Zn-bonded rare-earth transition-metal permanent magnets

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Zn-bonding was investigated as a mean of developing the coercivity in RE-TM permanent magnets of the type $Sm_2Fe_{17}X_y$ (X=N or C) and $Nd(Fe,Mo)_{12}N_{0.9}$. Coercivities $\mu_{0J}H_c$ up to 2.3 T were obtained for $Sm_2Fe_{17}N_y$ after an optimal heat treatment. The development of $_JH_c$ is connected with a modification of the grain boundaries by the reaction of Zn with the magnetic particles and is disturbed by the simultaneous formation of α-Fe during heat treatment. The decrease of polarization with increasing Zn-content is stronger after heat treatment than it corresponds to a simple dilution law.

1. INTRODUCTION

At present most of the permanent magnets based on RE-TM alloys are produced via powder metallurgy. Magnets for practical use are sintered or polymer bonded. Recently a series of interstitial ternary compounds of the type ReFeX (X=C and/or N) has been found from which $Sm_2Fe_{17}X_y$ [1, 2] and $Nd(Fe,TM)_{12}X_y$ [3] show intrinsic magnetic properties interesting for permanent magnet application. But there are serious difficulties to produce magnets by conventional sintering because these phases disproportionate at about 600 °C. To translate the intrinsic properties into useful magnet ones, bonding of the milled powders with low melting metals is useful [4]. In particular, additions of Zn-powder are succesful to increase the coercivity of $Sm_2Fe_{17}X_y$ powder after compaction and appropriate annealing processes. In this paper results concerning the development of coercivity in $Sm_2Fe_{17}N_y$, $Sm_2Fe_{17}C_y$ and $NdFe_{10.75}Mo_{1.25}N_{0.9}$ magnets by applying the Zn-bonding technique are reported.

2. EXPERIMENTAL DETAILS

Sm_2Fe_{17} powders were prepared from homogenized alloys. The nitrogenized (carbonized) powders of Sm_2Fe_{17} were obtained by a gas-solid reaction (GSR) with nitrogen (methane) at 450 °C for different periods of time [5, 6]. A similar method was used to prepare $NdFe_{12-x}Mo_xN_y$ powder [7].

$Sm_2Fe_{17}C_y$ was prepared also by arc-melting of Fe_3C, Fe, and a 50 wt-% Sm-Fe master alloy and by subsequent homogenization and milling [6]. The content of interstitials was determined by the pressure drop during GSR, the mass gain after the reaction, or by the heat extraction method. Zn-bonding was performed by mixing the milled powder with 5 to 90 wt-% Zn-powder, pressing in a magnetic field of 2 T and annealing at a temperature in the range from 250 °C to 500 °C for different times. In order to get more insight into the reactions of Zn with $Sm_2Fe_{17}N_y$ powder the samples were investigated by differential scanning calorimetry (DSC) at a heating rate of 20 K/min in nitrogen atmosphere. The phase compositions and structural changes were analysed by X-ray diffractometry and microprobe analysis. Magnetic measurements were performed by a VSM with fields up to 8 T.

3. RESULTS AND DISCUSSION

3.1. Zn-bonding of $Sm_2Fe_{17}N_y$ powder

Coercivities $\mu_{0J}H_c$ of about 0.4 T were found for powders with a mean grain size of about 10 μm after nitrogenation at 450 °C for 5 hours. Higher values were achieved by additionally milling these powders as shown in Figure 1. For resin fixed powders $_JH_c$ increases linearly up to a maximum value determined by a critical particle size. The oxygen content increases linearly over the whole milling time.
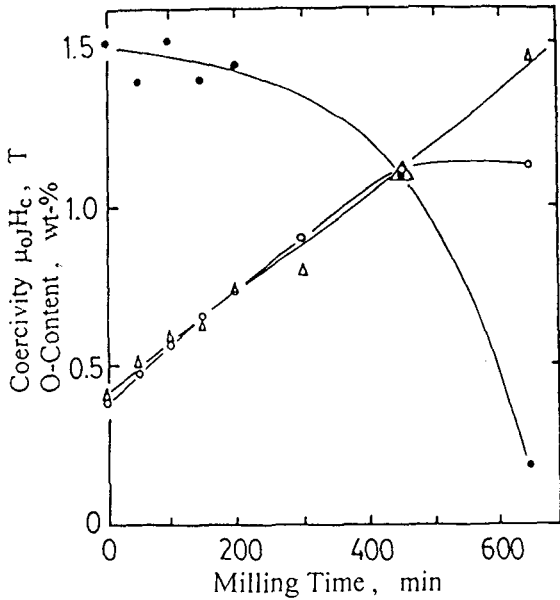
Figure 1. Coercivity of resin fixed (o) and 15 wt-% Zn-bonded (o) $Sm_2Fe_{17}N_y$ magnets and oxygen content (Δ) as a function of milling time.
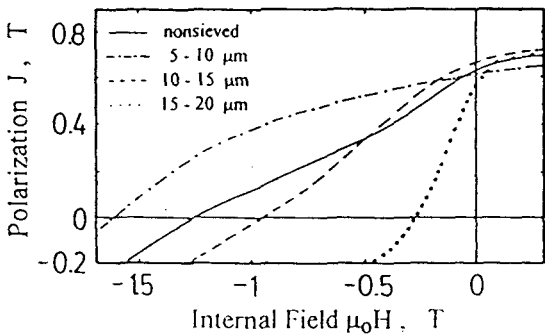

