Journal of Korean Magnetics Society, Volume 5, Number 5, October 1995

EFFECT OF BINARY ADDITIVES ON THE MAGNETIC PROPERTIES OF MECHANICALLY GROUND Fe-Nd-B MAGNETS

T.S. Jang[a], J.D. Park[b*], and W.Y. Jeung[b]

[a]Dept. of Metallurgical Engineering, Sun Moon University, Choongnam, Korea,
[b]Division of Materials, KIST, Seoul, Korea

Abstract**-----** The magnetic properties of the hot-pressed magnets made from the Fe-Nd-B alloys, mechanically ground and subsequently blended with binary additives such as Al-Cu and Ag-Zn before hot pressing, were investigated. The coercivities of the magnets increased as the concentration of Al-Cu increased up to 1 wt. %, or up to 3 wt. % in the case of Ag-Zn. At higher concentrations the coercivities decreased markedly. The maximum gain in coercivity by the addition was about 20 %. Typical values of ${}_iH_c$ and B_r of a hot-pressed magnet containing 1 wt. % Al-Cu were 18 kOe and 7 kG, respectively. It was found that Cu, Ag, and Zn, which diffused into the magnet during hot pressing, were mostly concentrated on the Nd-rich grain boundary phase whereas Al was present not only in the grain boundary region but also in the matrix grains.

I .INTRODUCTION

To make bonded or fully dense Fe-Nd-B magnets crushed melt-spun Fe-Nd-B ribbons are commonly used as the starting material. An alternative way to produce powders for making these magnets can be mechanical grinding and subsequent heat treatment of a cast Fe-Nd-B alloy. Probably due to the severe mechanical damage on hard magnetic grains and their boundaries [1], however, the magnetic properties, especially the coercivities, of a magnet made from the mechanically ground Fe-Nd-B are usually lower than those of the melt-spun counterpart. Thus, to improve the coercivities, it may be necessary to introduce small amount of other elements which may affect the grain boundary phase into the mechanically ground Fe-Nd-B.

In general, additives to modify the magnetic properties of $Fe_{14}Nd_2B$ type magnets are mixed into the Fe-Nd-B alloy at the initial melting and casting of the ingot. Previous work, however, showed that small amounts of powdered elements (especially, Zn) added into the crushed Fe-Nd-B ribbons just before hot working, so that they diffused into the ribbons during hot working, enhanced the coercivities of die-upset magnets [2,3]. The enhanced coercivities of the magnets are thought to be attributed to modification of the grain-boundary phase by the Zn (or other additives) diffused along the Nd-rich grain-boundary phase, which is molten or nearly molten at hot working temperature. This diffusion-alloying process is also effective to increase the coercivity of Zn-bonded $Fe_{17}Sm_2N_x$ magnets [4]. So far the diffusion alloying has been made only with pure elements, but the alloying with combined elements has not been tried. In the present work we have mixed metal powders of Al-Cu and Ag-Zn alloys with the mechanically ground Fe-Nd-B powder prior to hot pressing, and investigated the influence of these binary additives on the magnetic properties of the hot-pressed magnets.

II .EXPERIMENT

Ingots of $Fe_{78}Nd_{16}B_6$ were prepared by vacuum induction melting. The purity of the constituent elements was 99.9 % for Fe and Nd, and 99.5 % for B. Under a high-purity Ar atmosphere the ingots were crushed into particles under 35 mesh in a disc mill. Then, the mechanical grinding was carried out in a planetary ball mill for 12 hours after the particles were sealed in a cylindrical stainless-steel ball under the Ar atmosphere. Instead of using combined elemental powders for addition, ingots of intermetallic $Al_{67.5}Cu_{32.5}$ and $Az_{42}Zn_{58}$ (in at. %) were also prepared by vacuum induction melting the high-purity elements (Al, Cu, Ag, and Zn were all 99.9 %). These ingots were then pulverized by using a disc mill and a ball mill as described above.

Before hot pressing, the mechanically ground Fe-Nd-B and binary additives were blended for one hour in a ball mill. The binary additives were measured by weight such that a mixture would have 1 wt. % Al-Cu (or Ag-Zn) powder and 99 wt. %

* Current address: Dept. of Computer Aided Mechanical Engineering, Palbong Technical Institute, Inchon, Korea

Fe-Nd-B, in concentrations ranging from 1 to 10 wt. %. Hot pressing of a mixture was performed in a graphite die with the bore size of 8 mm. The mixture was heated to 750 °C in vacuum and pressed isostatically at 1 ton/cm^2.

