Preparation and Magnetic Property of $Sm_2Fe_{17}N_x$ Fine Powders Coated by Zn and In Metals Produced *via* Photodecomposition of Their Organometallic Compounds

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Fine powders of $Sm_2Fe_{17}N_x$ were stabilized by micro-capsulation with the In and Zn metals produced *via* photochemical decomposition of $In(C_2H_5)_3$ and $Zn(C_2H_5)_2$ under UV light irradiation and were molded to high-performance In metal-bonded magnets with the highest $(BH)_{max}$ value of 144 kJm^{-3} for $H_{cj} = 0.66$ MAm^{-1} among the metal-bonded $Sm_2Fe_{17}N_x$ magnets reported up to date.

Ternary samarium-iron-nitrogen intermetallic compound, $Sm_2Fe_{17}N_x$, have been noted as an attractive material to fabricate high-performance permanent magnets.[1,2] However, the excellent hard magnetic property is attained only on the finely ground $Sm_2Fe_{17}N_x$ powders down to a particle diameter below 3 μm[3,4] which are easily oxidized even in any atmosphere containing a trace of oxygen or moisture. To solve this serious problem, we have micro-capsulated such fine particles with the zinc metal derived from $Zn(C_2H_5)_2$ in a distilled organic solvent and have succeeded in producing a resin-bonded magnet with $(BH)_{max}$ = 176 kJm^{-3}. Meanwhile, metal-bonded magnets which are produced by using same metals with low melting points such as Zn should also be attractive materials because of their good mechanical strength, hardness, thermal stability, and so on.[5-7] In the present work, the $Sm_2Fe_{17}N_x$ fine powders were stabilized by a large amount of In and Zn metals and, by using the In metal component as the binder, the corresponding In metal-bonded magnets were fabricated without adding any other metal binder.

The $Sm_2Fe_{17}N_x$ fine powders were coated with the Zn and/or In metals produced *via* photochemical decomposition of $Zn(C_2H_5)_2$ and $In(C_2H_5)_3$ under UV light irradiation by the micro-capsulation method described elsewhere.[8,9] Nitrogen and oxygen contents of the resulting fine powders were checked on a nitrogen and oxygen analyzer and the Zn and In metal contents were also measured on an inductively coupled plasma atomic emission spectroscopy apparatus. X-ray photoelectron spectra (XPS) of the In/$Sm_2Fe_{17}N_x$ plate and Auger electron spectra (AES) of the Zn/$Sm_2Fe_{17}N_x$ one were recorded by an X-ray photoelectron spectroscopy apparatus (Mg*K*α radiation). The stabilized $Sm_2Fe_{17}N_x$ fine powders were served to fabricate the corresponding compression-type In metal-bonded magnets from the single or double coated powders, In/$Sm_2Fe_{17}N_x$ and In/Zn/$Sm_2Fe_{17}N_x$, by molding under conditions of 1.4 GPa, 450 K, and 1.4 MAm^{-1}. Magnetization hysteresis curves of the as-ground or surface-coated powders and molded materials of $Sm_2Fe_{17}N_x$ were recorded on a vibrating sample magnetometer (VSM) in a range of magnetic field up to ±1.6 MAm^{-1} at room temperature after magnetization at 4.8 MAm^{-1} by a pulsed field generator and the data obtained were also calibrated by a B-H loop tracer.

Figure 1 shows the In3p XPS and Zn LMM AES patterns observed on single metal-coated In/$Sm_2Fe_{17}N_x$ and Zn/$Sm_2Fe_{17}N_x$ platy samples. The surface-coating of In metal smoothly took place on the $Sm_2Fe_{17}N_x$ substrate, so that the strong In3p signals assigned to In metal were observed even on the surface without any Ar^+-ion bombardment. For the ZnLMM profile, the signal for Zn metal appeared on the Zn/$Sm_2Fe_{17}N_x$ sample etched for 20 nm (converted to SiO_2), suggesting that the Zn film on it was partly oxidized during the sample manipulation for setting on the XPS apparatus used here in air.

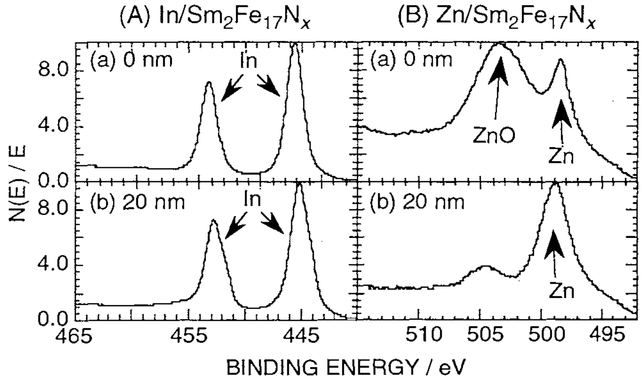

Figure 1. Spectrum patterns of the In3p and ZnLMM photoelectrons on the surface-coated $Sm_2Fe_{17}N_x$ plate coated with In and Zn metals before and after the surface etching for 20 nm (converted to SiO_2).

