Magnetic Property and Stability of $Zn/Sm_2Fe_{17}N_x$ Bonded Magnets Using the In Metal Derived from $In(C_2H_5)_3$ as a Binder

Kenji Noguchi, Masashi Nishimura, Ken-ichi Machida,* and Gin-ya Adachi*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

Received April 23, 1999. Revised Manuscript Received June 30, 1999

Fine powders of $Sm_2Fe_{17}N_x$ were stabilized by microcapsulation with the In and Zn metals produced via photochemical decompositions of $In(C_2H_5)_3$ and $Zn(C_2H_5)_2$ under UV light irradiation in an organic solvent to avoid any additional oxidation of them, and after the coating treatment, they still recorded high remanence ($B_r = \sim 1.30$ T) and coercivity ($H_{cj} = \sim 0.74$ MA m^{-1}) values to provide maximum energy products of $(BH)_{max} = \sim 279$ kJ m^{-3} despite the dilution effect by existence of the nonmagnetic In and/or Zn metals used for the protection. The photochemical decomposition of $In(C_2H_5)_3$ was smoothly performed compared with the case of $Zn(C_2H_5)_2$, so that a large amount of In metal was deposited on the surface of $Sm_2Fe_{17}N_x$ fine particles (~6.5 wt %) to be sufficient for serving as a metal binder for compression-type bonded magnets without any further addition of the same metals with low melting points. The single-layered metal-coated $In/Sm_2Fe_{17}N_x$ and double-layered metal-coated $In/Zn/Sm_2Fe_{17}N_x$ powders produced the corresponding In metal-bonded $Sm_2Fe_{17}N_x$ and $Zn/Sm_2Fe_{17}N_x$ magnets, of which the latter ones provided the highest $(BH)_{max}$ value of ~144 kJ m^{-3} among a series of metal-bonded $Sm_2Fe_{17}N_x$ magnets reported to date.

Introduction

The ternary samarium−iron−nitrogen intermetallic compound, $Sm_2Fe_{17}N_x$ ($x = \sim 3$), which possesses high saturation magnetization, strong uniaxial anisotropy, and high Curie temperature,[1,2] has been noted as an attractive material to provide high-performance permanent magnets, especially bonded ones, because it decomposes to SmN and α-Fe at the temperature above ca. 900 K. However, $Sm_2Fe_{17}N_x$ is needed to be ground into fine powders to generate the high coercivity for practical uses since the coercivity mechanism is controlled by the nucleation process.[3] Therefore, the sufficient hard magnetic property is attained only on the $Sm_2Fe_{17}N_x$ fine powders with a particle size (d) below 3 μm in diameter (the evaluated single domain sizes: 0.34 μm from the theoretical calculation, 1−2 μm from Kerr effect microscopy observations,[4,5] and 3−4 μm from powder pattern method used on scanning electron microscopy[6]), which are easily impaired by oxidation even in any atmosphere containing a trace of oxygen or moisture. To solve this serious problem, enormous efforts were made to stabilize them. From a series of studies on metal-bonded magnets using the metals with low melting points such as Zn, In, Bi, Pb, and Sn, it has been particularly found that Zn metal enhances the coercivity through the hot-pressing process at a temperature above the melting point (692.8 K), although the remanence value is considerably decreased.[7−13] This is due to the effective removal of the defects and the soft magnetic α-Fe phase on the surface of $Sm_2Fe_{17}N_x$ particles by the reaction with the Zn metal, where they play a role as the nucleation points to result in the rapid reversal of domain wall in the magnetic field applied along the inverted direction. Consequently, one can expect that the surface coating for the $Sm_2Fe_{17}N_x$ fine particles with Zn metal should be effective to improve both the coercivity and oxidation resistance. Mukai and co-worker[14] have first tried to coat the surface of $Sm_2Fe_{17}N_x$ coarse powders ($d = \sim 24$ μm, $H_{cj} = 0.06$ MA m^{-1}) with Zn metal by the electroplating method in an aqueous solution after the preliminary Cu coating, and by the successive heat treatment at ~743 K in an Ar

---

* To whom correspondence should be addressed. Phone +81, 6-6879-7352, +81, 6-6879-7353; FAX +81, 6-6879-7354; E-mail adachi@ap.chem.eng.osaka-u.ac.jp.

