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On the role of Zn in $Sm_2Fe_{17}N_x$ permanent magnets

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Coercivities up to 1.9 T were achieved by bonding micron-size $Sm_2Fe_{17}N_x$ particles with zinc. X-ray analysis of Zn-bonded samples indicates the presence of the ZnFe Γ phase and no unreacted Zn, after heat treatment at about 390 °C for 100 min for samples with Zn content varying from 5 to 35 wt. %. The increase of coercivity occurs only for a more intense heat treatment, e.g., at 390 °C for 300 min or 425 °C for 100 min. Differential scanning calorimetry (DSC) shows two exothermic peaks at 388 and 426 °C, but no endothermic peak related to the melting of Zn (at 419.6 °C) was observed. In dilatometric measurements two peaks were observed for the rate of length change near the same temperatures as the DSC peaks. Polarization-versus-field curves point to an additional ferromagnetic phase with (i) a Curie temperature near 180 K and (ii) 2% of the net magnetization at low temperatures. The corresponding dip in low-temperature demagnetization curves, however, is about 10% in depth. Most of the $Sm_2Fe_{17}N_x$ grains in the demagnetized Zn-bonded magnets are multidomain. We found $\gamma \approx 3.4 \times 10^{-2}$ J/m^2 and $D_c \approx 0.3$ μm for the wall energy and for the critical single-domain particle diameter, respectively.

I. INTRODUCTION

After the announcement of $Sm_2Fe_{17}N_x$ as a potential material for permanent magnet application by Coey and Sun,[1] good progress has been achieved towards developing useful coercive materials by applying different techniques.[2–4] Of these, metal bonding turns out to be a suitable technique for preparing anisotropic magnets.[3] Coercivities up to 1.8 T have been achieved in anisotropic magnets using Zn as the bonding material.[5,6] According to Otani *et al.*,[3] the effect of Zn in increasing the coercivity is to reduce the surface roughness of the $Sm_2Fe_{17}N_x$ particles and to decouple them magnetically by providing a paramagnetic ZnFe Γ phase in the interparticle space ($\sim Zn_7Fe_3$). Huang *et al.*[5] suggest that this increase in coercivity is also due to the elimination of deleterious α-Fe by combining it with Zn to form Zn-Fe paramagnetic phases. Furthermore, they only observed an increase in coercivity for binders such as Zn or Sn, which can form a nonmagnetic phase with Fe.

In this study we examine the formation of Zn-Fe phases in Zn-bonded magnets by different heat-treatment conditions and examine their effect on the magnetic properties.

II. EXPERIMENTAL METHODS

The preparation of our Zn-bonded $Sm_2Fe_{17}N_x$ magnets and the magnetic measurements were described elsewhere.[6,7] The reaction of Zn with the magnetic material was investigated by differential scanning calorimetry (DSC) and dilatometry. These investigations were carried out in nitrogen atmosphere at heating rates of 20 K/min (DSC) and 10 K/min (dilatometry). The samples were submitted to x-ray analysis after different stages of thermal treatment. Magnetic domains were analyzed by the Kerr technique.

III. RESULTS AND DISCUSSION

As shown in Fig. 1, the increase of coercivity after heat treatment with increasing Zn content is very clear, but it does not behave similarly for different combinations of time and temperature. Especially for intermediate Zn contents, more intense heat treatments are needed to further increase coercivity.

X-ray analysis shows the presence of the Γ phase after heat treatment at 390 °C for 100 min, and no unreacted Zn

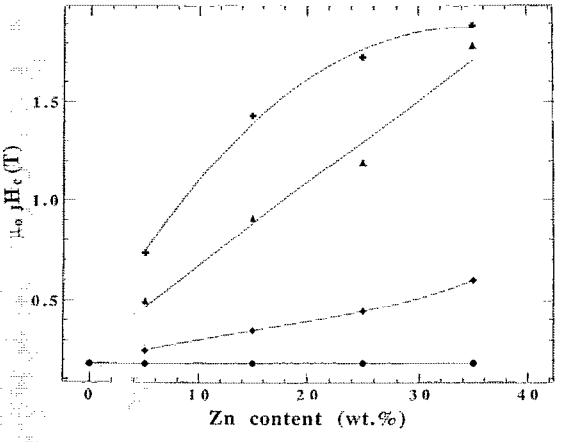

FIG. 1. Coercivity $_jH_c$ vs Zn content for different heat treatments conditions: before heat treatment; ♦—390 °C for 100 min; ▲—390 °C for 300 min; +—425 °C for 100 min, ●—mixed powder.

