Surface Modification for $Sm_2Fe_{17}N_x$ Fine Powders by Self-Assembled Monolayers Derived from Hydridosilane

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Surface of fine powder of $Sm_2Fe_{17}N_x$ was modified with self-assembled monolayer (SAM) film derived from hydridosilane. The oxidation resistance of $Sm_2Fe_{17}N_x$ bonded magnet was effectively improved by good hydrophobic property of the resulting SAM film.

Rare earth–iron intermetallic compound, $Sm_2Fe_{17}N_x$, has been reported to be one of attractive materials for high-performance permanent magnets.[1,2] However, such excellent hard magnetic characteristics are attained only with finely ground powder with particle size below 3 μm,[3,4] which is easily oxidized even in any atmosphere containing a trace of oxygen or moisture. To avoid this serious problem, the authors have studied on the improvement of the oxidation resistance of such fine powder by the surface coating with zinc metal.[5–7] Meanwhile, Fadeev et al.[8] have reported that hydridosilane compound ($R_{4-y}SiH_y$; $1 \le y < 4$) form the self-assembled monolayer (SAM) film on the surface of metals. The attachment reaction with the metal oxidized-surface progresses along with H_2 evolution. In addition, this film formation mainly proceeds in dehydrated nonpolar-organic solutions without any further oxidation of the metal. The resulting hydrophobic SAM films are expected to be suitable for protecting the fine powders of rare earth intermetallic compounds from moisture. Moreover, the attachment of the hydridosilane with organic groups should add good affinity for the resin binder of bonded magnet to the powder particles, and results in the enhancement for rotation of the magnetic powders during the alignment process in magnetic field. In this work, the surface modification of the $Sm_2Fe_{17}N_x$ fine powder was performed by the formation of the SAM films, and their magnetic properties were characterized directing toward the applicable uses as high-performance bonded magnet.

The $Sm_2Fe_{17}N_x$ fine powder was prepared by the ball-milling in *n*-hexane solution containing a surfactant according to procedure described elsewhere.[6,9] The resulting $Sm_2Fe_{17}N_x$ fine powder was treated in the *n*-hexane solutions containing the hydridosilane (*n*-octylsilane or diphenylsilane) at 340 K for 48 h. Nitrogen and oxygen contents of the resulting fine powders were checked by a nitrogen and oxygen analyzer. The $Sm_2Fe_{17}N_x$ fine powders modified by the SAM films were served to fabricate the corresponding compression-type resin-bonded magnets by molding under conditions of pressure (1.4 GPa) and magnetic field (1.4 MA m^{-1}). Magnetization hysteresis loops of the powder and molded samples were recorded by a vibrating sample magnetometer (VSM) in a range of magnetic field up to ±1.6 MA m^{-1} after magnetization at 4.8 MA m^{-1} by a pulsed field generator.

For X-ray photoelectron spectroscopy (XPS) patterns of the $Sm_2Fe_{17}N_x$ fine powders treated by the hydridosilanes, the Si 2p signal derived from *n*-octylsilane or diphenylsilane was observed at the binding energy value of 102.1 or 102.7 eV, respectively. These results indicate the formation of the SAM films on the $Sm_2Fe_{17}N_x$ particles through the reaction between the hydridosilanes and OH groups on the oxidized surface of metallic powder.

The oxidation-resistance properties of untreated- and SAM-modified-$Sm_2Fe_{17}N_x$ powders were evaluated by the thermogravimetric (TG) analysis under a flow system of dry-air (see Figure 1). For the SAM/$Sm_2Fe_{17}N_x$ powder, the weight loss was not observed at temperatures around the boiling points of hydridosilanes (*n*-octylsilane, 333 K; diphenylsilane, 361 K). This indicates that the hydridosilanes are attached to the powder surface with Si–O–M (M = Sm and Fe) covalent bonds and forms the SAM films. In the temperature range above 600 K, the weight gain was observed by the oxidation of $Sm_2Fe_{17}N_x$ powder. The starting temperature of oxidation was determined from an intersection point obtained by extrapolation of two lines recorded before and after such weight gain. The oxidation started at 644.8 and 650.7 K for *n*-octylsilane- and diphenylsilane-treated $Sm_2Fe_{17}N_x$ fine powders, respectively, in contrast to 595 K for the untreated one. These results demonstrate that the SAM film derived from hydridosilane, in particular diphenylsilane, as precursor is effective to improve the oxidation resistance of the $Sm_2Fe_{17}N_x$ fine powder.

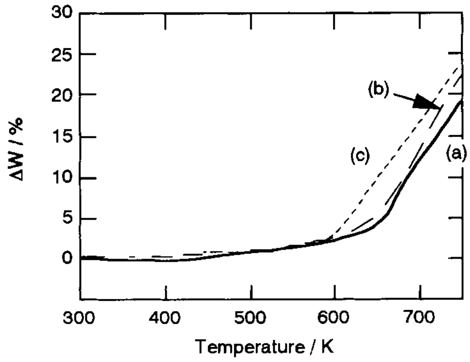

Figure 1. TG traces for $Sm_2Fe_{17}N_x$ powders treated by the solution that contained (a) 5 wt% diphenylsilane and (b) 5wt% *n*-octylsilane, and (c) untreated.

