Journal of Magnetics 3(4), 116-119 (1998)

A Study on the Magnetic Properties of Melt-Spun (Fe,T)-Nd-C Alloys (T=Al, Ti, Co, Ni)

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(Received 17 October 1998)

Influence of small additions ($\leq$2.0 at.%) of Al, Ti, Co, and Ni on the microstructural development and the magnetic properties of melt-spun Fe-Nd-C alloys was investigated. Addition of these elements tended to stabilize the crystallization of as-spun ribbons. Especially, Al and Ti preferred to stabilize $Fe_{17}Nd_2C_x$. The average grain size of $Fe_{14}Nd_2C$ (0.1~0.3 μm), obtained by a proper annealing, in the ribbon treated with 0.5 at.% additive was much smaller than that of additive-free ribbons, which would be the major source of large increase in coercivity. Among the additives, Ni was very effective to increase the coercivity whereas Co had beneficial effect on T_c. By adding 0.5 at.% Ni, intrinsic coercivities of more than 1.4 T, 40~50 % higher than that (~1.0 T) of additive-free ribbons, can be obtained after annealing at 750~800 °C.

1. Introduction

An iron-rich Fe-Nd-C alloy whose matrix is hard magnetic $Fe_{14}Nd_2C$ is one of good candidates for future magnets because the $Fe_{14}Nd_2C$ has the same structure as $Fe_{14}Nd_2B$ [1, 2] which is the matrix of high-performance Fe-Nd-B magnets and its intrinsic magnetic properties are similar to those of $Fe_{14}Nd_2B$ [3]. Unlike $Fe_{14}Nd_2B$, however, $Fe_{14}Nd_2C$ does not crystallize from the melt but is only transformed from $Fe_{17}Nd_2C_x$ and/or Fe through solid-state transformations in a cast alloy [2, 4]. It means that, like Alnico, Fe-Nd-C magnets can be made simply by casting and annealing. Unfortunately, it was not easy to obtain high-coercive cast magnets mainly due to extremely sluggish formation of $Fe_{14}Nd_2C$ [2, 4], and the fabrication of Fe-Nd-C magnets by liquid-phase sintering was also not successful due to the lack of a liquid phase in the temperature range where $Fe_{14}Nd_2C$ can exist [5]. Thus, for Fe-Nd-C alloys to be practical, it is prerequisite to increase the formation rate of $Fe_{14}Nd_2C$ by other means. It has been shown that fabrication of Fe-Nd-C alloys by melt spinning followed by a short annealing is an effective way to get not only the hard magnetic $Fe_{14}Nd_2C$ but also a relatively high coercivity (~1.0 T) [6, 7]. That is, this process enables us to utilize Fe-Nd-C alloys for making bonded magnets. However, comparing with magnetic properties of commercially available boride counterpart and considering possible reduction of coercivity by pulverization of the alloys [8], hard magnetic properties (especially, ${}_iH_c$) of melt-spun Fe-Nd-C alloys need to be improved for practical use. Therefore, as a part of an effort to improve the magnetic properties of melt-spun Fe-Nd-C, effect of small additions ($\leq$2.0 at.%) of Al, Ti, Co, and Ni on the microstructural development and the magnetic properties of the alloys was investigated in this study.

2. Experimental

The alloys of $Fe_{77-x}T_xNd_{15}C_8$ (T=Al, Ti, Co, and Ni, x= 0.5~2.0) were prepared by arc melting in high-purity argon using elements of more than 99.9% purity. They were crushed into several pieces and remelted in a quartz tube which has an orifice of 0.5 mm diameter. Then melt-spun ribbons were obtained by ejecting the molten alloy through the orifice onto a rotating copper wheel. Melt spinning was done at the wheel speed of 25 m/s. The ribbons were approximately 1.5~2 mm wide and 20~30 μm thick. They were annealed in evacuated and sealed quartz capsules at the specified condition, then quenched the capsules in water. Cu Kα X-ray diffraction (Mac Science M18XHF) and SEM observation (Hitachi S-2700) were performed on both as-spun and annealed ribbons. The magnetic properties were measured with a VSM (Lakeshore 7300) with the maximum applied field of 17 kOe.

