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Study of the temperature dependence of coercivity in MnBi

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Abstract

Two set of polycrystalline MnBi bulk samples, as-annealed and compacted powders, with different grain size, were prepared through powder metallurgy. Coercivity mechanisms were investigated by Kronmüller plot analysis, evaluating α and N_{eff} parameters, which take into account the effect of microstructure. The temperature dependence of coercivity of the as-annealed sample (α= 0.31) is compatible with pinning-type mechanisms, while that of the compacted powders (α= 0.41) indicates nucleation-type processes. Irreversible effects of temperature dependence of coercivity have been investigated.

Keywords: MnBi, rare-earth-free permanent magnets, coercivity

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1 Introduction

The intermetallic compound MnBi possesses many interesting magnetic properties. It displays a first order magneto-structural transition from a ferromagnetic low temperature phase (LTP), α, to a paramagnetic high temperature phase (HTP), β, at 628 K (Chen & Stutius, 1974). The LTP has the hexagonal NiAs-type structure and the HTP shows a Ni_2In-type structure. At the magneto-structural transition the cell parameters change and Mn atoms may diffuse into the bipyramidal interstices (Andresen, 1967). The ferromagnetic α phase, shows a strong uniaxial magnetocrystalline anisotropy which has the peculiar feature to increase with temperature up to 500 K where $K_u = 2.2\ 10^6\ J/m^3$. This makes the compound an interesting candidate as a rare-earth-free permanent magnet, especially for high temperature applications.

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Several strategies were developed to optimize the coercivity by refining grain size without appreciable reduction of phase fraction and magnetization. Cryomilling (Rao, 2013), surfactant addition (Liu, 2014) and milled ribbon (Zhang, 2012) have been shown to be effective, but the process becomes rather complex. These problems also calls for a better understanding of the magnetization processes of MnBi. Guo et al. studied the coercivity of melt-spun material by a pinning model taking into account the thermal fluctuations (Guo, 1992). Rao et al. (Rao, 2013) found that the coercivity is due to nucleation process. A similar result was confirmed by Kronmuller (Kronmuller, 2014).

The aim of this work is to better clarify the magnetization process of MnBi by the study of the temperature dependence of coercivity in samples with different microstructure. This study is carried out on two set of polycrystalline samples with different grain size: large grains for a the as-annealed samples and small grains for samples made by compacted powders. The magnetization reversal mechanisms were investigated through Kronmüller plot, by evaluation of the α and N_{eff} parameters, which take into account the effect of microstructure (Kronmuller, 1988). Furthermore the irreversible effects on microstructure were analyzed, after the samples have been subjected to first-order magnetostructural transition α-β at 628 K.

2 Experimental

Polycrystalline samples were prepared with a nominal composition $Mn_{50}Bi_{50}$. Because of the presence of a peritectic decomposition at $T_p = 720$ K, the preparation of high phase fraction of MnBi can be done by elemental powder mixing and subsequent annealing at $T < T_p$. The elemental starting materials (Mn purity 99.95 %, Bi purity 99.99 %) were high-energy ball mixed in Zirconia jar (sealed in a glove box in nitrogen atmosphere in order to avoid oxidation) for 2 hours at a revolution speed of 450 rpm and with a volume ratio of ball to powders of 200:1. Then the mixed powders were compacted as a green pellet (pressure of 470 MPa), with a diameter of 5 mm and thickness in the range 0.5-1 mm. The “as-annealed pellets” were prepared by annealing the green parts at 580 K for 1 hour in an applied magnetic field of 1 T (along pellet diameter) in order to promote the phase formation and the growth of aligned grains, reaching 90 wt% of MnBi phase fraction. The “compacted powders pellets” were obtained through high-energy ball milling of the as-annealed material in Zirconia jar, sealed in nitrogen atmosphere (revolution speed 450 rpm and volume ratio of ball to powders 40:1) for 30 min and the obtained powders were compacted (pressure of 470 MPa).

The sample morphology was characterized through Scanning Electron Microscopy (SEM). The magnetic measurements were performed by Vibrating Sample Magnetometer (VSM) equipped with a heating system in a field up to $\mu_0 H_{appl}$ 1.7 T. No correction was made for the demagnetization field effect in the magnetic measurements.