(1) Coey, J. M. D.; Sun, H. *J. Magn. Magn. Mater.* **1990**, *87*, L251.
(2) Li, H.-S.; Coey, J. M. D. In *Handbook of Magnetic Materials*; Buschow, K. H. J., Ed.; North-Holland: Tokyo, 1991; Vol. 6, Chapter 1.
(3) Schnitzke, K.; Schultz, L.; Wecker, J.; Katter, M. *Appl. Phys. Lett.* **1990**, *57*, 2853.
(4) Mukai, T.; Fujimoto, T. *J. Magn. Magn. Mater.* **1992**, *103*, 165.
(5) Hu, J.; Dragon, T,; Sartorelli, M.-L.; Kronmullar, H. *Phys. Status Solidi* **1993**, *136*, 207.
(6) Kobayashi, K.; Iriyama, T.; Yamaguchi, T.; Kato, H.; Nakagawa, Y. *J. Alloys Compd.* **1993**, *193*, 235.
(7) Otani, Y.; Moukarika, A.; Sun, H.; Coey, J. M. D. *J. Appl. Phys.* **1991**, *69* (9), 6735.
(8) Huang, M. Q.; Zhang, L. Y.; Ma, B. M.; Zheng, Y.; Elbicki, J. M.; Wallace, W. E.; Sankar, S. G. *J. Appl. Phys.* **1991**, *70* (10), 6027.
(9) Kuhrt, C.; O'Donnell, K.; Schnitzke, K.; Schultz, L. *Appl. Phys. Lett.* **1992**, *60* (26), 3316.
(10) Rodewald, W.; Wall, B.; Katter, M.; Velicescu, M.; Schrey, P. *J. Appl. Phys.* **1993**, *73* (10), 5899.
(11) Velicescu, M.; Wall, B.; Rodewald, W.; W.Reppel, G. *IEEE Trans. Magn.* **1993**, *29*, 2827.
(12) Wall, B.; Katter, M.; Rodewald, W.; Velicescu, M. *IEEE Trans. Magn.* **1994**, *30*, 675.
(13) Iriyama, T.; Katsumata, T.; Mitsui, R. *Trans. Mater. Res. Jpn.* **1994**, *14B*, 1063.
(14) Mukai, T.; Fujimoto, T. Japanese Patent 93-234729.

10.1021/cm990234l CCC: $18.00

atmosphere, a high coercivity value of 0.54 MA m^{-1} has been observed on them. However, this method was only effective on the $Sm_2Fe_{17}N_x$ coarse powders with a relatively large particle size above 20 μm in diameter, owing to the serious damage by additional oxidation in the aqueous solution used here for the electroplating. Meanwhile, the vacuum evaporation method[15] as one of dry processes has been applied to stabilize the $Sm_2Fe_{17}N_x$ fine powders. By the Zn metal evaporation over the fine powders, the thermal stability of $Sm_2Fe_{17}N_x$ is considerably improved, and the coercivity is also increased by the subsequent heat treatment. However, their remanence values are considerably decreased because the reaction between the $Sm_2Fe_{17}N_x$ phase and the Zn metal takes place to produce the intermetallic compounds, such as $Sm_2(Fe,Zn)_{17}N_x$[16] and Sm_2FeZn_2,[10] of which the hard magnetic properties are fairly inferior to that of the original $Sm_2Fe_{17}N_x$ one. In addition, the aggregation among the $Sm_2Fe_{17}N_x$ fine powders becomes significant, so that the remanence is lowered by the poor alignment of the primary particles.

Contrary to the above works, the present authors have microcapsulated the $Sm_2Fe_{17}N_x$ fine particles with the Zn metal produced via the photochemical decomposition of $Zn(C_2H_5)_2$[18,19] in the degassed and dehydrated organic solvent and have succeeded in producing high-performance resin-bonded magnets with $(BH)_{max} = \sim 176$ kJ m^{-3}, where the observed energy product is the largest one among the values reported on the resin- and metal-bonded $Sm_2Fe_{17}N_x$ magnets to date.[18,20] This is due to the fact that the additional oxidation of $Sm_2Fe_{17}N_x$ fine powders hardly occurs during surface-modification processes compared with the cases of the electroplating and vacuum evaporation methods, because the surface coating of the Zn metal derived from $Zn(C_2H_5)_2$ is performed in the organic solvent which hardly contains the oxidants such as oxygen and water, and thus the incident frequency of oxygen and water molecules over the surface of $Sm_2Fe_{17}N_x$ fine particles is much more depressed than those in the aqueous solution and the evacuated atmospheres even in the pressure range $10^{-9}-10^{-7}$ Pa. However, the Zn metal film formed on the surface of $Sm_2Fe_{17}N_x$ fine powders is only of the thickness around 1.0 nm (about several Zn atom layers), which is too thin to protect them effectively against the attack of oxygen and water, and unfortunately, the thickness of Zn metal film hardly increases even by prolonging the irradiation time of UV light because the recombination rate of the resulting Zn metal and ethyl radicals is high. Therefore, it can be expected that the oxidation resistance of $Sm_2Fe_{17}N_x$ powders should be much improved if the metal amount for the surface coating is increased. In addition, if the above-mentioned metals with low melting points can also be derived from the their organometallic compounds such as $In(C_2H_5)_3$ as well as $Zn(C_2H_5)_2$, multilayered metal films should be prepared by repeating the surface-coating processes using them as the precursors.

On the other hand, as mentioned above, the metal-bonded magnets as produced by using some metals with low melting points as binders are also expected to be attractive because of their good mechanical strength, hardness, thermal stability, and so on.[7−13] Among the metal-bonded magnets prepared from the $Sm_2Fe_{17}N_x$ fine powders up to date, Iriyama et al.[14] have recorded the highest magnetic $(BH)_{max}$ value (134 kJ m^{-3}) on a compression-type anisotropic Zn metal-bonded $Sm_2Fe_{17}N_x$ magnet ($\rho = \sim 7.5$ g cm^{-3}) fabricated by hot-pressing at ∼723 K after aligning and pressing. Although the other metals such as Sn, Al, In, and Ga also serve as the binder to produce the metal-bonded $Sm_2Fe_{17}N_x$ magnets, their $(BH)_{max}$ values (100−125 kJ m^{-3}) are lower than that of the Zn metal-bonded magnet as well as their low coercivity ($H_{cj} = 0.36-0.44$ MA m^{-1}). The results mean that these metals scarcely contribute to enhance the coercivity contrary to Zn.