Table 1. Metal and oxygen contents, and magnetic properties for the as-ground and surface-coated $Sm_2Fe_{17}N_x$ fine powders

powders	Metal content		Oxygen	Magnetic properties		
	Zn (wt%)	In (wt%)	content (wt%)	B_r (T)	H_{cj} (MAm^{-1})	$(BH)_{max}$ (kJm^{-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

The fundamental magnetic data measured on the as-obtained and surface-coated $Sm_2Fe_{17}N_x$ fine powders were summarized in Table 1, together with the metal and oxygen contents. The surface-coating was effectively performed *via* the following photochemical decomposition of $In(C_2H_5)_3$ as:

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

so that a large amount of In metal (~ 5 wt%) was deposited on the surface of $Sm_2Fe_{17}N_x$ fine particles compared with the case of Zn metal-coating (~ 0.3 wt%). This is due that the rate of recombination between the Zn metal and ethyl radical is faster than that for the In metal. Indeed, the zinc metal amount of Zn/$Sm_2Fe_{17}N_x$ (0.22 wt%) was considerably decreased by the subsequent coating with In metal to produce In/Zn/$Sm_2Fe_{17}N_x$

(0.09 wt%), possibly according to the following exchange reaction:

$$2In(C_2H_5)_3 + 3Zn \rightarrow 2In + 3Zn(C_2H_5)_2.$$

The In/$Sm_2Fe_{17}N_x$ and In/Zn/$Sm_2Fe_{17}N_x$ fine powders still kept the high fundamental magnetic values (B_r=~1.30 T, H_{cj}=~0.74 MAm^{-1}, and $(BH)_{max}$=~271 kJm^{-3}), although the B_r and H_{cj} values were somewhat decreased after the In metal-coating owing to the dilution effect of the non-magnetic In metal.

Typical anisotropic hysteresis loops were observed on the In metal-bonded Zn/$Sm_2Fe_{17}N_x$ magnet produced from the In/Zn/$Sm_2Fe_{17}N_x$ powders (see Figure 2). The In metal-bonded magnet obtained under the optimized condition provided the higher $(BH)_{max}$ value (144 kJm^{-3} for B_r = 0.96 T and H_{cj} = 0.66 MAm^{-1}) than that of the In metal-bonded one from the In/$Sm_2Fe_{17}N_x$ powder. This is due to the superior thermal stabilization effect of Zn metal-coating and the improvement of the oxidation resistance by the double-metal coating layer, consequently, the decrease of the hard magnetic property of the raw material, In/Zn/$Sm_2Fe_{17}N_x$, was depressed during the molding process at the temperature around melting points of the binder metals compared with the case of the magnets made from the uncoated $Sm_2Fe_{17}N_x$. powders as raw materials. It is noted that the $(BH)_{max}$ value of 144 kJm^{-3} observed on the In metal-bonded Zn/$Sm_2Fe_{17}N_x$ magnet is the highest one among a series of metal-bonded $Sm_2Fe_{17}N_x$ magnets reported up to date (e.g. $(BH)_{max}$ = 134 kJm^{-3} for the Zn metal-bonded magnet[7]).

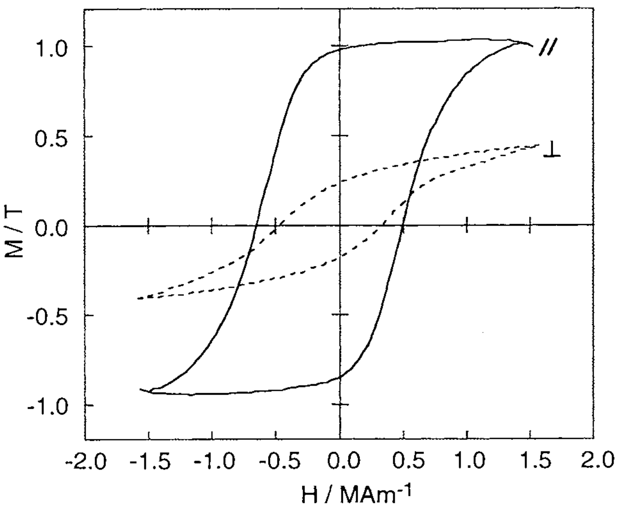

Figure 2. Anisotropic hysteresis loops of In metal-bonded magnet measured parallel (solid line) and perpendicular (dotted line) to a magnetization direction.

In conclusion, the In/Zn/$Sm_2Fe_{17}N_x$ powders provide high-performance permanent metal-bonded magnets owing to the good stabilization effect of the thick In and Zn metal coating film without any further addition of metal binders.

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