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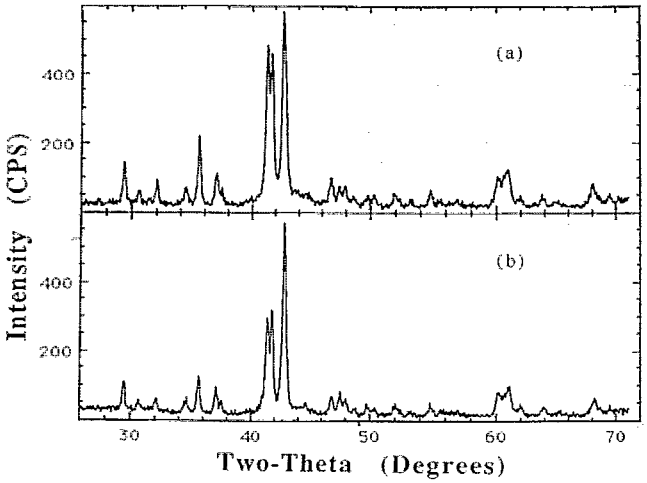

FIG. 2. X-ray diffraction patterns of 25% Zn bonded samples after heat treatment: (a) 390 °C for 300 min; (b) 425 °C for 100 min.

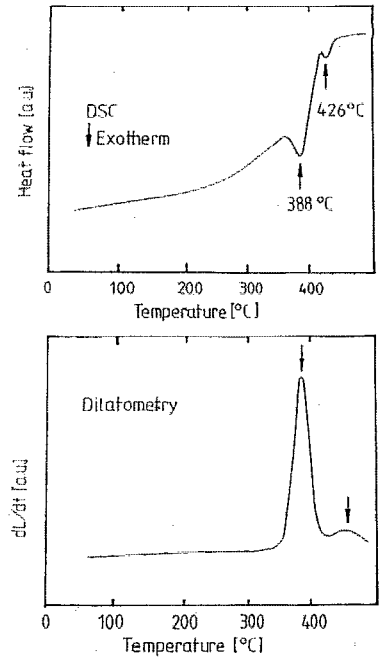

FIG. 4. Differential scanning calorimetry (DSC) curve (heating rate 20 K/min) and dilatometry curve (heating rate 10 K/min) for a sample made from a mixture of $Sm_2Fe_{17}N_x$ with 15 wt % Zn.

could be detected. It is noteworthy that at this stage the coercivity is not yet fully developed. It increases after more intense heat treatments for longer times or at higher temperatures. Possibly an improvement in coating of the magnetic particles by the Γ phase takes place when more intense heat treatments are applied, and this leads also to the observed decrease in the relative intensity of the x-ray reflections of the $Sm_2Fe_{17}N_x$ phase: e.g., for the peaks between 41° and 42° (Fig. 2).

In Fig. 3 the variation of magnetization measured at 4 T, before and after heat treatment, is shown. As would be expected, the magnetization before heat treatment decreases with Zn content approximately according to a simple dilution law. After heat treatment, however, this decrease is much stronger. Furthermore, the magnetization, unlike the coercivity, seems to decrease simultaneously with the formation of the Γ phase, not apparently changing after the complete consumption of Zn. The reduction is caused by the reaction of Zn with some magnetic phase, which can be α-Fe or $Sm_2Fe_{17}N_x$.

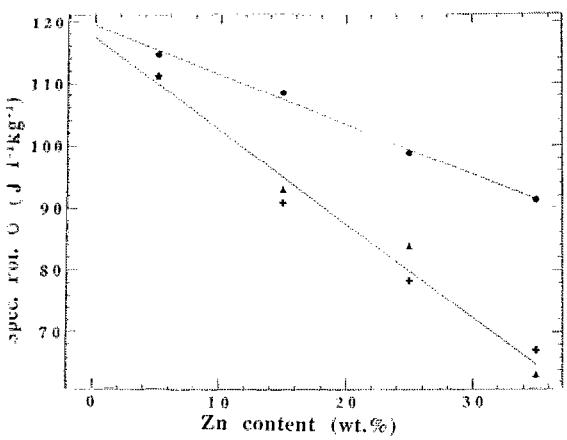

FIG. 3. Specific polarization σ, measured at an external field of 4 T, as a function of Zn content for different heat treatments conditions: ●—before heat treatment; ▲—390 °C for 300 min; +—425 °C for 100 min.