3. Results and Discussion

Fig. 1 shows the x-ray diffraction patterns obtained from as-spun $Fe_{76.5}T_{0.5}Nd_{15}C_8$ (T=Al, Ti, Co, and Ni) ribbons. As shown in the figure, soft magnetic rhombohedral $Fe_{17}Nd_2C_x$ crystallizes from the melt as a primary phase in all cases, impling that hard magnetic $Fe_{14}Nd_2C$ has to be

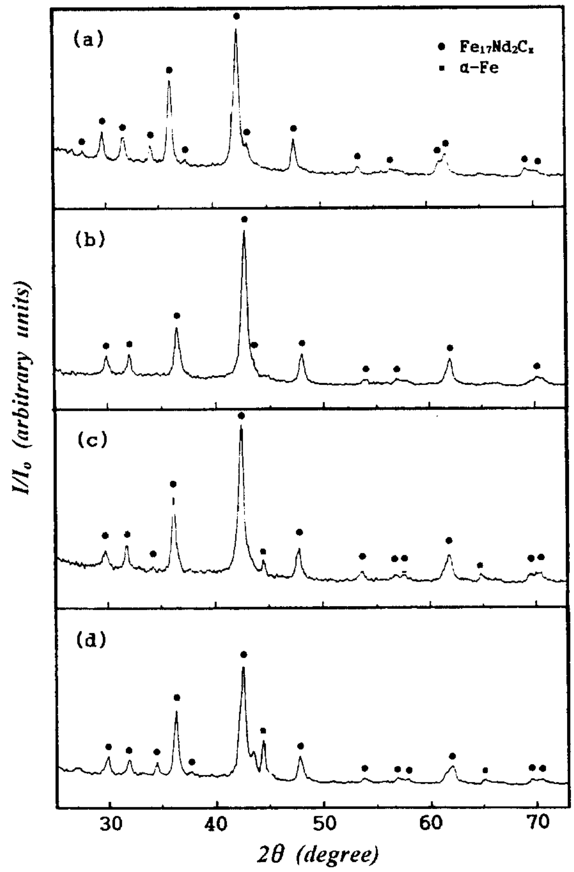


Fig. 1. X-ray (Cu Kα) diffraction patterns of as-spun $Fe_{76.5}T_{0.5}$-$Nd_{15}C_8$ ribbons spun at 25 m/s: (a) T=Al, (b) T=Ti, (c) T=Co, and (d) T=Ni.

formed by an annealing regardless of the kind of additive elements. The as-spun additive-free Fe-Nd-C ribbons were mainly composed of α-Fe, $Fe_{17}Nd_2C_x$ and an amorphous phase, and their qualitative ratio varied depending on the cooling rates [7]. Consequently, the ribbons spun at 20 m/s consisted of the primary $Fe_{17}Nd_2C_x$ and the secondary α-Fe together with some amorphous phase while the ribbons spun at 30 m/s were mostly amorphous [7]. From this fact, the occurrence of $Fe_{17}Nd_2C_x$ as a primary phase in the as-spun ribbons spun at 25 m/s is fully forecasted. However, as shown in the figure, there is no indication of amorphous phase which should be characterized by a broad diffraction feature around 2θ=30~50°. It tells us that, likewise to the case of small Cu additions [9], small additions of Al, Ti, Co, or Ni stabilize the crystallization of as-spun alloys. This crystallization tends to be more stabilized as the amount of additives increases. It is interesting that, as revealed in Fig. 1a and 1b, small Al or Ti additions totally suppress the crystallization of α-Fe but stabilize $Fe_{17}Nd_2C_x$, while small Cu additions prefer to stabilize α-Fe [9]. Suppression of α-Fe by Co or Ni addition is less severe than that of Al or Ti addition.

