Synthesis and characterization of Mn₂B nanocrystals by mechanical alloying method

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Abstract

In this study, elemental Mn and B initial materials were used to synthesize pure MnB nanocrystals by ball milling. Milling experiments were conducted with high-energy planetary ball mill in a hardened steel vial with hardened steel balls, under Ar atmosphere at 40:1 ball-to-powder ratio and 300 rpm rotating speed. As synthesized MnB nanocrystals phase structures and morphological/microstructural investigation were analyzed by X-Ray diffractometry (XRD) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX), respectively. Particle size of MnB were calculated as 34.5 nm by Rietveld refinement. Furthermore, the magnetic behavior of nanocrystals were determined by vibrating sample magnetometer (VSM). MnB sample shows ferromagnetic behavior at room temperature with saturation magnetization of 13 emu/g and coercivity of 90 Oe.

1. Introduction

The properties such as relatively high melting temperature, hardness and brittleness makes the transition metal boride of manganese as good candidates in the hard materials. Hard materials are used commonly as cutting tools and hard coating in various industrial fields [1]. Numerous synthesis methods have been used for the production of refractory borides such as combustion synthesis, which is also known as self-propagating high-temperature synthesis (SHS), solvothermal, carbothermal and mechanical alloying (MA) methods [2-5]. Among these methods, MA is intensively preferred for the advantages such as relatively low-cost equipment, simplicity, low-temperature processing, great flexibility in the selection of the processing parameters, and ability to produce large quantities of material with the same physical properties [6-9]. The powders are subjected to continuous cold-welding, flattened, fracturing and re-welding mechanisms due to impacts on the balls and grinding medium. A lot of unique alloying materials such as nanocrystalline, quasicrystalline, amorphous and supersaturated solid solutions alloys can be synthesized with this method [6]. In the literature, it is obvious that metal borides studies with MA method have exponentially increased in recent years due to its simple and favorable features [10-12].

The boron and its alloys form various compounds and alloys with many elements found in nature. In the literature, there are many allotropic phases of boron with transition elements. [13-16]. Five different solid state phases have been reported in the Mn-B binary phase diagram: the phase of MnB (tetragonal structure of the Al₄Cu type, I4/mcm), MnB (orthorhombic structure of Fe-B type, Pnma), MnB₄ (orthorhombic structure of the Ta₄B₄ type, Immm), MnB₄ (hexagonal structure of the AlB₂ type, P6/mmm), and MnB₄ (monoclinic structure of the MnB₄, C2/m). [1, 17-21]. However, there is a lack of available information on the synthesis of manganese borides in the literature. Meng et al. synthesized various kinds of manganese borides by liquid-solid reaction from manganese and amorphous boron powders at high pressure and high temperature. They have reported that mixing the boron and manganese powder at various atomic ratios, temperatures and pressures, Mn₁₂B₃, Mn₁₂B₄, MnB, MnB₂, MnB₃, MnB₄, and MnB₅ phases were synthesized effectively [22]. In another study conducted by Zhu et al., MnB alloy was synthesized by starting from Mn and B chips with arc melter [23]. Guo et al. conducted high-pressure synthesis experiments of single-crystal of MnB₄ and characterized their structure and hardness. They also theoretically examined the relative stability, as well as mechanical, electronic, and magnetic properties of MnB₄, in both the AlB₂ and ReB₂-type structures by means of first-principles calculations within DFT [24].

There are also studies by an arc melting methods for synthesis of MnB₁₀₀ₓ and MnB₁₂₀ₓ-Co₁₀₀₋ₓ alloys [25-26]. In this study, to the best of our knowledge, MnB was...
synthesized for the first time with Mn and B powders mixture by using planetary type ball under Ar atmosphere. The phase and morphological structures were investigated with X-Ray Powder Diffractometry and crystal structures were analyzed by Rietveld refinement and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX). Magnetic properties of as-synthesized sample was characterized by using vibrating sample magnetometer (VSM).

