Texturing hard Nd-Fe-B powdered ribbons in High Magnetic Field

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Abstract. A new route to texture NdFeB alloys in magnetic field was presented in a recent paper \([1]\), constituting an attempt towards the preparation of anisotropic bonded magnets. NdFeB ribbons composed of Nd\(_2\)Fe\(_{14}\)B grains embedded in a Nd-Cu eutectic matrix, were annealed under an applied magnetic field up to 16T, at temperatures above the Nd-Cu melting temperature. A crystallographic texture was found to progressively develop at annealing temperatures, above 700 °C. In this paper, it is proposed that the grain orientation mechanism involves a competition between the aligning magnetic field torque acting on the magnetic grains and thermal disordering effects which becomes more and more significant as the temperature is increased. A simple model is developed to evaluate these effects. It is shown as well that a lowering of the alloy coercivity takes place during annealing.

1. Introduction

There exist two main types of NdFeB hard magnets. In the first type, the micron-size grains, obtained by grinding bulk ingots, have low coercive field values (typically, \(\mu_0H_c\) is below 0.1 T). The large coercivity, which characterizes the magnets, develops only during sintering. In the second type, melt-spun amorphous Nd-Fe-B ribbons constitute the precursor material used for the preparation of bonded magnets. The sub-micrometer-size grains, formed during crystallization of melt-spun ribbons, are randomly oriented. Bonded magnets may be obtained by mixing ribbon flakes within a polymer. As a result of the crystallographic orientation, the magnetization remanence, \(\mu_0M_r\), is generally below 0.8T. Compared with these isotropic magnets, it may be hoped that anisotropic magnet powders with crystallographic alignment will lead to higher remanence, better rectangularity of the demagnetization curve, and, in turn, an increase in the energy product, \((BH)_{\text{max}}\).

Several routes have been explored with the aim of producing textured NdFeB hard nanostructured materials. This includes the development of a specific protocol of the HDDR process and various powdering processes applied to already textured bulk materials (die-upset ribbons or hot deformed...
alloys) [2-4]. The subtle effects involved in the texturing mechanisms have been described in recent reviews [5-7].

In permanent magnet alloys, texturing under magnetic field may be envisaged. In previous studies [8-9], magnetic texturing was tested at the alloy solidification temperature. The solidification of Sm-Co alloys under 7T led to a crystallographic preferential orientation of the c-axis (easy axis) of the solidified individual grains along the applied magnetic field direction. However, in Nd-Fe-B, the results showed that the magnetocrystalline anisotropy energy, in a magnetic field of 5 T, is not sufficient to align the Nd$_2$Fe$_{14}$B crystallites, during their solidification, with the easy magnetization axis parallel to the field direction. In other studies, the crystallization of amorphous nano-composite magnets under magnetic field induced nanostructure refinement and better exchange coupling, but no significant texture effect was obtained [10,11].

In a recent study, we have demonstrated the possibility of orienting Nd$_2$Fe$_{14}$B solid particles in an Nd-Cu liquid eutectic phase under a magnetic field applied on a ribbon heated above the melting temperature of the Nd-Cu eutectic phase [1]. In the present work, a quantitative analysis of the orientation mechanism in a magnetic field at high temperature is proposed, and the coercivity of field process samples is examined.

2. Experimental details
Ribbons were obtained by melt spinning an as-cast alloy of composition Nd$_{31.45}$Fe$_{66.34}$B$_{0.92}$Cu$_{1.31}$ equivalent to 50% wt Nd$_2$Fe$_{14}$B and 50% wt Nd$_{70}$Cu$_{30}$. The set-up used for annealing in high magnetic field is described in [1]. The magnetic field, $\mu_0 H_{\text{app}}$, up to 16 T, was applied during the whole thermal treatment process consisting in two successive annealing steps.

The first step was aimed at orienting the particles under field. It was realized at temperatures $T_1$ above the melting temperature of the Nd-Cu eutectic, up to a maximum temperature of 1173 K. The plateau temperature was reached at a rate of 0.5 K/s and the duration of the temperature plateau was either 3 minutes or 1 hour. The second step, aiming at developing coercivity, was realized at 800 K for 30 minutes.

The samples were characterized by X-Ray Diffraction (not shown) and Scanning Electron Microscopy (SEM). The magnetic measurements were performed at room temperature, on bulk treated samples using a cryomagnet with 10 T maximum applied magnetic field. The macroscopic texture ratio, $r_\text{c} = (M_{r//} - M_{r\perp})/(M_{r//} + M_{r\perp})$ was taken as a measure of the degree of texture. With this definition, $0 \leq r < 1$, $\mu_0 M_{r//}$ and $\mu_0 M_{r\perp}$ are the remanent magnetizations measured in the parallel and perpendicular directions with respect to the direction of the applied field, $H_{\text{app}}$.