Magnetic properties (B_r and $_iH_c$) of a hot-pressed magnet magnetized at 25 kOe were measured by a DC-flux meter. X-ray diffraction was performed for phase identification, and SEM and AES were employed for microstructural investigation and chemical analyses.

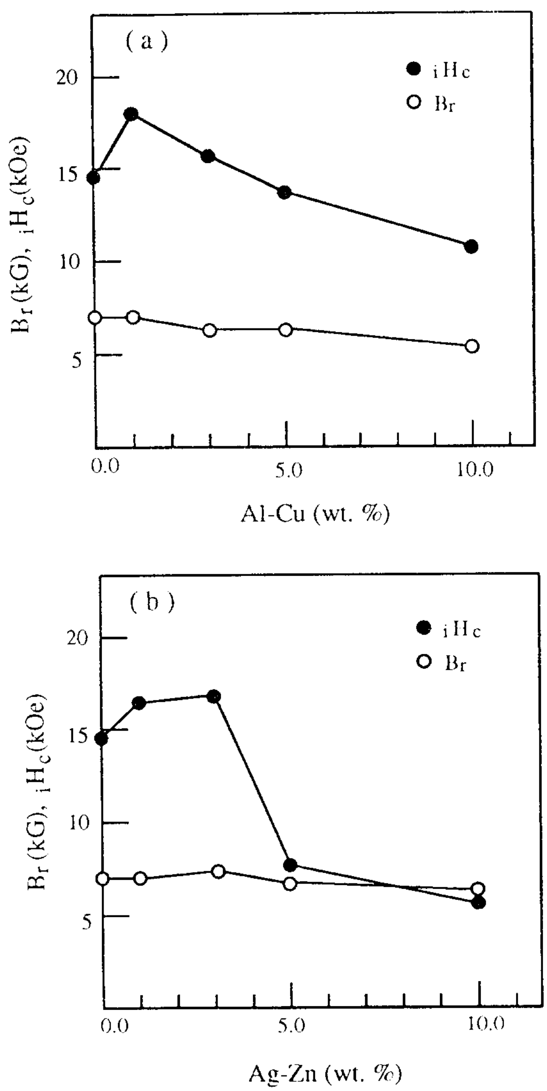

Fig. 1 Dependence of $_iH_c$ and B_r on (a) Al-Cu and (b) Ag-Zn content in hot-pressed magnets with the starting composition of $Fe_{78}Nd_{16}B_6$.

III. RESULTS AND DISCUSSION

Fig. 1 shows the variation of $_iH_c$ and B_r of the hot-pressed magnets along with the increase of the amount of binary additives. As shown in the figure, the coercivities of the magnets increase as the concentration of Al-Cu increases up to 1 wt. %, or up to 3 wt. % in the case of Ag-Zn. At higher concentrations the coercivities decrease markedly,

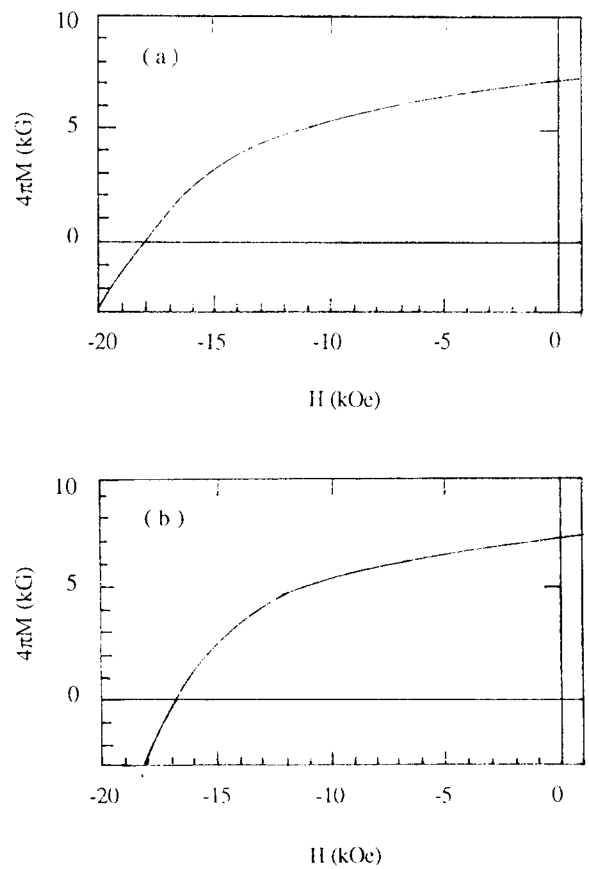

Fig. 2 Demagnetization curves for hot-pressed magnets containing (a) 1.0 wt. % Al-Cu and (b) 3.0 wt. % Ag-Zn.

