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Bulk Fe-Nd-Al amorphous alloys with hard magnetic properties

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Bulk amorphous alloys with hard magnetic properties were produced by a copper mold casting method for $Fe_{45}Nd_{45}A_{10}$, $Fe_{45}Nd_{40}Al_{15}$ and $Fe_{42.5}Nd_{42.5}Al_{15}$ alloys in a cylindrical form with diameters of 3, 3 and 4 mm, respectively. The crystallization temperature (T_x) and melting temperature (T_m) of the $Fe_{42.5}Nd_{42.5}Al_{15}$ bulk amorphous alloy are 813 and 877 K, respectively. Accordingly, the temperature interval between T_m and T_x, ΔT_m (=T_m-T_x), is as small as 64 K and the reduced crystallization temperature (T_x/T_m) is as high as 0.93. The small ΔT_m and high T_x/T_m values are presumed to be the origin for the achievement of the high amorphous-forming ability of the Fe-Nd-Al alloy. The $Fe_{45}Nd_{45}A_{10}$, $Fe_{45}Nd_{40}Al_{15}$ and $Fe_{42.5}Nd_{42.5}Al_{15}$ bulk amorphous cylinders with a diameter of 1 mm exhibit hard magnetic properties of 0.212-0.248 T for magnetization, 0.124-0.171T for remanence and 156-245kA/m for intrinsic coercive field at room temperature. The hard magnetic properties for these bulk amorphous alloys tend to transform to the soft type with decreasing diameter of the cylindrical samples. These Fe-Nd-Al bulk amorphous alloys with hard magnetic properties and high amorphous-forming ability are promising for future progress as a new type of Fe-based magnetic material.

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1. Introduction

Since the first successful synthesis of Fe-based multicomponent metallic glasses in an Fe–Al–Ga–P–C–B system by copper mold casting in 1995 [1], various kinds of bulk metallic glasses with rather good soft magnetic properties have been prepared in a number of ferrous-group alloy systems by a copper mold casting method [2]. In addition to these metallic glasses exhibiting soft magnetism, one can list Nd–Fe–Al [3, 4] and Pr–Fe–Al [5] amorphous alloys with hard magnetic properties. The peculiar features of these amorphous alloys are reported as follows: (1) high amorphous-forming ability (AFA) which enables us to fabricate the bulk amorphous alloys with a maximum diameter of 12mm [4], (2) significant change in magnetic properties with sample thicknesses, that is, the ribbon specimens with a thickness of approximately 20μm exhibit soft magnetism while the bulk specimens exhibit hard magnetism with coercive force ranging 300 to 400 kA/m at room temperature [3-5]; (3) rather high reduced crystallization temperature (T_x/T_m) of nearly 0.90 [3-5], where T_x and T_m are onset temperature of crystallization and melting temperature, respectively. Although the Nd-Fe-Al and Pr-Fe-Al amorphous alloys have high AFA to be formed in a bulk shape, the saturation magnetization of the alloys are as small as 0.1-0.3T because of the low Fe content of the alloy ranging 60-70 at.%.

With an aim to improve the disadvantage of the magnetization of the Nd-rich Nd-Fe-Al bulk amorphous alloys, we have started investigating the Fe-rich Fe-Nd-Al bulk amorphous alloys with high magnetization, intrinsic coercive force and large AFA. As a result, we have succeeded in fabricating $Fe_{50}Nd_{35}Al_{15}$ bulk amorphous alloy with a diameter of 1.5 mm by the cooper mold casting [6]. This bulk amorphous alloy exhibits good thermal stability of 106K for ΔT_m (=T_m-T_x) and 0.88 for the reduced crystallization temperature (T_x/T_m), and semi-hard magnetic properties of 0.117 T for remanence and 50 kA/m for intrinsic coercive field at the room temperature. However, the properties of this alloy are still dissatisfaction as a bulk amorphous alloy for practical usage and as a hard magnetic alloy as well.

