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Magnetic properties of zinc-coated $Sm_2(Fe_{0.9}Co_{0.1})_{17}N_x$ powders

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Abstract

High-performance magnetic powders of the $Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.9}$ compound were prepared by ball milling in an organic solution containing surface active agent (Aerosol OT). The subsequent zinc-coating process allows the powders to be stabilized against oxidation by O_2 or H_2O. The above two steps were optimized by investigating the powder particle size (i.e. milling time) dependence and the influence of zinc content on the treatment efficiency, in order to obtain powerful magnets. © 1998 Elsevier Science S.A.

Keywords: Rare earth magnets; 2:17 nitrides; Cobalt; Zinc coating; Thermal stability

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1. Introduction

Owing to their excellent intrinsic magnetic properties, interstitially modified materials have been regarded as promising candidates for permanent magnet applications. Especially, $Sm_2(Fe_{1-x}Co_x)_{17}N_x$ $(0 \leq x \leq 0.3)$ compounds are of great interest [1–6]. Nevertheless, the metastability of nitrides and the high reactivity of rare earth metals with H_2O, O_2, CO and CO_2 still remain a serious problem, because this leads to a large loss of the original magnetic properties of the fine-powder.

Recently, we have reported that Zn metal, used as a protection layer for the $Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.9}$ powders, is very efficient for improving both stability and magnetic properties of this compound and those of epoxy-bonded magnets made of such powders [7]. The zinc metal deposition was made by coating the surface of the ground powder particles with the Zn metal derived from the photodecomposition of $Zn(C_2H_5)_2$ irradiated for 5 h (≤0.26 wt.%). Such zinc coated powders exhibited good magnetic properties (after 4 h of milling: $(BH)_{max}=46.8$ MG Oe; $4\pi M_r=15.1$ kG; ${}_iH_c=11.1$ kOe) but a weak corrosion resistance, and we have concluded that the zinc protection layer thickness (=1 nm) was not enough to suppress the corrosion process.

In this paper, the aim of our study was to improve the stability of such high magnetic performance Zn/$Sm_2(Fe_{0.9}Co_{0.1})_{17}N_x$ powders by increasing the thickness of the zinc layer. The magnetic behaviour of the fine powders was examined as a function of the milling time, and furthermore, optimized with a view to producing new high performance permanent magnets.

2. Experimental

2.1. Ball milling conditions

Raw $Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.9}$ powders were prepared elsewhere according to the conventional technique [8]. Each sample (6 g) of the raw powder (particle size≈40 μm; density=7.93 g cm^{-3}; $T_c=798$ K) was ground by ball milling in a hexane solution containing 2.5×10^{-3} mol l^{-1} of Aerosol OT (di-2-ethylhexyl sodium sulfosuccianate, $C_{20}H_{37}O_4{-}SO_3{-}Na^+$) by using a glass vessel and steel balls [7,9,10]. The hexane used was distilled several times in the presence of Na metal to remove water. The manipulations were carried out in a purified argon atmosphere (less than 8 ppm of oxygen and water). After the ball milling operation, the hexane solution was removed and the powder was washed with distilled hexane and dried in vacuo.

The powders, denoted hereafter $Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.9}$ and $Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.6}$, correspond, respectively, to the raw nitride and to the powder samples ground for 4 h.

2.2. Zinc coating conditions

The resulting fine powder was introduced in a quartz cell with 20 ml of a *n*-hexane solution containing 13.1 mol% of $Zn(C_2H_5)_2$. The photodecomposition of $Zn(C_2H_5)_2$ was performed by ultra-violet irradiation for 5

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h or 20 h, by using a low pressure mercury arc. Finally, the zinc coated powder was dried in vacuo after evaporation of the $Zn(C_2H_5)_2$ residues. The thickness of the zinc layer deposited on one particle was calculated by considering the zinc content and the powder mean particle size (the particle shape was assumed to be spherical).

Composites powders, denoted hereafter $Zn_{0.2}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ and $Zn_{0.6}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$, correspond to the samples milled for 4 h and zinc coated for 5 h (0.26 wt. % of zinc) and 20 h (0.73 wt. % of zinc) respectively.

2.3. Production of bonded magnets

The ground $Zn/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_x$ powders were mixed with 2.5 wt. % of epoxy resin, isotropically pressed under 1.4 GPa in a magnetic field of 18 KOe, and cured at 353 K for 4 h, according to a technique described elsewhere [9].

