Bulk Nd–Fe–Al Amorphous Alloys with Hard Magnetic Properties

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An amorphous phase in Nd–Fe–Al system was formed in an extremely wide composition range of 0 to 90 at% Fe and 0 to 93 at% Al by melt spinning. Based on the information on the amorphous formation, ferromagnetic Nd95Fe5Al8 bulk amorphous alloys with high coercive force at room temperature were obtained by a copper mold casting method. The maximum diameter of the cylindrical amorphous samples with a length of 50 mm is about 7 mm for the 20%Fe alloy and about 4 mm for the 30%Fe alloy. Neither glass transition nor supercooled liquid region is observed in the temperature range before crystallization, being different from previous bulk glassy alloys exhibiting a wide supercooled liquid region before crystallization. The onset temperature of crystallization (\(T_c\)) and melting temperature (\(T_m\)) are measured to be 778 and 863 K, respectively, for the Nd95Fe5Al8 alloy. The resulting reduced ratio of \(T_c/T_m\) is as high as 0.90 and the temperature interval between \(T_c\) and \(T_m\) is as small as 85 K. The extremely high \(T_c/T_m\) and small \(\Delta T_m(=T_m-T_c)\) values are the reason for the achievement of the large glass-forming ability. The bulk amorphous Nd95Fe5Al8 alloy has a ferromagnetism with the Curie temperature (\(T_c\)) of about 600 K which is much higher than the highest \(T_c\) (about 480 K) for the Nd–Fe binary amorphous alloy ribbons. The remanence (\(B_r\)) and intrinsic coercive force (\(H_c\)) for the bulk Nd95Fe5Al8 alloy are 0.122 T and 277 kA/m, respectively, in the as-cast state and 0.128 T and 277 kA/m, respectively, in the annealed state for 600 s at 600 K. The \(B_r\) and \(H_c\) decrease to 0.045 T and 265 kA/m, respectively, for the crystallized Nd95Fe5Al8 sample consisting of Nd+Al14Nd+\(\delta\) phases and the maximum hard magnetic properties are achieved in the amorphous state. The hard magnetic properties for the bulk amorphous alloys are presumably due to the homogeneous development of ferromagnetic clusters with large random magnetic anisotropy. The finding of the bulk amorphous alloys exhibiting hard magnetic properties at room temperature is promising for the future development as a new type of magnetic amorphous permanent magnet.

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I. Introduction

Since the first success of preparing a bulk amorphous alloy with a diameter of about 7 mm in La–Al–Cu system in 1989(1), bulk amorphous alloys have attracted rapidly increasing interest because of the importance in materials science and the extension of their application fields. Bulk amorphous alloys by conventional solidification methods have been obtained in a number of alloy systems such as Ln–Al–TM(2), Mg–Ln–TM(3,4), Zr–Al–TM(5–9), Ti–Zr–Al–TM–Be(10) and Ti–Zr–TM–Be(11) (Ln = lanthanide metal, TM = transition metal). However, these alloy systems have been limited to the nonferrous metal base alloys without ferromagnetism at room temperature. Based on the series of findings of a number of amorphous alloys with large glass-forming ability, we have proposed(12–16) the three empirical rules for the achievement of large glass-forming ability for metallic alloys, i.e., (1) multicomponent systems consisting of more than three components, (2) significantly different atomic size ratios above about 12% among the main three constituent elements, and (3) large negative heats of mixing among the main three constituent elements. According to the three empirical rules, we have searched new Fe-based amorphous alloys with large glass-forming ability and ferromagnetism at room temperature. More recently, it has been found(17) that bulk amorphous alloys are formed in the multicomponent Fe-based systems such as Fe–Al–Ga–P–C–B and Fe–Al–Ge–P–C–B consisting of the three group elements of Fe, (Al, Ga) and (P, C, B, Ge) which satisfy the above-described three empirical rules. As was found for the above-described Ln–, Mg–, Zr– and Ti-based glassy alloys(12–16), the multicomponent Fe-based amorphous alloys also showed a high thermal stability of supercooled liquid(17–19), as is evidenced by a wide supercooled liquid region, \(\Delta T_c\) exceeding 60 K which is defined by the difference between crystallization temperature (\(T_c\)) and glass transition temperature (\(T_g\)). Furthermore, the bulk Fe-based amorphous alloys exhibit ferromagnetism with a Curie temperature of about 600 K and the saturation magnetization and coercive force are measured to be about 1.3 T and 60 A/m, respectively, at room temperature(17,19). The bulk Fe-based amorphous alloys with rather good soft magnetism have attracted attention as a new type of soft magnetic material. In the series of studies on the search of bulk Fe-based amorphous alloys with ferromagnetism at temperatures above room temperature, we have succeeded in finding bulk Nd–Fe–Al amorphous alloys with permanent magnetic properties. The ternary alloy system also satisfies the three empirical rules for the achievement of large glass-forming ability.

