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Original Research Paper

Mechanochemical processing and microstructural characterization of pure Fe_2B nanocrystals

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ABSTRACT

The results of current investigation demonstrate that mechanochemical processing can be used to synthesize high purity Fe_2B nanocrystals by selecting well-optimized milling conditions, reaction paths and proper starting materials. Microstructure, phase analyses, specific surface area, and magnetic properties of the synthesized nanocrystals were examined by using X-ray diffraction/spectroscopy, electron microscopy, nitrogen adsorption–desorption methods following Brunauer-Emmett-Teller equation and vibrating sample magnetometer techniques, respectively. Removal of MgO impurity phase by leaching the resulting powder in the acetic acid solution yielded single phase Fe_2B nanocrystals with the crystallite size and specific surface area of 12.5 nm and 29 m^2/g, respectively. Magnetization results clearly indicated the ferromagnetic behavior of Fe_2B nanocrystals with saturation magnetization observed around 96.26 $emu \cdot g^{-1}$. Electron microscope images revealed coaxial/spherical powder shape and morphology of the single-phase Fe_2B nanocrystals.

1. Introduction

Metal borides are mainly characterized with their high level of hardness, high melting temperatures, excellent wear-resistance and chemical stabilities for production of industrial tools. While some applications involve the use of these materials as semi conductive diffusion barriers, melt crucibles or cutting tool materials, others require stable materials for high temperature uses [1–3]. In addition to related properties of metal borides for industrial uses, the synthesis methods to obtain the materials in different physical forms, such as thin films, bulk pieces and nanocrystals, are also crucial. A wide range of synthesis methods, such as self-propagating high temperature synthesis (SHS) [4,5], chemical vapor deposition method (CVD) [6], electrolysis method [7,8], sol-gel [9,12], solvothermal [13,15] and mechanochemical process [16–20] are used. Among these methods, mechanochemical synthesis, which is also known as high energy milling method is preferred to obtain high purity macro and nano-scale ceramics, borides and composite materials. Mechanochemical process allows low cost production at low temperatures and simple controlling on synthesis parameters. Basically, mechanochemical process involves some repeated mechanisms, such as cold welding, flattened and fracturing. The cold welding and fracturing mechanisms reduce the particle size, and increase the surface area and diffusion rate, causing the reaction to take place at low temperatures [21–27].

Recently, borides of magnetic metals, mostly produced via solvothermal method, such as Co, Ni, Ru and Fe, have increasingly attracted attention due to their potential as a hydrogen catalyst in the aqueous solution of $NaBH_4$ [28–34]. Among these magnetic borides such as Ru, Ni, and Co are widely known materials synthesized by mechanochemical method [35–37]. There are also a few studies about production of Fe_2B alloys using elemental boron and iron as initial reactants [38–48]. However, to the best of our knowledge, there has been no experimental study about the production of pure Fe_2B nanoparticles with starting materials such as Iron (Fe), Boron Oxide (B_2O_3) and Magnesium (Mg) via mechanochemical synthesis method so far. Here we report; (*i*) the synthesis of pure Fe_2B nanocrystals using mechanochemical process, and (*ii*) the characterization of the nanocrystals using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), and vibrating sample magnetometer (VSM) techniques in detail.

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2. Experimental

Fe (Merck, 10 μm, 99.5%), B_2O_3 (Eti Maden, 598 μm, 98.00%), and Mg (Sigma Aldrich, 138 μm, 99.00%) were used as starting materials. Sample handling and milling experiments were performed under Argon gas (99.999%) atmosphere. Purification process was performed in the acetic acid (CH_3COOH, Merck, 99.50%) solution. Experimental studies were conducted using high-energy planetary ball mill (Fritsch, P6, Monomill). Particle size measurements were conducted in a Malvern Mastersizer-2000 analyzer in order to determine the accurate particle size distributions of the starting powders. Appropriate amounts (Eq. (1)) of starting materials, at the ratio of 4:1.1:3.3 mol. that corresponds to 10% excess amount of B_2O_3 and Mg, were weighted in inert argon atmosphere using high precision balance. Mechanical milling was performed in a 80 ml hardened steel grinding vial using three hardened steel balls with diameter of 15 mm and following the flowchart presented in Fig. 1. Milling parameters are listed in Table 1.

$$4Fe + B_2O_3 + 3Mg \rightarrow 2Fe_2B + 3MgO \quad (1)$$

The powder mixture obtained after milling process was purified with room temperature leaching using a magnetic stirrer at the ratio of 1/250 g mL^{-1} within 5 M aqueous acetic acid solution for 30 min at 400 rpm rotational speed. These leaching parameters were optimized after a series of pre-experiments. For solid-liquid separation, the solution was centrifuged at 5000 rpm rotational speed for 10 min after leaching. Then, the particles were washed with distilled water-ethanol, and dried in vacuum of 20 mbar for 10 h at 70 °C.

