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Coercivity of SmFeN permanent magnets produced by various techniques

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Abstract

The coercivity mechanism of SmFeN permanent magnets produced by various techniques is studied within the framework of a micromagnetism model by analyzing the temperature dependence of the coercive field. The studied materials include isotropic magnets produced by mechanical alloying and by HDDR plus Zn-bonding and anisotropic magnets produced by Zn-bonding. It follows from these analyses that, in general, a nucleation process initiated on the grain boundary where the demagnetizing field is the largest determines the magnetization reversal process in SmFeN magnets.

Keywords: Coercivity mechanism; High coercive materials; Micromagnetism; $Sm_2Fe_{17}N_x$

1. Introduction and motivation

$Sm_2Fe_{17}N_x$ has excellent intrinsic magnetic properties [1,2], i.e. high Curie temperature (~750 K), high saturation magnetization (~1.56 T at 300 K) and extremely high uniaxial magnetocrystalline anisotropy (>12 MA m^{-1} at 300 K). The high uniaxial anisotropy, which is vital in establishing coercivity, makes SmFeN a promising material for permanent magnet fabrication. To date, many sophisticated techniques have been developed to produce SmFeN magnets. This is due to the chemical instability of $Sm_2Fe_{17}N_x$ which decomposes into SmN_x and α-Fe at temperatures above 800 K. The chemical instability of $Sm_2Fe_{17}N_x$ therefore prevents the well-established techniques, e.g. sintering or rapid quenching, from being used. However, the mechanical-alloying technique [3,4], the Zn-bonded technique [5,6] and also the explosion-sintered technique [7] have proved to be successful in establishing coercivity for $Sm_2Fe_{17}N_x$ interstitial compound. The highest coercive field, 2.4 MA m^{-1} at room temperature, has so far been achieved in isotropic magnets produced by mechanical alloying [3,4]. The coercivity mechanism of mechanically alloyed SmFeN magnets has been studied [8] and a nucleation mechanism was proposed to be a leading mechanism in determining the magnetization reversal process of that type of magnet. However, a pinning process was reported by Ding et al. [4] and Kobayashi [9]. Isotropic Zn-bonded SmFeN magnets and explosion-sintered anisotropic SmFeN magnets have also been investigated [6,7]. In the present report, the main emphasis is on a comparative study of the coercivity mechanism of SmFeN permanent magnets produced by the mechanical-alloying, the hydrogenation–disproportionation–desorption–recombination (HDDR) [10] and the Zn-bonding techniques. The materials of interest include anisotropic as well as isotropic SmFeN magnets. These three types of magnets were chosen because mechanically alloyed SmFeN magnets consist only of single-domain particles, whereas Zn-bonded anisotropic SmFeN magnets are composed of only multi-domain particles. The Zn-bonded HDDR SmFeN magnets can be either, depending on the preparation parameters.

2. Experimental details

The preparation process of the various SmFeN magnets studied in the present investigation was described in detail in separate publications [5,8,11,12]. The hysteresis loops of the various SmFeN magnets were measured in the temperature range from 5 to 700 K using a vibrating sample magnetometer with a maximum field strength of 6.4 MA m^{-1}. Since the value of the coercive field depends strongly on the applied magnetizing field strength [8], the magnet has to be magnetized to saturation for measuring the full hysteresis loop, from which the value of H_c is taken. For measurements at or above room temperature, a field strength of 6.4 MA m^{-1} is sufficient to achieve the saturated state (see Fig. 1). However, for measurements at low temperatures, a field strength of 6.4 MA m^{-1} is too