The aim of this paper is to investigate the possibility to fabricate other Fe-rich Fe-Nd-Al bulk amorphous alloys than $Fe_{50}Nd_{35}Al_{15}$ bulk amorphous alloy and to measure their hard magnetic properties.

2. Experimental

Ternary alloys with compositions of $Fe_{45}Nd_{45}A_{10}$, $Fe_{45}Nd_{40}Al_{15}$ and $Fe_{42.5}Nd_{42.5}Al_{15}$ (at.%) were prepared by induction-melting a mixture of pure Nd, Fe and Al metals in an argon atmosphere. These alloy compositions were selected according to our previous results on the composition range in which an amorphous phase is formed in the Fe-Nd-Al ternary system by melt spinning, combined with the consideration of the composition of $Fe_{50}Nd_{35}Al_{15}$ alloy [6]. From these pre-alloyed ingots cylindrical samples with a length of about 50 mm and diameters ranging 1 to 5 mm were prepared by injection casting of the molten alloy into copper molds with cylindrical cavities. The injection pressure was fixed to 0.1 MPa. For comparison, amorphous ribbons with thickness of about 20-30 μm and width of 1mm were also produced by a single-roller melt spinning method in an argon atmosphere. The structure of the as-cast cylindrical samples was examined by X-ray diffractometry. The thermal stability was measured by differential scanning calorimetry (DSC) at a heating rate of 0.67K/s. Magnetic properties were measured with vibrating sample magnetometer (VSM) under an applied field of 1432kA/m at room temperature.

3. Results and discussion

Fig. 1(a) shows the X-ray diffraction patterns of the $Fe_{45}Nd_{45}A_{10}$ cylinders with diameters of 1-4mm, together with the data of the melt-spun ribbon specimen for comparison. The diffraction profiles of the alloys with diameter ranging 1 to 3mm show a broad pattern at around 2θ from 25 to 35°. Furthermore, no diffraction peaks resulting from a crystalline phase are seen over the entire diffraction angle. In contrast, appreciable diffraction peaks corresponding to α-Nd are discerned in the X-ray pattern of the alloy with a diameter of 4 mm. Thus, it can be concluded that the bulk amorphous alloy with the maximum diameter of 3 mm is obtained for $Fe_{45}Nd_{45}Al_{10}$ alloy. From the Figs. 1(b) and (c), it is found that bulk amorphous sample are obtained for the $Fe_{45}Nd_{40}Al_{15}$ and $Fe_{42.5}Nd_{42.5}Al_{15}$ alloys up to 3 and 4 mm, respectively.

