MECHANISMS AND EFFECTS OF VARIOUS REDUCING AGENTS ON THE FABRICATION OF ELEMENTAL BORON

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Abstract

Elemental boron powder was fabricated by high-energy ball milling of powder mixtures containing stoichiometric amounts of boron oxide as boron source and magnesium, calcium and aluminum as reducing agents. The reaction was carried out by Spex 8000 D Mixer/Mill with a rotation speed of 1200 rpm with different ball-to-powder weight ratios in the range of 10:1 to 30:1. The effects of milling durations, reducing agents and ball-to-powder weight ratios on the production efficiency of elemental boron were investigated. The milled products include the mixture of boron, borates and oxides which can be removed by selective acid leaching. Eventually, elemental boron in amorphous structure was obtained. Characterization studies of the milled and leached products were performed by X-ray Diffraction technique (XRD) and Atomic Absorption Spectrometer (AAS).

Keywords: Boron oxide, high-energy ball milling, reducing agent, mechanochemical synthesis

1. INTRODUCTION

Boron which is a very hard element exhibits the properties of high melting point, high chemical resistance and high strength. These superior properties enable to use it in several high-tech applications from metallurgy to electronics. The most widely used area of elemental boron is as a reinforcement material for metals and plastics. Besides, it is used as a dopant in semi-conductors, as a neutron inhibitor in nuclear reactors and as a target material for the beam sputtering and physical vapor deposition processes. It may be used in abraders thanks to its property of being the second hardest element after diamond. Additionally, it provides to obtain high-tech boron products such as transition metal borides, boron nitride, boron carbide, boron trichloride, etc.

Elemental boron is produced by several methods including metallothermic reduction, mechanochemical synthesis, electrolytic reduction and gas phase reduction. In metallothermic reduction process, elemental boron is fabricated by the reduction of boron compounds (B₂O₃, H₃BO₃, HBO₂, Na₂B₄O₇, etc.) with molten reducing agents (Mg, Na, etc.) [1-4]. The reaction between boron compounds and reducing agents result in 85-95 % pure boron in amorphous structure. Electrolytic reduction is based on the deposition of boron on the cathode material through the electrolysis of molten salt bath which includes various combinations of alkali metal chlorides (KCl, NaCl, etc.), alkali metal boron fluorides (KBF₄, NaBF₄, LiBF₄, etc.), boron fluoride (BF₃) and other boron compounds (B₂O₃, Na₂B₄O₇, etc.) [5-8]. Boron can be produced by thermal dissociation of boron halides or boron hydrides by hydrogen on a hot substrate surface. The most significant point of this process is that the substrate surface must be essentially inert to the deposited boron, boron halides and boron hydrides. The preferred deposition method of boron is conducted by passing boron trichloride and hydrogen over electrically heated wires such as tungsten, titanium and tantalum [9-12]. Another way to obtain
elemental boron is mechanochemical synthesis of the powder mixtures containing boron compounds (B₂O₃, H₃BO₃, Na₂B₄O₇, etc.) and reducing agents (Mg, Al, Ca, etc.) [13-14]. The review in literature shows that the mechanochemically synthesized boron has not been investigated comprehensively.

In this study, elemental boron was produced by high-energy ball milling of powder mixtures containing boron oxide and various reducing agents. The effects of reducing agents (Mg, Ca and Al) on the production efficiency of elemental boron have been broadly investigated. Moreover, the parameters of milling durations and ball-to-powder weight ratios have been examined.

2. EXPERIMENTAL PROCEDURE

Boron oxide (B₂O₃, ETI Mine, 98 % purity, 466.901 µm average particle size) was used as an economical boron source. Magnesium (Mg, MME, 99.7 % purity, 142.688 µm average particle size), calcium (Ca, Riedel-de Haën, 98 % purity, 0.2-3 mm average particle size) and aluminum (Alfa Aesar™, 99.5 % purity, 12 µm average particle size) were used as reducing agents. Powder mixtures containing stoichiometric amounts of reactants were prepared according to the overall displacement reactions given in Eq. (1)-(3). At each run, powder batches of 6 g (2.93 g B₂O₃ and 3.07 g Mg; 2.2 g B₂O₃ and 3.80 g Ca; 3.38 g B₂O₃ and 2.62 g Al) for 10:1 ball-to-powder weight ratio and powder batches of 4 g (1.95 g B₂O₃ and 2.05 g Mg; 1.47 g B₂O₃ and 2.53 g Ca; 2.25 g B₂O₃ and 1.75 g Al) for 30:1 ball-to-powder weight ratio were weighed in a Precisa™ XB320M sensitive balance.

