

## Enhanced Magnetic Squareness in Manganese-Bismuth Mechanical Alloys Incorporating Magnesium Oxide

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Manganese-bismuth (MnBi) mechanical alloys have been under development for novel permanent magnets without rare-earth elements. The ball-milling of bismuth (III) oxide and manganese powders in this work leads to soft magnetic MnBi alloys with rod-like MnO impurity and highly unbalanced compositions. Interestingly, the introduction of magnesium (Mg) as reducing element during the milling gives rise to unique magnetic properties. The obtained MnBi alloys incorporating plate-like MgO has an enhanced magnetic squareness but minimal coercive field. The magnetic squareness remains high after the heat treatment and washing. The washing in ammonia also brings about a balanced composition between Mn and Bi.

**Keywords:** manganese-bismuth, magnesium oxide, mechanical alloying, coercive field, magnetic squareness.

### 1. INTRODUCTION

The quest for rare-earth free permanent magnets has led to the interest in manganese-bismuth (MnBi) alloys [1]. With the low temperature phase (LTP), the alloys exhibit large energy products and coercive fields at room temperature [2–4]. Furthermore, the coercive field has a unique positive temperature coefficient, in contrast to the conventional magnets which lose hard magnetic characteristics at high temperature [5]. MnBi has also been tested as hard phase in hard-soft composite magnets [1, 6]. In spite of these advantages, this novel permanent magnet is still in development. One challenge is to upscale the fabrication for mass production. The syntheses of MnBi by redox reaction [7], arc melting [8] and melt spinning [9] are not straightforward. The peritectic reaction segregates the primary Mn phase from the MnBi liquid at high temperatures [10]. As a result, the LTP MnBi is not always obtained from melting routes.

High energy ball milling has received a great deal of attention as a pathway to fabricate MnBi alloys. Since Mn powders are easily oxidized and reacted with water, the milling has to be carried out in either inert gas atmosphere [11–18] or liquid nitrogen [2]. The method is also demonstrated to enhance the coercive field of MnBi synthesized by hydrogen plasma metal reaction [19].

Permanent magnets are characterized by the maximum energy product. Large coercive field and remanence, two magnetic parameters attributed to large energy product, are desirable. However, high values of both parameters are not always obtained in some circumstances. For composites with dominant ferromagnetic-ferromagnetic exchange interactions, the remanence is enhanced at the expense of coercive field [20]. It follows that the magnetic squareness,

the ratio remanence to saturation magnetization, is also increased in these composites.

In this work, magnetic squareness of MnBi powders prepared by ball-milling with and without magnesium (Mg) are compared. The precursors of metallic Mn mixed with the Bi<sub>2</sub>O<sub>3</sub> oxides can be used to produce nanostructured magnets in the presence of dispersant with large yield [13, 14, 21]. Mg can simultaneously act as a dispersant and a reducing element. The mechanochemistry combining the mechanical and chemical reactions has been explored because external forces by milling affects chemical bonds and the transformation into novel structures [22, 23]. Since the phase composition is a major factor influencing the magnetic properties, the ratio of Bi to Mn as well as formation of oxide before and after heat treatment was monitored. Effects of Mg addition and heat treatment on the morphology of MnBi powders, which dictates magnetic properties via the shape anisotropy [24], were also reported.

### 2. MATERIALS AND METHODS

Two sets of samples were synthesized by mechanical alloying. Bismuth (III) oxide (Bi<sub>2</sub>O<sub>3</sub>) (10 μm, 99.9 % trace metals basis, Aldrich) and Mn (–325 mesh, ≥ 99 % trace metals basis, Aldrich) powders were mixed with atomic ratio of 1:3 under argon atmosphere. The powders were milled in a ball-milling machine (Retsch PM100), at 600 rpm with balls to powders weight ratio of 10:1, for 20 min. The milled powders were sintered at 800 °C for 20 min, quenched and then continued annealing at 300 °C for 12 h. The other set of samples was prepared with the addition of Mg (98 %, turnings, Aldrich) as a reducing element. The annealed powders were washed by either acetic acid or ammonia (1 % v/v). Morphology and elemental composition were respectively probed by field emission scanning electron microscopy (FESEM: Zeiss

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Merlin Compact) and energy dispersive spectroscopy (EDS: Oxford Aztec connected Zeiss Merlin Compact). Magnetic properties were measured by means of vibrating sample magnetometry (VSM: Lake Shore 2000) in sweeping  $\pm 10$  kOe field. The coercive field was the x-intercept of hysteresis loops and the magnetic squareness was computed from the ratio of magnetization in zero field (remanence) to that in 10 kOe field.

### 3. RESULTS AND DISCUSSION

#### 3.1. MnBi

FESEM images for as-milled sample in Fig. 1 a reveal clustered particles of varying diameters from 100 to 500 nm. According to the EDS spectra, the difference in Mn and Bi compositions are associated to different shapes of particles. The clusters with irregular shape and rough surface are Bi-rich.