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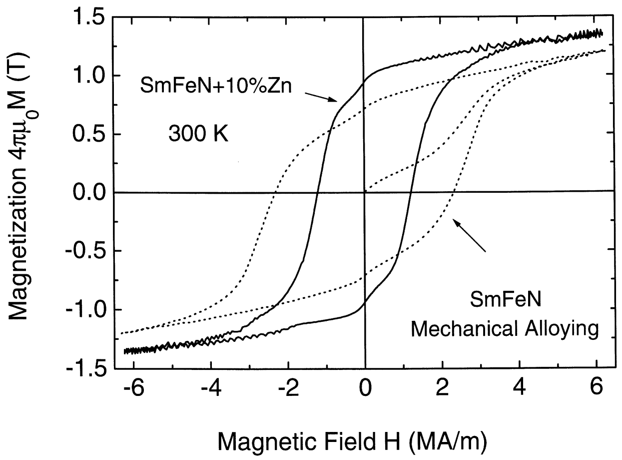

Fig. 1. The hysteresis loop at 300 K of a Zn-bonded anisotropic SmFeN magnet and an isotropic SmFeN magnet produced by the mechanical alloying technique.

low. In order to achieve magnetization saturation, the sample was first heated to 300 K and magnetized at this temperature with a field strength up to 6.4 MA m^{-1} and then cooled to the given temperature in a field of 6.4 MA m^{-1}. The value of H_c was obtained from the demagnetization curve as the field where the irreversible susceptibility, χ_{irr}, shows a maximum [8], and not, as is customary, as the field where the magnetization becomes zero. These two definitions give the same results for a magnet whose grains are well aligned, subjected to a field applied anti-parallel to the alignment direction. However, they can differ strongly when, in addition to irreversible processes, reversible rotations become important. Therefore, the physical meaning of H_c for the present definition is the field where most domains irreversibly reverse their magnetization due to the applied inverse field.

3. Micromagnetic concept of the coercivity of permanent magnets

According to the micromagnetic theory [13,14], the coercive field H_c of a magnet can generally be expressed as

$$H_c = \alpha H_n - N_{eff} M_s \quad (1)$$

where H_n is the nucleation field of a spherical single-domain particle when the external inverse field is applied exactly anti-parallel to the easy magnetization direction (EMD). The value of H_n depends only on the intrinsic magnetic parameters, i.e. the magnetocrystalline anisotropy and the spontaneous magnetization, of the hard magnetic phase included in the magnets and has been calculated by Martinek and Kronmüller [15]. α and N_{eff} are micromagnetic parameters which reflect the differences between the nucleation of a reversed domain in a spherical single-domain particle and that in a magnetized large crystal (a size larger than the critical size of the single-domain particle). The former parameter, α, describes the reduction of the nucleation field due to the appearance of crystallographic defects in the magnetic inhomogeneous region (α_K) on the grain surface, where a reversed domain is preferentially nucleated, and due to the unavoidable misalignment of the grains (α_φ). In fact, the nucleated reversed domain must have the EMD anti-parallel to the EMD of the magnetized grain. From this argument, it follows that there are at least two terms which are included in α, i.e. $\alpha = \alpha_K \alpha_\varphi$. Theoretically, both α_φ and α_K are temperature dependent. For magnets with strong magnetocrystalline anisotropy, it was shown that the coercivity H_c can be correlated to the minimum nucleation field H_n^{min} [15]. Eq. (1) can be rewritten in this case as

$$H_c = \alpha_K H_n^{min} - N_{eff} M_s \quad (2)$$

For SmFeN permanent magnets, the minimum nucleation field is determined only by the intrinsic magnetic properties of $Sm_2Fe_{17}N_x$ and can be expressed as [17]

$$H_n^{min} = \frac{1}{2\sqrt{2}\mu_0 M_s}\left(K_1 + \frac{K_2}{4}\left(W - \frac{K_1}{K_2} + 3\right)\right) \times \sqrt{\left(W\left(\frac{K_1}{K_2}+1\right) - \left(\frac{K_1}{K_2}\right)^2 - \frac{2K_1}{K_2} + 3\right)}$$