Figure 2. Influence of the particle size distribution of $Sm_2Fe_{17}N_y$ powder on the shape of demagnetization curves of Zn-bonded magnets (the pore sizes of sieves were 5, 10, 15 and 20 μm).

As a result of additional milling not only the particle size is reduced but also the chemical composition, the surface state as well as the amount of phases may be changed. These factors can influence the coercivity. For very fine powders obtained after long milling times Zn-bonding is not useful because of the sharp decrease of $_jH_c$ after the heat treatment (e.g. at 425 °C for 2 hours). For longer milling times the coercivity and mainly the remanence decrease
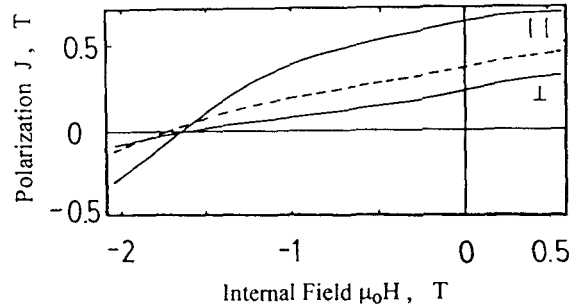

Figure 3. Demagnetization curves of a textured Zn-bonded $Sm_2Fe_{17}N_y$ magnet measured parallel ($\|$) and perpendicularly ($\perp$) to the texture axis in comparison with an isotropic magnet (- - -).
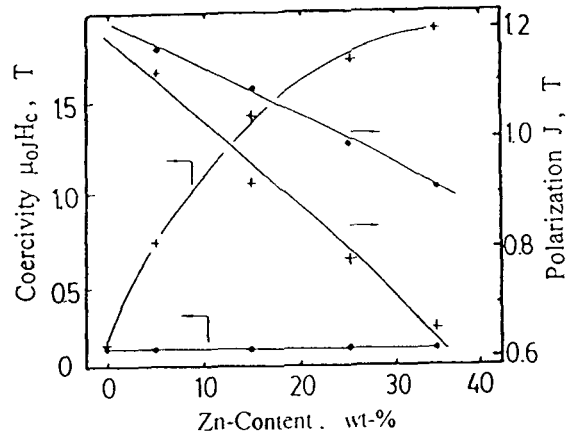

Figure 4. Polarization (measured at an applied field of 4 T) and coercivity of $Sm_2Fe_{17}N_y$ samples, before (o) and after (+) heat treatment, versus Zn-content.

strongly due to the presence of α-Fe.

The shape of demagnetization curves can be remarkably improved by sieving the powder before the compaction, i.e. by narrowing the particle size distribution as shown in Figure 2. The demagnetization curves in Figure 3 indicate a good alignment of the easy axes (c-axes) of the $Sm_2Fe_{17}N_y$ grains in our textured Zn-bonded magnets.

The influence of Zn-content and heat treatment is shown in Figure 4. Before heat treatment, the coercivity does not change with Zn-content and the polarization decreases by a simple dilution law. After annealing, however, a strong increase of the coercivity is observed and the polarization decreases

more rapidly.

Demagnetization curves of Zn-bonded $Sm_2Fe_{17}N_y$ with different degrees of texture were measured very accurately in the first quadrant of the J-H plane in fields up to 8 T between 20 °C and 260 °C. By means of a fit procedure the anisotropy constants K_1 and K_2 as well as the anisotropy field H_A, shown in Table 1, were calculated from these demagnetization curves [8]. The good agreement of our values with results for H_A and K_1 of pure $Sm_2Fe_{17}N_y$, obtained by the SPD method and by a fitting procedure [9], shows that Zn-bonding does not influence the intrinsic magnetic properties.