Phase analyses of nanocrystals were examined by XRD using a powder diffractometry (XRD, Rigaku, D/MAX-2200) equipped with copper anode. The Cu-Kα radiation (λ = 1.54 Å) was generated at 40 kV and 30 mA, anode voltage and current, respectively. Intensity data was collected over a 2θ range from 2° to 90° at 4°/min scanning rate. International Center for Diffraction Data (ICDD) powder diffraction files were used in the identification of crystalline phases. Microstructural characterization, shapes-morphologies and structure conformation of the synthesized particles were specified via SEM (FEI, Quanta 200F) and high resolution TEM (FEI, Tecnai G2 F30), respectively. TEM images were analyzed using Image J digital software [49]. Specific surface areas of the purified products were calculated using nitrogen adsorption-desorption method following Brunauer-Emmett-Teller equation (BET, Nova, 220E). For magnetic characterization at room temperature, magnetic field depended (within ±20 kOe magnetic field ranges) DC magnetization measurements were performed by using Quantum Design Physical Properties Measurement System (PPMS) with VSM option.

Table 1
Milling parameters of Fe_2B nanocrystals.

Milling parameters	
Ball diameter (mm)	15
Number of balls	3
Ball to powder ratio	40:1
Rotation speed (rpm)	400
Milling period (h)	1, 2, 3, 4, 5, 20

Scherrer's formula was employed to calculate the crystallite size (Eq. (2)). In Eq. (2), τ represents the crystallite size, K is a constant taken depending on the crystal shape (0.89), λ is the X-ray wavelength (1.54 Å), β is the full width at half maximum (FWHM) of the peak and θ is the Bragg angle. The FWHM and the position of (1 0 0) peak in the XRD pattern of FeB_2 phase were used for crystallite size calculations.

$$\tau = \frac{K \cdot \lambda}{B \cdot \mathrm{Cos}\theta} \quad (2)$$

3. Results and discussion

The identification of crystalline phases in starting mixture is given in Fig. 2. The XRD pattern (Fig. 2) of starting mixture points out intensive Fe (ICDD Card No: 01-089-7194) and Mg (ICDD Card No: 01-089-5003) peaks, while B_2O_3 phase is not seen due to its amorphous nature. SEM images of the starting materials given in Fig. 3 indicate the flat-irregular shape of Fe and Mg, and irregular form and morphology of B_2O_3. The d(0.5) particle sizes of the Fe, Mg and B_2O_3 starting powders were measured as 6.3 μm, 137.6 μm and 597.9 μm, respectively (Fig. 3a–c). The small peak in the particle size distribution of Fe, located in 20–80 μm range, can be attributed to intense agglomerations in the starting powder.

The starting materials used for mechanochemical synthesis (MCS) are widely available commercially and mostly in pure powder forms that have particle sizes in the range of 1–200 μm. Starting with the materials which have bigger particles sizes would also be sufficient since the powder particle size is not very critical, and decreases to few micrometers exponentially within a very short time of milling (typically a few minutes) [50]. The small particle size of the starting materials shortens the reaction time since the energy required to reduce the grain size at the beginning of the milling is transferred to the reaction [22].

The ball to powder ratio (weight ratio of the milling balls to the powder charge) is 40:1. The mixed powders were ball milled for 1–20 h (Table 1). XRD patterns of the sample group ball milled for 1–5 h are presented in Fig. 4a. In the XRD pattern of 1 h milled sample, the peaks of starting materials showed a decreasing tendency during the milling. The XRD patterns reveal decreasing the peak

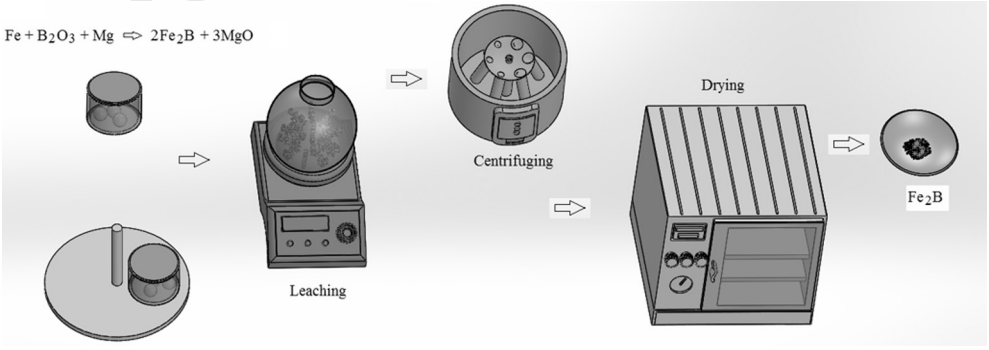

Fig. 1. Flowchart for producing a pure Fe_2B nanocrystals.

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