with

$$W = \sqrt{\left(1 + \frac{K_1}{K_2}\right)^2 + 8}$$

where K_1 and K_2 are anisotropy constants and M_s the spontaneous magnetization. The parameter N_{eff} describes the local demagnetization field which assists in nucleating the reversed domains under the action of the applied inverse field. The reason for the presence of $N_{eff}M_s$ is due to the fact that the nucleated reversed domain in a magnetized large grain is not of spherical shape. In fact, for a uni-axial material, the nucleated reversal domain is of plate-like shape [16]. It must be noted that N_{eff} is a temperature independent coefficient. Only because of this fact can a linear relationship between H_c/M_s and H_n/M_s be used to justify the model correlated to Eq. (1) and/or Eq. (2). According to the above discussion, it becomes evident that the micromagnetic parameter α_K provides information on the defects on the grain surface. A large value of α_K indicates a narrow inhomogeneous region, a low density of defects, difficulty in nucleating inverse domains on the grain surface and, therefore, resulting in high coercivity. The micromagnetic parameter N_{eff} gives information on the smoothness of the grain surface. A low value of N_{eff} indicates a more round grain surface, less opportunity to find a sharp edge where an inverse domain is preferentially nucleated, and therefore leads to high coercivity. By studying the micromagnetic parameters α_K and N_{eff}, a clear picture of the reversed domain, and therefore the magnetization reversal process, can be obtained.

4. Experimental results, micromagnetic analysis and discussion

Fig. 1 shows the hysteresis loop measured at room temperature for a Zn-bonded anisotropic SmFeN permanent magnet. Compared to an isotropic SmFeN magnet produced by the mechanical-alloying technique, the coercive field strength of the Zn-bonded magnets is low. Since the hard magnetic phase in both magnets is the same, i.e. $Sm_2Fe_{17}N_x$, the rather large difference in the coercive field strength between the two magnets reflects the sensitivity of the coercive field strength to the microstructure. The mechanically alloyed SmFeN magnets were shown to consist mainly of single-domain particles [8]. The mean grain size of the Zn-bonded magnets is between 1.5 and 5 μm which is much larger than the critical size (0.32 μm) of the single-domain particle of $Sm_2Fe_{17}N_x$ [5,8]. The anisotropic Zn-bonded magnets are assumed therefore to contain mainly multi-domains grains. For a given magnetic material, single-domain particles provide the highest achievable coercive field. However, the remanence of an anisotropic magnet is higher, thanks to magnetic alignment. Due to the intrinsic isotropic particles, magnetic alignment is impossible for mechanically alloyed magnets.

The temperature dependence of H_c measured for anisotropic SmFeN magnets produced by Zn-bonding and for isotropic magnets produced by mechanical alloying is shown in Fig. 2. Fig. 3 shows the temperature dependence of H_c of isotropic Zn-bonded HDDR SmFeN magnets. The value of H_c measured at room temperature for $Sm_2Fe_{17}N_x$ recombined at 1048 K and bonded with 15% Zn is 2.4 MA m^{-1}, which is comparable to the value of H_c achieved

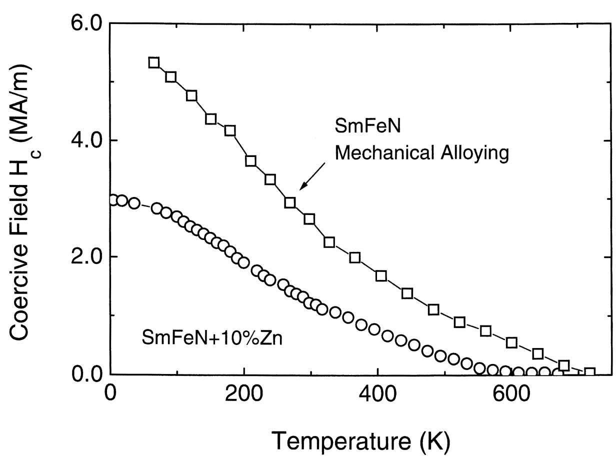

Fig. 2. Temperature dependence of the coercive field H_c of a Zn-bonded anisotropic SmFeN permanent magnet and an isotropic mechanically alloyed SmFeN permanent magnet.