Table 1.
Fitted values of K_1, K_2, J_s and H_A for $Sm_2Fe_{17}N_y$

T (°C)	K_1 (MJm^{-3})	K_2 (MJm^{-3})	J_s (T)	$\mu_0 H_A$ (T)
20	8.89	1.46	1.54	19.3
100	6.62	0.70	1.47	13.7
180	4.69	0.25	1.36	9.6
260	3.00	0.049	1.22	6.4

The DSC trace of $Sm_2Fe_{17}N_y$ powder mixed with Zn shows an exothermic peak in the first run of experiment at 390 °C (see trace 1) in Figure 5). X-ray analysis reveals that this exothermic reaction is
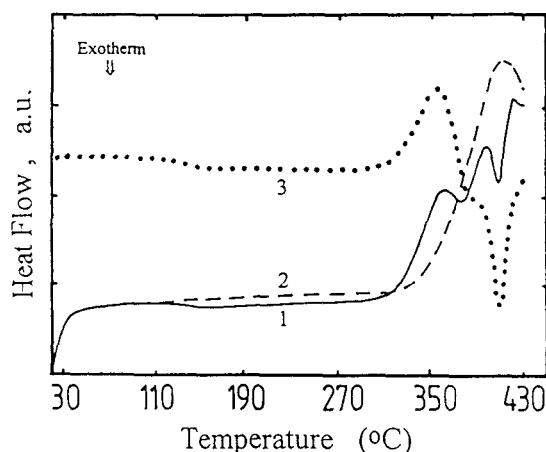

Figure 5. DSC traces of a 15 wt-% Zn-bonded $Sm_2Fe_{17}N_y$ magnet (heating rate 20 K/min, nitrogen atmosphere): first run (1 : ———) and second run (2 : – – –) of the same sample. Curve 3) results from the difference between 1) and 2) (• • • •).

related to the formation of a Γ-phase assigned as Zn_7Fe_3 [4]. The second run of the same sample (trace 2) and mainly the difference curve 3 show that all Zn has reacted with $Sm_2Fe_{17}N_y$ and there is no sign of Zn melting at 419 °C. For this heating rate the endothermic reaction peak (characteristic for melting of Zn) only appears for higher Zn-contents (e.g. 30 wt-% Zn). After annealing Zn-bonded samples for short times at 390 °C, the coercivity is not fully developed and increases with annealing for longer times or at higher temperatures. Possibly an improvement of coating of the $Sm_2Fe_{17}N_y$ particles by the Γ-phase as well as a smoothing of their surface by the chemical reaction take place and these effects could enhance the coercivity. They also lead to a decrease in the relative intensity of the X-ray reflections of the $Sm_2Fe_{17}N_y$ phase [11].

The microprobe analysis of a Zn-bonded $Sm_2Fe_{17}N_y$ magnet indicates the presence of Sm, Fe and Zn at the boundary of the $Sm_2Fe_{17}N_y$ grains with concentrations of 5 at-% Sm, 45 at-% Fe and 50 at-% Zn. A phase with a similar composition was synthesized in the ternary Sm-Fe-Zn system [12]. There is no direct evidence for the existence of such ternary phase in the magnets. According to [12] the formation of the Γ-phase dissolving about 5-at% Sm is connected with α-Fe precipitation. This can explain the degradation of the magnetic properties mainly of fine $Sm_2Fe_{17}N_y$ powders due to Zn-bonding because they react more vehement compared with coarser powders.