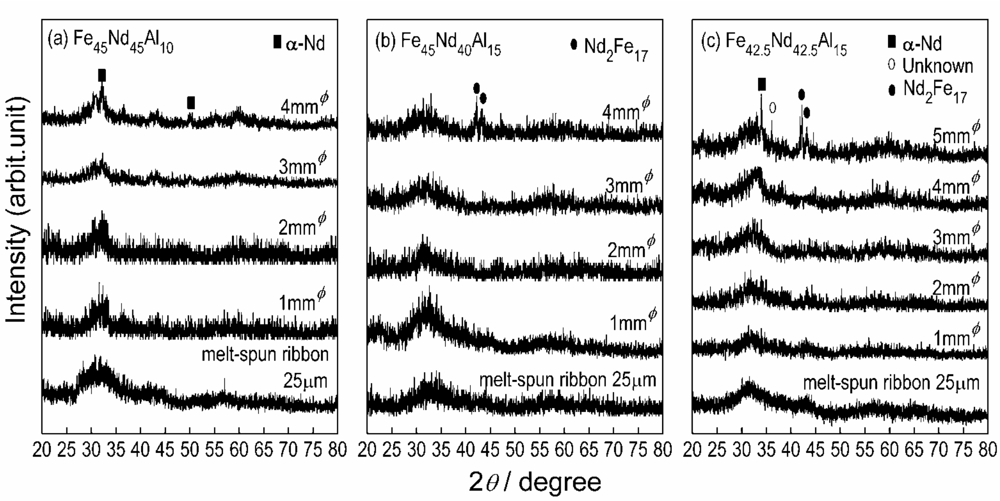

Fig. 1. The XRD patterns of (a) cast $Fe_{45}Nd_{45}Al_{10}$ cylinders with diameters of 1-4 mm (b) cast $Fe_{45}Nd_{40}Al_{15}$ cylinders with diameters of 1-4 mm and (c) cast $Fe_{42.5}Nd_{42.5}Al_{15}$ cylinders with diameters of 1-5 mm. The data of the melt-spun ribbon specimen (25 μm) are shown for comparison.

Fig. 2 shows the DSC curves of the as-cast $Fe_{45}Nd_{45}Al_{10}$, $Fe_{45}Nd_{40}Al_{15}$ and $Fe_{42.5}Nd_{42.5}Al_{15}$ cylinders with a diameter of 1mm. In Fig. 2, the T_x and T_m are crystallization and melting temperature, respectively. These alloys show a distinct exothermic reaction due to crystallization marked with T_x, followed by an endothermic reaction due to eutectic reaction marked with T_m. From Fig. 2, T_x is measured to be 805 K for $Fe_{45}Nd_{45}Al_{10}$, 790 K for $Fe_{45}Nd_{40}Al_{15}$, and 813 K for $Fe_{42.5}Nd_{42.5}Al_{15}$ alloys. On the other hand, T_m is measured to be 925 K for $Fe_{45}Nd_{45}Al_{10}$, 880 K for $Fe_{45}Nd_{40}Al_{15}$, and 877 K for $Fe_{42.5}Nd_{42.5}Al_{15}$ alloys. As it is carried out in our previous data [3-5], the AFA of the specimens was evaluated by T_x/T_m, which is the reduced crystallization temperature. For the alloys shown in Fig. 2, the T_x/T_m is calculated to be 0.87 for $Fe_{45}Nd_{45}Al_{10}$ alloy, 0.90 for $Fe_{45}Nd_{40}Al_{15}$ alloy, and 0.93 for $Fe_{42.5}Nd_{42.5}Al_{15}$ alloy. The extremely high T_x/T_m value and the small ΔT_m imply a steep increase in viscosity with decreasing temperature in the supercooled liquid of the Fe-Nd-Al liquid. Thus, Fe-Nd-Al supercooled liquid is considered to have the high degree of the dense random packing density in the supercooled liquid by satisfying the factors: (1) multicomponent elements, (2) significant difference in atomic size ratios, and (3) large and negative heat of mixing. These factors are frequently used for the development of bulk metallic glasses with high glass-forming ability.

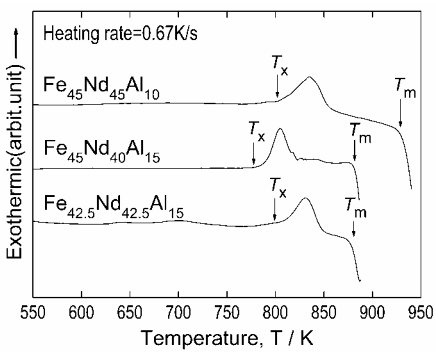

Fig. 2. DSC curves of the as cast $Fe_{45}Nd_{45}Al_{10}$, $Fe_{45}Nd_{40}Al_{15}$ and $Fe_{42.5}Nd_{42.5}Al_{15}$ cylinders with a diameter of 1 mm. The T_x and T_m are crystallization and melting temperature, respectively.