The as-spun ribbons contained nano-sized Nd$_2$Fe$_{14}$B crystallites embedded in the Nd-Cu eutectic matrix consisting of the β-Nd phase and the orthorhombic NdCu compound. A Nd$_2$Fe$_{14}$B grain size of less than 10 nm was derived from the Scherrer formula. The melting temperature of the Nd-Cu eutectic is 783K [1]. Therefore, at temperature above 783 K, the Nd$_2$Fe$_{14}$B grains are solid whereas the intergranular Nd-Cu phase is liquid. All thermal treatments reported in this work were performed under such conditions.

3. Results and discussion
The application of a magnetic field during annealing was found to have a remarkable effect on the alignment of the Nd$_2$Fe$_{14}$B grains. As shown in Figure 1, an anisotropic magnetic behaviour is evidenced in the sample annealed at 1173K for 3 min, in a magnetic field of 16T. The direction parallel to the annealing field direction and in the ribbon plane is found to be the direction of preferred c-axis crystallite orientation. Figure 1 shows as well that the coercive field is significantly reduced upon annealing, from 2.5T in the un-annealed samples to 0.9T in the annealed ones. Additionally, in the sample treated in magnetic field, the coercivity decrease is more pronounced. After annealing at 1173K for 3min, the coercive field reaches 0.5T in the sample treated in 16T and 0.9T in the sample treated in zero field. This effect is attributed to a texture dependence of coercivity which is generally observed in this type of materials [12].
The field dependence of the texture ratio $r$ measured after 3 min annealing at $T_1=1173$ K, is plotted in Figure 2; $r$ is approximately proportional to $H$, it reaches 0.6 under the maximum applied field of 16 T. Note that for $H=0$ T, $r=-0.1$, i.e. a weak basal plane texture is present [1].
The Nd$_2$Fe$_{14}$B crystallites appear to be essentially equiaxed and no particular shape alignment of the Nd$_2$Fe$_{14}$B grains is found in the samples treated under magnetic field. No free iron or other soft magnetic phase is detected. The occurrence of large grains in the annealed samples may explain the low value of coercivity then observed. Indeed, it is well known that the coercivity of hard magnetic materials tend to decrease as the grain size is increased.

Within the mechanism proposed in the already cited paper [1], a liquid phase is required for efficient grain texturing. The texturing effect of the magnetic field occurs above the Curie temperature of the Nd$_2$Fe$_{14}$B phase. The orientation of the tetragonal phase c-axes is determined by the magnetic field torque, $\Gamma_{mag}$. The friction torque within the liquid matrix is negligible, because of the low viscosity of the molten metal. Assuming that the magnetization of the considered Nd$_2$Fe$_{14}$B grain is along the field, the magnetic torque, $\Gamma_{mag}$, may be expressed as

$$\Gamma_{mag} = K(T, H) V \sin(2\theta)$$

where $V$ is the grain volume, $H_{appl}$ is the applied magnetic field, $\theta$ is the angle between the field and the easy direction and $K(T, H_{appl})$ is the magnetic anisotropy which, in the paramagnetic state, is a function of both $T$ and $H_{appl}$. This equation shows that the magnetic torque is far much higher for the coarser grains than for the submicron size population of grains. It implies that, within the best experimental conditions (1173K and field up to 16T), the magnetic anisotropy is not the limiting factor for the coarse grains to orientate. Rather, friction between coarse grains will hinder their orientation, in regions where the amount of liquid phase is not sufficient. On the contrary, nanosized grains can rotate more easily but thermal activation may limit their orientation process.

For the purpose of discussing the respective role of both $T$ and $H_{appl}$ on the orientation mechanism of the small size grains, $K(T, H_{appl})$ has been calculated and a Boltzmann statistical calculation developed to numerically obtain the anisotropy ratio as a function of $T$ and $H_{appl}$.