2.4. Characterizations

The structural analysis of raw and zinc coated fine powders was performed on a MAC Science-M18XHF-SRA diffractometer (monochromatasised Cu Kα radiation). Oxygen content was measured by using an oxygen analyser (Horiba-EMGA 550). The zinc content was evaluated with an inductively coupled plasma atomic spectroscopy apparatus (Shimadzu ICPS 1000IV). Magnetic hysteresis loops were recorded at room temperature using a vibrating sample magnetometer in a field range of ±15 KOe after magnetization at 60 KOe by a pulsed magnetic field generator. Particle size was checked by means of SEM observations and specific surface area (SSA) of the powder was measured by a conventional (BET) nitrogen adsorption method (Micrometrics Flow Sorb II 2300).

3. Results and discussion

3.1. The $Sm_2(Fe_{0.9}Co_{0.1})_{17}N_x$ fine powders

The particle size variations, as estimated from SEM pictures and as converted from SSA measurements, are compared in Fig. 1. For the raw nitride, which is full of micro-cracks (clearly identified on SEM pictures), the particle size calculated from the SSA data (proportional to the inverse of the SSA value) is far smaller than that obtained by SEM observations (SEM: 40 μm; SSA: 4.9 μm (0.15 $m^2\ g^{-1}$)). The difference between the two curves decreases with the milling time, and after 4.5 h, the particle sizes estimated from both SEM pictures and SSA values become very close (SEM: 1.0 μm; SSA: 0.3 μm (2.42 $m^2\ g^{-1}$)). This indicates that the variation of the particle size with the milling time mainly results from the reduction in quantity of the cracks in the powder.

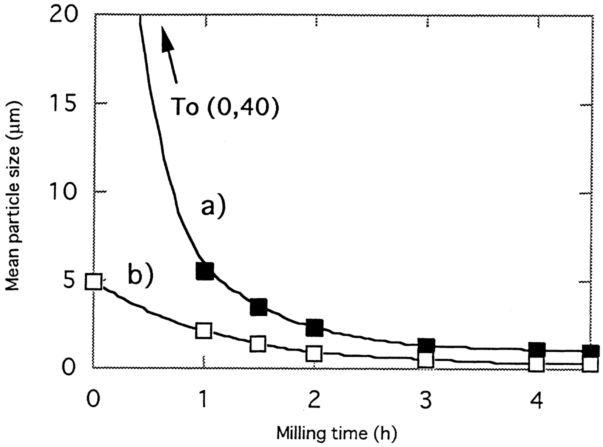

Fig. 1. Mean particle size versus milling time of $Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.9}$, as estimated from (a) SEM pictures, and (b) SSA measurements.

XRD patterns of the powder samples of $Sm_2(Fe_{0.9}Co_{0.1})_{17}N_x$ are fully indexed in the space group $R3m$. These patterns showed that up to 4 h of milling, there is no evidence of decomposition into SmN and Fe or Fe/Co. Also, this was supported by the small oxygen content (0.30~0.38) and the hysteresis loop squareness value (51%~35%) measured for the different samples, as the squareness value$=H_k/{}_iH_c$, where H_k is the H value at $0.9\times 4\pi M_r$. After 4.5 h of milling, the partial amorphization of the powder and the appearance of soft phase(s) (Fe or/and FeCo) damage the magnetic properties of the powders (confirmed by XRD and VSM).

3.2. The stabilization of fine powders with zinc-metal coating

As previously reported, the magnetic properties of both powders obtained just after milling (free powders) and zinc-coated powders are improved with an increase of the milling time (Fig. 2). For both irradiation times, we obtained our best results for a milling time of 4 h.

As expected, the coercivity values of $Sm_2(Fe_{0.9}Co_{0.1})_{17}N_x$ and $Zn/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_x$ particles vary as the inverse of the mean particle size (Fig. 2(a)). The coercivity then seems to be controlled by a nucleation process [11]. Nevertheless, the coercivity decreases slightly as the amount of zinc is increased. We have concluded that the oxygen residues present as ZnO in the Zn metal film decompose the nitride partially, and lower the coercivity of zinc coated powders [7,9]. Oxygen contents measured on the zinc coated powders (0.41 wt. % and 0.49 wt. % respectively after 5h and 20 h of irradiation) are always higher than those of corresponding free powders (0.38 wt. %, 4 h of milling) and seem to confirm the latter assertion.