Fig. 3 shows the change in the hysteresis *J–H* loops for the as-cast amorphous $Fe_{45}Nd_{45}Al_{10}$ $Fe_{45}Nd_{40}Al_{15}$ and $Fe_{42.5}Nd_{42.5}Al_{15}$ cylinders. The data of the melt-spun amorphous ribbons with a thickness of about 25 μm are shown for comparison. From the hysteresis *J-H* loops, the remanence (B_r), Intrinsic coercive force ($_iH_c$) and magnetization under an applied field of 1432 kA/m (J_{1432}) at room temperature are summarize in the Table 1. It is noted that the magnetic properties of the cast cylinders significantly depend on the sample diameter. For instance, when the sample thickness decreases from 1 mm to 25 μm, B_r for $Fe_{45}Nd_{45}Al_{10}$ $Fe_{45}Nd_{40}Al_{15}$ and $Fe_{42.5}Nd_{42.5}Al_{15}$ alloys decrease from 0.171, 0.124 and 0.137 T to 0.072, 0.086 and 0.099 T, respectively. In a similar way, the $_iH_c$ of these three alloys decrease from 245, 156 and 163 kA/m to 8.5, 9 and 10 kA/m, respectively. Thus, the soft to hard magnetic transition between ribbons and bulk specimens has been observed in the bulk Fe-Nd-Al amorphous alloys.

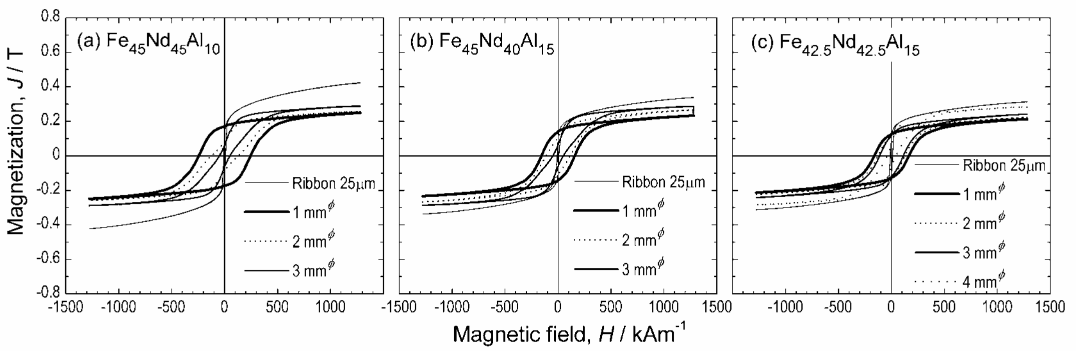

Fig. 3. Hysteresis J-H loops of (a) cast $Fe_{45}Nd_{45}Al_{10}$ cylinders with diameters of 1-3 mm (b) cast $Fe_{45}Nd_{40}Al_{15}$ cylinders with diameters of 1-3 mm and (c) cast $Fe_{42.5}Nd_{42.5}Al_{15}$ cylinders with diameters of 1-4 mm. The data of the melt-spun ribbon specimen (25 μm) are shown for comparison.

This phenomenon is also reported in the bulk amorphous Nd-Fe-Al systems [7]. Besides, the *J-H* loop curves for the cast cylinders with different diameters are recognized as hard–type, and are completely different from that of the ribbon samples exhibiting soft magnetism. The hard magnetic properties of the as-cast cylinders are presumably due to the formation of an amorphous phase with much relaxed disordered structure as compared with that for the ribbon samples, which is caused by the lower cooling rate of the copper mold casting method than the single-roller melt spinning method. The presumption is also supported by the previous result [8] in which the total enthalpy for structural relaxation of a $Zr_{60}Al_{10}Co_3Ni_9Cu_{18}$ amorphous alloy decreases from 683 J/mol of the melt-spun ribbon to 147 J/mol of the cast cylinder of 5 mm$^\phi$ in diameter and 133 J/mol of the cast cylinder of 7 mm$^\phi$ in diameter. The lower relaxation enthalpy means formation of short-range ordered structure in the cylinder samples. For Nd-Fe-Al bulk amorphous cylinders, the precipitation of crystalline phases α-Nd and Nd_2Fe_{17} can reduce the hard magnetic properties [9]. Thus, it is clear that the cylinders of these bulk Fe-Nd-Al amorphous with diameters of 1mm exhibit good hard magnetic properties due to random magnetic anisotropy [10,11] caused by the development of short-range Nd-Fe and Nd-Fe-Al atomic pairs. On the contrary, the hysteresis curves of the ribbon specimen show soft magnetic properties, as can be seen in Fig. 3 and Table 1. Here, it is important to point out that there is clear tendency for B_r and $_iH_c$ to decrease with increasing diameter of cylinders in these bulk Fe-Nd-Al amorphous alloys. For instance, the B_r and $_iH_c$ value decrease from 0.124 T and 163 kA/m to 0.059 T and 42 kA/m for the $Fe_{42.5}Nd_{42.5}Al_{15}$ alloy when the diameter of cylinder increases from 1 to 4 mm.