In Fig. 1 b, the heat-treated MnBi powders are composed of larger particles size in ranges of 100 nm–1  $\mu$ m. The EDS composition analysis similarly revealed the imbalanced composition between Mn and Bi, depending on the particle shape. Moreover, the morphology of these heat-treated powders is not homogeneous and some filaments are grown on some part of their surfaces as exemplified in the inset. According to the EDS analysis, this filament-like feature is MnO impurity.

Magnetic properties of ball-milled MnBi powders before and after heat treatment are compared in Fig. 2. The as-milled sample exhibits room temperature soft ferromagnetism with a narrow hysteresis loop. The magnetization in the zero applied field is largely dropped from the value in the 10 kOe applied field resulting in a magnetic squareness as small as 0.15. After the heat treatment, the magnetization is more saturated in the 10 kOe applied field and the magnetic squareness is doubled. The coercive field is increased from 169 to 454 Oe, suggesting that the LTP MnBi is increased during the annealing [15, 19].

#### 3.2. MnBi with MgO

The morphology of clustered particles in Fig. 3 a is similar to those from the synthesis without Mg. EDS spectra indicate a large variation of composition with Mn-rich and Bi-rich clusters. After the heat treatment, the compositions in Fig. 3 b remains nonuniform but an FESEM image shows agglomerations into round clusters with some embedded nanoplates. Such morphology likely occurs due to the reduction of reducing element in the following chemical reaction.



These plate-like structures are more evident after washing the mechanical alloys in either acid or base, and identified as magnesium oxide (MgO) by EDS (Fig. 3 c).

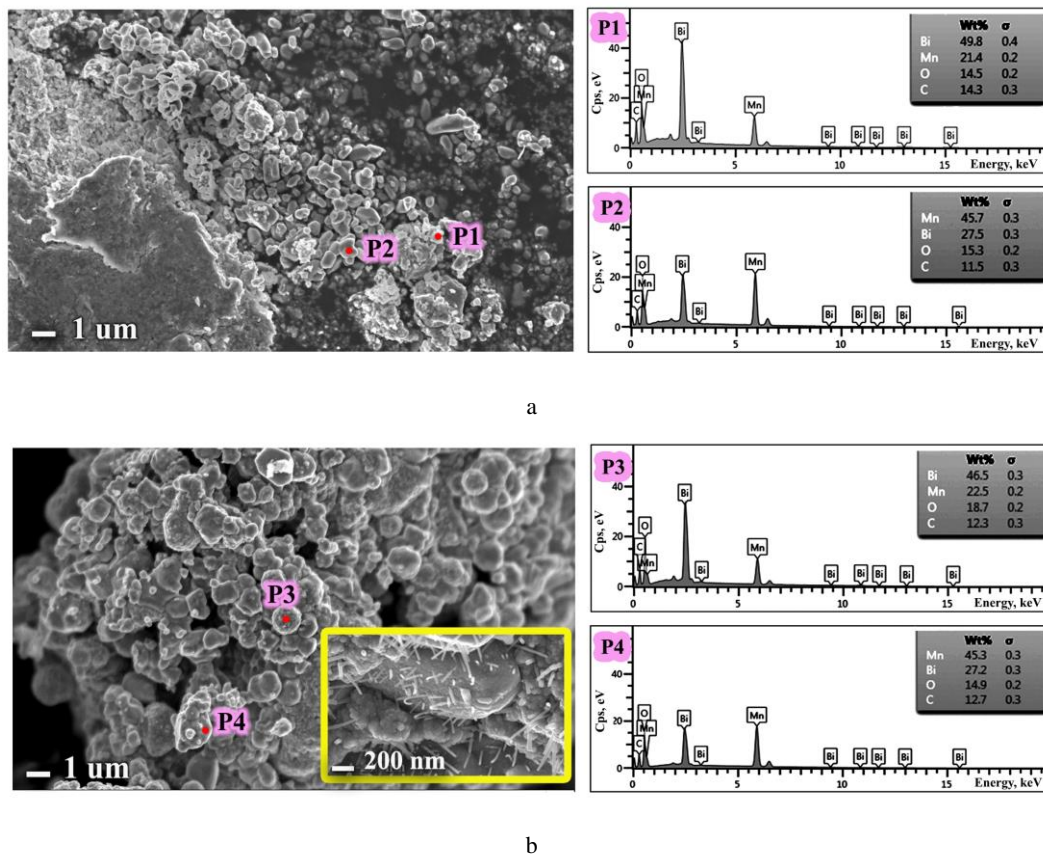


Fig. 1. FESEM images and corresponding EDS spectra of: a – as-milled MnBi powders and; b – MnBi powders after heat treatment