$K(T, H_{appl})$ has been evaluated based on simple considerations. In the tetragonal structure of the Nd$_2$Fe$_{14}$B phase, second order anisotropy terms are expected to dominate and to first order, the anisotropy constant $K$ is assumed to be proportional to $\mu^3_{Fe}$ where $\mu_{Fe}$ is the field induced Fe magnetic moment in the paramagnetic state expressed as a function of temperature within the molecular field.
model [1,13]. Thus, assuming $\theta \approx T_c$ (585 K) the Nd$_2$Fe$_{14}$B paramagnetic Curie temperature, the anisotropy energy, $K(T, H_{appl})$ may be expressed as:

$$K(T, H_{appl}) = 3.2 \times 10^6 \left(\frac{\mu_0 H_{appl}}{T - \theta}\right)^3$$

(2)

Calculated $K(T, H_{appl})$ values are presented in Figure 4 as a function of temperature and for different magnetic field intensities.

![Figure 4. Anisotropy constant as a function of temperature for different magnetic field intensities.](image)

The anisotropy constant value follows a logarithmic decrease as the temperature is increased. Moreover, a drastic increase of $K(T, H_{appl})$ is observed as the magnetic field is increased which implies, in turn, that the magnetic torque is much higher under high field. This means that magnetic orientation can be achieved for lower grain sizes under higher magnetic field.

Within Boltzmann statistics, it is assumed that the magnetization of all individual Nd$_2$Fe$_{14}$B particles is saturated along the magnetic field. However, the crystallographic c-axes may be distributed about the field axis. Let $\theta$ be the angle between the applied field and the c-axis in a given grain. The texture ratio, $r$, is expressed as:

$$r = \cos \theta = \frac{\int_0^{\pi/2} \sin \theta \cos \theta e^{-\frac{K(T, H_{appl}) V}{k_B T} \cos^2 \theta} d\theta}{\int_0^{\pi/2} \sin \theta e^{-\frac{K(T, H_{appl}) V}{k_B T} \cos^2 \theta} d\theta}$$

(3)

The texture ratio calculated as a function of the applied magnetic field for $T=1173$K and grains with 100 nm and 200 nm diameter is presented in Figure 2.

The calculated texture ratio for 200 nm diameter grains shows an upturn increase above 6T. At 12T the texture ratio reaches 0.75 and varies little under higher magnetic field. For 100 nm diameter grains, the effect of the magnetic field on texturing is significantly reduced. Under 16T, $r$ is of the order of 0.5
only. These calculations show that thermal activation affects significantly the efficiency of grain texturing under field at this annealing temperature. However, calculations show that this degree of texture is already very significant, with $\cos \theta = 0.85$ for $r=0.45$.

Globally, these results illustrate the fact that thermal disordering effects decrease as the grain size is increased, as a result of the increased particle whole anisotropy. A grain diameter of 200 nm is considered to be a minimum for satisfactory orientation to be achieved under the maximum available applied field of 16 T. Consequently, starting from grain sizes below 10nm in the as-cast ribbons, some grain coarsening is necessary as a first step for orientation to occur. Concomitantly, the number of grains which can orientate for a given magnetic field increases with magnetic field intensity. In the general case of magnet powders, where grain sizes are typically of the order of several hundred of nanometers, the high magnetic field texturing process may be very efficient.

The variation of the experimentally measured texture ratios lies between the curves calculated for 100nm and 200nm grain diameters. Actually, the experimental variation is in fair agreement with the calculation for 200 nm particles up to 7T. Such particle diameter corresponds approximately to the experimental diameter seen in the grey regions of Figure 3. At higher field values, the calculated texture ratio is above the experimental ones. This discrepancy may be attributed to the bimodal grain size distribution existing in the samples, whereas, a uniform grain size is considered in the calculation and coarse grains are not taken into account. The lower texture found experimentally with respect to the calculated ones suggests that orientation of the coarser grains is difficult. The same conclusion was reached in the initial study describing the effects of texturing NdFeB ribbons under field [1]. It was proposed that the difficulty in orienting large grains was due to the insufficient liquid phase amount which impeded free rotation of the grains under the effect of the aligning field.

4. Conclusion
An original approach towards the preparation of anisotropic hard magnetic alloys was explored in this work. Nd-Fe-B ribbons were annealed at various temperatures above the melting temperature of the liquid Nd-Cu eutectic. The application of a high magnetic field was found to result in a remarkable texturing effect. The crystallographic texture progressively developed with increasing the annealing temperatures, above 973 K. However, the alloy coercivity decreases concomitantly because of grain growth. The magnetic torque responsible for the texturing effect increases with increasing magnetic field intensity, leading to a texture ratio of 0.6 after annealing in 16T.

The calculation presented in this study indicates that grains diameters above 200 nm are required for satisfactory texturing to develop. At the same time, large micron-size grains are present in the alloy after annealing, which cannot orientate easily due to the fact that they come into contact during rotation. It is suggested that efficient orientation would require the use of alloys in which the amount of liquid phase is increased.

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