and above 5 wt. % for both cases the coercivities drop below that of the additive-free magnet. The magnets containing high Ag-Zn exhibit severer deterioration of the coercivities than their counterparts containing high Al-Cu. The maximum gain in coercivity by the addition, in the case of Al-Cu, is about 20 %. The addition of Ag-Zn yields lower gain than that of Al-Cu. The variation of the remanence is less sensitive to the addition although the remanences of the magnets decrease monotonically with increasing the concentrations of the additives in the magnets. The demagnetization curves for the hot-pressed magnets containing 1 wt. % Al-Cu and 3 wt. % Ag-Zn are shown in Fig. 2. Typical values of ${}_iH_c$ and B_r of a hot-pressed magnet containing 1 wt. % Al-Cu are 18 kOe and 7 kG, respectively, which are almost equivalent to those of the magnet made from melt-spun precursors containing 0.5 wt. % Zn [3]. Comparing with the magnets made from the melt-spun precursors, lower values of B_r frequently encountered in the magnets made from the mechanically ground precursors are primarily attributed to the stoichiometry of the precursors, in

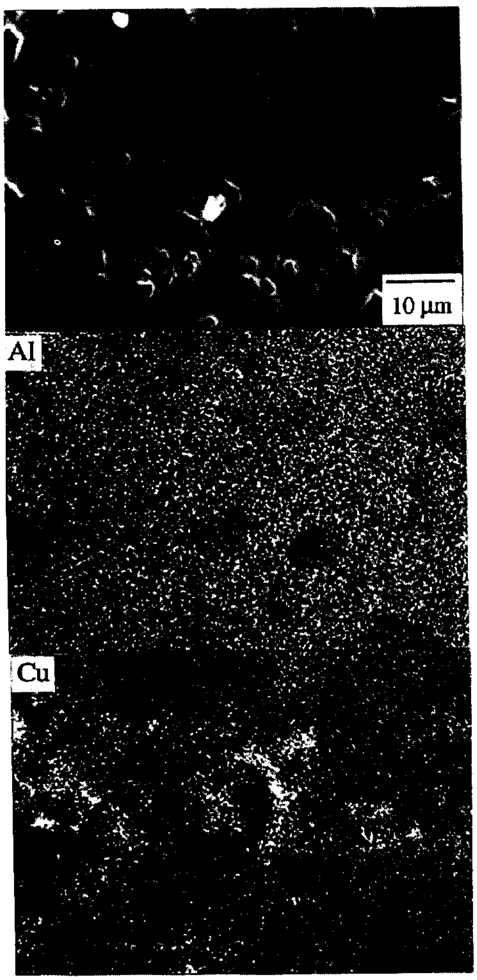

Fig. 3 Distribution of Al and Cu in a hot-pressed magnet containing 5.0 wt. % Al-Cu: (a) SEM micrograph, (b) corresponding distribution of Al, and (c) corresponding distribution of Cu.

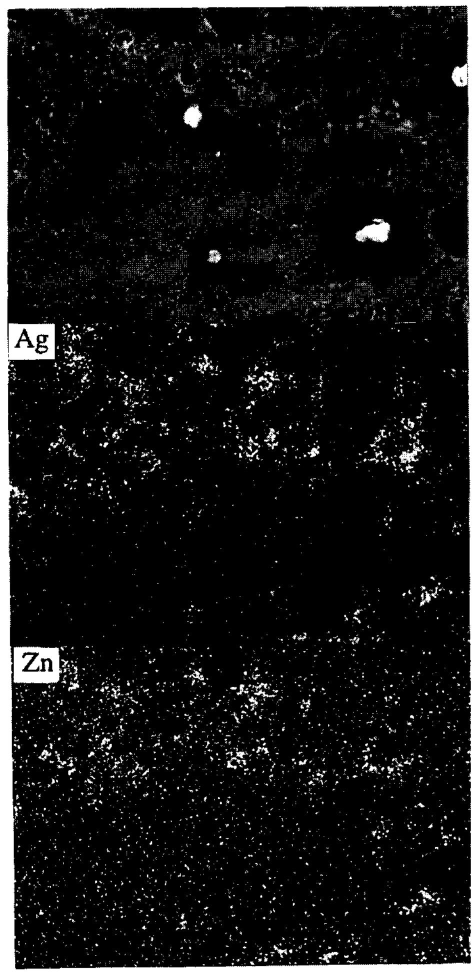

Fig. 4 Distribution of Ag and Zn in a hot-pressed magnet containing 5.0 wt. % Ag-Zn: (a) SEM micrograph, (b) corresponding distribution of Ag, and (c) corresponding distribution of Zn.

which more Fe is contained in the melt-spun precursors whose composition is closer to the stoichiometric $Fe_{14}Nd_2B$. The squareness of both curves in Fig. 2 may be improved by die upsetting the hot-pressed precursors as in the case of melt-spun magnets [2,3].

