

Investigation on mechanochemical behavior of Al/Mg–B₂O₃–Nb system reactive mixtures to synthesize niobium diboride



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ABSTRACT

Aluminum and magnesium were used in the M–B₂O₃–Nb (M = Al, Mg) system to synthesize niobium diboride (NbB₂) via a mechanochemical process. The phase transformation and structural evaluation were investigated by means of X-ray diffractometry, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and differential thermal analysis techniques (DTA). Unlike thermodynamic possibility and DTA results, negligible aluminothermic reaction was occurred in the system and AlNb₂ intermediate phase was formed during milling. On the other hand, nanostructure NbB₂ was mechanochemically synthesized by the magnesiothermic reduction after 2.4 h of milling and the type of reactions was mechanically induced self-sustaining reaction (MSR). DTA results revealed that Mg₃(BO₃)₂ was largely formed during the thermal process, while the quantity of this by-product extremely decreased during the mechanochemical synthesis and completely eliminated after 5 h of milling. Scanning and transmission electron microscopy observations confirmed that the range of particle size was within 100 nm.

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1. Introduction

In recent years, niobium diboride (NbB₂) as a transition metal boride is recognized as potential candidate for high-temperature structural applications because of some outstanding properties such as high hardness, high-temperature strength, high melting points, good chemical stability, wear resistance and electrical conductivity [1–3]. Furthermore, it is important to prepare the powder mixture of NbB₂ with fine, homogeneous microstructure, because it is known that ceramic materials with fine microstructures exhibit improved mechanical properties [4]. The discovery of superconductivity at 39 K in MgB₂ has motivated new investigations on similar transition metal diborides such as those in the Ti–B, Zr–B, Hf–B, Nb–B, and Ta–B systems [5–10]. There are relatively few studies available on the synthesis of niobium boride powders compared with investigations of other transition metal borides. Niobium diboride can be conventionally prepared with solid state reaction between niobium and boron and molten salt electrolysis. However, investigations of the solid state reaction have been confined to temperatures above 1500 °C [11]. Formation of a variety of transition metal diborides MB₂ (M = Be, Al, Nb, Mo, Ta, Ti, Hf, V, and Cr) has been conducted by combustion synthesis from constituent elements in the mode of self-propagation of high temperature (SHS) [5–10]. In this regard, Yeh and Chen [6] have prepared niobium borides NbB and NbB₂ using the SHS approach from elemental powder compacts. In another attempt, they investigated the feasibility of producing specific boride

compounds (such as Nb₃B₂, NbB, Nb₅B₆, Nb₃B₄, and NbB₂) from elemental powder compacts with relating stoichiometric ratios by combustion synthesis [12]. Takeya et al. [5] found a superconducting phase with a transition up to 8 K in Nb_xB₂ (x = 0.67–1.11) produced by combustion synthesis. Tsuchida and Kakuta [4] demonstrated that the nanocomposite of NbC/NbB₂ was successfully synthesized by mechanical activation assisted SHS (MA-SHS) as a unique and energy-saving technique. In addition, they investigated in detail the effect of the particle size of Nb metal, the mixing ratio of Nb/B/C and the weight ratio of sample to balls on the MA-SHS in air process [13]. Moreover, niobium diboride was synthesized and consolidated by the spark plasma sintering technique (SPS) [14].

Besides these techniques, there have been various studies [15,16] on the use of active metals like Al and Mg as a reducing agent to generate a great amount of heat, which can be used as a heat source for activation of synthesis reactions. Yeh and Li [17] investigated the synthesis of NbB₂–Al₂O₃ composite by SHS of Al–Nb₂O₅–B₂O₃ system. Due to formation of various by-products together with some general problems in SHS process such as grain growth, non-uniform phase and others, it is necessary to find an effective technique that could overcome disadvantages.

Mechanochemical activation as a type of in-situ method is a solid state powder processing which involves inducing chemical reactions in a mixture of as-received powders at room temperature or at least much lower temperatures. An increase in the kinetic of reactions during high energy milling can be a result of microstructural refinement, repeated cold deformation and fracture of particles [18,19]. In recent years, the mechanochemical technique has been widely used to fabricate interpenetrating phase composites with nanosized microstructures. A

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mechanochemical was process proposed by Iizumi et al. [20] to prepare NbB₂ powder via reaction between powder mixtures of Nb–B (1:2).

The aim of this work is to explore the possibility of in-situ synthesis of niobium diboride powder via mechanochemical method by using Al/Mg–B₂O₃–Nb mixtures as precursor materials at room temperature. Thermodynamic calculations and thermal analysis were performed to get an insight about the probable reactions.

2. Experimental

The precursor materials were aluminum (Merck, 99.7% purity, particles size 40 ± 5 μm), magnesium (Merck, 99.7% purity, particles size 40 ± 5 μm), boron trioxide (Merck, 99.95% purity, mean particles size 30 ± 5 μm) and niobium metal (Strem Chemicals, 99.8% purity, mean particles size 45 ± 5 μm). The specifications of the samples and values of the precursor materials are presented in Table 1.

The precursor materials were milled in a planetary ball mill for various times at room temperature. Details of ball mill machine and milling conditions are given in Table 2. To prevent the oxidation process, the vial of milling was filled by high purity argon gas before ball milling.