3 Results and discussion

Fig. 1(a) shows a backscattered electron image of the polished cross-section of the as-annealed sample. In the image it is possible to distinguish three phases with different grey levels: dark-grey for Mn, medium-grey for MnBi and bright-grey for Bi. The grain size of MnBi is in the range 10-70 µm. Fig. 1(b) shows SEM image for powders milled for 30 min. Milling produces particles with average size of 0.5 µm, which result clustered.

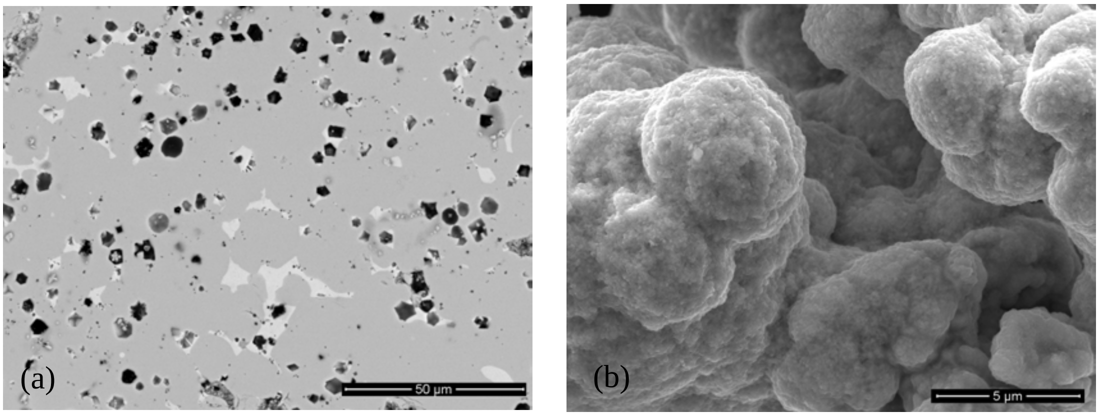

Figure 1: (a) (left) Backscattered electron image of the polished cross-section of as-annealed sample, the gray level identifies the phase: dark-grey for Mn, medium-grey for MnBi and bright-grey for Bi. (b) (right) SEM image of clustered powders milled for 30 min.

In order to investigate the effect of different grain size on hard magnetic properties, the magnetic hysteresis loops were measured at different temperatures in the range 300-640 K. Fig. 2(a) shows the hysteresis loops of the as-annealed material with the magnetic field applied parallel to the easy axis of the sample, which exhibits magnetic anisotropic behavior. The hysteresis loops shape of compacted powders sample displays isotropic orientation due to the subsequent milling (Fig. 2(b)). Only a portion of the hysteresis loops for T $\geq$ 390 K is shown in Fig. 2(b) because the coercivity μ_0H_c is higher than the maximum applied field (1.7 T). The as-annealed sample has a high magnetic remanence M_r of 52 Am^2kg^{-1} and a relative small coercivity μ_0H_c of 0.08 T at room temperature, while the compacted powders pellet has lower magnetic remanence M_r equal to 26 Am^2kg^{-1} (because of the magnetic isotropic orientation), but a high coercivity μ_0H_c equal to 0.85 T at room temperature.