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\begin{align*}
B₂O₃ + 3Ca & \rightarrow 2B + 3CaO & (1) \\
B₂O₃ + 3Mg & \rightarrow 2B + 3MgO & (2) \\
B₂O₃ + 2Al & \rightarrow 2B + Al₂O₃ & (3)
\end{align*}
\]

The solid-state reaction of the prepared powder mixtures were carried out in a Spex 8000 D Mixer/Mill with a rotation speed of 1200 rpm. Different ball-to-powder weight ratios (10:1 and 30:1) were used. The weight of the powder mixtures were 4 g when the ball-to-powder weight ratio was 30:1 since it is necessary to leave enough space for the balls and the powder particles to move around freely in the milling container. Milling containers were hardened steel vials with a capacity of 50 ml and milling media was hardened steel balls with a diameter of 6 mm. Before milling, the vials were evacuated to about 10⁻² Pa and back filled with Argon gas (BOSTM, 99.999 % purity) in a Plaslabs™ glove-box. After sealing the vials, milling was continually performed during 10 min., 1 h, 3 h, 6 h and 10 h. Milled products were unloaded again at Argon atmosphere in glove-box. Subsequently, the undesired products were removed from the mechanochemically synthesized powders by hydrochloric acid (HCl, Merck, 37 %) leaching under ultrasonic stirring (Bandelin Sonorex). Powder batches of 2 g were leached at each run. Leaching parameters such as HCl concentration, duration and solid/leachant ratio were designated respectively as 0.5 M, 15 min. and 1 g/20 cm³. Centrifuging (TD3™ Centrifuge, 3500 rpm, 15 min.), decanting, washing and drying (FN 500 stove, 120°C, 24 h) treatments were conducted repeatedly. The phase compositions of mechanochemically synthesized powders were analyzed by X-ray diffraction (XRD) technique using Bruker™ D8 Advanced Series Powder Diffractometer with CuKα (1.54060 Å) radiation in the 2θ range of 10-120° with 0.02° at a rate of 2°/min. The International Center for Diffraction Data® (ICDD) powder diffraction files were used for the identification of crystalline phases. Gibbs free energy change-temperature relations were interpreted.
by HSC Chemistry Ver. 4.1 program. The amount of boron (ppm) in the supernatant liquid was analyzed by Perkin Elmer™ 1100B Atomic Absorption Spectrometer (AAS).

3. RESULTS AND DISCUSSION

Solid-solid chemical reactions reported in the literature have demonstrated that metal oxide powders could be reduced to its pure metals by high-energy ball milling with reactive metals at room temperature. In order to investigate the possibilities of boron oxide reduction with Ca, Mg and Al, the relation between Gibbs free energy change and temperature of the overall displacement reactions was drawn as shown in Figure 1. The reactions given in Eq. (1)-(3) have negative free energy changes which mean that reactions take place spontaneously and therefore they are thermodynamically feasible at room-temperature. Moreover, negative enthalpy changes of the reactions imply that heat is released during milling due to the exothermic reactions and the vial temperature increases significantly. The conversion of mechanical energy into chemical energy provides to bring out chemical reactions that it has been referred as mechanochemical synthesis. Two different reaction kinetics could be possible to explain the mechanochemical synthesis. The first one may be explained by extending of the reaction to a very small volume with each collision and resulting in a gradual transformation. The second one can arise from the occurrence of ignition attained by critical milling duration. It is considered that there is only particle refinement during milling until the ignition temperature is reached [15].

![Figure 1. Gibbs free energy change-temperature relation of the overall displacement reactions given in Eq. (1)-(3)](image)

Figure 2 represents the XRD patterns of the \( B_2O_3+3Ca \) powder mixtures after milling for 1 h, 3 h and 6 h with 10:1 ball-to-powder weight ratio. As seen in Figure 2, the reduction reaction was completed after 1 h milling that it forms CaO (ICDD Card No: 037-1497, cubic) and \( Ca_3(BO_3)_2 \) (ICDD Card No: 070-0868, rhombohedral) phases as reaction products. However, Eq. (1) do not involve \( Ca_3(BO_3)_2 \) phase. In addition to these phases, a very slight peak of boron arose near 20°. With prolonging milling duration, CaO peaks broadened and the intensities of \( Ca_3(BO_3)_2 \) phase decreased.