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aim of this paper is to present the sample morphology, structure, thermal stability and magnetic properties of bulk Nd$_{90-x}$Fe$_x$Al$_{10}$ amorphous alloys prepared by a copper mold casting method.

II. Experimental Procedure

Ternary Nd–Fe–Al alloys were prepared by induction-melting a mixture of pure Nd, Fe and Al metals in an argon atmosphere. The formation of bulk amorphous alloys was tried for Nd$_{90-x}$Fe$_x$Al$_{10}$ (at%) alloys. The alloy series were chosen because the alloys containing 10 at% Al had much larger glass-forming ability as compared with Nd–Fe binary alloys. From the pre-alloyed Nd$_{90-x}$Fe$_x$Al$_{10}$ ingots, cylindrical samples with a constant length of about 50 mm and different diameters in the range of 1 to 10 mm were prepared by injection casting of the molten alloy into copper molds with cylindrical cavities. The injection pressure was fixed to be as low as 0.05 MPa. For comparison, amorphous Nd$_{90-x}$Fe$_x$Al$_{10}$ ribbons with a cross section of 0.03–0.04 × 1 mm$^2$ were also produced by a single-roller melt spinning method in an argon atmosphere. Furthermore, the composition range in which an amorphous phase is formed in the Nd–Fe–Al system was examined for the melt-spun ribbon samples. The amorphous structure of the as-cast and melt-spun samples was examined by X-ray diffractometry, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and optical microscopy (OM). The OM sample was etched for 10 s at 293 K in a solution of 0.5% hydrofluoric acid and 99.5% distilled water in volume ratio. The distribution of the constituent elements in the transverse and longitudinal cross sections for the cast bulk alloys was examined by an energy dispersive X-ray (EDX) spectroscope which was set in the scanning electron microscope. The thermal stability associated with crystallization, magnetic transition from ferromagnetism to paramagnetism and melting temperature was measured by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Magnetization and coercive field under an applied field of 1432 kA/m were measured in a temperature range from room temperature to 873 K with a vibrating sample magnetometer (VSM).

III. Results

1. Formation of bulk Nd–Fe–Al amorphous alloys and their thermal stability

Figure 1 shows the composition range in which an amorphous phase is formed in the Nd–Fe–Al ternary system by melt spinning. It is seen that the amorphous phase is formed in an extremely wide composition range of 0 to 90 at% Fe and 0 to 93 at% Al. The amorphous phase region is much wider than that$^{[18]}$ for La–Al–Ni ternary amorphous alloys with the widest amorphous formation range reported up to date. The wide amorphous formation range appears to result from the wide amorphous formation ranges for the Nd–Fe and Nd–Al binary alloys. The details of the thermal stability and mechanical properties for the melt-spun Nd–Fe–Al amorphous alloys will be presented elsewhere. As is the case with the La–Al–TM (TM＝Ni or Cu)$^{[20,21]}$ systems, the amorphous formation in the wide composition range implies the possibility that the Nd–Fe–Al ternary alloys also have a large glass-forming ability which enables the production of bulk amorphous alloys by conventional solidification methods.

