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Low-temperature phase MnBi compound: A potential candidate for rare-earth free permanent magnets

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ABSTRACT

The low-temperature phase (LTP) MnBi is one of the few rare-earth free compounds that exhibit a large magnetocrystalline anisotropy energy in the order of 10^6 J/m^3. A large coercive field ($\mu_0 H_{cj}$) above 1 T can be obtained readily by reducing the crystallite size (D) through mechanical grinding (MG). The room-temperature H_{cj} values follow a phenomenological expression $\mu_0 H_{cj} = \mu_0 H_a(\delta/D)^n$ where the anisotropy field ($\mu_0 H_a$) is ~4 T, the Bloch wall width (δ) is 7 nm and the exponent (n) is about 0.7 in our study. The grain refinement upon MG is accompanied by suppression of the spin reorientation transition temperature (T_{SR}) from 110 K to below 50 K. The coercive field starts to exhibit positive temperature dependence approximately 50 K above T_{SR} and the room-temperature magnetic hardening induced by MG could partially be brought about by the lowered onset of this positive temperature dependence. The suppression of T_{SR} by MG is likely to be induced by the surface anisotropy with which the 2nd order crystal field term is enhanced. One of the shortcomings of LTP-MnBi is its poor phase stability under the ambient atmosphere. The spontaneous magnetization decreases considerably after room-temperature aging for 1 week. This is due to oxidation of Mn which leads to decomposition of the MnBi phase. Hence, the surface passivity needs to be established before this material is considered for a permanent magnet in practical uses. Another shortcoming is the limited spontaneous magnetization. The theoretical upper limit of the maximum energy product in LTP-MnBi remains only a quarter of that in $Nd_2Fe_{14}B$. Nevertheless, owing to the unique positive temperature dependence of the first-order anisotropy constant (K_1), the hardness parameter (κ) of LTP-MnBi is enhanced above room temperature; κ reaches as large as 2.8 at 580 K. This makes LTP-MnBi a possible candidate for the hard phase in rare-earth free nanocomposite magnets.

1. Introduction

Since the discovery of large magnetocrystalline anisotropy in $SmCo_5$ compound [1,2], rare-earth elements have almost always been a key component of high-performance permanent magnets [3–6]. In recent years, with ever increasing global demand, these elements have become the focus of attention because of the risk of a limited supply chain. Hence, the development of high performance permanent magnets with reduced rare-earth content or the magnets free of rare-earth elements has become one of the hottest topics in the field of magnetic materials. With this background, the low temperature phase (LTP) MnBi with $P6_3/mmc$ structure has attracted much attention primarily because of its large anisotropy field ($\mu_0 H_a \sim 4.5$ T at room temperature) [7,8]. It has been reported that LTP-MnBi powders processed by ball milling exhibit a large intrinsic coercivity ($\mu_0 H_{cj}$) above 1.5 T at room temperature [9,10]. Moreover, the first-order magnetocrystalline anisotropy constant (K_1) of LTP-MnBi is known to exhibit a positive temperature dependence up to ~500 K [8]. This unique temperature dependence of K_1 results in a large $\mu_0 H_{cj}$ value above 2.5 T at 540 K [11,12], making LTP-MnBi an attractive material as a candidate for permanent magnets used at elevated temperatures.

In this report, a brief overview of the processing routes and the magnetic properties of mechanically-ground LTP-MnBi will be given. The effect of nanoscale grain refinement on the spin reorientation transition and the coercive field of LTP-MnBi will be discussed along with the potential of LTP-MnBi as a rare-earth free permanent magnet.

2. Experimental procedures

Melt-spinning was carried out using a Cu roller at a circumferential speed of 30 m/s. The melt-spun samples were annealed for 0.6 ks at 538 K. The annealed samples were pulverized into powders with a size smaller than 200 μm under an Ar atmosphere. Mechanical grinding (MG) of the pulverized powders was carried out on a Super MISUNI vibration mill. X-ray diffraction (XRD) patterns were

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obtained using Cu Kα radiation. Susceptibility was measured using a Lake Shore 7130 susceptometer operating at 137 Hz and 100 A/m. Magnetization curves were acquired on a vibrating sample magnetometer; the maximum magnetic field applied was 1.2 MA/m for room-temperature measurements and 0.8 MA/m for low temperature measurements. The MnBi powders for these magnetic measurements were sealed in an epoxy resin droplet.

3. Preparation of low-temperature phase MnBi

Attempts to prepare a single-phase state of LTP-MnBi by conventional melting and casting usually fail primarily because of the peritectic reaction in the Mn–Bi binary phase diagram [13] at 628 K where the LTP-MnBi forms upon solidification process. Hence, processing routes other than conventional casting have often been employed for preparing LTP-MnBi samples. Yang et al. [10] prepared their MnBi samples by sintering a mixture of pure Mn and Bi powders and reported that a highest fraction (up to 60 wt%) of LTP-MnBi was obtained with a nominal alloy composition of $Mn_{55}Bi_{45}$. The problematic peritectic reaction can be avoided effectively by using amorphous MnBi as a precursor. Guo et al. [8] employed this approach and they prepared the precursor amorphous phase by melt-spinning. A LTP-MnBi sample with an impurity Bi content of 5% was successfully prepared by heating the precursor amorphous to 570 K at 80 K/min. This low impurity level demonstrates the effectiveness of using a melt-spun precursor for preparation of LTP-MnBi and thus, this processing route has been adopted in many reports [14,15].