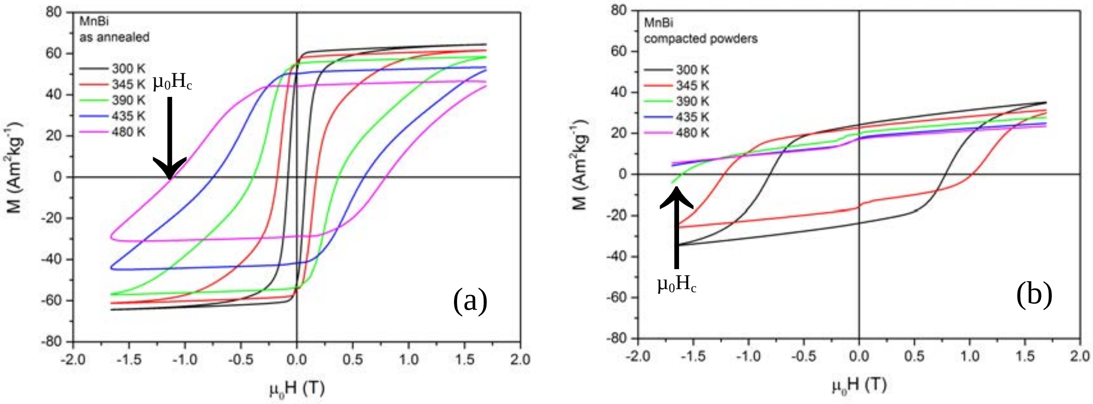

Figure 2: (a) (left) Anisotropic hysteresis loops of the as-annealed sample in the range 300-480 K with magnetic field applied parallel to the easy axis. (b) (right) Isotropic hysteresis loops of the compacted powders sample, only a portion of the hysteresis loops for T $\geq$ 390 K is shown because the coercivity μ_0H_c is higher than the maximum applied filed (1.7 T).

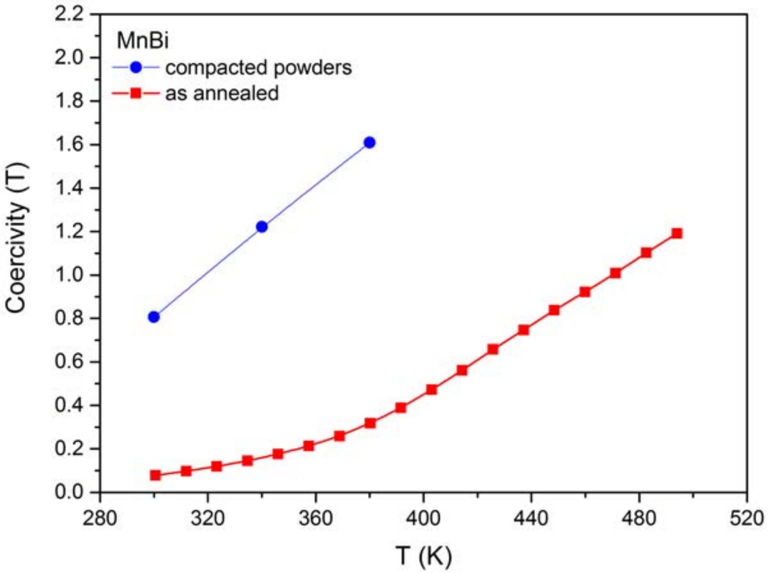

Figure 3: Temperature dependence of coercivity of the as-annealed (in red) and the compacted powders samples (in blue), respectively in the range 300-390 K and 300-495 K.

Fig. 3 displays the coercivity of the samples as function of temperature in the range 300-495 K. The coercive fields are obtained from the demagnetizing branches of hysteresis loops. The coercivity values measured with VSM (maximum applied field 1.7 T) were compared before and after magnetizing the samples by a pulsed magnetic field of 7 T. The loops before and after the magnetization process display the same demagnetizing curves, which reveals that the demagnetizing branches can be considered as saturated and the negative μ_0H_c values can be taken as a good estimation of the real coercivity. When changing the temperature, a constant magnetic field of 1 T was always switched on, in order to keep the samples close to the positive saturation.

The comparison of Fig.3 between the as-annealed and the compacted powders samples reveals a significant change in hard magnetic properties at high temperature. Surprisingly, the as-annealed material acquires a non negligible coercivity above room temperature, which probably means that some coercivity mechanism, not active at room temperature, comes into play.