3.2. Zn-bonding of $Sm_2Fe_{17}C_y$

Homogeneous $Sm_2Fe_{17}C_y$ samples could be prepared by arc-melting up to y=1 and by GSR up to y=2.5 [6]. Compacted powders produced from arc-molten carbides show coercivities of about 0.04 T, only slightly higher than $_jH_c$ of Sm_2Fe_{17}. On the other hand carbides prepared by GSR have a coercivity of about 0.2T. By Zn-bonding the coercivity of arc-molten carbides could be increased up to 0.1 T. A stronger increase was found by Zn-bonding of GSR-carbides as shown in Figure 6. The maximum values of coercivity achieved for carbides are only about half of those obtained for nitrides, though the anisotropy fields of both compounds are comparable [8]. X-ray diffraction pattern of Zn-bonded magnets of both compounds have revealed that the carbide magnets contain a higher amount of
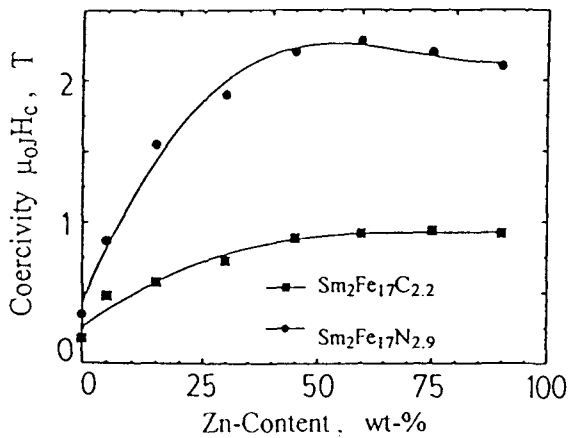
Figure 6. The influence of Zn-content on the coercivity of $Sm_2Fe_{17}C_{2.5}$ and $Sm_2Fe_{17}N_{2.9}$.
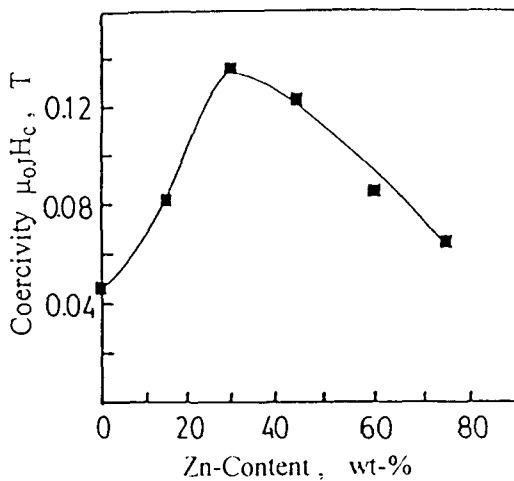

Figure 7. Influence of the Zn-content on the coercivity of $NdFe_{10.75}Mo_{1.25}N_{0.9}$ magnets.

α-Fe, which probably decreases the coercivity. For our Zn-bonded $Sm_2Fe_{17}C_y$ magnets no decrease in the intensity of the α-Fe peaks could be found after different stages of heat treatment.

3.3. Zn-bonding of $NdFe_{12-x}Mo_xN_{0.9}$

The coercivity of $NdFe_{12-x}Mo_xN_{0.9}$ with low Mo concentration x=1.25 and 1.5 can be also increased by means of both additional ball milling and Zn-bonding [7]. Figure 7 shows the influence of the Zn-content on the coercivity for $NdFe_{10.75}Mo_{1.25}N_{0.9}$

without additional milling procedure. The effect of Zn is much less than that found for $Sm_2Fe_{17}X_y$. Additional tests with Al, Sb, and Sn, as well, did not give positive results. A possible reason for this observation might be that the Sm-containing boundary phase detected in Zn-bonded $Sm_2Fe_{17}X_y$ magnets (X=N or C) is not present in these 1:12 materials.

Acknowledgment

REFERENCES

[1] J.M.D. Coey and H. Sun, J. Magn. Magn. Mater. 87 (1990) L251.

[2] J.M.D. Coey, H. Sun, Y. Otani and D.P.F. Hurley, J. Magn. Magn. Mater. 98 (1991) 76.

[3] M.S. Anagnoston, C. Christides and D. Niarchos, Solid Sate Commun. 78 (1991) 681.

[4] Y. Otani, A. Moukarika, H. Sun, J.M.D. Coey, E. Devling and I.R. Harris, J. Appl. Phys. 69 (1991) 6735.

[5] P.A.P. Wendhausen, A. Handstein, P. Nothnagel, D. Eckert and K.-H. Müller, phys. stat. sol. (a) 127 (1991) K121.

[6] P.A.P. Wendhausen, Bo-Ping-Hu, B. Gebel, D. Eckert, A. Handstein and K.-H. Müller, Digest of EMMA'93 Conf., Kosice, Slovakia, 1993, paper B-P-06.

[7] Bo-Ping Hu, P.A.P. Wendhausen, D. Eckert, W. Pitschke, A. Handstein and K.-H. Müller, as [6], paper B-P-21.

[8] K.-H. Müller, D. Eckert, P.A.P. Wendhausen, A. Handstein, S. Wirth and M. Wolf, as [6], paper P-O-06.

[9] M. Katter, J. Wecker, C. Kuhrt, L. Schultz and R. Grössinger, J. Magn. Magn. Mater. 114 (1992) 35.

[10] K.-H. Müller, G. Leitner, W. Pitschke, P.A.P. Wendhausen, A. Handstein and D. Eckert, phys. stat. sol. (a) 133 (1992) K37.

[11] P. Wendhausen, D. Eckert, A. Handstein and K.-H. Müller, J. Appl. Phys. 73 (1993) 6044.

[12] B. Reinsch, H.H. Stadelmaier and G. Petzow, Digest of the INTERMAG'93 Conference, Stockholm, Sweden, 1993, paper FC-07.