We have examined the possibility of preparing the bulk amorphous alloys in the wide amorphous formation range of the Nd–Fe–Al ternary system by a copper mold casting method. As a result, it was found that the Nd–Fe–Al alloys containing 10 to 50%Fe and 10%Al have a glass-forming ability which is large enough to form an amorphous phase even in the cylindrical bulk samples with diameters above 1 mm. Figure 2 shows the morphology and outer surface appearance of the cylindrical
Nd<sub>50</sub>Fe<sub>25</sub>Al<sub>15</sub> samples with lengths of 38 to 50 mm and different diameters of 1, 3, 5 and 7 mm prepared by the copper mold casting method. The cast samples have smooth outer surface and good metallic luster typical for an amorphous phase without grain boundaries and no distinct contrast revealing the precipitation of a crystalline phase is seen over the outer surface. Furthermore, the dimensions of these samples are nearly the same as those for the inner cavities of the copper mold, indicating that the Nd–Fe–Al alloys have a good castability. Figure 3 shows the X-ray diffraction patterns taken from the outer surface region for the cylindrical Nd<sub>50</sub>Fe<sub>25</sub>Al<sub>15</sub> samples with diameters of 3, 5 and 7 mm, together with the data of the melt-spun ribbon with a cross section of 0.04 x 1 mm<sup>2</sup>. A broad diffraction peak is seen around the wave vector (K<sub>0</sub> = 4π sin θ/λ) of about 22 nm<sup>-1</sup> for all of the samples and no appreciable diffraction peaks corresponding to a crystalline phase are seen over the entire diffraction angle. The X-ray diffraction data indicate clearly that the cylindrical alloys with diameters of 3, 5 and 7 mm consist of an amorphous phase. With the aim of clarifying the absence of any crystalline phase in the cast cylindrical alloys, we examined the microstructure of the central regions in the transverse and longitudinal cross sections after the deep etching treatment. The transverse cross sectional structure of the Nd<sub>50</sub>Fe<sub>25</sub>Al<sub>15</sub> alloy with a diameter of 3 mm shown in Fig. 4(a) is composed only of featureless contrast region. However, in the optical micrograph Fig. 4(b) taken from the transverse cross section of the Nd<sub>50</sub>Fe<sub>25</sub>Al<sub>15</sub> alloy with a diameter of 3 mm, one can see a weak contrast of acicular shape with a length of about 4 μm and a diameter less than about 0.1 μm. As is evident from the comparison between Fig. 4(a) and (b), the acicular contrast is seen only for the Nd<sub>50</sub>Fe<sub>25</sub>Al<sub>15</sub> alloy with a diameter of 3 mm. In order to investigate the reason for the appearance of the acicular contrast, the difference in alloy components between the acicular contrast region and the featureless matrix was examined by the EDX spectroscopic analysis. However, as shown for the Nd<sub>50</sub>Fe<sub>25</sub>Al<sub>15</sub> alloy in Fig. 5, no appreciable distinction in composition between the acicular and the featureless contrast regions is seen in the scanning electron micrograph and EDX spectroscopic profiles. The problem whether or not the acicular contrast corresponds to a crystalline phase with nearly the same alloy composition as that for the amorphous matrix remains unclear in the present study. Considering that the featureless contrast region corresponds to the amorphous phase region, the cast alloy is concluded to consist of a mostly single amorphous phase even at the composition Nd<sub>50</sub>Fe<sub>25</sub>Al<sub>15</sub>. Figure 6 shows the maximum diameter (d<sub>max</sub>) for the formation of the mostly single amorphous phase as a function of Fe content for the cast Nd<sub>50−x</sub>Fe<sub>x</sub>Al<sub>15</sub> cylinders with a length of 50 mm. The maximum diameter increases with decreasing Fe content, shows a maximum value of 7 mm at 20%Fe and then decreases with further increasing Fe content. Furthermore, one can notice that no amorphous alloy with a diameter above 1 mm is formed in the composition ranges of 0 to 5%Fe and 60 to 90%Fe. Here, it is important to point out that the residual existence of amorphous phase in coexistence with crystalline phases is recognized for the cast Nd<sub>50</sub>Fe<sub>25</sub>Al<sub>15</sub> cylinder with a diameter of 10 mm.

