5-1-2000

Order–disorder effects in nitrided Sm–Fe permanent magnets

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Order–disorder effects in nitrided Sm–Fe permanent magnets

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Rapidly solidified $Sm_{11}Fe_{89}$ was observed to form partially ordered Sm_2Fe_{17}. The ordering increased systematically with annealing temperature, reaching an order parameter of 0.8 after annealing at 950 °C for 15 min. The coercivity of the corresponding interstitial compound $Sm_2Fe_{17}N_x$ varied with annealing temperature and thus order parameter. The coercivity reached a maximum for an order parameter of 0.45–5, then dramatically decreased as the order increased. This behavior is characteristic of demagnetization controlled by domain wall pinning by antiphase boundaries. © *2000 American Institute of Physics.* [S0021-8979(00)91008-9]

I. INTRODUCTION

Order–disorder transformations and the development of antiphase boundaries (APB) strongly influence the magnetic properties of materials. Specifically, improved domain wall pinning occurs as the APB density increases, resulting in coercivity enhancement. The APB density is directly related to the amount of long-range order. An excellent example of enhancing magnetic properties by modifying the long-range order is the Fe–Pt system, which undergoes an ordering transformation at 50 at % Pt. Increases of more than a factor of 3 in the coercivity have been associated with an increase in long-range order.[1] This increase is followed by a rapid decrease when the long-range order exceeds a critical value and the APB density decreases.

Certain rare earth–transition metal compounds similarly contain order–disorder transformations from the disordered $TbCu_7$-type structure[2] to the ordered Th_2Zn_{17}-type structure.[3] The ordering in this case involves the Fe–Fe dumbbell placement on the Sm sublattice. In the Sm–Co system, this order–disorder temperature has been reported to be on the order of 1280 °C.[4] In the Sm–Fe system, the ordering temperature is much higher and conventional solidification processing results in the formation of the ordered Sm_2Fe_{17} structure. However, the disordered $TbCu_7$-type $SmFe_7$ structure has been reported to form under rapid solidification conditions.[5–8] The ordered Sm_2Fe_{17} structure is recovered upon subsequent annealing. The magnetic properties of interstitially modified Sm_2Fe_{17} were also reported to improve over those of interstitially modified disordered $SmFe_7$.[5,6] This improvement was speculated to be due to intrinsic differences in the magnetic anisotropy between the ordered and disordered states. However, it has also been shown that increasing the APB density and configuration leads to increased domain wall pinning.[9]

Through appropriate annealing treatments, the amount of long-range order can be modified. The long-range order parameter S describes the amount of long-range order and is defined as[10]

$$S=\frac{r_A-f_A}{1-f_A}, \tag{1}$$

where r_A is the fraction of A sites occupied by the ''right'' atom and f_A is the fraction of A atoms in the alloy. In the case of the Sm–Fe compound, A corresponds to the Fe–Fe dumbbell pair of atoms. S varies from 0 (totally disordered) to 1 (fully ordered) and can be experimentally determined by x-ray diffraction by monitoring the intensity of the superlattice reflections relative to the intensity of the fundamental reflections according to

$$S^2=\frac{I_s|F_f|^2p_f\mathrm{LP}_f}{I_f|F_s|^2p_s\mathrm{LP}_s}, \tag{2}$$

where I is the integrated intensity of the x-ray peak, F is the structure factor, p is the multiplicity, and LP is the Lorentz polarization factor which is equal to $(1+\cos^2 2\theta)/(\sin^2\theta\cos\theta)$. The subscripts s and f correspond to superlattice and fundamental, respectively.

In this paper, the development of long-range order upon heat treatment of rapidly solidified Sm–Fe alloys and the effect of long-range order on the coercivity of interstitially modified Sm_2Fe_{17} permanent magnets is reported.

II. EXPERIMENTAL PROCEDURES

An alloy of nominal composition $Sm_{11}Fe_{89}$ was arc melted under high purity Ar from 99.97% pure Fe and 99.9% pure Sm. The ingot was then rapidly solidified by melt spinning in a highly purified Ar atmosphere with a tangential Cu wheel velocity of 30 m/s. For heat treatment, samples were gently pulverized in a mortar and pestle, wrapped in Ta foil, and sealed in quartz ampoules under high purity Ar. The quartz ampoules were annealed at temperatures ranging from 500 to 1000 °C for 15 min, after which they were quenched in water. The samples were reduced to less than 45° for x-ray diffraction and nitrogenation. Nitrogenation took place at 475 °C for 4 h under a flowing nitrogen atmosphere. After nitrogenation, the samples were again examined by x-ray diffraction to confirm complete nitrogenation. The x-ray diffraction was performed on a Phillips X'Pert-MPD system utilizing Cu $K\alpha$ radiation. The magnetic measurements