The positive effect of zinc coating on the magnetization of the $Sm_2(Fe_{0.9}Co_{0.1})_{17}N_x$ samples is clearly observed on Fig. 2(b), but it does not appear with the same efficiency

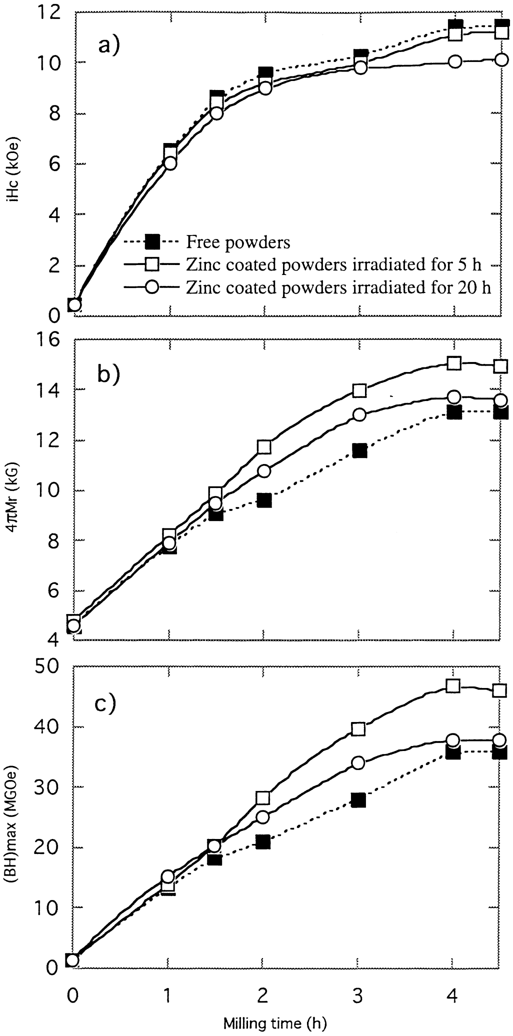

Fig. 2. Milling time dependence of (a) the coercivity, (b) the remanent magnetization and (c) the $(BH)_{\max}$ for free powders and for zinc coated powders irradiated for 5 h and 20 h.

for the different irradiation times. The saturation magnetization of the zinc-coated powder, as obtained after irradiation of 5 h, is 15.9 kG, the remanent magnetization is 15.1 kG and the thickness of the zinc layer was estimated to be 1 nm (zinc content=0.26 wt. %). For the irradiation time of 20 h, both the saturation magnetization (14.4 kG) and the remanent magnetization (13.7 kG) are decreased by the zinc layer which was estimated to be 3 nm (zinc content=0.73 wt. %), since the magnetic phase is more screened by the zinc metal. The magnetic square values remain of the same order (around 35%) for both zinc contents.

The influence of zinc content on magnetic performance at room temperature is summarized in Fig. 3. The $(BH)_{\max}$ value of our best samples reaches 46.8 MG Oe (371 kJ m^{-3}) and 37.9 MG Oe (300 kJ m^{-3}) for the $Zn_{0.2}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ and $Zn_{0.6}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ powders, respectively. Also, the hysteresis curve of these samples exhibits anisotropic behaviour.

Magnetic characteristics of our best samples were also studied from the viewpoint of their practical use as a permanent magnet. In this sense, powder samples were measured after heat treatments at 423 K (150°C) for 1, 5 and 10 h (under argon). This temperature is twice as high as the conventional one used to cure bonded magnets. The time dependence of heat treatment as a function of the fundamental magnetic parameters of both $Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.6}$, $Zn_{0.2}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ and $Zn_{0.6}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ powders obtained under the optimized ball milling conditions (4 h) are shown in Fig. 3. The positive influence of a larger amount of zinc on the stability of powders is clearly identified.

For the free powder, the oxygen content is considerably increased with the time of heating (0.38 wt. %~0.76 wt. %). Thus, coercivity and remanent magnetization values are also decreased (Fig. 3(a) and (b)). The values for the $Zn_{0.2}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ powder are not constant, but still remain at a very high level after the heat treatment, with ${}_iH_c=10$ kOe, $4\pi M_r=13.6$ kG and $(BH)_{\max}=35.8$ MG Oe (285 kJm^{-3}). For the larger amount of zinc ($Zn_{0.6}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ powder), magnetic properties are kept constant after 10 h at 150°C under argon, with ${}_iH_c=10.2$ kOe; $4\pi M_r=13.7$ kG; $(BH)_{\max}=37.9$ MG Oe (301 kJ m^{-3})). Also, the magnetic square remains constant (~35%) only for the $Zn_{0.6}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ powder. We can compare these results to those obtained from the $Zn/Sm_2Fe_{17}N_3$ powder of Ref. [9]. In this case, the corresponding thickness of the zinc layer was estimated to be 2 nm, and the $(BH)_{\max}=40$ MG Oe (318 kJ m^{-3}) was also kept constant under the same conditions.