Figure 7 shows the DSC curves of the cast Nd<sub>50−x</sub>Fe<sub>x</sub>Al<sub>15</sub> (x = 10, 20, 30, 40 and 50 at%) cylinders with a diameter of 1 mm prepared by copper mold casting. The DSC curves consist only of an exothermic peak due to crystallization for all the alloys. Neither appreciable endothermic reaction due to the glass transition nor the subsequent supercooled liquid region is seen in the
temperature range before crystallization. The absence of the glass transition is recognized for all the alloys and the glass transition phenomenon is not related to the ease of the amorphous formation for the present alloys. This is in good contrast to the previous results\(^{10-11}\) that all the amorphous alloys with large glass-forming ability exhibit a distinct glass transition and wide supercooled liquid region before crystallization. The reason for the large glass-forming ability for the Nd–Fe–Al alloys where no glass transition phenomenon is observed before crystallization is discussed later. Figure 8 shows the DSC curves of the cylindrical Nd\(_{40}\)Fe\(_{50}\)Al\(_{10}\) samples with diameters of 1, 2 and 3 mm prepared by copper mold casting. Only an
exothermic peak due to crystallization is seen in the temperature range of 770 to 825 K for all the samples and no appreciable difference in the exothermic peak behavior with sample diameter is seen. This result indicates that the crystallization behavior of the amorphous phase is independent of the existence of the acicular contrast. The absence of the appreciable change in the DSC curve with diameter is also recognized for the other Nd$_{90-x}$Fe$_x$Al$_{10}$ (x=20 and 40 at%) alloys.

The crystallized structure was examined for the cast Nd$_{90}$Fe$_{30}$Al$_{10}$ alloy annealed for 600 s at 873 K by X-ray diffractometry. The crystallization structure was identified to consist of hcp-Nd, cubic Al$_3$Nd and tetragonal $\delta$ (Nd$_{77}$Fe$_{23}$Al)$_{22}$ phases. Considering that the structure agrees with that for the precast ingot prepared by arc melting, it is concluded that the achievement of the large glass-forming ability is not due to an extrinsic factor such as the dissolution of oxygen.

2. Magnetic properties

The cylindrical bulk amorphous samples were found to exhibit ferromagnetism at room temperature. Figure 9 shows the change with Fe content in the hysteresis J-H loops of the as-cast amorphous Nd$_{90-x}$Fe$_x$Al$_{10}$ (x=20, 30 and 35 at%) cylinders with diameters of 3 to 5 mm. It is to be noticed that the 20%Fe and 30%Fe amorphous alloys exhibit high coercive force combined with high squareness ratios in the second quadrant. Based on the data of the hysteresis J-H loops, the remanence ($B_r$), intrinsic coercive force ($H_c$), maximum energy product ($BH$)$_{max}$ and magnetization in a field of 1432 kA/m ($J_{sat}$) at room temperature are plotted as a function of Fe content in Fig. 10. The $B_r$, $H_c$ and ($BH$)$_{max}$ increase with decreasing Fe content and show high values of 0.112 T, 288 kA/m and 19 kJ/m$^3$, respectively, for the 30%Fe alloy and 0.059 T, 209 kA/m and 5 kJ/m$^3$, respectively for the 20%Fe alloy. On the other hand, the $J_{sat}$ value increases significantly with increasing Fe content, i.e., from...
0.103 T for the 20%Fe alloy to 0.370 T for the 45%Fe alloy. Figure 11 shows the change in the hysteresis J-H loops with sample diameter for the as-cast amorphous Nd$_{90}$Fe$_{20}$Al$_{10}$ cylinders, together with the data of the melt-spun amorphous ribbon with a thickness of about 30 μm. It is seen that the J-H loop behavior of the cast cylinders is significantly dependent on the sample diameter. There is a clear tendency for $B_r$ and $H_c$ to increase with increasing diameter in the diameter range of 1 to 5 mm. Besides, the decrease in the sample thickness from 1 mm to 0.03 mm causes the much significant change in the J-H loop behavior. That is, the $B_r$ and $H_c$ decrease from 0.059 T and 209 kA/m, respectively, for the cast cylinder with a diameter of 1 mm to 0.010 T and 5 kA/m, respectively, for the ribbon sample. This result indicates that the hard magnetic properties are strongly sensitive to the disordered structural state in the amorphous phase. There is a clear tendency for the hard magnetic properties to increase with increasing development of short-range order caused by the decrease in cooling rate from melt. The J-H loop curves for the cast cylinders with diameters of 1 to 3 mm are similar with each other, in comparison with that for the ribbon sample. The similarity is presumably due to the formation of the amorphous phase with much relaxed disordered structure as compared with that for the ribbon sample. The presumption is supported from the previous result$^{(23)}$ that the total enthalpy of structural relaxation for a Zr$_{60}$Al$_{20}$Co$_3$Ni$_8$Cu$_{18}$ amorphous alloy decreases from 683 J/mol for the melt-spun ribbon to 133 J/mol for the cast 7 mm$^3$ sample through 147 J/mol for the cast 5 mm$^3$ sample. In order to confirm the significant difference in the hysteresis J-H loop behavior between the amorphous cylinder with relaxed atomic configurations and the melt-spin amorphous ribbons with more unrelaxed atomic configurations, the J-H loops of the melt-spin Nd$_{90-x}$Fe$_x$Al$_{10}$ (x = 20 to 70 at%) amorphous ribbons are shown in Fig. 12. The $J_{145}$ values increase significantly from 0.044 to 0.745 T with increasing Fe content, but the $H_c$ values are in the range of 0.1 to 13.3 kA/m and do not show any systematic change with Fe content. Thus, the $H_c$ values are much smaller for the melt-spin amorphous ribbons. The much lower $H_c$ values also allow to presume that the relaxed atomic configurations are necessary for the achievement of higher $H_c$ values. The subsequent annealing causes a slight increase in hard magnetic properties of the cast amorphous cylinder and the melt-spin amorphous ribbon, as shown for the Nd$_{90}$Fe$_{20}$Al$_{10}$ alloy in Fig. 13. For instance, the $B_r$, $H_c$ and $(BH)_{max}$ values for the amorphous cylinder with a diameter of 3
mm change from 0.122 T, 277 kA/m and 18 kJ/m³, respectively, in the as-cast state to 0.128 T, 277 kA/m and 18 kJ/m³, respectively, in the annealed state for 600 s at 600 K. Similarly, the B, and Hc, for the amorphous ribbon increase from 0.01 T and 5 kA/m, respectively, in the as-spun state to 0.03 T and 11 kA/m, respectively, in the annealed state for 1.8 ks at 623 K. The reason for the significant differences in the remanence and coercive force between the cast cylinders and melt-spun ribbon is presumably due to the difference in the short-range disordered structure. Furthermore, the significant difference in Hc between the cast cylinder and the annealed ribbon samples also suggests that the development of relaxed atomic configurations including the irreversible structural relaxation is important for the achievement of the high Hc. A subsequent detailed study on the relation between magnetic properties and relaxation-induced atomic configurations on a short-range scale is required for the clarification of the mechanism.