In any case, as in additive-free alloys [7], hard magnetic $Fe_{14}Nd_2C$ is not formed in as-spun state but transformed from the as-spun precursors by a short heat treatment.

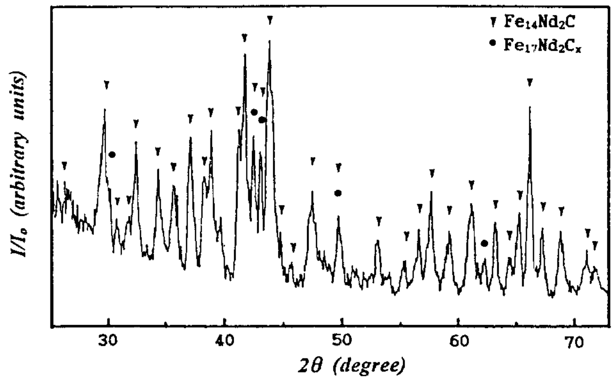


Fig. 2. X-ray (Cu Kα) diffraction pattern of $Fe_{76.5}Co_{0.5}Nd_{15}C_8$ ribbons annealed 15 min. at 700 °C.

DTA results indicate that the temperature range in which $Fe_{14}Nd_2C$ can be formed remains virtually as same as that of additive-free alloys. An example of diffraction patterns obtained from the annealed ribbons is shown in Fig. 2. As shown in the figure, $Fe_{14}Nd_2C$ became the major phase after annealing 15 min. at 700 °C. The rapid formation of $Fe_{14}Nd_2C$ in melt-spun alloys by such short annealing is mainly due to the structural instability of the as-spun alloys which lowers the degree of order of the crystalline phases and accelerates the solid state transformation by thermal energy [6]. But residual $Fe_{17}Nd_2C_x$ which was not eliminated completely after 15 min. at 700 °C coexists with $Fe_{14}Nd_2C$, indicating that proper combinations of annealing time and temperature are important for producing fully developed $Fe_{14}Nd_2C$. They also determine magnetic properties of the annealed ribbons, which will be discussed later.

Typical microstructures observed in both as-spun and annealed ribbons are shown in Fig. 3. As shown in Fig. 3a~3d, as-spun ribbons treated with 0.5 at.% of Al, Ti, Co, or Ni and subsequently spun at 25 m/s are filled with very fine crystallites, resulting in XRD patterns in Fig. 1. It was found that the average size of the crystallites tended to increase as the amount of additive in the as-spun ribbons increased. After annealing at proper conditions, the ribbons treated with the same amount of additives are filled with tiny spherical grains of $Fe_{14}Nd_2C$ as shown in Fig. 3e~3h. The average grain size is 0.1~0.3 μm which is much smaller than that (0.5~0.7 μm) of additive-free ribbons spun at 20 m/s and subsequently annealed 10 min. at 750 °C [7]. It is close to the single domain size of the hard magnetic phase [10, 11], and the alloys possessing $Fe_{14}Nd_2C$ grains of this grain size yield higher coercivities (See Table 1).

As shown in Fig. 4, $Fe_{14}Nd_2C$ grains in annealed ribbons tend to grow up as the amount of additive in the ribbons increases, and the grain growth of $Fe_{14}Nd_2C$ is more obvious in the ribbons annealed at higher temperature. Fig. 4a shows a typical configuration of $Fe_{14}Nd_2C$ in the ribbons treated with 2.0 at.% of Al, Ti, or Co and annealed 15 min. at 800 °C. Particularly, as shown in Fig.