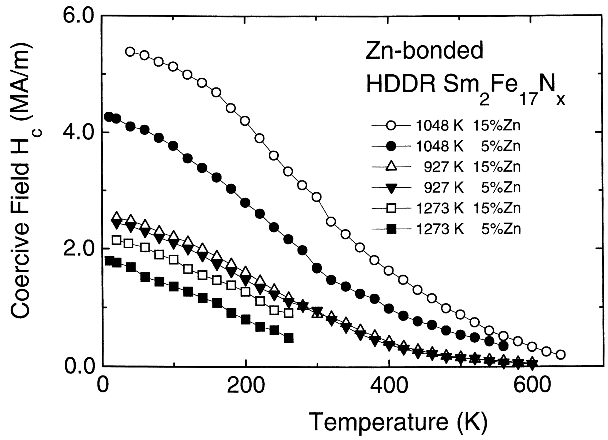

Fig. 3. Temperature dependence of the coercive field H_c of various Zn-bonded isotropic SmFeN permanent magnets produced by HDDR with different recombination temperatures and/or Zn contents.

by mechanical alloying. This might suggest that this Zn-bonded material mainly consists of single-domain grains.

The analysis of the temperature dependence of the coercive field is based on the nucleation model. It must be noted that for a quantitative analysis of the coercive field one has to take into account a probability distribution, $P(\varphi)$, of grain orientation with respect to the c-axis. Therefore, the effective α_φ^{eff} values representative for H_c have to be determined by appropriate averaging. The type of averaging depends on the magnetic coupling between neighboring grains. Generally, the following two extreme cases are considered [8,14,16]. Firstly, $\alpha_\varphi^{eff} = \alpha_\varphi^{int} = \int p(\varphi)\alpha_\varphi \, d\varphi$. In this case, all grains are assumed to be magnetically isolated from each other and reverse their magnetization individually without influencing neighboring grains. This is the case for most isotropic permanent magnets [8]. The second case is described by $\alpha_\varphi^{eff} = \alpha_\varphi^{min}$, where all grains are assumed to be strongly magnetically coupled and a reversed grain also induces reversion of the magnetization of the neighboring grains. The bulk coercive field in this case depends only on the grains which have the minimum nucleation field. This is the case for most anisotropic permanent magnets [16]. For simplicity, in the present analysis, only the second case, i.e. assuming $\alpha_\varphi^{eff} = \alpha_\varphi^{min}$, was taken into account.

Fig. 4 shows a plot of H_c/M_s versus H_n^{min}/M_s for anisotropic Zn-bonded SmFeN magnets. A linear relationship is found over a wide temperature range from 5 to 494 K. By fitting this linear relationship, one obtains $\alpha_K = 0.71$ (>0.3) and $N_{eff} = 1.50$. A linear relationship between H_c/M_s and H_n^{min}/M_s is also found (Fig. 5) for isotropic SmFeN magnets produced by the mechanical alloying technique. Values of $\alpha_K = 1.15$ and $N_{eff} = 1.96$ are obtained by fitting the linear relationship between H_c/M_s and H_n^{min}/M_s. Compared to the data obtained for anisotropic Zn-bonded magnets, both α_K and N_{eff} are bigger for mechanically alloyed magnets. Furthermore, a value of α_K

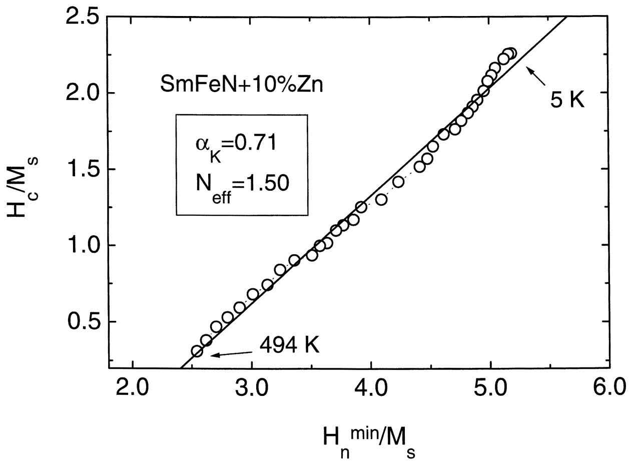

Fig. 4. H_c/M_s versus H_n^{min}/M_s for a Zn-bonded anisotropic SmFeN permanent magnet. A linear relationship between H_c/M_s and H_n^{min}/M_s indicates that the nucleation of the reversed domains controls the magnetization reversal process of Zn-bonded anisotropic magnets.