Figure 14 shows the change in magnetization under a field of 1432 kA/m (Jc) with temperature for the cast amorphous Nd₈₀Fe₂₀Al₁₀ alloy with a diameter of 5 mm. The magnetization begins to decrease significantly at about 400 K and almost disappears in the vicinity of 600 K, indicating that the Curie temperature of the ferromagnetic Nd-Fe-Al amorphous alloy is located at about 600 K. It is further seen that the magnetization at room temperature for the sample heated once to 873 K is as small as 0.02 T. The heating to 873 K is recognized to cause the formation of the mixed structure of Nd + Al₂Nd + δ phases. It is therefore concluded that the present hard magnetic properties of 277 kA/m for Hc and 18 kJ/m³ for (BH)max are obtained only for the bulk amorphous alloy with relaxed atomic configurations and decrease significantly upon crystallization.

**IV. Discussion**

1. The reason for the large glass-forming ability of the Nd₈₀-Fe₂₀Al₁₀ (x=20 and 30 at%) alloys

We discuss the reason for the large glass-forming ability of the Nd₈₀Fe₂₀Al₁₀ and Nd₆₀Fe₃₀Al₁₀ alloys which enables the production of the bulk amorphous alloy with a maximum thickness of about 7 and 4 mm, respectively. The DSC data shown in Figs. 7 and 8 indicate that neither distinct glass transition nor supercooled liquid region is observed for these bulk amorphous alloys. The absence of the supercooled liquid region before crystallization implies that the supercooled liquid for these Nd-Fe-Al alloys does not have high thermal stability. This result is different from the previous close relation between \( \Delta T_c \) and glass-forming ability for a number of amorphous alloys in Ln-Al-TM \(^{20(21)}\), Mg-Ln-TM \(^{24-26}\), Zr-Al-TM \(^{12(27)}\), Ti-Zr-TM \(^{28}\) and Ti-Zr-TM-B \(^{41}\) systems. That is, there is a clear tendency for the critical sample thickness for glass formation to increase with increasing \( \Delta T_c \). This tendency is not satisfied for the present Nd-Fe-Al alloys. Here, one can remind of another important factor of the reduced glass transition temperature \( \left( T_g/T_m \right) \) in the evaluation of the glass-forming ability. It is well known \(^{29}\) that the large glass-forming ability is obtained for the amorphous alloy with higher \( T_g/T_m \) value. Here, the melting temperature \( (T_m) \) of the Nd-Fe-Al alloys was measured by differential scanning calorimetry. As shown in Fig. 15, the \( T_m \) value is measured to be 863 K for the Nd₈₀Fe₂₀Al₁₀ alloy and 921 K for the Nd₆₀Fe₃₀Al₁₀ alloy. Furthermore, the absence of the glass transition phenomenon for these amorphous alloys also implies that \( T_g \) is higher than \( T_c \) and hence the use of \( T_c \) in the evaluation of \( T_g/T_m \) corresponds to the lower limit of the reduced glass transition temperature. The \( T_g/T_m \) is evaluated to be as high as 0.90 for the