The DSC traces of samples made from $Sm_2Fe_{17}N_x$ powder mixed with Zn show two exothermic reactions at approximately 390 and 425 °C (Fig. 4). At nearly the same temperatures, the dilatometry shows two expansion peaks (Fig. 4). To check the relation of these peaks with reactions involving the Zn-Fe system we performed DSC and dilatometry on an additional 75:25 sample made from powders of these elements. It turns out that the same peaks appear at approximately the same temperatures. Hence they are related to reactions involving the Zn-Fe system. As checked by x-ray analysis the first exothermic reaction occurring around 390 °C is related to the formation of the Γ phase. The observed expansion peak (~8 vol %) near this temperature is probably due to voids caused by the preferential diffusion of Zn into iron (Kirkendal effect).[8] The nature of the second exothermic peak, however, is not known. No endothermic peak related to the melting of Zn can be seen in the DSC traces, meaning that either the endothermic peak is suppressed by the exothermic one at around 426 °C or, for the given conditions, the reaction between Zn and the magnetic particles takes place below the melting point of Zn.

At low temperatures the demagnetization curves of Zn-bonded $Sm_2Fe_{17}N_x$ show a dip, about 10% in depth, in the second quadrant of *J-H* plane (Fig. 5). A spin-reorientation transition cannot account for the effect since none was found for this compound.[7,9] Another possible cause is the presence of an additional ferromagnetic phase with a Curie temperature T_C not much below 200 K. In-

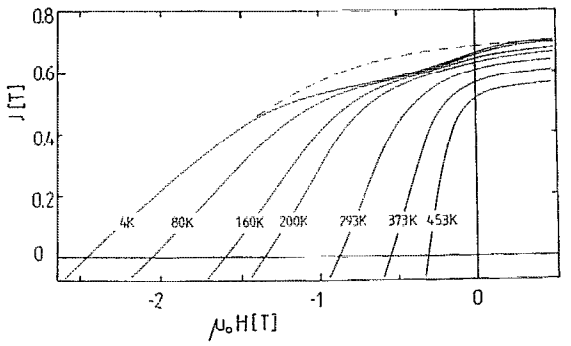

FIG. 5. Demagnetization curves of a 15-wt. % Zn-bonded magnet measured at different temperatures.

deed, thermomagnetic analysis points to a phase with $T_C \approx 180$ K (Fig. 6). But the contribution of this phase to saturation polarization is only 2%. It probably favors the nucleation of movable domain walls in $Sm_2Fe_{17}N_x$ grains which are mostly larger than the critical diameter D_c for

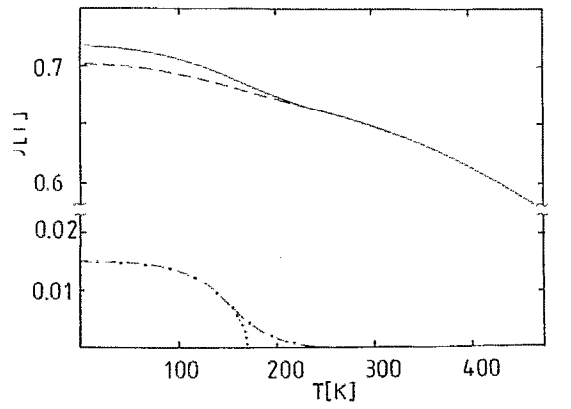

FIG. 6. Thermomagnetic phase analysis for the magnet of Fig. 5: —, experimental polarization-versus-temperature curve measured on the major demagnetization curve at an applied field of 1 T; ----, $T^{3/2}$ fit for the low-temperature behavior of the magnetic main phase; – · – · –, resulting J-vs-T curve for an additional ferromagnetic phase; ··· extrapolation to zero-field condition.

single-domain particle behavior. We estimated $D_c \approx 0.3\ \mu$m using the formula[10] $D_c \sim \gamma/J_s^2$ with J_s being the intrinsic saturation polarization and $\gamma = 3.4 \times 10^{-2}$ J/m^2 the wall energy, which was determined from the width d of the domains in a grain of diameter D using the formula[10] $\gamma \sim J_s^2 d^2/D$.

IV. CONCLUSIONS

We showed that the coercivity of Zn-bonded $Sm_2Fe_{17}N_x$ magnets can be improved by heat treatment after the formation of the paramagnetic Γ phase. The effect can be simply explained by a better distribution of the paramagnetic phase in the interparticle space, but the possibility of formation of another phase which decouples the $Sm_2Fe_{17}N_x$ more effectively, for instance, $Sm_5Fe_{42}Zn_{53}$,[11] has not been excluded. As discussed above, the dip observed in the demagnetization curves measured below 200 K possibly indicates the existence of another paramagnetic phase besides the Γ phase. X-ray analysis, however, gives no evidence of such a phase.

ACKNOWLEDGMENTS

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