Table 1. The magnetic properties of melt-spun ribbons and as-cast cylinders of $Fe_{45}Nd_{45}Al_{10}$, $Fe_{45}Nd_{40}Al_{15}$ and $Fe_{42.5}Nd_{42.5}Al_{15}$ amorphous alloys.

Alloy	Shape		J_{1432} / T	B_r / T	$_iH_c$ / kAm^{-1}
$Fe_{45}Nd_{45}Al_{10}$	Ribbon	25 μm	0.311	0.072	8.5
	Cylinders	1 mm$^{\phi}$	0.248	0.171	245
		2 mm$^{\phi}$	0.257	0.084	126
		3 mm$^{\phi}$	0.288	0.061	50
$Fe_{45}Nd_{40}Al_{15}$	Ribbon	25 μm	0.338	0.086	9
	Cylinders	1 mm$^{\phi}$	0.232	0.124	156
		2 mm$^{\phi}$	0.267	0.104	114
		3 mm$^{\phi}$	0.289	0.060	47
$Fe_{42.5}Nd_{42.5}Al_{15}$	Ribbon	25 μm	0.312	0.099	10
	Cylinders	1 mm$^{\phi}$	0.212	0.137	163
		2 mm$^{\phi}$	0.223	0.117	142
		3 mm$^{\phi}$	0.241	0.116	128
		4 mm$^{\phi}$	0.283	0.059	42

4. Conclusions

With the aim of fabricating new Fe-rich Fe-Nd-Al bulk amorphous alloys with higher amorphous-forming ability and better hard magnetic properties than those of the bulk amorphous $Fe_{50}Nd_{35}Al_{15}$ alloy. The structure, thermal stability and magnetic properties were investigated for cast $Fe_{45}Nd_{45}A_{10}$, $Fe_{45}Nd_{40}Al_{15}$ and $Fe_{42.5}Nd_{42.5}Al_{15}$ (at. %) alloys. The results obtained in the present study are summarized as follows:

(1) The X-ray diffraction results show that the maximum diameters of $Fe_{45}Nd_{45}Al_{10}$, $Fe_{45}Nd_{40}Al_{15}$ and $Fe_{42.5}Nd_{42.5}Al_{15}$ bulk amorphous alloy rods are 3, 3 and 4 mm, respectively.

(2) The reduced crystallization temperature (T_x/T_m) of these alloys are about 0.87-0.93, where T_x and T_m are crystallization and melt temperature, respectively, and ΔT_m (=T_m–T_x) are about 63-120 K, The large amorphous-forming ability is due to the extremely high T_x/T_m and small ΔT_m.

(3) The $Fe_{45}Nd_{45}Al_{10}$, $Fe_{45}Nd_{40}Al_{15}$ and $Fe_{42.5}Nd_{42.5}Al_{15}$ bulk amorphous cylinders with a diameter of 1mm exhibit hard magnetic properties: 0.212-0.248T for magnetization, 0.124-0-171T for remanence and 156-245kA/m for intrinsic coercive field.

(4) The transition from soft to hard magnetism between ribbon and bulk specimens takes place in Fe-rich Fe-Nd-Al amorphous as well as Nd-rich amorphous alloys.

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