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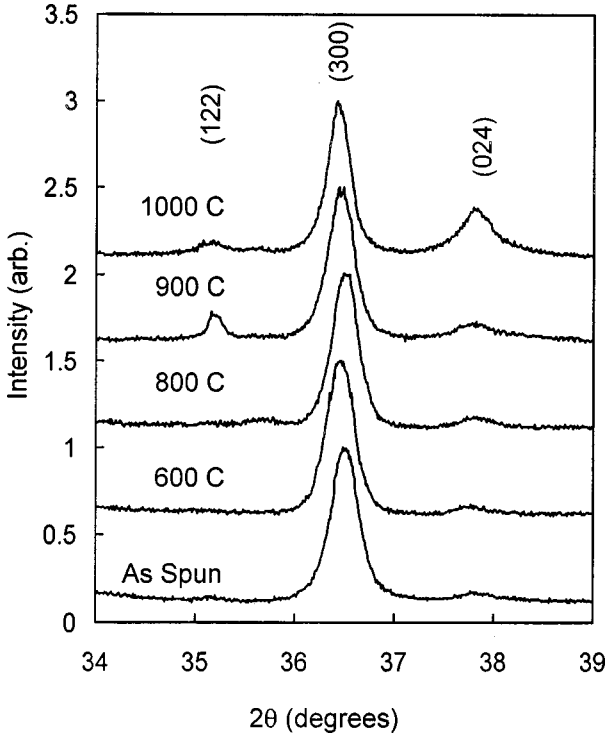

FIG. 1. X-ray spectra of different annealing temperatures. The (300) peak remains the same but the (024) peak increases with annealing temperature.

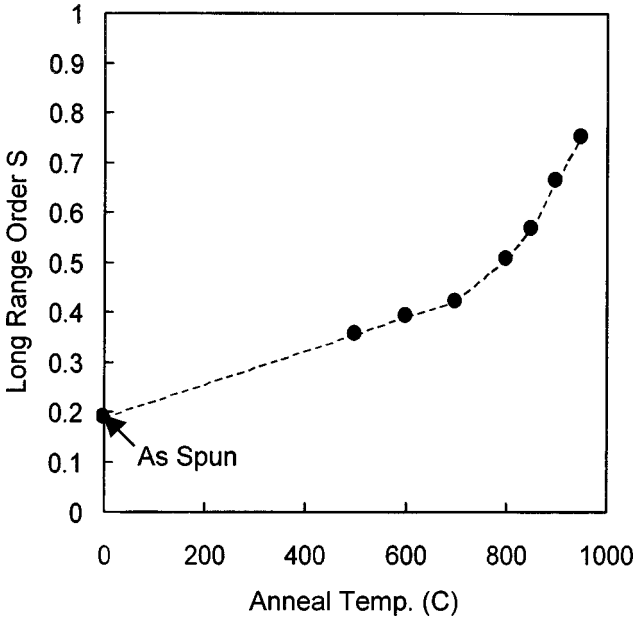

FIG. 2. Long-range order parameter S as a function of annealing temperature for the $Sm_{11}Fe_{89}$ alloy (circle).

were made with a Lakeshore vibrating sample magnetometer, which has a maximum field of 2.3 T, after pulse magnetization at 3.5 T.

III. RESULTS AND DISCUSSION

X-ray diffraction of the as-solidified $Sm_{11}Fe_{89}$ revealed the presence of Sm_2Fe_{17} with a small degree of long-range order and a small amount of α-Fe. The microstructure consisted of equiaxed grains on the order of 500 nm in size.[8] The presence of long-range order was indicated by the observance of superlattice reflections in the x-ray spectrum. Figure 1 shows a portion of 2θ space containing both fundamental (the {300}) and superlattice (the {024} and {122}) reflections. As observed, the {024} reflection is present in the as-solidified material, albeit with a very low intensity, indicating the presence of long-range order.

After heat treatment, the samples contained approximately the same phase constitution; there was no significant increase in α-Fe content. Grain growth occurred, resulting in a grain size of approximately 1 μm after annealing at 700 °C. Annealing did, however, result in a systematic increase in the intensity of the {024} superlattice reflection, indicating an increase in long-range order (Fig. 1). The long-range order, as indicated from the intensity of the {024} reflection, appeared to increase with increased annealing temperature.

