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One step pressing-annealing to produce LTP MnBi magnets

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Abstract

The production process for the high-purity low-temperature-phase (LTP) manganese bismuth (MnBi) magnets requires arc-melting, grinding and annealing materials under inert atmosphere. However, the formation of MnO is practically unavoidable during these steps since both Mn and MnBi are easily oxidized even by trace amounts of oxygen. In this work, an oxygen-free pressing-annealing system is developed to facilitate the synthesis of LTP MnBi with minimal oxidization. The semi-automatic pressing is carried out by using the compression piston and the load cell is used to measure the pressing force. The copper plate and cylindrical container are heated by nichrome filament heating. Mn and Bi precursors in powder form are simultaneously pressed and annealed allowing one step formation of LTP MnBi in argon atmosphere chamber. The vibrating sample magnetometry reveals the hysteresis loop of MnBi samples with ferromagnetic characteristics.

1. Introduction

Permanent magnets are essential components in many electric and electronic devices from computers, appliances to medical equipment. Power-related novel devices become smaller, lighter and more efficient in the 21st century [1]. Emergent applications of permanent magnets in renewable energy have come to the landscape recently, for instance the large-scale applications in electrical vehicles and wind turbines. It has been proven that the energy efficiency of traction motors and wind turbine generators using permanent magnets is superior to other types. Due to the remarkable magnetic properties, rare-earth-based materials have been the key ingredient in permanent magnet applications for several decades. However, the limited availability and high price of rare-earth elements, such as neodymium, dysprosium and samarium, have a severe impact on modern high-performance magnets. Also, mining and refining rare-earth metals lead to environmental problems [2]. These concerns have driven a new round of search for rare-earth free magnetic materials to be used as a hard phase in exchange coupling nanocomposite magnets [3].

The low-temperature phase (LTP) manganese bismuth (MnBi) is one of the most investigated permanent magnets without rare-earth elements, especially the ones for elevated applications [4]. MnBi has attracted much recent attention in the development of rare-earth-free permanent magnets due to its unique increase in coercivity with increasing temperature. However, the pure MnBi phase is difficult to obtain, partly because the reaction between Mn and Bi is peritectic, and partly because Mn reacts readily with oxygen. MnO formation is irreversible and detrimental to magnet performance [5]. Mn metals are normally antiferromagnetic. By increasing the atomic distance between Mn atoms to 2.96 Å or more, the element becomes ferromagnetic [6].

Synthesis of the high performance LTP MnBi compound is the principle step for fabrication of MnBi-based exchange coupled magnets [7,8]. Various approaches have been developed to obtain single phase MnBi, including arc-melting, melt-spinning followed by ball milling, sintering and chemical synthesis. The annealing process must be also applied to maximize the LTP content in a peritectically solidified alloys. According to the phase diagram of Mn-Bi system, the annealing temperature must be lower 340 °C in order to preserve the ferromagnetic phase of $Mn_{50}Bi_{50}$.

Since the solidification of MnBi alloys is peritectic, their microstructures always consist of the starting phases of Mn and Bi as well as the resulting phase MnBi. Moreover, the oxidation was controlled by preparing the samples at low pressure. The time-controlled annealing process plays a key role in regulating the microstructure with the main ferromagnetic phase matrix, in which the rest of Mn and the Bi accumulations are embedded [9]. In this work, the annealing process is incorporated into the same step with the pressing. Phases, morphology and magnetic properties of samples annealed and pressed for 6, 12 and 18 h in argon atmosphere were characterized and compared.

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2. Experimental

2.1 Development of one-step pressing-annealing machine

The one-step pressing-annealing system shown in Figure 1 was developed. The 250 × 250 × 420 mm^3 vacuum chamber was built from the 10 mm-thick stainless steel (STL304), having the transparent 175 × 235 × 4.5 mm^3 acrylic window. Inside the chamber, starting materials in a cylindrical copper mold were pressed by a compression piston. A load cell was used as a transducer to convert the pressure up to 40 N/cm^2 into electrical signals. The maximum temperature of 450 °C was obtained for continuous 200 h by the heating plate with a nichrome heater. The refractory bricks (SK) were used as insulators with argon gas flow during the process.

2.2 Fabrication and characterization of Mn-Bi magnets

Mn and Bi powders (≥99% trace metals basis, Aldrich) were mixed with Mn:Bi atomic ratio of 2:1 and then put into the cylindrical copper mold. This mold was placed on the heating plate and pressed with 50 psi by a piston, controlled by a load cell. The operating temperature of 280 °C is higher than the melting point of Bi but lower than the upper limit of the LTP MnBi. Three samples were prepared using varying times of 6, 12 and 18 h in argon atmosphere.