![Fig. 15 High-temperature DSC curves of the cast amorphous Nd₈₀Fe₂₀Al₁₀ and Nd₆₀Fe₃₀Al₁₀ cylinders with diameters of 5 and 3 mm, respectively.](image-url)
Nd₅₀Fe₂₀Al₁₀ and 0.85 for the Nd₅₀Fe₂₀Al₁₀ alloy. These values are much higher than about 0.6²⁵ for the previous amorphous alloys with large glass-forming ability. The extremely high $T_c / T_m$ values seem to be the reason for the achievement of the large glass-forming ability which enables the formation of the bulk amorphous alloys even for the alloys without the glass transition. It has been reported⁶⁰ that a Z₅₆Al₁₀Ni₁₀Cu₁₃Pd₃ alloy with large glass-forming ability is supercooled by about 385 K corresponding to the magnitude of 0.35 $T_m$ even at a low cooling rate of about 40 K/s. The $T_c$ and/or $T_k$ values of the Nd–Fe–Al alloys are much higher than 0.65$T_m$ and hence the small $\Delta T_m (= T_m - T_g$ or $= T_m - T_s)$ values of 85 to 138 K seem to be another factor which enables the achievement of the large glass-forming ability. The extremely high $T_c / T_m$ and the small $\Delta T_m$ values also imply a steep increase in viscosity with decreasing temperature in the supercooled liquid. The steep increase in viscosity for the Nd–Fe–Al supercooled liquids seems to be attributed to the high degree of dense random packing density for the supercooled liquid consisting of the multiple constituent elements with significantly different atomic size ratios and large negative heats of mixing. The actual measurement of the viscosity will be required for the clarification of the appropriateness of the mechanism for the achievement of the large glass-forming ability.

In any event, it is believed that the $T_c / T_m$ values of 0.85 to 0.90 are the highest and the $\Delta T_m (= T_m - T_g$ or $= T_m - T_s$) of 85 to 138 K is the smallest among all the amorphous alloys reported up to date. In addition to the large $\Delta T_m$ values, a subsequent search of an amorphous alloy with high $T_c / T_m$ and small $\Delta T_m$ is expected to cause the appearance of another series of bulk amorphous alloys with large glass-forming ability.

2. The reason for the appearance of hard magnetic characteristics for the Nd-rich Nd–Fe–Al bulk amorphous alloys

Here, we discuss the reason why the bulk amorphous Nd₅₀Fe₂₀Al₁₀ and Nd₅₀Fe₂₀Al₁₀ alloys prepared by the casting method exhibit the hard magnetic properties at room temperature. The features of the magnetic properties obtained in the present study are summarized as follows: (1) The high coercive forces exceeding 234 kA/m (3 kOe) are obtained in the high Nd concentration range of 50 to 75 at% and in the cast bulk amorphous state with relaxed disordered atomic configurations. (2) There is a tendency for the coercive forces to increase with increasing diameter of the cast cylinders in the range of 1 to 5 mm. (3) The coercive forces and Curie temperatures for the cast Nd₅₀Fe₂₀Al₁₀ amorphous alloys are about 1.9 and 1.3 times higher, respectively, than the highest values⁶¹ for the binary Nd₁₀₀−ₓFeₓ amorphous ribbons. (4) There is no appreciable difference in the hard magnetic properties between the cast amorphous alloys with acicular contrast and without appreciable contrast in the optical micrographs of the transverse cross section. (5) The hard magnetic properties are obtained only for the bulk amorphous alloys and the crystallization into the equilibrium crystalline mixture causes a drastic decrease in the hard magnetic properties. These experimental results must be taken into consideration for the interpretation of the appearance of the hard magnetic properties.