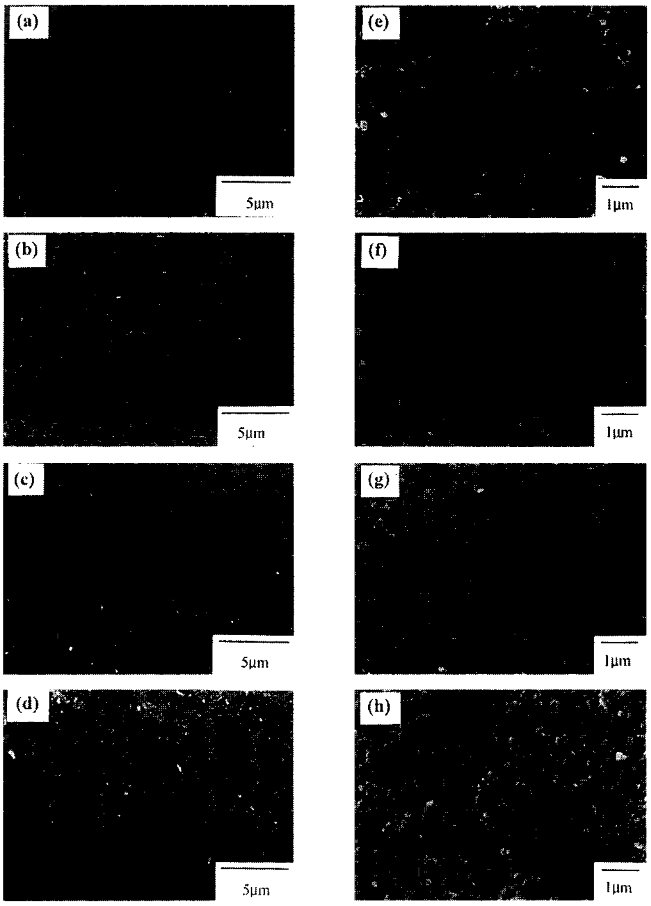
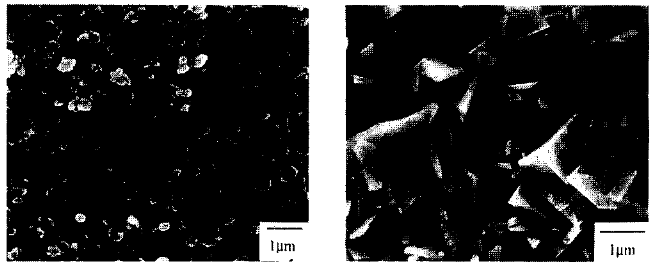


Fig. 3. Fracture surfaces of $Fe_{76.5}T_{0.5}Nd_{15}C_8$ ribbons. From (a) to (d), as-spun ribbons for (a) T=Al, (b) T=Ti, (c) T=Co, and (d) T=Ni. From (e) to (h), annealed ribbons for (e) T=Al, (f) T=Ti, (g) T=Co, and (h) T=Ni. Annealing was done for 15 min. at 750 °C.



(a) (b)

Fig. 4. SEM micrographs of the fracture surface of (a) $Fe_{75}Al_{2.0}Nd_{15}C_8$ annealed 15 min. at 800 °C and (b) $Fe_{75}Ni_{2.0}Nd_{15}C_8$ annealed 15 min. at 850 °C.

4b, Ni-treated ribbons reveal remarkable grain growth after annealing at higher temperature, i.e., 850 °C. Such an abnormal grain growth was also found in Cu-treated ribbons [9]. It was found that Cu was highly concentrated in the Nd-rich grain boundary phase rather than the matrix of $Fe_{14}Nd_2C$, providing a high interfacial mobility that was responsible for the rapid growth of $Fe_{14}Nd_2C$ [9]. However, it is not clear why small nickel additions also cause abnormal grain growth of $Fe_{14}Nd_2C$. EDX results show that Ni is not concentrated in the grain boundary phase whose amount is much less than that of Cu-treated one but distributed more uniformly throughout the microstructure. Nevertheless, high interfacial mobility should be also responsible for the grain growth.