Magnetic properties were examined using an in-house developed vibrating sample magnetometer (VSM, calibrated with Lakeshore 730908 using a 3mm-diameter Ni sphere). Morphology was inspected by a scanning electron microscope (SEM: FEI Quanta 450 FEG). The elemental compositions were measured using the energy dispersive spectrometry (EDS), attached to the SEM. The phases were identified using single-crystal X-ray crystallography (Rigaku Oxford Diffraction-XtaLAB SuperNova) with CuKα radiation in the powder mode.

3. Results and discussion

The one-step pressing-annealing machine successfully combines the pressing and annealing of MnBi powders into a single step. In addition to the time saving, magnetic properties are improved by the reduction in oxidation. Table 1 lists the room temperature coercive field and magnetizations derived from hysteresis loops shown in Figure 2. The sample prepared at 6 h has the largest coercive field of 1103 Oe, approximately twice those of the samples prepared at 12 and 18 h. Without initial melting, this value also represents a marked improvement from the fabrication of MnBi magnets [10]. However, the highest coercive field occur in the sample has the least magnetization whereas the highest magnetization is obtained in the sample prepared at 12 h with 35 emu/g at 10 kOe. The magnetization of the sample prepared at 18 h is reduced to 25 emu/g while its coercive field remains comparable to that of the sample prepared at 12 h. The high performance of MnBi bulk magnets requires both high saturation magnetization and coercive field [9]. However, the tradeoff between coercive field and remanent magnetization often occurs as a result of the intergranular exchange interaction.

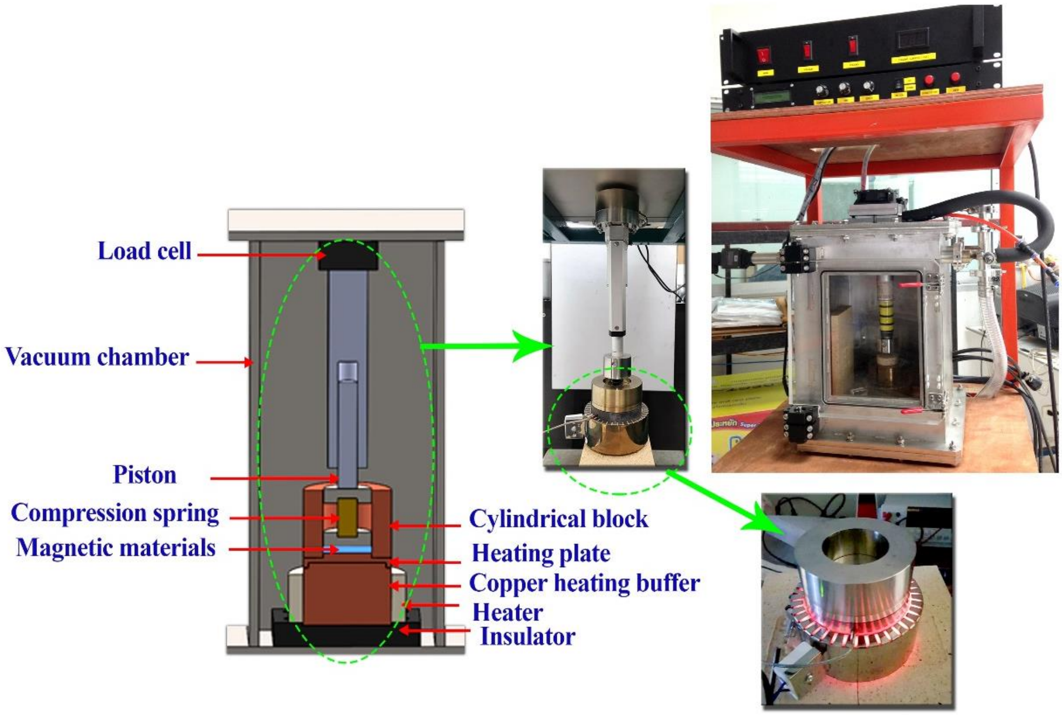

Figure 1. Photograph and diagram of the one step pressing-annealing machine.

Prepared in the one-step pressing-annealing machine with varying times, each sample exhibits three different features as exemplified in Figure 3. SEM micrographs and corresponding EDS spectra in the case of 12 h reveal areas corresponding to MnBi, Mn and Bi phases. The EDS detects most weight percent of non-reacting Mn in the region with bulky figures and sleek surfaces. The moderately coarse regions are ascribed to the Bi-rich matrix embedded by Mn with more than twice amount of Bi over Mn. Oxygen contents found in this region correspond to oxidations of Mn and Bi [12].