3.3. Magnetic properties of $Zn/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_x$ bonded magnets

The magnetic behaviour of $Zn_{0.2}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.9}$ and $Zn_{0.6}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ powders and corresponding magnets are presented in Fig. 4. The $(BH)_{\max}$ value of the $Zn_{0.2}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ powder is higher

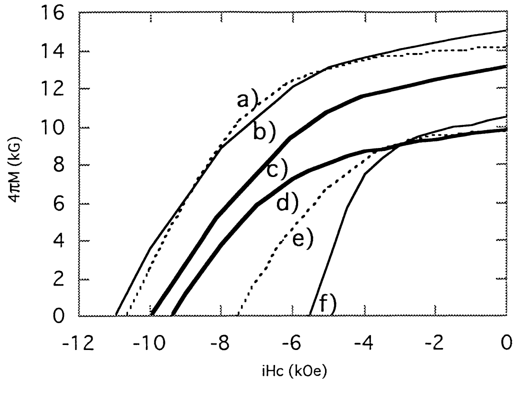

Fig. 3. Comparison of the hysteresis curves of the: (a) $Zn/Sm_2Fe_{17}N_3$ powder [9], (b) $Zn_{0.2}/Sm_2(Fe_{0.9},Co_{0.1})_{17}N_{2.7}$ powder, (c) $Zn_{0.6}/Sm_2(Fe_{0.9},Co_{0.1})_{17}N_{2.7}$ powder and (e), (f), (d) corresponding magnets.

because of a dramatic improvement in the magnetization and a weaker screening of the magnetic phase by zinc metal than in the $Zn_{0.6}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ powder. Nevertheless, the results of the corresponding magnets are reversed, with $(BH)_{max}$ values of 18.3 MG Oe (146 kJ m^{-3}) and 19 MG Oe (151 kJ m^{-3}), respectively. Especially, the coercivity of the magnet made of the $Zn_{0.6}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ powder (9.4 kOe; −5%) is less damaged during the pressing step than the coercivity of the magnet made of the $Zn_{0.2}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ powder (5.5 kOe; −50%). Also, the magnetization is slightly less decreased during that step (−28% as compared with −31%). This may be due to the difference of thickness between their zinc layers, as the zinc thickness on $Zn_{0.6}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ powder particles (3 nm) is three times higher than that of $Zn_{0.2}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ (1 nm). The magnet density slightly increases (up to 6.3 g cm^{-3}), and the magnet square decreases (44%~34%) with the amount of zinc. Also, the hysteresis curve of these magnets exhibits anisotropic behaviour. We can also compare these results with those of Ref. [9], obtained under the same conditions (Fig. 4).