In this work, the $Sm_2Fe_{17}N_x$ fine powders were stabilized by surface coating with multilayered films of the Zn and In metals produced via the successive photochemical decomposition processes of their organometallic compounds, $Zn(C_2H_5)_2$ and $In(C_2H_5)_3$, and the corresponding In metal-bonded $Zn/Sm_2Fe_{17}N_x$ magnets were fabricated by using the In metal component of coating films as the binder. Furthermore, the magnetic properties of the resulting microcapsulated powders and In metal-bonded magnets of $Sm_2Fe_{17}N_x$ were studied from a viewpoint of the practical use as permanent magnet materials by taking into account their oxidation resistance and thermal stability.

Experimental Section

The $Sm_2Fe_{17}N_x$ coarse powders prepared by nitrogenation of Sm_2Fe_{17} were ground by subsequent ball-milling according to the procedure described elsewhere.[20,21] The resulting fine powders were coated with the Zn and/or In metals produced via the photochemical decomposition of $Zn(C_2H_5)_2$ and $In(C_2H_5)_3$ under UV light irradiation in the vacuum glovebox charged by Ar gas according to the similar microcapsulation method as described elsewhere.[18,20] Nitrogen and oxygen contents of the resulting $Sm_2Fe_{17}N_x$ fine powders without and with the surface coating film were checked on a nitrogen and oxygen analyzer (Horiba, EMGA-550), and their Zn and In metal contents were also measured on an inductively coupled plasma atomic emission spectroscopy apparatus (Shimadzu, ICPS-1000IV). Signals for the X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) of $In/Sm_2Fe_{17}N_x$ and $Zn/Sm_2Fe_{17}N_x$ platy samples were obtained on an XPS apparatus (ULVAC-PHI, model 5500MT). Their surface was etched by Ar^+ ion bombardment, and the sputtered depth values were converted to those of SiO_2 for their references. The stabilized fine powders, $In/Sm_2Fe_{17}N_x$ and $In/Zn/Sm_2Fe_{17}N_x$, were served to fabricate the corresponding compression-type In metal-bonded magnets by molding under a pressure of 1.4 GPa at 450 K in a magnetic field of 1.4 MA m^{-1}. Magnetization hysteresis curves of the as-ground or surface-coated $Sm_2Fe_{17}N_x$ powders and their molded materials were recorded on a vibrating sample magnetometer, VSM (Tamakawa, TM-VSM2014-MHR type), in a range of magnetic fields up to ±1.6 MA m^{-1} at room temperature after magnetization at 4.8 MA m^{-1} by a pulsed field generator, and the

---

(15) Makita, K.; Hirosawa, S. *J. Alloys Compd.* **1997**, *260*, 236.

(16) Hiraga, K.; Okamoto, K.; Iriyama, T. *Mater. Trans. JIM* **1993**, *34* (6), 569.

(17) Izumi, H.; Machida, K.; Shiomi, A.; Iguchi, M.; Adachi, G. *Jpn. J. Appl. Phys.* **1996**, *35*, L894.

(18) Izumi, H.; Machida, K.; Iguchi, M.; Shiomi, A.; Adachi, G. *J. Alloys Compd.* **1997**, *261*, 304.

(19) Izumi, H.; Machida, K.; Shiomi, A.; Iguchi, M.; Noguchi, K.; Adachi, G. *Chem. Mater.* **1997**, *9*, 2759.

(20) Machida, K.; Shiomi, A.; Izumi, H.; Adachi, G. *Jpn. J. Appl. Phys.* **1995**, *34*, L741.

(21) Iriyama, T. Ph.D. Thesis, Tohoku University, Sendai, Japan, 1994.