larger than 1 is derived, which is not reasonable. These two facts suggest that, for mechanically alloyed magnets, the nucleation field is underestimated. In addition, it implies that the magnetic particles in the mechanically alloyed magnets are more isolated from each other. Each particle reverses its own magnetization without influencing the surrounding particles. Thus, the actual nucleation field has to be averaged over all particles. In the case of Zn-bonded anisotropic magnets, the magnetic coupling between grains is so strong that one reversed grain induces reversal of the surrounding grains. The coercive field is determined, therefore, by the grains which have the minimum nucleation field. From a micromagnetic analysis performed on various Zn-bonded HDDR SmFeN magnets (Fig. 6 and Table 1), a clear understanding of the role of the bonding material (Zn) and also the effect of recombination temperature on the coercivity can be obtained, although qualitatively [12]. From the data of Table 1, three

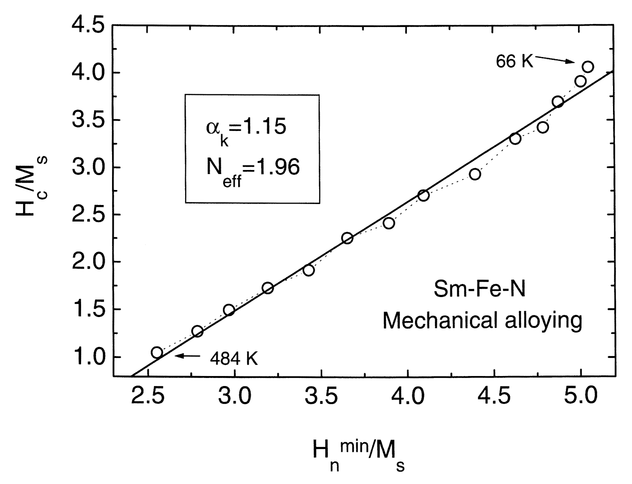

Fig. 5. H_c/M_s versus H_n^{min}/M_s for an isotropic SmFeN permanent magnet produced by the mechanical alloying technique.

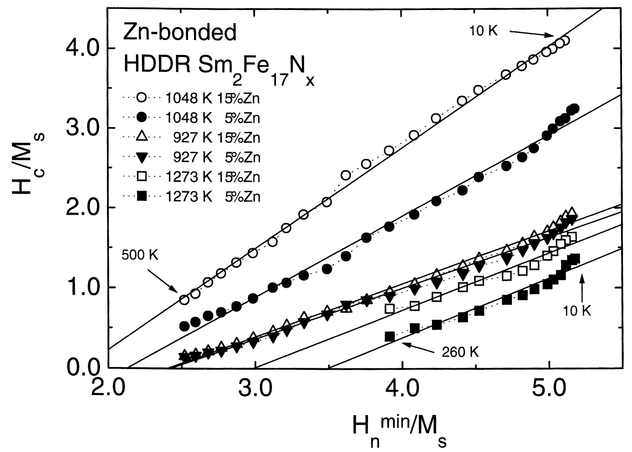

Fig. 6. H_c/M_s versus H_n^{min}/M_s for various isotropic SmFeN permanent magnet produced by Zn-bonding the HDDR-treated $Sm_2Fe_{17}N_x$ powders.