2. Materials and methods

The Mn₂B was synthesized by mechanical milling. Mn (Alfa Aesar, 99%) and B (Alfa Aesar, crystalline 98%) were used as initial materials. Sample preparation and milling experiments were conducted under Argon gas (99.5%) atmosphere. Milling experiments were performed using high-energy planetary ball mill (Retch, PM 100 CM, Monomill) with hardened steel balls and hardened steel vial. Milling experiments were performed at 300 rpm rotating speed and 40:1 ball to powder ratio and prolonged up to 10 h. The purification of the obtained powders was not required. Milling conditions were given in Table 1. The reaction for preparation of Mn₂B powder is given in Eq 1. Appropriate amounts (Eq.1) of initial powders were weighted in glove box using precision balance.

\[
2 \text{Mn} + \text{B} \rightarrow \text{Mn}_2\text{B} \quad (1)
\]

Rigaku D-max B horizontal diffractometer with CuKα radiation at a scanning rate of 0.02−1s.

| Milling conditions |
|--------------------|
| Vial material      | Hardened steel |
| Ball material      | Hardened steel |
| Ball diameter (mm) | 15             |
| Ball to powder ratio | 40:1          |
| Rotation speed (rpm) | 300          |
| Milling period (h)  | 0-10 h        |

Phase and structural analysis of as-made nanocrystals were analyzed via X-Ray Diffractometry (Rigaku, D/MAX B horizontal diffractometer) using Cu-Kα radiation at 40 kV and 30 mA, anode voltage and current for 2θ range from 20° to 100° at a scanning rate of 0.02−1s. International Center for Diffraction Data (ICDD) powder diffraction files were used in the identification of crystalline phases. The crystal structure of the synthesized Mn₂B phase was studied by multiphase Rietveld method using MAUD software [27]. Crystallography Open Database is used for the .cif files in the refinement. For the refinement of peak profiles, the Pseudo-Voigt function is used. Morphological and microstructural characterizations were determined by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX) using a FEI-Quanta FEG 450 microscope operated at 12.3 kV in secondary electron mode. The magnetic behavior of particles were determined using vibrating sample magnetometer (VSM) module of Physical Properties Measurement System (PPMS, Quantum Design).

3. Results and discussion

The Mn-B binary phase diagram is given in Figure 1. As seen in Figure 1, Mn₂B phase has tetragonal structure of the Al₂Cu type (space group; I4/mcm) while other phases such as MnB has orthorhombic structure of Fe-B type (space group; Pnma), Mn₃B₄ has orthorhombic structure of the Ta₃B₄ type (space group; Immm), MnB₂ has hexagonal structure of the AlB₂ type, (space group; P6/mmm), and MnB₂ has monoclinic structure of the MnB₂ (space group; C2/m) [1]. The Al₂Cu-type Mn₂B phase is easy to produce with low calculated enthalpy of formation as shown in Figure 1.

The phase analyses and microstructures of the initial materials mixtures are given in Figure 2 and Figure 3. As seen from the Figure 2, the reflections related to crystalline Mn (ICDD Card No:32-0637, Cubic, I-43m)
and B (ICDD Card No: 31-0207, Hexagonal, R-3m) were observed in diffraction pattern. The SEM images of initial powders reveal that both of Mn and B powders were in irregular shape and morphology and size range of the B powder before milling was in the 2-200 µm while Mn was in the range of 450 nm-5 µm.

The mixed powders were ball milled for 10 hours (Table 1) and weight ratio of milling balls to powder charge ratio is 40:1. XRD pattern of the sample ball milled are given in Figure 4. The XRD pattern shows that Mn$_2$B phase was successfully occurred after 10 h of ball milling processes. Multiphase Rietveld refinement showed that all the Mn$_2$B reflections are observed (ICDD Card No: 00-025-0535) and sample is single phase. Refinements confirm the tetragonal structure of Mn$_2$B in 14/mcm space group with the lattice parameters of $a=b=5.142$ (1) Å and $c=4.165$ (2) Å. The structural parameters obtained from Rietveld refinements are summarized in Table 2. After progressive cold-welding, flattened and fracturing mechanisms, reactions takes place at low temperature and particle size reduce to 34.5 nm.