It is generally known⁶²,⁶³ that amorphous rare earth(Ln)–Fe base thin films prepared by sputtering for magneto-optical storage media applications exhibit large coercive forces in the vicinity of the compensation temperature. The (Fe, Co)₉₅Ln₃ amorphous alloys exhibit magnetic exchange coupling between the magnetic moments of the Ln atoms and those of the Fe and Co atoms, leading to the appearance of ferromagnetism for light Ln elements and ferromagnetism for heavy Ln elements. Since the heavy Ln elements have a larger magnetic moment than the TM (Fe and Co) metals at low temperatures but the TM metals have the larger moment at high temperatures, it is possible to control the magnetic properties of the Ln–TM alloys by adjusting the alloy compositions. Thus, at some intermediate temperature, the Ln and TM magnetizations are equal and opposite, providing zero net magnetization. This temperature is usually known as the compensation temperature.⁶⁴,⁶⁵ As the compensation temperature is approached, the coercive force of the Ln–TM alloys tends toward infinity. This is because the energy per unit volume of sample coupled to the net magnetization $M$ by an external applied magnetic field $H$ is $\mu_0 MH$. As $M$ tends toward zero, $H$ must increase toward infinity to couple in the energy required to reverse the magnetization. On the other hand, as the temperature of these materials is raised above the compensation temperature, thermal energy causes the magnetization to be more easily changed in direction. Consequently, at high temperature, the coercive force decreases and approaches zero at the Curie temperature of the material where the thermal energy overcomes the exchange coupling causing the magnetic moments to align. This interpretation for the appearance of high coercive force can be applied for amorphous alloys in the (Fe, Co)–heavy Ln system with ferrimagnetism.

However, the compensation temperature cannot be detected in the magnetization curve as a function of temperature for the present Nd–Fe–Al amorphous alloys containing the light Ln element as a main component. Besides, the hysteresis J–H loops and the magnetization curve allow us to conclude that the cast amorphous Nd–Fe–Al alloys possess ferrimagnetism at room temperature. Consequently, the above-described concept that the high coercive force is due to agreement of the compensation temperature with room temperature cannot be applied for the present Nd–Fe–Al amorphous alloys. Furthermore, it has been reported⁶⁶ that binary Nd–Fe amorphous alloy ribbons prepared by melt spinning exhibit ferrimagnetism and the coercive force at room temperature increases with increasing Nd content and shows a maximum value of 150 kA/m at 60%Nd. The coercive force also increases with decreasing temperature and reaches about 4000 kA/m at 4.2 K for the melt-spun amorphous Nd₉₀Fe₁₀ alloy. Similar high coercive forces at room temperature have also been reported to be obtained for the
Nd–Fe binary amorphous films prepared by sputtering. The rather high coercive forces of the melt-spun Fe–Nd binary amorphous ribbons have been explained by the ferromagnetic cluster model with large random anisotropy. That is, the amorphous Nd–Fe alloys can be regarded as an ensemble of clusters composed of Fe and Nd atoms, supposedly of the order of 100 atoms. Based on the analytical data that the coercive force increases almost linearly with increasing anisotropy energy of the cluster, the coercive force of the homogeneous magnetic system has been presumed to result from the magnetic exchange coupling interaction among the clusters with large random anisotropy. This model also implies that the increases in the number and size of the clusters consisting mainly of Fe and Nd atoms cause the increase in coercive force of the alloy. This is consistent with the present result that the coercive forces of the amorphous Nd_{90−x}Fe_{x}Al_{10} alloys show maximum values in the vicinity of 60 to 70 at% Nd and are much higher for the cast bulk amorphous alloys with more relaxed disordered atomic configurations than for the melt-spun amorphous ribbon with more unrelaxed atomic configurations. The consistency suggests that the present high coercive forces of the Nd-rich Nd–Fe–Al bulk amorphous alloys originate from the homogeneous dispersion of Nd–Fe and Nd–Fe–Al clusters with large random magnetic anisotropy which optimally develop in the cast bulk alloys with relaxed disordered atomic configurations. In addition, the coercive forces at room temperature for the bulk Nd–Fe–Al amorphous alloys are considerably higher than the highest value (about 150 kA/m) of the Nd–Fe binary amorphous ribbons. The significant enhancement of coercive force may be due to the development of the more relaxed disordered structure resulting from the much larger sample thickness as well as to the significant increase in the Curie temperature from about 480 K for the amorphous Nd_{100−x}Fe_{x} (x=40 to 55 at%) alloys to about 600 K for the amorphous Nd_{90−x}Fe_{x}Al_{10} (x=20 to 40 at%) alloys. The detailed structure analysis of the Nd–Fe–Al amorphous alloys prepared by copper mold casting and melt spinning will shed light on the relation between the relaxed disordered structure containing the Nd–Fe and Nd–Fe–Al clusters and the hard magnetic properties as well as on the effect of additional Al element on the enhancements of coercive force and Curie temperature.