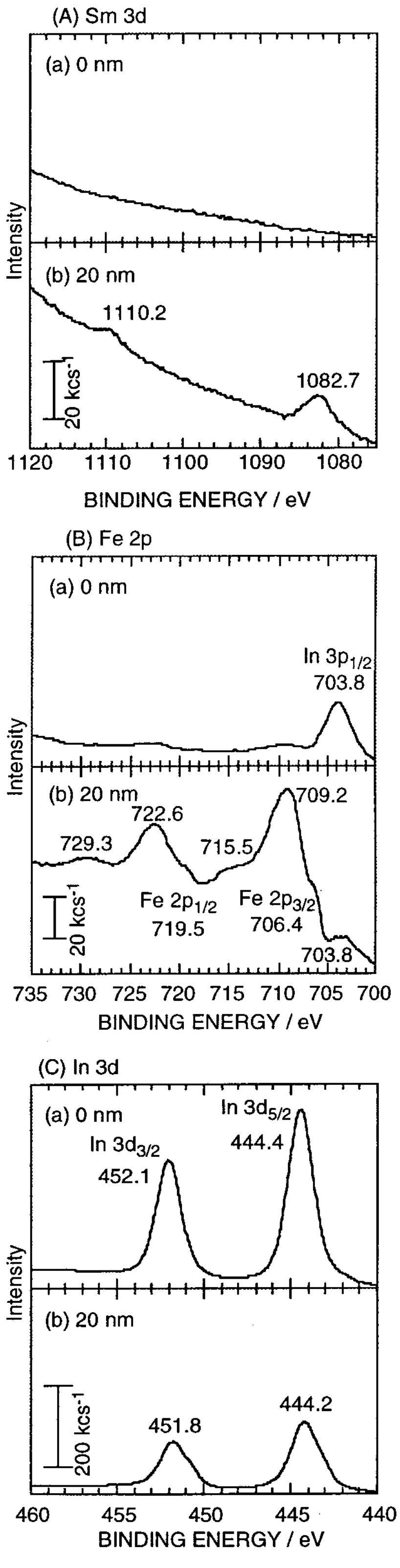

Figure 1. XPS profiles for the Sm 5d, Fe 2p, and In 3d signals observed on an In/Sm$_2$Fe$_{17}$N$_x$ plate (a) before and (b) after surface etching by Ar$^+$ ion bombardment for 20 nm (as converted to the depth value of SiO$_2$).

data obtained on the bonded magnets were also calibrated by a B-H loop tracer.

Results and Discussion

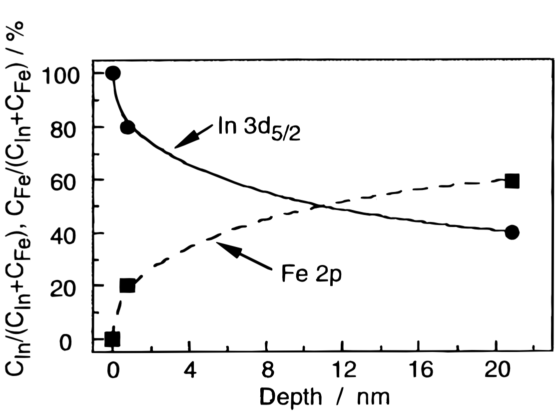

Figure 2. Depth profiles for the surface concentrations of Fe and In observed on the In/Sm$_2$Fe$_{17}$N$_x$ plate denoted in Figure 1. The etched depth of the platy sample was converted to that of SiO$_2$.

Powder Samples. The Sm$_2$Fe$_{17}$N$_x$ fine powders (~3 μm) were prepared by ball-milling in the degassed and dehydrated organic solution containing a surfactant (Aaerosol OT, di-2-ethylhexyl sodium sulfosuccianate) according to the previous papers.[20,21] The subsequent surface coating for the resulting fine powders was made by using the Zn and/or In metals produced via the photochemical decomposition of Zn(C$_2$H$_5$)$_2$ and In(C$_2$H$_5$)$_3$ under UV light irradiation at room temperature, respectively. Figure 1 shows the XPS patterns based on Sm 3d, Fe 2p, and In 3d electrons as observed on an In metal-coated Sm$_2$Fe$_{17}$N$_x$ platy specimen. No XPS pattern for the Sm 3d signals was observed on the unetched In/Sm$_2$Fe$_{17}$N$_x$ plate, but after the Ar$^+$ ion bombardment for 20 nm (as converted to the depth value of SiO$_2$), two peaks of Sm 3d$_{1/2}$ and Sm 3d$_{3/2}$ were clearly recorded to be assigned to Sm$_2$O$_3$. In a similar manner as the Sm 3d signals, the XPS pattern for the Fe 3p$_{3/2}$ and Fe 3p$_{1/2}$ signals was intensified after the surface etching. On the other hand, the intense In 3d signals were clearly detected on the In/Sm$_2$Fe$_{17}$N$_x$ plate even before the surface etching. The In 3d$_{3/2}$ and In 3d$_{5/2}$ signals derived from In metal were responsible for these sharp peaks. No XPS signal derived from the other metals, oxides, or hydroxides was detected. This result indicates that the In metal surface coating smoothly takes place on the Sm$_2$Fe$_{17}$N$_x$ substrate, so that the strong In 3d signals assigned to In metal are observed on it even without any Ar$^+$ ion bombardment.

Figure 2 shows the depth profiles for the atomic concentration ratio of Fe and In metals calculated from the peak intensity of In 3d and Fe 2p signals on the Sm$_2$Fe$_{17}$N$_x$ plate denoted in Figure 1. The In concentration ratio, $C_{\mathrm{In}}/(C_{\mathrm{In}} + C_{\mathrm{Fe}})$, on the sample prior to the surface etching was approximately 100% and decreased with the etching depth. In contrast, the concentration ratio of Fe was nearly 0% owing to the low intensity of XPS signals before the surface etching. These results indicate that the surfaces of the Sm$_2$Fe$_{17}$N$_x$ fine powders are completely covered with the In metal produced via the photochemical decomposition of In(C$_2$H$_5$)$_2$. Moreover, it can be expected that the oxidation resistance of the In metal-coated In/Sm$_2$Fe$_{17}$N$_x$ powders or magnets is superior to that of the Zn/Sm$_2$Fe$_{17}$N$_x$ ones owing to the thickness of the In metal film for the Sm$_2$Fe$_{17}$N$_x$ fine powders converted thickness: ~27 nm (4.5 wt %) for In/Sm$_2$Fe$_{17}$N$_x$; ~1.5 nm (0.3 wt %) for Zn/Sm$_2$Fe$_{17}$N$_x$. For the Zn LMM profiles observed on the Zn/Sm$_2$Fe$_{17}$N$_x$ platy specimen, the signals of Zn metal became signifi-