The intrinsic coercivities measured from annealed ribbons are listed in Table 1. Regardless of the kind of additives, in general, the ribbons treated with 0.5 at.% additive yield higher coercivities. It is believed to be due to grain refinement, as explained earlier, and the decrease of coercivity with the increase of the amount of additive is mainly due to grain growth. The high coercivity of melt-spun Fe-Nd-C alloys, as in boride counterpart, is thought to be originated from domain wall pinning at grain boundaries [9-12]. Thus, average grain size is critical, and it is desirable to get uniform grains with the size close to the single domain size or less for obtaining high $_iH_c$. In addition, it is prerequisite to remove residual soft magnetic α-Fe and $Fe_{17}Nd_2C_x$ showing easy-plane anisotropy as much as possible since the grain size alone does not determine the whole mechanism of the coercivity but a nucleation process also controls magnetization reversal [13]. Therefore, choosing an optimum annealing condition that can provide fully developed $Fe_{14}Nd_2C$ with the right grain size and distribution is important for obtaining high coercivity in the melt-spun Fe-Nd-C alloys. Within the given annealing times, annealing temperature around 750 °C seems to be adequate for obtaining high coercivity.

Table 1. Intrinsic coercivities ($_iH_c$) in $Fe_{77-x}T_xNd_{15}C_8$ (T=Al, Ti, Co, and Ni, x=0.5~2.0) ribbons melt spun at 25 m/s and subsequently annealed at various condition

Heat treatment		$_iH_c$ (kOe)															
		M=Al				M=Ti				M=Co				M=Ni			
Temp. (°C)	Time (min.)	x=0.5	x=1.0	x=1.5	x=2.0	x=0.5	x=1.0	x=1.5	x=2.0	x=0.5	x=1.0	x=1.5	x=2.0	x=0.5	x=1.0	x=1.5	x=2.0
700	15	13.0	12.4	10.0	9.1	12.6	10.0	10.1	9.8	11.3	10.9	9.0	8.6	13.8	11.6	10.6	8.9
	10	12.6	11.7	10.6	9.8	11.1	11.0	9.2	8.2	11.8	11.0	9.4	8.0	13.2	12.3	11.7	9.2
750	15	12.9	12.6	11.5	11.1	12.7	11.3	10.4	11.2	12.6	11.4	10.5	10.1	14.3	12.5	12.7	9.3
	20	12.4	12.4	11.5	10.9	12.0	10.7	9.8	9.1	11.7	10.8	10.0	9.3	14.7	11.8	10.9	8.7
800	15	11.8	11.5	10.7	10.5	10.0	10.6	9.4	8.3	10.5	9.2	10.0	8.7	14.1	12.3	9.5	7.8
850	15	8.9	8.5	8.1	7.8	10.5	10.2	8.1	6.5	8.6	8.5	7.3	6.8	9.8	8.0	6.5	5.7

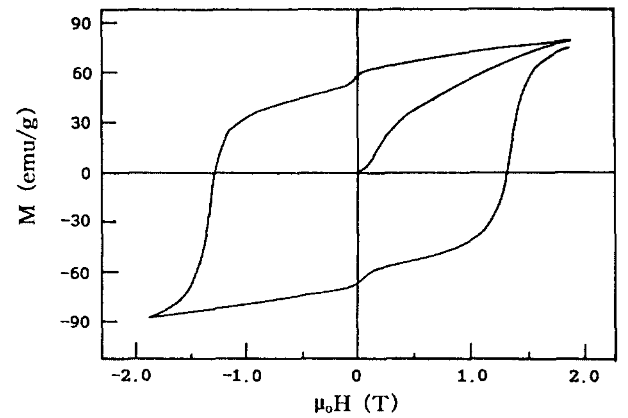


Fig. 5. Magnetization curve of a thermally demagnetized $Fe_{76.5}Al_{0.5}Nd_{15}C_8$ spun at 25 m/s and subsequently annealed 15 min. at 750 °C.