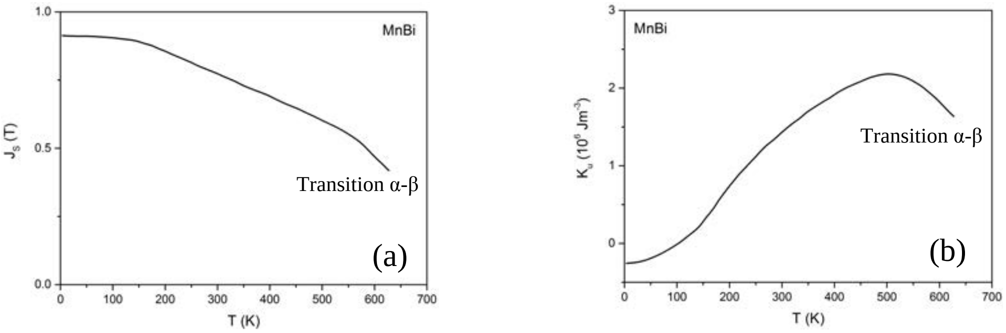

Figure 4: Temperature dependence of the saturation polarization J_S (a) and of the uniaxial magnetocrystalline anisotropy K_u (b) taken from (Chen & Stutius, 1974).

3.1 Kronmüller plot analysis

In order to investigate the reasons of the different behavior of the temperature dependence of coercivity of the two materials, the reversal mechanisms were studied through the Kronmüller model which parameters α and N_{eff} takes into account the effect of microstructure. The Kronmüller parameters were estimated by the equation $\mu_0 H_c = 2\alpha\mu_0 K_u/J_S - N_{eff} J_S$ (Kronmuller, 1988), where $\mu_0 H_c$ is the coercivity, K_u is the uniaxial magnetocrystalline anisotropy, α is a parameter taking into account both the effect of misalignment of the grains and the reduced anisotropy at the grain surfaces, J_S is the saturation polarization and N_{eff} describes the effect of the local stray fields. N_{eff} cannot be strictly interpreted as a geometric demagnetizing factor N_d because it takes into account more generally the shape of the reversed nuclei in the magnetization process (Kronmuller & Fahnle, 2003). Writing the equation as $\mu_0 H_c/J_S = 2\alpha\mu_0 K_u/J_S^2 - N_{eff}$ one has that, by plotting the data as $\mu_0 H_c/J_S$ versus $2\mu_0 K_u/J_S^2$, the Kronmüller law predicts a linear behavior in which the parameter α represents the slope and the parameter N_{eff} corresponds to the intersection with the ordinate

The Kronmüller parameters α and N_{eff} of the as-annealed and the compacted powders samples were calculated by performing a linear fit of $\mu_0 H_c/J_S$ versus $2\mu_0 K_u/J_S^2$ where $\mu_0 H_c$ is the coercivity measured in this work, while the saturation polarization J_S and the uniaxial magnetocrystalline anisotropy K_u are taken from (Chen & Stutius, 1974) as function of temperature (Fig. 4). Fig. 5 shows the Kronmüller plot for both samples. The results for the as-annealed sample, over the whole temperature range 300 - 495 K has not a linear relation of $\mu_0 H_c/J_S$ versus $2\mu_0 K_u/J_S^2$. The temperature dependence of coercivity of this sample shows two regimes: a 1st regime for T < 350 K with α=0.09 and N_{eff} = 0.41 and a 2nd regime for T > 350 K with α=0.31 and N_{eff} = 2.01 (Fig. 5). For the compacted powders sample a single regime is observed with α=0.41 and N_{eff} = 1.23 (Tab. 1).