Table 1. Metal and Oxygen Contents and Magnetic Properties for the As-Ground and Surface-Coated $Sm_2Fe_{17}N_x$ Powders

	metal content (wt %)		oxygen content	magnetic properties		
powder	Zn	In	(wt %)	B_r (T)	H_{cj} (MA m^{-1})	$(BH)_{max}$ (kJ m^{-3})
$Sm_2Fe_{17}N_x$			0.30	1.38	0.88	321
$In/Sm_2Fe_{17}N_x$		4.53	0.33	1.30	0.70	271
$Zn/Sm_2Fe_{17}N_x$	0.22		0.28	1.36	0.83	310
$In/Zn/Sm_2Fe_{17}N_x$	0.09	6.54	0.36	1.30	0.74	279

cant on the surface-etched sample, suggesting that the Zn film was partly oxidized during the setting on the XPS apparatus in air.

The In and Zn metal contents of the $Sm_2Fe_{17}N_x$ fine powders coated with In and/or Zn metals are summarized in Table 1, together with the oxygen content and magnetic parameters. The surface coating was effectively performed via the photochemical decomposition of $In(C_2H_5)_3$ under the UV light irradiation using a low-pressure mercury arc lamp as follows:

$$In(C_2H_5)_3 + Sm_2Fe_{17}N_x \xrightarrow{h\nu} In/Sm_2Fe_{17}N_x + C_mH_n$$

A large amount of In metal (~4.5 wt %) was deposited on the surface of $Sm_2Fe_{17}N_x$ fine particles compared with the case of single-layered Zn metal coating (~0.3 wt %). Since the $In(C_2H_5)_3$ ($\lambda_{max} = \sim 225$ nm) is the much more photosensitive against the UV lights compared with $Zn(C_2H_5)_2$ ($\lambda_{max} = 193$ and 248 nm), three In−C bonds in the $In(C_2H_5)_3$ molecule easily cleave because the latter compound tends to be excited by the UV light at 253.7 nm. In addition, the difference between the In and Zn metal amounts of the surface-coated films is due to the fact that the recombination between the Zn metal and ethyl radical generated by the photochemical decomposition of $Zn(C_2H_5)_2$ takes place more rapidly than that for $In(C_2H_5)_3$. Indeed, the Zn metal amount of $Zn/Sm_2Fe_{17}N_x$ (0.22 wt %) was considerably decreased by the subsequent surface coating with In metal to produce $In/Zn/Sm_2Fe_{17}N_x$. From qualitative and quantitative analyses by the ICP apparatus on the organic solution residues used for In meal coating, the Zn species were detected, and the content was approximately equal to the difference between the Zn contents of the starting $Zn/Sm_2Fe_{17}N_x$ powder and the resulting $In/Zn/Sm_2Fe_{17}N_x$ one. From these results, it was found that the exchange reaction between In and Zn metals proceeded as

$$In(C_2H_5)_3 \xrightarrow{h\nu} In(C_2H_5)_{3-m} + mC_2H_5^{\bullet} + In\downarrow \quad (1)$$

$$Zn + C_2H_5^{\bullet} \rightarrow ZnC_2H_5 \quad (2)$$

$$ZnC_2H_5 + C_2H_5^{\bullet} \rightarrow Zn(C_2H_5)_2 \quad (3)$$

$$C_2H_5^{\bullet} \rightarrow C_xH_y\ (C_2H_4,\ C_2H_6,\ C_4H_8,\ \text{or}\ C_4H_{10}) \quad (4)$$

where the Zn metal denoted in this reaction originated from that of the $Zn/Sm_2Fe_{17}N_x$ fine particles as preliminarily coated in the *n*-hexane solution of $Zn(C_2H_5)_2$. The recombination between Zn metal and ethyl radical is initiated by the generation of the ethyl radical fragments in the decomposition process as the initiating step shown in eq 1. The combination between the resulting ethyl radical and Zn metal on the surface of the $Sm_2Fe_{17}N_x$ powders occurs and produces the ZnC_2H_5 molecule as shown in eq 2. Further, the formation of $Zn(C_2H_5)_2$ molecules takes place in the subsequent reaction between the resulting ZnC_2H_5 and ethyl radical as in eq 3. On the other hand, the excess ethyl radicals react with each other in the terminating step as in eq 4. Moreover, it is expected that this exchange reaction enhances the deposition rate of In metal on the surface of $Sm_2Fe_{17}N_x$ fine powders, since the In contents of the doubly coated $In/Zn/Sm_2Fe_{17}N_x$ powders are usually larger than those of the singly coated $In/Sm_2Fe_{17}N_x$ ones. A model for the reaction mechanism to produce the $In/Zn/Sm_2Fe_{17}N_x$ fine powders is shown in Figure 3. The In metal coating for the $Zn/Sm_2Fe_{17}N_x$ particles should proceed through the following two processes: (1) the photochemical decomposition of $In(C_2H_5)_3$ and (2) the exchange reaction between Zn metal and $In(C_2H_5)_3$.