From EDX results, it is found that Al and Ti are mostly located in the grain boundary phase whereas Co is mostly distributed in the matrix replacing Fe of $Fe_{14}Nd_2C$. As mentioned before, Ni is distributed not only in the grain boundary phase but also in the matrix phase. That is, small Al, Ti, or Ni additions are believed to bring about some grain boundary modification during annealing, which may be also responsible for the increase of coercivity. Meanwhile, small Co additions seem to have more beneficial effect on T_c rather than ${}_iH_c$. In fact, the Curie temperature of $Fe_{14}Nd_2C$ in the annealed $Fe_{76.5}Co_{0.5}Nd_{15}C_8$ ribbons is 305 °C, about 15 °C higher than that (~290 °C) of additive-free ribbons, while the Curie temperature of $Fe_{14}Nd_2C$ in Al or Ti-treated ribbons are almost as same as that of additive-free ribbons. The increase in T_c of melt-spun Fe-Nd-C ribbons by Co addition is also reported in elsewhere [11]. But Co addition more than 4 at.% results in rapid decrease in coercivity [11]. Among the additives, Ni increases the coercivity more effectively. By adding just 0.5 at.% Ni, as shown in Table 1, the intrinsic coercivity which is 40~50 % higher than that (~1.0 T) of additive-free ribbons can be easily obtained. This coercivity is comparable to that (~1.5 T) of commercially available melt-spun Fe-Nd-B [10]. Furthermore, Ni also contributes to increase the Curie temperature of $Fe_{14}Nd_2C$ (~300 °C with 0.5 at.% Ni addition). It tells us that small nickel additions are very effective not only to increase the coercivity of melt-spun alloys but also to improve the thermal stability of $Fe_{14}Nd_2C$ in the alloys.

Typical hysteresis loop of high-coercive ribbons is shown in Fig. 5. Constriction of the loop at low magnetic field due to the presence of residual soft magnetic α-Fe and/or $Fe_{17}Nd_2C_x$ is clearly seen in the figure. Such constriction usually results in a lower remanence. In general, the remanence measured from the loops with minor constriction tends to decrease monotonously as the amount of Al, Ti, or Ni addition increases. The additive which has beneficial effect on the increase of *Br* is found to be Co only. The remanence as high as 70.2 emu/g, obviously larger than that (~62.5 emu/g) of additive-free ribbons, can be obtained from the ribbons treated with 0.5 at.% Co and annealed at 750 °C for 10 min. Further addition of Co, however, also results in the decrease of B_r. The ribbons exhibiting the highest coercivity with the addition of 0.5 at.% Ni yields the remanence of 61.3 emu/g. In any case, the degree of constriction of a hysteresis loop depends on the amount of residual soft magnetic phases, and they can be eliminated completely without loosing coercivity by careful control of annealing time and temperature.

4. Conclusions

Small additions of Al, Ti, Co, and Ni tend to stabilize the crystallization of as-spun ribbons. The average grain size of $Fe_{14}Nd_2C$, obtained by a proper annealing, in the ribbons treated with 0.5 at.% additive is much smaller (0.1~0.3 μm) than that of additive-free ribbons. It is close to the single domain size of the hard magnetic phase and believed to be the major source of large increase in coercivity. Among the additives, Ni seems to be very effective to increase the coercivity. By adding 0.5 at.% Ni, intrinsic coercivities of more than 1.4 T, 40~50 % higher than that (~1.0 T) of additive-free ribbons, can be obtained after annealing at 750~800 °C. Small amount of Ni addition is also found to contribute to the increase of thermal stability of $Fe_{14}Nd_2C$.

Acknowledgement

Support by Non Directed Research Fund, Korea Research Foundation, 1996 is gratefully acknowledged.

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