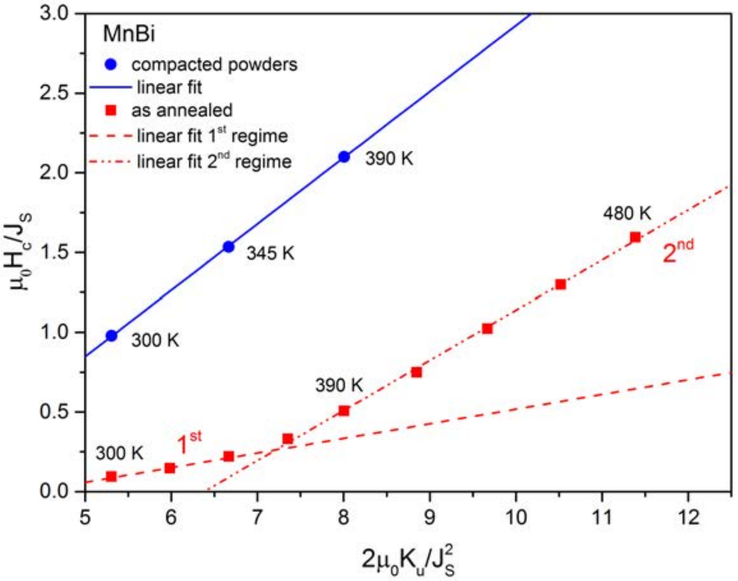

Figure 5: Blue circle and red squared points are the plot of $\mu_0 H_c/J_S$ versus $2\mu_0 K_u/J_S^2$ respectively for the compacted powders and the as-annealed samples. The blue and the red lines are linear fit of the data

MnBi	α	N_{eff}
As annealed 1st	0.09	0.41
As annealed 2nd	0.31	2.01
Compacted powders	0.41	1.23

Table 1: Kronmüller parameters α and N_{eff}

The value of the Kronmüller parameters α could identify the predominant coercivity mechanism: with $\alpha < 0.3$ the mechanism could be both pinning-type or nucleation-type, while with $\alpha > 0.3$ can be only nucleation-type (Kronmuller, 1988). For the compacted powders sample ($\alpha = 0.41$) the coercivity appears to be nucleation-type. For the as-annealed sample the magnetization reversal could be of both types for the 1st regime and at the limit of nucleation-type for 2nd regime. For the as-annealed material the existence of two regimes is also noticed in the changes of the hysteresis loop shape shown in Fig. 2(a): for T > 345 K the shape of hysteresis loops appears as there are two mechanisms active. At room temperature the loop shape is more squared than the shape of loops for T < 345 K. A separated discussion is needed to comment the values found for N_{eff}. As matter of fact, values of N_{eff} larger than 1 are unexpected on the base of a purely geometric interpretation, however these are often reported in the literature (Kronmuller, 2014). This could mean that the analyzed data could not be described with the model, or that in any case the results must be discussed on a physical ground. In this work the results of the 2nd regime of the as-annealed sample show slightly large value of the parameter N_{eff}. This may be due to a large contribution of local stray fields in the case of large grains or to the inclusions of nonmagnetic particles, as reported in the literature (Kronmuller, 1988).

3.2 Instability effects

In order to investigate in depth the temperature dependence of the coercivity and the stability of the magnetic properties of the MnBi under temperatures cycling, the VSM measurements at different temperatures T_{max} were performed. The coercivity as function of temperature was measured up to a maximum temperature in both heating (from 300 K to T_{max}) and cooling (from T_{max} to 300 K) for three different T_{max} and for both the samples. Fig. 6 shows the results for the as-annealed sample for T_{max} equal to 495 - 585 - 640 K. The coercivity behavior is reversible up to T_{max} = 495 K, instead for T_{max} > 495 K the coercivity measured in cooling strongly decreases with respect to heating curve and the reduction is irreversible.

It should be noted that this relatively low temperature value (495 K) is $0.9T_{melting}$ of Bi (540 K), so the atomic diffusion of Bi atoms becomes very high and plays a relevant role in the redistribution of defects.

When the as-annealed sample undergoes for the first time the first order magneto-structural transition α-β at 628 K its coercivity decreases drastically (Fig. 7). On the other hand, the hard magnetic properties of the compacted powders sample are rather stable. Only after the α-β transition the sample shows an appreciable reduction of coercivity. Fig. 7 displays the temperature dependence of coercivity of both samples before and after the transition.

The strong reduction of coercivity after α-β transition of the as-annealed sample suggests that the coercivity of the starting material was mainly due to lattice imperfections, such as defects and dislocations representing pinning centres for domain wall motion. On the other hand, at 628 K the atomic displacement produced by the phase transformation may be the cause of the elimination of the defects giving rise to coercivity. The estimated value $\alpha = 0.31$ (close to the Kronmüller limit $\alpha < 0.3$) may be compatible with pinning mechanisms. The stability of the compacted powders sample and its slight decrease of coercivity after the transition indicate that the predominant mechanism for the magnetization reversal is nucleation-type. This assumption is consistent with the results of the Kronmüller analysis.