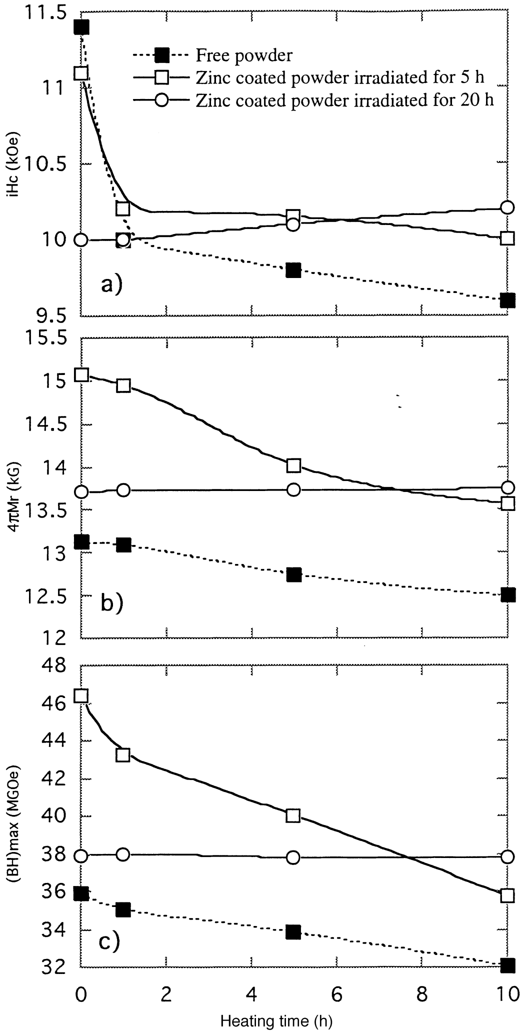

Fig. 4. Variation of (a) the coercivity, (b) the remanent magnetization and (c) the $(BH)_{max}$ versus the heating time (Ar, 150°C) for free powders and for zinc coated powders irradiated for 5 h and 20 h.

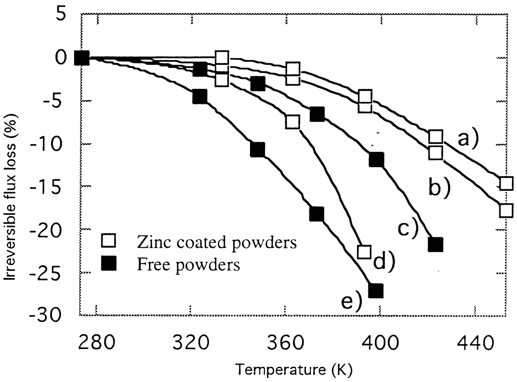

Fig. 5. Irreversible flux loss curves of some bonded magnets (measured in air): (a) $Zn_{0.6}/Sm_2(Fe_{0.9},Co_{0.1})_{17}N_{2.7}$; (b) $Zn_{0.2}/Sm_2(Fe_{0.9},Co_{0.1})_{17}N_{2.7}$; (c) $Sm_2(Fe_{0.9},Co_{0.1})_{17}N_x$; (d) $Zn/Sm_2Fe_{17}N_3$ [9]; (e) $Sm_2Fe_{17}N_x$.

The irreversible flux loss curve (measured in air) of the bonded magnet made of $Zn_{0.2}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ and $Zn_{0.6}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ powders are presented in Fig. 5, together with those reported on the magnets made of $Sm_2(Fe_{0.9}Co_{0.1})_{17}N_x$ ($x \approx 3$), $Zn/Sm_2Fe_{17}N_3$ [9] and $Sm_2Fe_{17}N_x$ ($x \approx 3$) powders.

Three major remarks can be drawn from these curves. First of all, it is clearly shown that a small amount of cobalt magnetically stabilizes the 2:17 nitrides, which exhibit the lower irreversible flux loss than for cobalt-free 2:17 nitrides, for temperatures up to 453 K. Also, the magnets prepared from zinc coated powders exhibit lower irreversible flux loss than free powders, for both $Zn/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_x$ and $Zn/Sm_2Fe_{17}N_x$. Finally, the magnet stability is increased for the larger amount of zinc.

The best results are obtained with $Zn_{0.6}/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.7}$ powders, with irreversible flux loss values of −1.35% at 363 K, and −14.5% at 453 K. To our knowledge, these values are the best values ever reported for this compound. This is due to a combined effect of cobalt substitution and zinc coating on the magnetic stability and on the corrosion resistance of the 2:17 nitrides.

4. Conclusion

We have shown that powders of the interstitial compound $Sm_2(Fe_{0.9}Co_{0.1})_{17}N_{2.9}$ exhibit better intrinsic properties than the pure 2:17 nitride and have a very high potential as a new material for powerful anisotropic bonded magnets. The zinc coating based on the $Zn(C_2H_5)_2$ photodissociation provides the stability to keep the magnetic properties at their excellent level. The particle size dependence and the influence of zinc content on the magnetic performances of $Zn/Sm_2(Fe_{0.9}Co_{0.1})_{17}N_x$ powders and corresponding magnets are of prime importance. Finally, the best results are obtained, by adjusting the particle size to 1.1 μm, and the zinc content to 0.73 wt. %, with the $(BH)_{max}$ value of 37.9 MG Oe (301 kJ m^{-3}), providing the smallest irreversible flux loss coefficients with −1.35% at 363 K, and −14.5% at 453 K for the epoxy bonded magnet with the $(BH)_{max}$ value of 19 MG Oe (151 kJ m^{-3}).

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