The formation of MnBi phase reveals in the region with spherical shapes in SEM micrographs and equal amount of Mn and Bi in EDS spectra. By pressing and annealing at 280 °C, the diffusion of Mn (solid) into Bi liquid through the peritectic reaction promote MnBi phase formation [5,12,13]. The annealing significantly enhances the LTP MnBi content [11], although most works initially use the melt-spinning or arc-melting prior to the annealing [14,15].

The different EDS spectra measured at different spots suggest the phase inhomogeneity. The mixed phase was further characterized by XRD in Figure 4. Diffraction peaks at 2θ = 28.14°, 29.21°, 38.14°, 42.20°, 51.49°, 52.14°, 58.18° and 68.68° assigned to the (101), (002), (102), (110), (201), (112), (202) and (211) planes are indexed as MnBi (Reference: 03-065-8164 Bismuth manganese). The diffraction peaks at 27.16°, 39.62°, 44.55°, 46.02°, 48.70°, 56.03°, 62.18° correspond to the (012), (110), (015), (113), (202), (024) and (116) planes of Bi (Reference: 01-085-1329 Bismuth). The diffraction peaks at 43.02° and 47.83° are due to the (411) and (332) planes of the Mn phase (Reference: 01-089-2412 Manganese).

Table 1. Magnetic properties of MnBi samples prepared by the one step pressing and annealing machine for 6, 12 and 18 h.

Annealing time	M_{max} (emu/g)	M_r (emu/g)	H_c (Oe)
6 h	17.86	8.87	1103.53
12 h	34.93	12.20	551.42
18 h	25.05	8.13	506.05

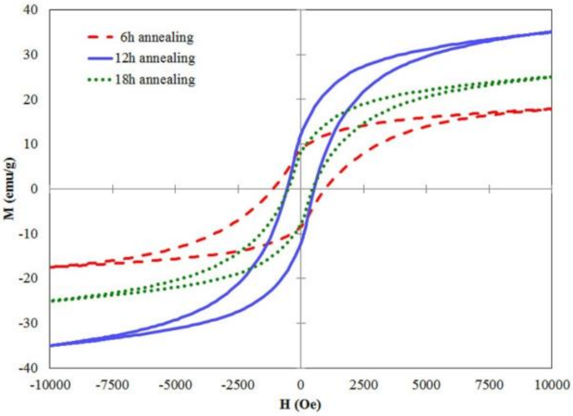

Figure 2. Hysteresis loops of MnBi magnets prepared by the one step pressing-annealing machine for 6, 12 and 18 h.

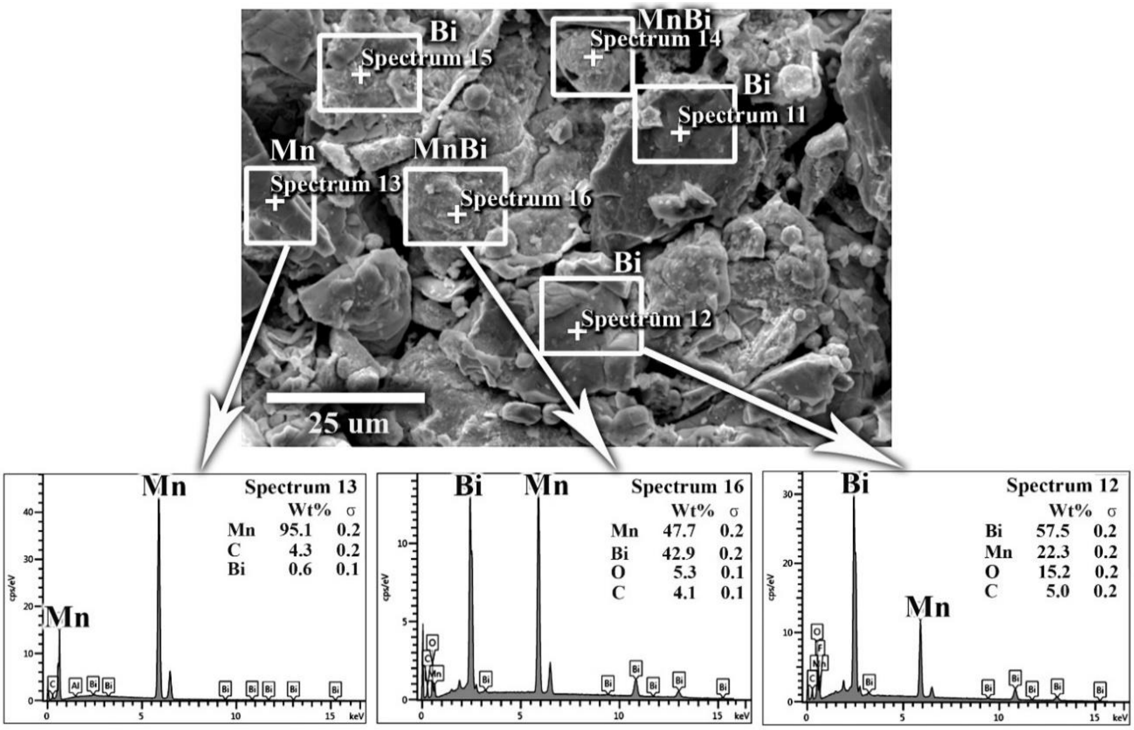

Figure 3. FESEM image and EDS spectra of MnBi magnets prepared by the one step pressing-annealing machine for 12 h.