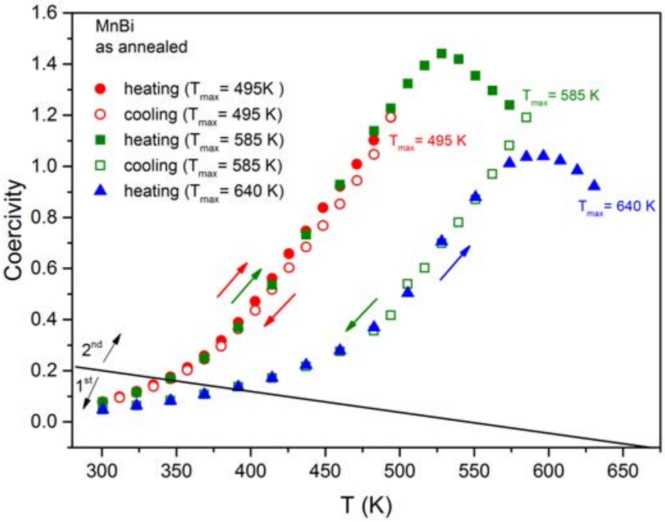

Figure 6: VSM measurements at different temperatures T_{max} of the as-annealed sample. The coercivity as function of temperature up to a maximum temperature in both heating (from 300 K to T_{max} = 495-585-640 K) and cooling (from T_{max} = 495-585-640 K to 300 K).

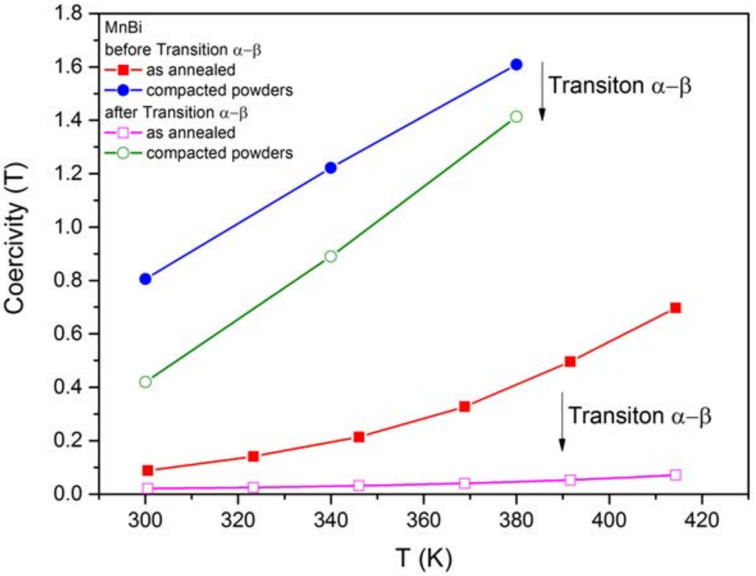

Figure 7: Temperature dependence of coercivity of the as-annealed and the compacted powders samples, respectively in the range 300-390 K and 300-415 K, before and after its underwent for the first time the magneto-structural transition α-β at 628 K.

4 Conclusions

Temperature dependence of coercivity of rare-earth free magnetic material MnBi was investigated for two set of polycrystalline samples with different grain size: as-annealed and compacted powders. The results of Kronmüller analysis show two regimes for the as-annealed sample. The instability under temperature cycling of this material suggests that coercivity is due to pinning mechanisms. For the compacted powders sample the Kronmüller analysis and the stability of magnetic properties are compatible with nucleation-type processes. The results about the parameter N_{eff} shows a large contribution of local stray field in the case of large grain size.

The non negligible coercivity above room temperature of the as-annealed sample highlights the significant role played by the pinning centres, such as the defects. Following this route one may lead the formation of defects in order to develop high coercivity, for instance introducing a third element in the MnBi compounds. To this aim, the role of the partial substitution of Mn with Ti is currently under investigation.

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