Figure 5 shows the SEM image of the synthesized Mn$_2$B nanocrystals. It is seen that size of Mn$_2$B particles are within the range of 50-500 nm, and have irregular/coaxial shape and morphologies. It has been also
observed that particles are agglomerated. It is known that particle size reduction takes due to some mechanisms such as cold welding, flattening and repeated fractures in mechanical alloying processing. Consequently, new unstable surfaces are formed by continuous fractures and deformations, and as a result agglomeration occurs. The EDX elemental analysis confirms the Mn and B phases together with little Cr and Fe impurities. Due to the nature of the milling process, impurities are frequently observed originating from to the milling vial.

In order to obtain information about the magnetic properties, magnetic field dependence of magnetization (M(H)) of the as-made Mn$_2$B powder is measured at 300 K (Figure 6). This measurement can be divided into 4 quadrants. In the 1st quadrant, external magnetic field is applied to powder sample and swept from 0 – 3 T range, which is also called virgin curve. Magnetization of the sample was measured continuously under the applied field. Then in the second quadrant, magnetic field is swept from 3 – 0 T. The direction of the applied field was then reversed during the 3rd quadrant and field is applied from 0 – (-3) T. Finally applied field was swept from -3 – 0 T in the 4rd quadrant and magnetization of the sample was measured continuously. Significant physical parameters such as; saturation magnetization, saturation field, coercivity, anisotropy constant and maximum energy product can be obtained from M(H) measurement. As can be seen in Figure 4, Mn$_2$B sample has weak ferromagnetic signal with the saturation magnetization of 13 emu/g. Sample has coercivity of 90 Oe at 300 K, as depicted in the inset of figure. Among the manganese borides only MnB with positive exchange interaction between Mn atoms shows ferromagnetic behavior while MnB$_2$ and Mn$_3$B$_4$ are antiferromagnetic. MnB$_4$ phase is paramagnetic and Mn$_2$B is non-magnetic [28]. The ferromagnetic behavior observed in our sample (Figure 6) could be attributed to the small amount of Fe/Cr impurities, which originates from milling experiment carried using hardened steel vial.

| 2θ (degree) | hkl | f | Relative intensity | d calculation (Å) | d experimental (Å) |
|-------------|-----|---|-------------------|-------------------|-------------------|
| 24.435      | 110 | 10 | 10.0              | 3.6400            | 3.6494            |
| 34.826      | 200 | 15 | 15.0              | 2.5740            | 2.6050            |
| 42.952      | 002 | 25 | 25.0              | 2.1040            | 2.0952            |
| 44.833      | 211 | 100| 100.0             | 2.0200            | 2.0185            |
| 50.020      | 112 | 11 | 11.0              | 1.8220            | 1.8180            |
| 56.441      | 202 | 25 | 25.0              | 1.6290            | 1.6228            |
| 73.461      | 312 | 12 | 12.0              | 1.2880            | 1.2861            |
| 78.767      | 330 | 9  | 9.0               | 1.1240            | 1.1270            |
| 80.029      | 213 | 30 | 30.0              | 1.1980            | 1.2006            |
| 84.017      | 420 | 1.0 | 1.0              | 1.1510            | 1.1460            |
| 89.102      | 402 | 6  | 6.0               | 1.0980            | 1.0923            |

Table 2. Phase structures of Mn$_2$B nanocrystals.
4. Conclusion

The synthesis of Mn$_2$B nanocrystals were studied with the initial powders of Mn and B at 300 rpm rotating speed and 40:1 ball to powder ratio via planetary ball mill. It is seen that after 10 h ball milling Mn$_2$B nanocrystals were synthesized. The synthesized particles are characterized using x-ray diffraction/spectroscopy, electron microscopy, and vibrating sample magnetometer measurements. Particle sizes of the nanocrystals were calculated as 34.5 nm by Rietveld refinement. In contrary to the reported works in the literature, Mn$_2$B sample was found to be ferromagnetic at room temperature with small saturation magnetization of 13 emu/g. This weak ferromagnetic signal is attributed to the Fe impurity caused from the hardened steel milling vial.

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