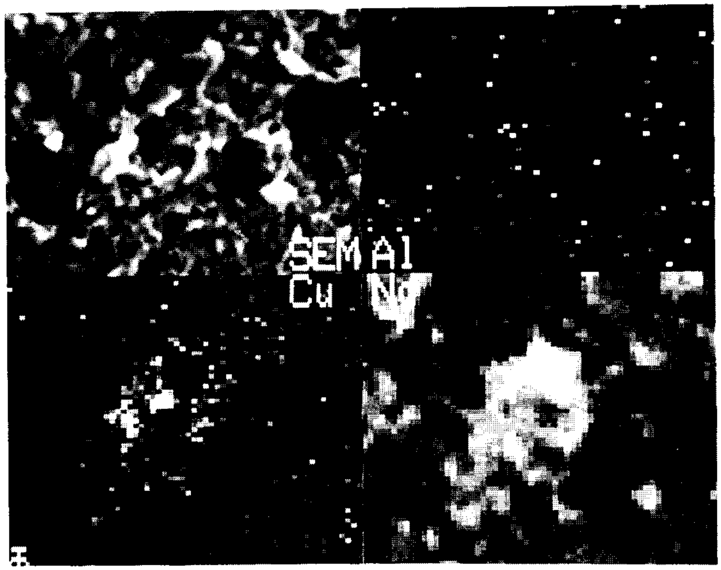

Fig. 5 Fractured surface of a hot-pressed magnet containing 3.0 wt. % Al-Cu and the corresponding maps of Al, Cu, and Nd.

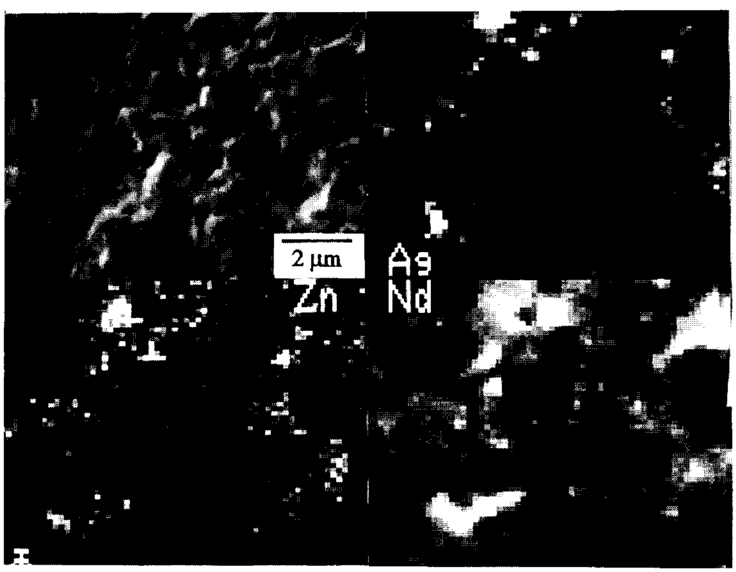

Fig. 6 Fractured surface of a hot-pressed magnet containing 3.0 wt. % Ag-Zn and the corresponding maps of Ag, Zn, and Nd.

The grain size of the hard magnetic $Fe_{14}Nd_2B$ is well less than 5 μm in the additive-free magnets and in the magnets containing small amount (< 3 wt. %)of binary additives (see Fig. 5 and 6) However, larger grains (5 ~ 10 μm) are occasionally observed in the magnets containing more additives (refer to Fig. 3 and 4), and the portion of the larger grains apparently increases as the amount of the additives increases. In the magnets containing 10 wt. % Al-Cu (or Ag-Zn), grains larger than 10 μm are often found. These large grains indicate the grain growth of the matrix phase during hot pressing, and the grain growth is mainly responsible for the poor coercivities of the magnets containing higher amount of the additives. Similar grain growth was also observed in the hot-pressed Fe-Nd-B magnets treated with small amount of Cu [5].