The magnetic properties and oxygen contents of the SAM/$Sm_2Fe_{17}N_x$ fine powders treated in the hydridosilane solutions with various concentrations are summarized in Table 1. Oxygen contents of the SAM/$Sm_2Fe_{17}N_x$ fine powders increased with the increase in the hydridosilane concentration as compared with that of the untreated powder. However, any damage for the magnetic properties by oxidation was not observed on the SAM/$Sm_2Fe_{17}N_x$ fine powders. Hence, the increase of the oxygen contents was responsible for the oxidation of the SAM films, which possess the active Si–H groups against H_2O and O_2. This suggests that the residual Si–H groups in the SAM film play an efficient role to depress from the attack of H_2O and O_2 to the magnetic powder.

Table 1. Oxygen content and magnetic properties of the $Sm_2Fe_{17}N_x$ powders treated by hydridosilanes

Hydridosilane	Concentration / wt%	Oxygen content / gcm^{-3}	Magnetic properties B_r / T	H_{cj} / Mam^{-1}	$(BH)_{max}$ / kJm^{-3}
-	-	0.44	1.37	0.79	311
n-Octylsilane	5	0.44	1.35	0.75	309
	10	0.62	1.37	0.75	318
	50	0.60	1.35	0.75	311
Diphenylsilane	5	0.49	1.34	0.78	298
	10	063	1.34	0.75	296
	50	0.76	1.32	0.67	298

The SAM/$Sm_2Fe_{17}N_x$ bonded magnets produced from the powder samples treated by *n*-octylsilane and diphenylsilane showed the $(BH)_{max}$ values of ~147 kJ m^{-3} and ~151 kJ m^{-3}, respectively, which were superior to that of the bonded one of the untreated powder (~134 kJ m^{-3}). In addition, the B_r values of the SAM/$Sm_2Fe_{17}N_x$ bonded magnets (0.96 T for *n*-octylsilane and 1.00 T for diphenylsilane) were higher than that of the untreated $Sm_2Fe_{17}N_x$ one (0.92 T). It should be due to addition of the affinity for the resin binder by the SAM film with the organofunctional groups. The additional chemical affinity makes the magnetic particle to rotate easily along the direction of applied magnetic field during the alignment process. Moreover, the demagnetization curves observed on the SAM/$Sm_2Fe_{17}N_x$ bonded magnets showed the superior rectangularity (H_k/H_{cj} = 46%) to the bonded magnet produced from the as-ground powder (42%). This means that the chemical affinity of the SAM films for the resin binder improves the dispersibility of the powder materials in the molding process.

Figure 2 shows the exposure time dependence of flux losses of the resin-bonded magnets produced from the SAM/$Sm_2Fe_{17}N_x$ powders at 393 K in air after magnetization by pulsed magnetic field of 4.8 MA m^{-1}. The SAM/$Sm_2Fe_{17}N_x$ bonded magnets showed the smaller flux losses than that of the magnets produced from the Zn/$Sm_2Fe_{17}N_x$ powder produced by photodecomposition of $Zn(C_2H_5)_2$.[5,6] Among the hydridosilane compounds, it is obvious that the SAM film derived from diphenylsilane effectively depress the decrease of magnetic flux as compared with the case of *n*-octylsilane.

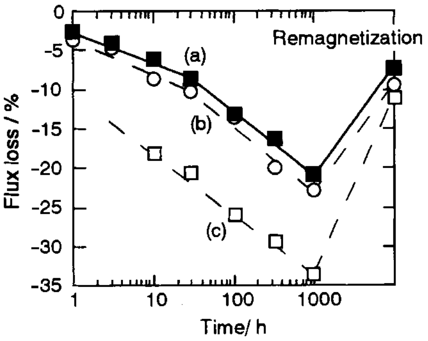

Figure 2. Standing time dependence of the flux loss of the bonded magnets produced from $Sm_2Fe_{17}N_x$ powders covered by (a) diphenylsilane, (b) *n*-octylsilane, and (c) Zn-metal (in air, at 393 K).

In conclusion, the formation of the self-assembled monolayer (SAM) films derived from hydridosilanes is one of the efficient methods for $Sm_2Fe_{17}N_x$ fine powders to improve the oxidation resistance and add the affinity for the resin binder due to their hydrophobic organic groups.

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References

1 J. M. D. Coey and H. Sun, *J. Magn. Magn. Mater.*, **87**, L251 (1990).
2 T. Iriyama, K. Kobayashi, and H. Imai, European Patent, 0-369-097-A1 (1989).
3 K. Kobayashi, T. Iriyama, T. Yamaguchi, H. Kato, and Y. Nakagawa, *J. Alloys Compd.*, **193**, 235 (1993).
4 J. Hu, T. Dragon, M. -L.Sartorelli, and H. Kronmüllar, *Phys. Status Solidi A*, **136**, 207 (1993).
5 H. Izumi, K. Machida, A. Shiomi, M. Iguchi, and G. Adachi, *Jpn. J. Appl. Phys.*, **35**, L894 (1996).
6 H. Izumi, K. Machida, A. Shiomi, M. Iguchi, K. Noguchi, and G. Adachi, *Chem. Mater.*, **9**, 2759 (1997).
7 K. Noguchi, M. Nishimura, K. Machida, and G, Adachi, *Chem. Lett.*, **1999**, 555.
8 A. Y. Fadeev and T. J. McCarthy, *J. Am. Chem. Soc.*, **121**, 12184 (1999).
9 K. Machida, A. Shiomi, H. Izumi, and G. Adachi, *Jpn. J. Appl. Phys.*, **34**, L741 (1994).