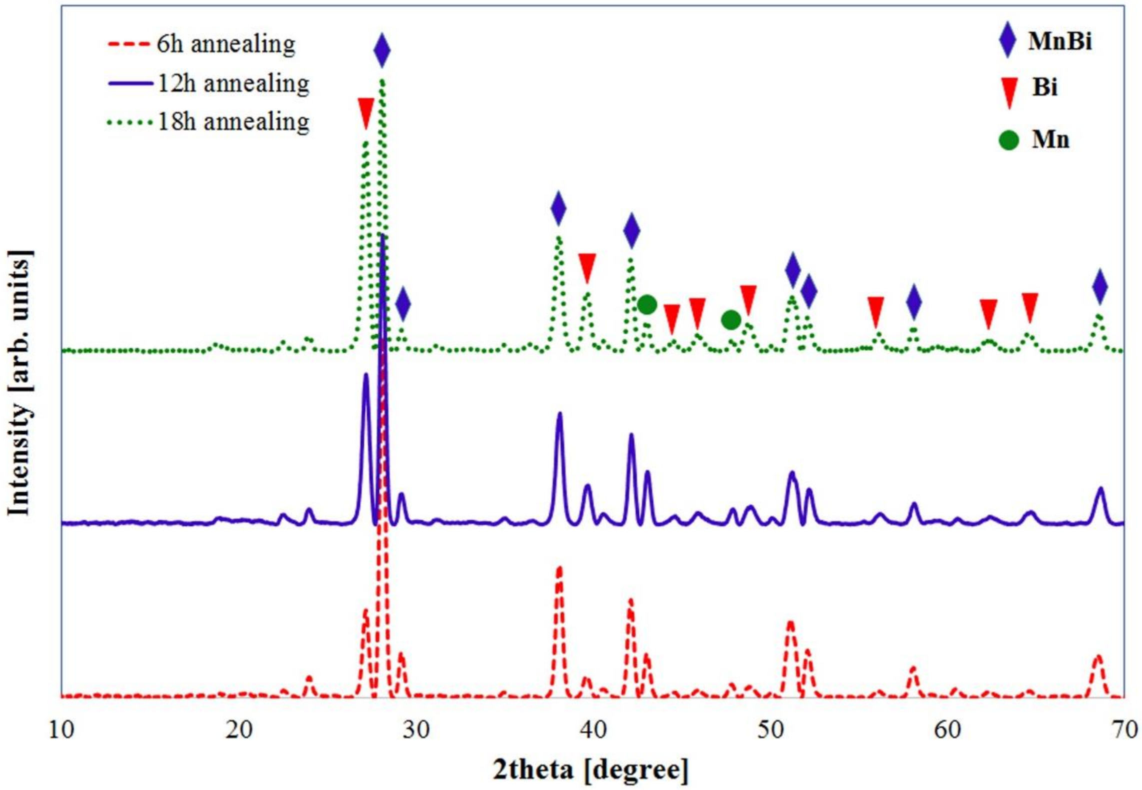

Figure 4. XRD pattern of MnBi magnets prepared by the one step pressing-annealing machine for 6, 12 and 18 h.

The finding confirms previous reports that the LTP MnBi is difficult to obtain in high-purity [15-19]. It can be inferred that the ferromagnetic properties observed in Figure 2 are solely attributed to the MnBi phase. By comparing the XRD patterns in Figure 4, the most intense MnBi peaks are observed in the sample annealed for 6 h which explains its largest coercive field. In addition to the relation between the phase and coercive field, MnBi also varies in size and differently distributes in each sample after the peritectic reaction in the pressing-annealing process. The longer annealing tends to increase the grain size of MnBi. The resulting exchange interaction between magnetic grains increases the magnetization while the coercive field is reduced in the observed tradeoff [9,11].

4. Conclusions

In order to prepare the LTP MnBi desirable for rare-earth free magnets, the system was developed to combine pressing-annealing into a single step with minimal oxidation. The system can be operated up to 200 h but the processing time of only 6 h results in larger coercivity than those prepared using longer times. All ferromagnetic properties are attributable to the MnBi phase with a spherical shape but such phase exists among oxides non-interacting Mn and Bi-rich phases. Nevertheless, the phase formation can be controlled by parameters regulated by the pressing-annealing system.

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