The distribution of Al and Cu in the magnet containing 5 wt. % Al-Cu and that of Ag and Zn in the magnet containing 5 wt. % Ag-Zn, which were mapped by SEM, are shown in Fig. 3 and 4, respectively. While Al is distributed uniformly throughout the magnet, except for the inside of larger grains, the distribution of Cu is uneven, gathering at certain areas. In the case of Ag-Zn, although the distribution of Zn looks more even, Ag and Zn largely behave in a same manner, collecting more at some particular areas. In other words, Al only diffuses thoroughly through the magnet at the hot-pressing condition. For Cu, Ag, and Zn, in contrast, hot pressing temperature and/or time may not enough to diffuse more completely. Die-upset may lead to more even distribution of these additives. EDX results obtained from several points within both magnets confirm the locations of the additives as in Fig. 3 and 4. EDX analyses also indicate that the locations where Cu, Ag, and Zn collect mostly are the Nd-rich grain boundary areas. On the other hand, Al is present also in the matrix grains, except for the inside of larger grains as already shown in Al map, suggesting that it not only diffuses through the magnets but also reacts with the grains during hot pressing.

As shown in Fig. 5 and 6, Auger maps of Cu, Ag and Zn, obtained from the magnets containing 3 wt. % Al-Cu and Ag-Zn, respectively, clearly manifest that these elements collect mainly at Nd-rich regions which ought to be the grain-boundary areas in the magnets. Unfortunately, locations of Al are not clear in Fig. 5. But it was confirmed by SEM that the distribution of Al was uniform in the magnet. It is well known that Cu is located at Nd/Pr-rich grain boundary areas [6-10], altering the boundaries and consequently increasing the coercivities. EDX analysis indicates that the additive-containing grain boundaries are multiphase regions. X-ray diffraction fails to identify any new intermetallic phase that might be form between Nd and the additives. EDX results show, however, that the atomic ratio Nd: (Al, Cu) or Nd: (Ag, Zn) in certain parts is approximately 2:1 or 4:1 depending upon the location. In some parts their ratio approaches 1:1. The existence of the intermetallic phase CuNd was reported elsewhere [9]. The Al-stabilized [11] or Zn-stabilized [2] Laves phase was less obvious.

Ⅳ.CONCLUSIONS

The coercivity of the magnet prepared from the mechanically ground precursors can be improved by small amount of additions (1 wt. % for Al-Cu or 3 wt. % for Ag-Zn). The maximum gain in coercivity by the addition is about 20 %, and the values of ${}_iH_c$ and B_r of a hot-pressed magnet containing 1 wt. % Al-Cu are 18 kOe and 7 kG, respectively. The enhancement of coercivities in the hot-pressed magnets containing binary additives is attributed to modification of the grain-boundary phases, by diffusion-alloying the additives with the grain-boundary phases during hot pressing, even though the nature of the grain-boundary phases is not clear and some additives react with the hard magnetic grains.

REFERENCES

[1] H.H. Stadelmaier and N.C. Liu, *Materials Lett.* **4** (1986), 304.
[2] C.D. Fuerst and E.G. Brewer, *Appl. Phys. Lett.* **56** (1990), 2252.
[3] C.D. Fuerst and E.G. Brewer, *J. Appl. Phys.* **69** (1991), 5826.
[4] C. Kuhrt, H. Cerva, and L. Schultz, *Appl. Phys. Lett.* **64** (1994), 797.
[5] J.D. Park, T.S. Jang, W.Y. Jeung, and C.S. Kwak, *IEEE Trans. Magn.* **29** (1993), 2881.
[6] J.F. Herbst, C.D. Fuerst, R.K. Mishra, C.B. Murphy, and D.J. Van Wingerden, *J. Appl. Phys.* **69** (1991), 5823.
[7] H. Sakamoto, M. Fujikura, and T. Mukai, *J. Appl. Phys.* **69** (1991), 5832.
[8] T.S. Jang and H.H. Stadelmaier, *Materials Lett.* **9** (1990), 483.
[9] B. Grieb, K. Fritz, and E.-Th. Henig, *J. Appl. Phys.* **70** (1991), 6447.

[10] T. Shimoda, K. Akioka, O. Kobayashi, and T. Yamagami, *J. Appl. Phys.* **64** (1988), 5290.

[11] B. Grieb, K.G. Knoch, E.-Th. Henig, and G. Petzow, *J. Magn. Magn. Mater.* **80** (1989), 75.