The decomposition behavior of melt-spun amorphous Mn–Bi alloys can be traced by thermo-magneto-gravimetric analysis (TMGA). Fig. 1 shows the TMGA curve of a melt-spun $Mn_{52.5}Bi_{47.5}$ alloy acquired on a Perkin–Elmer TGA7 thermo-gravimetric analyzer with a small magnetic field gradient applied. The TMGA signal shows an increase at 538 K due to polymorphic crystallization of LTP-MnBi from the amorphous precursor. The curve then shows an abrupt decrease at 630 K. This temperature agrees well with the upper limit of the phase field for LTP-MnBi on the equilibrium phase diagram (628 K) [13], indicating that the abrupt drop of TMGA is due to the first order Curie transition where the a/c ratio of the $P6_3/mmc$ structure changes due to the phase transformation from LTP-MnBi to the high temperature phase (HTP) MnBi. The Curie temperature on the TMGA curve upon cooling is 610 K, slightly lower than the T_C obtained on the heating curve. Furthermore, the TMGA signal below T_C on the cooling curve is clearly lower than that on the heating curve. This indicates that the fraction of nonmagnetic impurities in the sample increases considerably once the phase transformation from LTP-MnBi to HTP-MnBi takes place. Hence, the precursor amorphous ribbons should be annealed between 538 and 630 K. In the present study, the precursor ribbons were annealed at 538 K for 0.6 ks under a vacuum ($<10^{-3}$ Pa).

Although the nominal composition of the ingots used for melt spinning was identical ($Mn_{52.5}Bi_{47.5}$) in the present study, the room-temperature magnetization (J) values of our LTP-MnBi samples prepared by crystallization of amorphous precursors varied considerably from 0.47 T to 0.65 T, presumably because of the subtle difference in the melt-spun conditions which were hard to control. To investigate the effect of alloy composition on the J values, annealed MnBi samples were chemically analyzed. Fig. 2 shows the relationship between Mn or Bi content and the room-temperature magnetization for MnBi samples annealed at 538 K for 0.6 ks. It is clear that the highest J value is obtained when the alloy composition is at the stoichiometric MnBi composition and the deviation of the chemical composition from this stoichiometry results in a significant reduction of J. Hence, the large variation of the magnetization values can be attributed to the alloy composition.

In addition to the challenge of obtaining LTP-MnBi with low levels of impurities, the poor surface passibily of MnBi is a potential hindrance in the development of permanent magnets based on LTP-MnBi. Fig. 3 shows the effect of room temperature aging on the magnetization of a MnBi sample. The magnetization after aging was measured at 77 K under an applied field of 0.8 MA/m. The sample used was epoxy-bonded LTP-MnBi powders prepared by crystallization of a melt-spun precursor. The sample kept under an Ar atmosphere shows no appreciable change in the magnetization value for an aging period up to 80 days whereas the sample

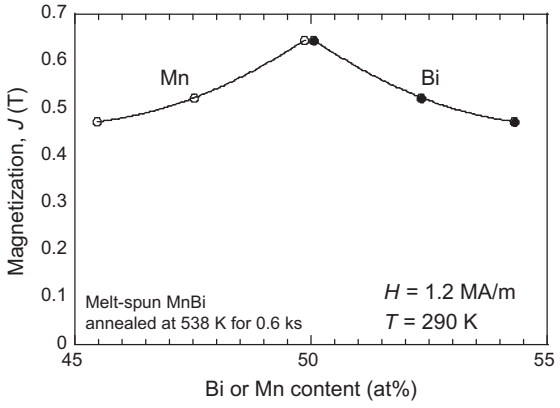

Fig. 2. Dependence of room-temperature magnetization (J) for melt-spun Mn–Bi alloys annealed at 538 K for 0.6 ks.

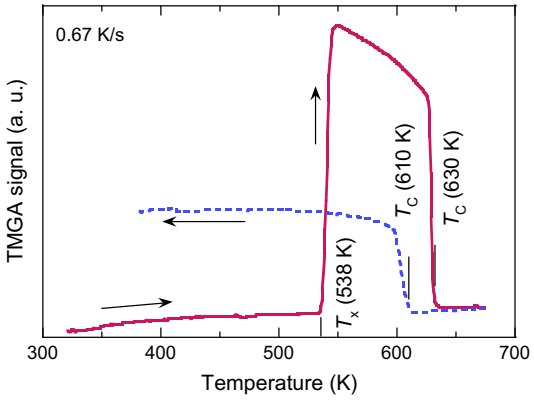

Fig. 1. Thermo-magneto-gravimetric curves for a melt-spun $Mn_{52.5}Bi_{47.5}$ alloy.

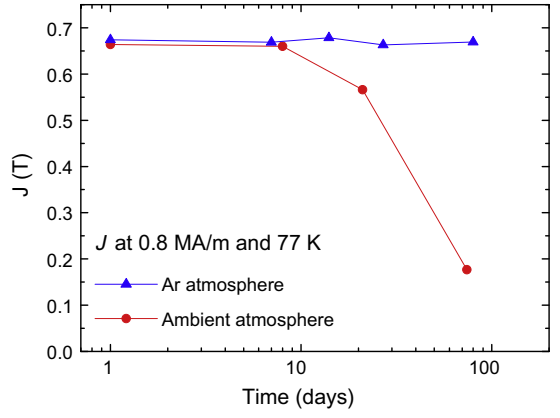

Fig. 3. Effect of room-temperature aging under Ar and ambient atmospheres on magnetization (J) for LTP-MnBi.