-x}$Co$_9$Nd$_3$DY$_{0.5}$B$_x$ ($x = 17.5$ to 35) and Fe$_{60}$Co$_{9}$Nd$_3$DY$_{0.5}$B$_{25}$TM$_2$ (TM = V, Nb, Ta, Cr, Mo and W) glassy alloys. The results obtained are summarized as follows.

1. The supercooled liquid region $\Delta T_c$ and reduced glass transition temperature $T_g/T_c$ are 56 K and 0.56, respectively, for the Fe$_2$Co$_9$Nd$_3$DY$_{0.5}$B$_{25}$ glassy alloy. The Fe$_2$Co$_9$Nd$_3$DY$_{0.5}$B$_{25}$ glassy alloy rods were produced in the diameter range up to 0.75 mm by copper mold casting.

2. The Fe$_{62}$Co$_{9}$Nd$_3$DY$_{0.5}$B$_{25}$ glassy alloy annealed at 773 K for 600 s exhibits good soft magnetic properties of 1.41 T for saturation magnetization $I_x$, 2.6 A/m for coercive force $H_c$, and 12000 for permeability $\mu_r$ at 1 kHz.

3. The substitution of 2 at% elements TM ($= \text{Nb, Ta, Mo and W}$) for Fe and Co in the Fe$_{62}$Co$_9$Nd$_3$DY$_{0.5}$B$_{25}$ glassy alloy significantly increases $T_c$ and decreases liquidus temperature $T_l$, leading to the increases in $\Delta T_c$ and $T_g/T_c$ from 56 to 87 K and from 0.56 to 0.57, respectively, for the Fe$_{60}$Co$_{9}$Nd$_3$DY$_{0.5}$B$_{25}$TM$_2$ glassy alloys.

4. By the substitution of 2 at% elements TM (TM = Cr, V, Nb, Ta, Mo and W) for Fe and Co, the $I_x$ decreases slightly and $H_c$ remains almost unchanged. The $I_x$ and $H_c$ of the glassy Fe$_{60}$Co$_{9}$Nd$_3$DY$_{0.5}$B$_{25}$TM$_2$ alloys are in the range from 1.13 to 1.19 T and 3.98 to 4.98 A/m, respectively.

5. The bulk glassy alloy rods were produced in the diameter range up to 1.2 mm by copper mold casting of the Fe$_{60}$Co$_{9}$Nd$_3$DY$_{0.5}$B$_{25}$Nb$_2$ alloy. The bulk glassy rods also exhibit high $I_x$ of 1.15 T. The magnetic properties are nearly the same as those for the melt-spinning glassy ribbon.

REFERENCES