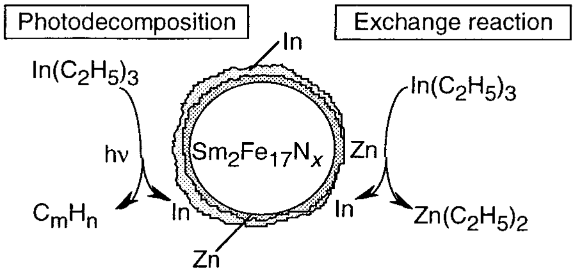

Figure 3. A proposed microcapsulation model for the $Zn/Sm_2Fe_{17}N_x$ fine particle with the In metal derived from $In(C_2H_5)_3$. Prior to the In metal coating, the preliminary surface coating was made by the Zn metal produced via the photochemical decomposition of $Zn(C_2H_5)_2$ under UV light irradiation.

For the magnetic parameters of the as-ground and metal-coated $Sm_2Fe_{17}N_x$ fine powders as summarized in Table 1, the B_r and H_{cj} values were somewhat decreased by the treatment for In metal coating. The decrease of the B_r value is due to the dilution effect caused by a large amount of nonmagnetic In metal. Furthermore, it is presumed that the aggregation of each magnetic particle occurs because a large amount of In metal plays a role as a binder for the $Sm_2Fe_{17}N_x$ fine powders. This aggregation leads to depression for the rotation of the $Sm_2Fe_{17}N_x$ fine particles along the direction of the applied magnetic field during the alignment process before the VSM measurements for the hard magnetic properties of the In metal-coated $Sm_2Fe_{17}N_x$ powders and, consequently, to provide the formation of the misalignment domains.

Demagnetization curves for the fine powders of $Sm_2Fe_{17}N_x$ (as-ground), $In/Sm_2Fe_{17}N_x$, $Zn/Sm_2Fe_{17}N_x$, and $In/Zn/Sm_2Fe_{17}N_x$ are shown in Figure 4. On the magnetic properties of the In metal-coated powders, $In/Sm_2Fe_{17}N_x$ and $In/Zn/Sm_2Fe_{17}N_x$, the decrease of the H_{cj} value after the treatment for In metal coating was larger than that of the B_r value. This is due to the remaining isotropic domains even after alignment in the applied magnetic field of ~4.8 MA m^{-1}, since these domains work as nucleation points for the reversal domain walls in the aggregated secondary particles because of the weak interaction between the misaligned powders compared with the case of the completely aligned ones. However, the $In/Sm_2Fe_{17}N_x$ and $In/Zn/Sm_2Fe_{17}N_x$ fine powders still kept the fundamental magnetic param-

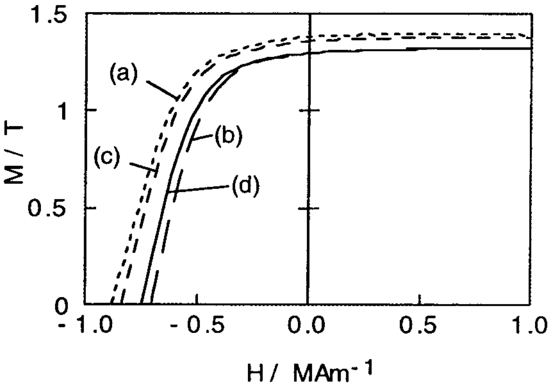

Figure 4. Demagnetization curves for the fine powders of (a) $Sm_2Fe_{17}N_x$ (as-ground), (b) $In/Sm_2Fe_{17}N_x$, (c) $Zn/Sm_2Fe_{17}N_x$, and (d) $In/Zn/Sm_2Fe_{17}N_x$.

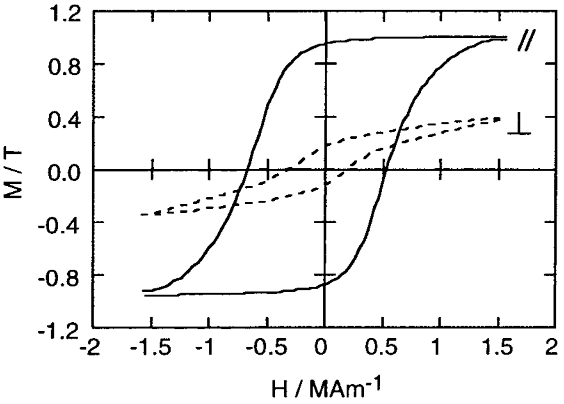

Figure 5. Anisotropic magnetic hysteresis loops recorded on a In metal-bonded $Zn/Sm_2Fe_{17}N_x$ magnet along (solid line) and perpendicular to (dash line) the magnetization direction.

eters at high levels (B_r = ~1.30 T, H_{cj} = ~0.74 MA m^{-1}, and $(BH)_{max}$ = ~279 kJ m^{-3}), which were enough to mold the high-performance In metal-bonded $Sm_2Fe_{17}N_x$ magnets. In addition, the oxygen contents of the $In/Zn/Sm_2Fe_{17}N_x$ and $In/Sm_2Fe_{17}N_x$ powders were lowered because the stability of $Sm_2Fe_{17}N_x$ fine powders against attack of oxygen or moisture was effectively improved by the In and/or Zn metal coatings.