In Fig. 4, magnetic properties of MnBi powders after ball-milling for 20 min with Mg as a dispersant and a reducing element are drastically different from those synthesized without Mg. The magnetization is close to the saturation under 10 kOe field and is moderately decreased when the applied field is reduced to zero. This substantial remanence leads to a magnetic squareness around 0.5. Enhanced squareness is a characteristic of a hard magnetic material but the maximum energy product is much lower than those in the literatures [11–18]. A lower coercive field is an indication of a lower fraction of LTP MnBi obtained in this work. Exemplified EDS spectra in Fig. 3 indicate the separation between Mn-rich and Bi-rich clusters. High magnetic squareness with low coercive field indicates the dominant ferromagnetic-ferromagnetic exchange interactions [20]. With these magnetic properties, magnets with substantial external field can be realized with low switching field.

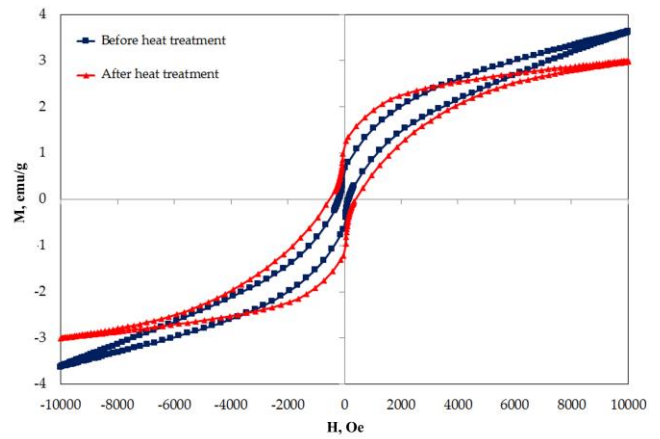


Fig. 2. Magnetic hysteresis loops of MnBi powders before and after heat treatment