V. Summary

With the aim of preparing a bulk amorphous alloy with ferromagnetism at room temperature, the structure, thermal stability and magnetic properties were examined for cast Nd–Fe–Al alloys prepared by the copper mold casting method. Besides, the amorphous formation range in melt-spun Nd–Fe–Al alloys was determined. The results obtained are summarized as follows:

1. The amorphous formation range for the melt-spun Nd–Fe–Al alloys extends over an extremely wide composition range of 0 to 90 at% Fe and 0 to 93 at% Al.

2. Cylindrical bulk amorphous samples with a length of 50 mm and diameters of 1 to 7 mm were prepared for the Nd_{90−x}Fe_{x}Al_{10} alloys containing 10 to 50 at% Fe. The cast cylindrical samples have a smooth outer surface and good metallic luster.

3. No appreciable glass transition is observed in the temperature range below the onset temperature of crystallization for the bulk Nd_{90−x}Fe_{x}Al_{10} amorphous alloys with diameters below 7 mm. The crystallization takes place through a single stage for all the alloys and the crystallized structure consists of Nd, Al, Nd and δ phases for the Nd_{90}Fe_{20}Al_{10} alloy.

4. The \( T_m \) and \( T_c \) are measured to be 863 and 778 K, respectively, for the Nd_{90}Fe_{20}Al_{10} alloy and 922 K and 784 K, respectively, for the Nd_{90}Fe_{20}Al_{10} alloy and the resulting \( T_c / T_m \) values are as high as 0.85 to 0.90. The temperature interval between \( T_m \) and \( T_c \), \( \Delta T_m = T_m - T_c \), is also as small as 85 to 138 K. The large glass-forming ability is due to the extremely high \( T_c / T_m \) and the small \( \Delta T_c \) values. This is different from the previous glassy alloys with large glass-forming ability where the wide supercooled liquid is observed before crystallization.

5. The amorphous Nd_{90−x}Fe_{x}Al_{10} bulk alloys with 20 to 30 at% Fe were found to exhibit hard magnetic properties of 0.90 to 0.122 T for \( B_r \), 262 to 277 kA/m for \( H_c \) and 18 to 19 kJ/m³ for \( (BH)_{max} \) at room temperature. The Curie temperature \( T_c \) of the Nd_{90}Fe_{20}Al_{10} alloy is measured to be about 600 K which is much higher than that (about 480 K) for the binary Nd_{100−x}Fe_{x} (x=40 to 55 at%) amorphous alloys. The significant increase in \( T_c \) by the addition of Al seems to cause a remarkable enhancement of coercive force from about 150 kA/m for the Nd–Fe binary amorphous alloys to about 280 kA/m.

6. The \( B_r \) increases to 0.128 T and the \( H_c \) keeps a constant value of 277 kA/m, respectively, for the amorphous Nd_{90}Fe_{20}Al_{10} sample annealed for 600 s at 600 K. The crystallization causes the significant decrease in the magnetic properties to 0.128 to 0.045 T for \( B_r \) and 265 to 277 kA/m for \( H_c \). The maximum hard magnetic properties are obtained in the amorphous state. The high coercive forces are presumably because the cast bulk amorphous alloys have a relaxed disordered structure which can be regarded as an ensemble of Nd–Fe and Nd–Fe–Al clusters with large random magnetic anisotropy. The achievement of the hard magnetic properties for the bulk amorphous alloys is promising for a further extension of application fields of amorphous alloys.

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