Bonded Magnets. Since the $In/Sm_2Fe_{17}N_x$ and $In/Zn/Sm_2Fe_{17}N_x$ fine powders contained large amounts of In metal as the coating film (~6.5 wt %; as listed in Table 1), the In metal-bonded magnets of $Sm_2Fe_{17}N_x$ were molded using them without any further addition of In metal. The In metal of coating films served as the binder for the In metal-bonded magnets, since the In metal melt formed at ~453 K rapidly permeated into the interfaces and the cracks around the surface of the $Sm_2Fe_{17}N_x$ fine particles and resulted in reduction of their mutual frictional force for the rotation of the particles, and consequently, the resulting In metal-bonded magnets provided the excellent magnetic properties. Typical magnetization hysteresis loops observed on the In metal-bonded $Zn/Sm_2Fe_{17}N_x$ magnet produced from the $In/Zn/Sm_2Fe_{17}N_x$ powder as denoted in Table 1 without any further addition of In metal are shown in Figure 5. The solid line corresponds to the loop measured along the orientation direction, and the dashed line is for the pattern recorded perpendicular to the above direction. The magnetic anisotropy was fairly observed on the resulting In metal-bonded $Zn/Sm_2Fe_{17}N_x$ magnet even without any addition of In metal. This indicates that the quantity of the In metal produced via photochemical decomposition of $In(C_2H_5)_3$ is enough to mold the $Sm_2Fe_{17}N_x$ fine powders in the applied magnetic field of ~1.4 MA m^{-1}. The resulting remanence ratio $(B_r)_{hard}/(B_r)_{easy}$ was 0.19.

The magnetic properties for the In metal-bonded magnets of $Sm_2Fe_{17}N_x$ produced in this work are summarized in Table 2, together with those for similar kinds of metal-bonded magnets as reported to date. The In metal-bonded magnet molded from the $In/Zn/Sm_2Fe_{17}N_x$ fine powder under the optimized conditions of 1.4 MA m^{-1}, 1.4 GPa, and 453 K provided a value of $(BH)_{max}$ = 144 kJ m^{-3} for B_r = 0.96 T and H_{cj} = 0.66 MA m^{-1}, which was higher than those of the In metal-bonded one produced using the $In/Sm_2Fe_{17}N_x$ powder. The magnetic properties of the In-coated powders used as the raw materials for the bonded magnets are summarized in Table 1. The excellent magnetic parameters for the In metal-bonded $Zn/Sm_2Fe_{17}N_x$ magnet are due to the superior effect of Zn metal for the thermal stability, and particularly, the B_r value is high compared with those of the other metal-bonded magnets reported elsewhere[7−13,21] although the H_{cj} value is somewhat lower than that of Zn metal-bonded magnet.[8,9,12,13] It has been reported that an amorphous-like layer forms on the surface of $Sm_2Fe_{17}N_x$ particle via the partial oxidation, and the reaction between such amorphous-like layer and the Zn metal in the coating film takes place by heating at ~723 K to enhance the H_{cj} value. However, such enhancement was not observed on the H_{cj} value of the In metal-bonded magnet molded from the single-layered coated $In/Sm_2Fe_{17}N_x$ fine powder. In addition, the crystal lattice was distorted to induce an internal stress by the applied uniaxial pressure of 1.4 GPa during the molding process, resulting in further decrease of the H_{cj} value. On the other hand, the B_r value of the bonded magnet was slightly lower than the calculated one by taking into account the reduced density value. This must be due to the local demagnetization field induced by the nonmagnetic spaces as resulted from the incompleteness in the dentisification of the bonded magnets. It is noted that the $(BH)_{max}$ value (144 kJ m^{-3}) observed on the In metal-bonded $Zn/Sm_2Fe_{17}N_x$ magnet (with ρ = 6.38 g cm^{-3}), as molded from the $In/Zn/Sm_2Fe_{17}N_x$ powder without any In metal addition, is still the highest one among the similar kinds of metal-bonded $Sm_2Fe_{17}N_x$ magnets reported until now (e.g., $(BH)_{max}$ = 135 kJ m^{-3} for the Zn metal-bonded $Sm_2Fe_{17}N_x$ magnet reported by Iriyama et al.[13]).