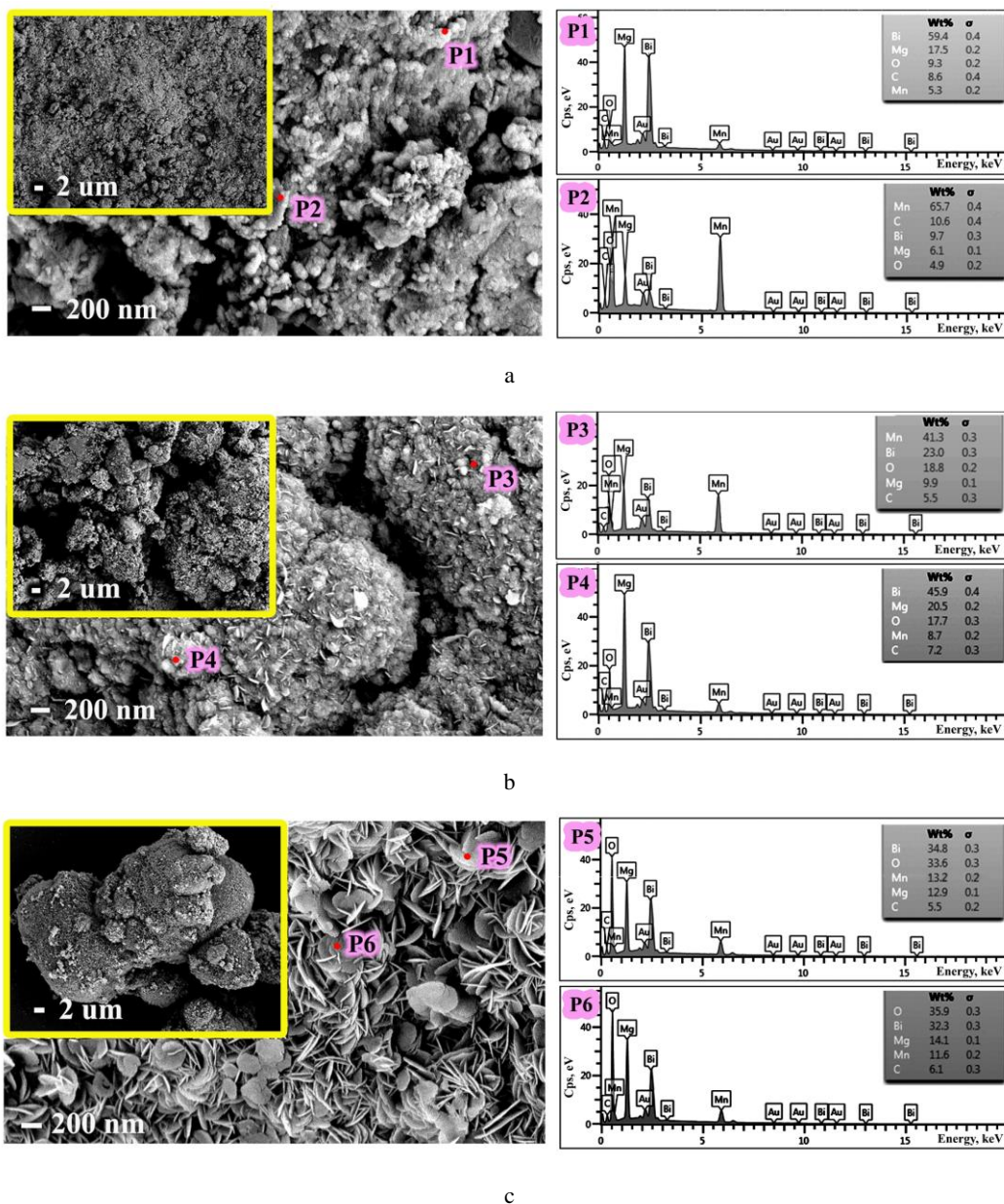
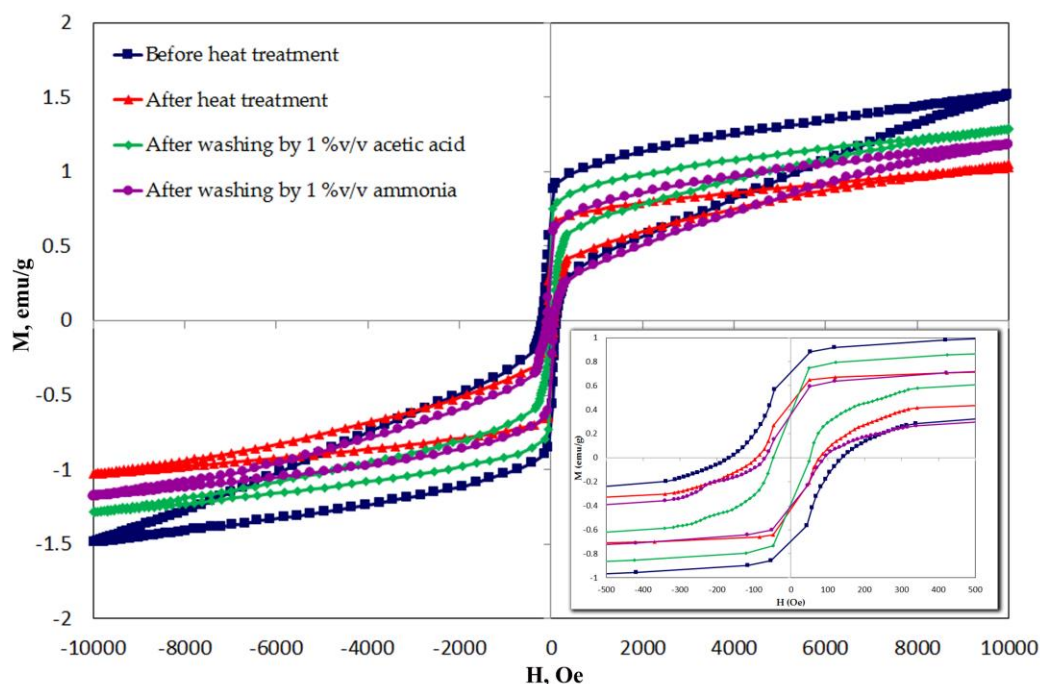


Fig. 3. FESEM images and EDS spectra of MnBi powders with Mg after: a–ball-milling for 20 min; b–after the heat treatment; c–subsequent washing by 1 % v/v ammonia



**Fig. 4.** Magnetic hysteresis loops of ball-milled MnBi powders with Mg before and after heat treatment, and after washing by 1 % v/v acetic acid and 1 % v/v ammonia, respectively (insets are magnified loops at low fields)

Magnetic characteristic is retained after the heat treatment and the magnetic squareness is also related to the formation of MgO nanoplates in magnetic clusters. The washing reduces the squareness down to 0.3 due to excessive amount of MgO. Nevertheless, the difference between Mn-rich and Bi-rich clusters is reduced after the washing in ammonia and the overall composition is more consistent.

#### 4. CONCLUSIONS

The enhancement of magnetic squareness in the MnBi alloys incorporating MgO was demonstrated and related to the morphology and phase composition. A balanced composition between Mn and Bi was successfully obtained after the heat treatment and base-washing ball-milled MnBi powders with Mg. The milling without Mg gave rise to MnO nanorods and soft magnetic characteristics. On the other hand, the incorporation of Mg in the ball-milling enhanced magnetic squareness and led to plate-like MgO in MnBi mechanical alloys. Because of minimal coercive fields, large hysteresis and the maximum energy product required for permanent magnets were not obtained. Nevertheless, this composite has potential applications for supplying substantial magnetic field with moderate switching field in miniature devices.

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