To quantify the increase in long-range order upon annealing, the long-range order parameter S was calculated for each sample utilizing Eq. (2) considering the {024} and {300} reflections. The structure factors in Eq. (2) were calculated using coefficients from the International Tables for Crystallography[11] and atom positions for the Th_2Zn_{17} structure.[12] S was determined to be approximately 0.2 for the as-solidified material, and it increased to close to 0.8 for the sample annealed at 950 °C. The long-range order parameter S is shown as a function of reduced annealing temperature in Fig. 2. S was observed to depend on the annealing temperature and increased rapidly with annealing temperature due to the higher diffusivity associated with higher temperature.

The magnetic measurements were conducted after nitrogenation of the various samples. Formation of the interstitial $Sm_2Fe_{17}N_x$ compounds was confirmed by monitoring peak shifts in the x-ray diffraction patterns associated with lattice expansion. The coercivity was observed to vary with annealing temperature and reached a maximum for the sample annealed at 700 °C; anneals at 850 °C and above resulted in a rapid decrease in H_c. The observed values of H_c also strongly depended on the long-range order parameter S (Fig. 3). The coercivity increased with S to a short plateau, then dropped abruptly as S continued to increase. This behavior is similar to that observed between H_c and S in other order–disorder systems.[1] The strong dependence of H_c on S is explained by domain wall pinning by APBs. At low S, the APB structure is not well developed and thus the APBs are ineffective as domain wall pinning sites. As previously reported,[9] at $S \approx 0.5$ the defect structure consisted of planar defects normal to the c axis. As the order further increased to $S \approx 0.7$, the APBs developed additional components parallel to the c axis and more effectively pinned domain walls. Further increases in ordering resulted in a decrease in APB density. For instance, the number of misplaced atoms per unit cell can be estimated from Eq. (1). For an order parameter of 0.7, there is approximately one defect every four unit cells, while for an order parameter of 0.9 there is approximately one defect every seven unit cells. The effectiveness of APBs in pinning domain walls is clearly closely tied to the degree of order and the characteristics of the defects resulting from

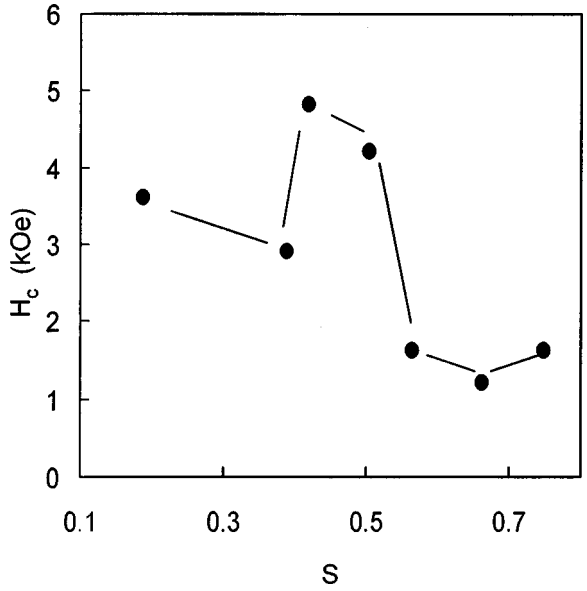

FIG. 3. Coercivity as a function of long range order parameter S for the $Sm_{11}Fe_{89}$ alloy (circle).

the disorder. Further work is underway to more clearly understand this relationship in the Sm–Fe system.

Previous work[5–6] also observed an increase in H_c with annealing but was attributed to intrinsic changes in magnetic anisotropy related to the more ordered Sm_2Fe_{17} structure. While the anisotropy is likely affected somewhat by the structural changes occurring during the development of long-range order, the results here indicate that the enhancement in coercivity is due to microstructural changes occurring in the samples.

IV. CONCLUSIONS

In this study, the development of long-range order in rapidly solidified $Sm_{11}Fe_{89}$ was monitored as a function of annealing temperature. The as-solidified material was determined to have an order parameter of 0.2, which increased with annealing temperature to 0.8 at 950 °C. The coercivity was observed to increase to a maximum at an order parameter of 0.5, and then decreased dramatically with more ordered structures. This relationship of the coercivity with the long-range order parameter indicated that coercivity is controlled by domain wall pinning by antiphase boundaries. The results here also will allow the tailoring of microstructural features to maximize magnetic properties in the Sm–Fe–N system.

ACKNOWLEDGMENTS

The authors are grateful to the National Science Foundation Division of Materials Research for support of this work (Grant No. 9714946). Research at INEEL was supported by the DOE Division of Basic Energy Sciences under DOE Idaho Operations Office Contract No. DB-AC07-94ID13223.

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