Figure 6 shows the typical irreversible flux loss curve of the In metal-bonded $Zn/Sm_2Fe_{17}N_x$ magnet as measured in a temperature range 273−393 K in air, together with those of the epoxy resin-bonded magnets of as-obtained $Sm_2Fe_{17}N_x$ and surface-coated $Zn/Sm_2Fe_{17}N_x$ powders as reported elsewhere.[13,19] The flux loss curve of the In metal-bonded magnet obtained in this work was more gradually decreased than that of the injection-type resin-bonded one of the as-obtained $Sm_2Fe_{17}N_x$,[13] although the latter-type bonded magnet usually contains a large amount of resin (~10 wt %) and tends to show good oxidation resistance and traced the same curved pattern as that of compression-type resin-bonded $Zn/Sm_2Fe_{17}N_x$ one.[19] This is attributed to the

Table 2. Metal Contents, Density, and Magnetic Properties of the Metal-Bonded $Sm_2Fe_{17}N_x$ Magnets

	metal binder			magnetic properties				
raw powder	metal	content (wt %)	density (g cm^{-3})	B_r (T)	H_{cj} (MA m^{-1})	$(BH)_{max}$ (kJ m^{-3})	H_k/H_{cj} (%)	ref
$In/Sm_2Fe_{17}N_x$	In	4.53	6.39	0.89	0.60	122	41	this work
$In/Zn/Sm_2Fe_{17}N_x$	In	6.54	6.38	0.96	0.66	144	44	
$Sm_2Fe_{17}N_x$	Zn	15.0			0.44	84		7
	Zn	9.0	~6.70	0.83	0.86	86		8
	Zn	20.0	6.00	0.41	3.47			9
	Zn	15.0	5.85	0.73	0.60	68		10
	Zn	15.0	5.50	0.77	1.07	97	25	12
	In	10.0		0.94	0.39	122		21
	Zn		7.50	~0.95	~1.19	~135		13

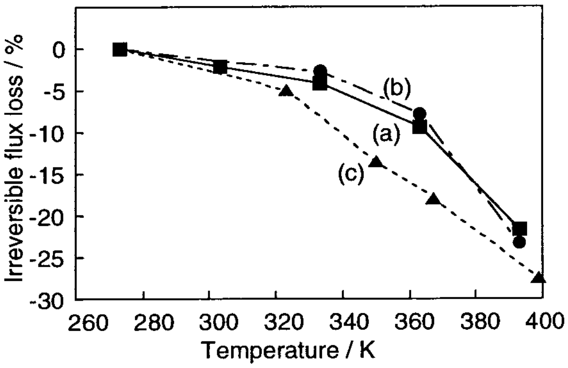

Figure 6. Irreversible flux loss curves for bonded magnets: (a) In metal-bonded one of $Zn/Sm_2Fe_{17}N_x$ (this work); (b) resin-bonded one of $Zn/Sm_2Fe_{17}N_x$ (ref 19); and (c) injection-type resin-bonded one of $Sm_2Fe_{17}N_x$ (ref 13).

good oxidation resistance of the Zn metal-coating film over the $Sm_2Fe_{17}N_x$ fine particles. It is concluded that the metal-bonded $Zn/Sm_2Fe_{17}N_x$ magnets with good oxidation resistance and thermal stability can be produced from the In metal-coated $Zn/Sm_2Fe_{17}N_x$ fine powders without any further addition of In metal. The reason why they show the good oxidation resistance is due to the fact that the In metal on the surface melts and permeates rapidly into the grains and cracks around the surface of the $Sm_2Fe_{17}N_x$ fine particles to cover them uniformly and serve to neutralize the nucleation points for inverting the magnetic domain walls.

The temperature coefficient of the In metal-bonded $Zn/Sm_2Fe_{17}N_x$ magnet produced from the $In/Zn/Sm_2Fe_{17}N_x$ fine powders as the raw materials was evaluated to be $\alpha(B_r) = -0.065\%\ K^{-1}$ by the measurements in the range 273−393 K. This value was comparable with that of the Zn metal-bonded $Sm_2Fe_{17}N_x$ magnet ($\alpha(B_r) = -0.06\%\ K^{-1}$) reported elsewhere[12,13] and was superior to those of injection-type resin-bonded $Sm_2Fe_{17}N_x$ magnet ($\alpha(B_r) = -0.07\%\ K^{-1}$) as commercial use. These results make it clear that the In metal-bonded $Zn/Sm_2Fe_{17}N_x$ magnet prepared in this work is also excellent in the thermal stability.

Conclusions

The $In/Zn/Sm_2Fe_{17}N_x$ fine powders provide high-performance In metal-bonded $Zn/Sm_2Fe_{17}N_x$ magnets without any further addition of In metal because the photochemical decomposition of $In(C_2H_5)_3$ proceeds more rapidly than that of $Zn(C_2H_5)_2$ to deposit sufficient amounts of In metal on the $Sm_2Fe_{17}N_x$ fine particles for molding them to the In metal-bonded ones as the metal binder. The resulting $(BH)_{max}$ value of ~144 kJ m^{-3} is the highest among the energy products reported on similar kinds of metal-bonded magnets produced from the as-obtained (uncoated) $Sm_2Fe_{17}N_x$ fine powders to date. This means that the $Sm_2Fe_{17}N_x$ fine powders are effectively stabilized by the effective microcapsulation with In and Zn metals, and the good thermal stability of the resulting In metal-bonded magnets is due to such surface coating.

Acknowledgment. The authors thank to Drs. T. Iriyama and N. Imaoka for their helpful suggestions on the preparation and characterization of raw powders and bonded. This work was supported by Grant-in-Aid for Scientific Research No. 10555218 from the Ministry of Education, Science, Sports, and Culture of Japan.

CM990234L