In this study, the amount of the remained B₂O₃ was calculated to understand the reaction mechanism. For calculation of this value, firstly, the obtained powder from the milling process was weighed and considered as W₁. Then, the powder was washed by hot water (80–90 °C) for 1 h with magnetic stirrer and then the solution was filtered and the residue on the filter was dried at the 90 °C for 3 h, and then weighed as W₂. The different W₁–W₂ = W₃ is the amount of remained B₂O₃. Finally, to report changes in data as percentage change, the following formula was used: [(obtained value/initial value) × 100].

XRD analysis was carried out using Cu–Kα radiation to identify different phases of the starting powders and mechanically alloyed powders. The diffractometer (Philips X-ray diffractometer) was operated at 40 kV and 30 mA. Scans were performed between 10° < 2θ < 90°. “PANalytical X’Pert HighScore” software was also used for the analysis of different peaks. The diffraction patterns of products were compared to proposed standards by the Joint Committee on Powder Diffraction and Standards (JCPDS).

The crystallite size and lattice strain of samples are calculated by using Williamson–Hall method [18,19] according to Eq. (1):

$$\beta_s \cos \theta = \frac{k\lambda}{d} + 2\eta \sin \theta \quad (1)$$

where β_s is the peak broadening in radians, 2θ is the position of peak maximum, k is the Scherrer constant (0.9), λ is the X-ray wavelength (λ CuKα₁ = 1.540598 Å), d is the so-called crystallite dimension and is an approximate upper limit of the lattice distortion. The instrumental broadening (β_i) was removed by applying the following equation according to Gaussian–Gaussian [18,19] relationship by using an annealed Mg powder:

$$\beta_s^2 = \beta_e^2 + \beta_i^2 \quad (2)$$

where β_e is the FWHM of the measured XRD peak.

The reaction process and features were also investigated by thermal analyses (DTA; model BÄHR 503). A small amount of the reactants weighing about 50 ± 5 mg was held in an alumina crucible and heated

Table 1
Specifications of the specimens and contents of the precursor materials.

Type	Compositions contents (wt.%)			
	Al	Mg	B ₂ O ₃	Nb
Aluminothermic reduction	37.53	–	48.40	14.07
Magnesiothermic reduction	–	43.80	41.83	14.37

Table 2
Details of ball mill machine and milling conditions.

Rotation speed of vial (rpm)	500
Diameter of vial (mm)	100
Vial material	Hardened chromium steel
Ball material	Hardened carbon steel
Diameter of balls (mm)	20
Number of balls	5
Balls to powder weight ratio	20:1
Total powder mass (g)	7

under argon flow (flow rate: 50 ml/min) at a heating rate of 10 °C/min up to 1300 °C.

The morphology and the agglomerate size distribution of the milled powders were studied by field emission scanning electron microscopy (FE-SEM, Hitachi 4160, 15KV). In addition, the size and morphology of fine powders were studied thoroughly by transmission electron microscopy, TEM (Philips CM10, Eindhoven, The Netherlands) which operated at 100 kV.

Magnesium oxide was removed by leaching the as-milled powder in a 1 M-HCl solution at 80 °C for 1 h.

The reported values of adiabatic temperature (T_{ad}) for systems would be calculated by using the equation below:

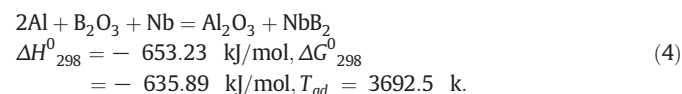
$$\Delta Q = -\Delta H_{298}^0 + \int_{T_m}^{T_{ad}} \sum C_p(\text{Solid}) \cdot dT + \Delta H_m + \int_{T_m}^{T_{ad}} \sum C_p(\text{Liquid}) \cdot dT = 0 \quad (3)$$

where C_p, and ΔH₂₉₈⁰ and ΔQ are specific heat capacity, standard enthalpy changes of formation at 298 K and heat of reaction, respectively.

3. Results and discussion

3.1. Aluminothermic reduction

Considering the basis of reaction thermodynamics can contribute to understanding the basic information about reactions and to estimate their behavior and formation of the possible phase compositions during the mechanochemical process [16]. If aluminum is selected as the metallic reducing agent, the main reaction is as follows:



According to ΔG⁰ and ΔH⁰, this sample has high negative values which means that this reaction is highly favorable and exothermic. However, reactions with negative ΔG₂₉₈⁰ do not necessarily occur at room temperature because of their slow kinetics.

DTA (Fig. 1a) was utilized to investigate thermite reaction behavior and initial reaction temperatures in Al, B₂O₃ and Nb powder mixtures (under argon gas at a heating rate of 10 K min⁻¹). The first endothermic peak at about 660 °C is related to the melting of Al. This curve also shows two exothermic peaks, around 850, 1035 °C. In order to make clear the reactions that occurred within exothermic peaks, after DTA analysis, the coarse samples were ground into powder and then characterized by XRD (Fig. 1b). As can be seen, the phase compositions of the synthesized products mainly contain Al₂O₃, aluminum borate (Al₄B₂O₉) and low amount of remaining unreacted powders (remained Al and Nb). It can be found that two exothermic peaks in DTA curve are attributed to initiation of aluminothermic reaction (5) and subsequently formation of the aluminum borate phase (6)



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