typical features are evident. (i) In the case of materials recombined at 927 K, both α_K and N_{eff} do not differ much for magnets bonded with 15% and 5% Zn. (ii) For materials recombined at 1048 K, N_{eff} is nearly constant while α_K is much higher for magnets bonded with 15% Zn. (iii) For materials recombined at 1273 K, α_K is nearly constant while N_{eff} is lower for magnets bonded with 15% Zn. From these data, the role of Zn in Zn-bonding SmFeN magnets can be studied. Before a detailed discussion of the role of Zn in enhancing the coercivity in Zn-bonded isotropic HDDR SmFeN magnets, it is necessary to clarify the microstructure of HDDR SmFeN. The main difference of HDDR Sm_2Fe_{17} to the parent alloy is their much smaller randomly oriented grains within particles. No change of the microstructure of HDDR Sm_2Fe_{17} is assumed to occur during the nitrogenation process due to the very low nitrogenation temperature (723 K). Bonding HDDY SmFeN with Zn, the particle surface can be modified during subsequent heat treatment, however the grain boundaries inside particles will be less influenced. The coercivity of HDDR SmFeN recombined at 927 K is probably controlled by the presence of α-Fe and the 1:7 phase, but not by modification of the materials by Zn. Therefore, α_K and N_{eff} and also H_c are almost independent of the Zn content. The HDDR SmFeN powders recombined at 1048 K show a coercivity of about 1.2 MA m^{-1}

Table 1
The fitted micromagnetic parameters α_K and N_{eff} for Zn-bonded HDDR SmFeN magnets with fine grained Sm_2Fe_{17} recombined at different temperatures (RT) and bonded with different Zn contents

Zn (wt.%)	RT (K)	α_K	N_{eff}
15	1273	0.71	2.12
5	1273	0.74	2.57
15	1048	1.26	2.30
5	1048	1.01	2.16
15	927	0.66	1.59
5	927	0.63	1.54

even without Zn bonding [17]. The present micromagnetic analysis suggests that the enhancement of coercivity of this material by Zn bonding is mainly due to the reduction of the inhomogeneous region on the grain surface (large α_K in higher Zn content magnets). This is surprising because SmFeN particles consist of randomly oriented fine grains, and most of the grain boundaries between them will not be modified by Zn. However, it is understandable that an inverse domain will be preferentially nucleated in grains which partly share their grain boundaries with the particle surface. As soon as those grains are demagnetized, the internal grains will be demagnetized due to the strong magnetic interaction between the grains. If this argument is correct, any improvement of the particle surface by Zn may be experienced by all grains. The enhancement of the coercivity of the materials recombined at 1273 K by Zn is suggested mainly to be due to the modification of the smoothness of the SmFeN grain boundary (smaller N_{eff} in higher Zn content magnets). This can be understood as resulting from the much larger $Sm_2Fe_{17}N_x$ grains compared to those recombined at 1048 K [17].

From the above analysis, it is evident that the nucleation model gives a satisfying description of the coercivity for SmFeN permanent magnets produced by means of Zn-bonding and mechanical alloying. The fitted values of α_K are all larger than 0.3 which leads to the conclusion that the magnetization reversal process of those magnets is determined by the nucleation mechanism. This conclusion is helpful for magnet fabrication because it implies that, in order to produce high coercive SmFeN magnets, it is much more useful to try to obtain small grains than to try a complex heat treatment.

5. Conclusions

(1) The magnetization reversal process of SmFeN permanent magnets produced by Zn-bonding as well as mechanical alloying is determined by the nucleation process of reversed domains.

(2) The reversed domain, due to the applied inverse magnetic field, is nucleated preferentially in mis-aligned grains (determined by α_φ) on the grain surface (determined by α_K) where the demagnetizing field is the highest (determined by N_{eff}), e.g. at sharp edges on the grain surface.

(3) The temperature dependence of the coercive field H_c of Zn-bonded SmFeN magnets can be well described by $H_c = \alpha_K H_n^{min} - N_{eff} M_s$, suggesting that the $Sm_2Fe_{17}N_x$ grains in these magnets are strongly magnetically coupled.

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