Figure 3 illustrates the XRD patterns of the \( B_2O_3+3Mg \) powder mixtures after milling for 3 h, 6 h and 10 h with 10:1 ball-to-powder weight ratio. It is evident from Figure 3 that there is no reduction reaction after 3 h milling because Mg (ICDD Card No: 035-0821, hexagonal) phase is still present in the powder mixture.
Surprisingly, the peaks of $\text{B}_2\text{O}_3$ phase were not seen in the patterns of 3 h milled powders. The absence of $\text{B}_2\text{O}_3$ peaks could be due to its amorphous nature. The reduction reaction is completed after 6 h milling since MgO (ICDD Card No: 071-3631, cubic) and a very small amount of $\text{Mg}_3(\text{BO}_3)_2$ (ICDD Card No: 075-1807, orthorhombic) phases occur as reaction products. The formation of $\text{Mg}_3(\text{BO}_3)_2$ phase is unexpected according to the Eq. (2). In addition to these phases, there should be some amount of elemental boron in the product in regard of Eq. (2). However, it can also be in an amorphous form. Analogously to these results, Ricceri and Matteazzi have reported the XRD analysis of the $\text{B}_2\text{O}_3$+Mg powder mixture milled for 10 min. with a 27:1 ball-to-powder weight ratio [13]. Extended milling up to 10 h results in broadening of MgO peaks that it represents crystallite refinement.

The XRD patterns in Figure 2 and 3 are in good agreement with the curves in Figure 1. Mechanochemical synthesis of the $\text{B}_2\text{O}_3$+3Ca powder mixtures takes place earlier than $\text{B}_2\text{O}_3$+3Mg powder mixtures due to the fact that Ca has more negative free energy change than Mg. Calciothermic reduction reaction was completed 5 h earlier than that of magnesiothermic reduction. Although Ca has positive effect on the duration of the reaction, it has a great tendency to become a borate which raises difficulties in acid leaching.
Figure 4 demonstrates the XRD patterns of the patterns of the $\text{B}_2\text{O}_3+3\text{Al}$ powder mixtures after milling for 1 h and 6 h with 10:1 ball-to-powder weight ratio. Figure 4 points out that there is no reduction reaction up to 6 h milling since Al (ICDD Card No: 004-0787, cubic) phase is still present and there is no $\text{Al}_2\text{O}_3$ formation. This result can not be surprising considering Figure 1 and thereby the complete reaction can be occur after 10 h or more milling.

![Figure 4](image)

**Figure 4.** XRD patterns of the $\text{B}_2\text{O}_3+3\text{Al}$ powder mixtures mechanochemically synthesized for different durations with 10:1 ball-to-powder weight ratio (a) 1 h, (b) 6 h

Figure 5 demonstrates the XRD patterns of the $\text{B}_2\text{O}_3+3\text{Ca}$ powder mixtures after milling for 10 min., 1 h and 3 h with 30:1 ball-to-powder weight ratio. The ball-to-powder weight ratio has a significant effect on the time required to achieve a particular phase in the powder being milled. At a high ball-to-powder weight ratio, because of an increase in the weight proportion of the balls, the number of collisions (particle-vial and particle-ball) per unit time increases and consequently more energy is transferred to the powder particles and so mechanochemical synthesis takes place faster. As seen from Figure 5, only 10 min. milled $\text{B}_2\text{O}_3+3\text{Ca}$ powder mixture has a distinct peak of Ca (ICDD Card No: 071-4619, cubic) phase. It can be said that almost total amorphization comes out in the 1 h milled powder mixture. With further milling, the amorphous structure turns into $\text{Ca}_2\text{B}_2\text{O}_5$ (ICDD Card No: 022-0139, monoclinic) phase.

![Figure 5](image)

**Figure 5.** XRD patterns of the $\text{B}_2\text{O}_3+3\text{Ca}$ powder mixtures mechanochemically synthesized for different durations with 30:1 ball-to-powder weight ratio (a) 10 min., (b) 1 h, (c) 3 h
After leaching of $\text{B}_2\text{O}_3 + 3\text{Ca}$ powders milled for 6 h with a 10:1 ball-to-powder weight ratio, AAS analysis revealed the presence of 10.2 mg boron content in the leachant due to the dissolution of unreacted boron oxide in the powder. On the basis of theoretical boron content of the powder mixture and the amount of boron found in leachant, the conversion yield of boron oxide is calculated as about 95.5%. Likewise, 0.6 mg boron was detected in the leachant after leaching of $\text{B}_2\text{O}_3 + 3\text{Mg}$ powders milled for 10 h with a 10:1 ball-to-powder weight ratio and the conversion yield of boron oxide is determined as about 97%. Although high conversion yields of boron oxide are obtained, it should be taken into consideration that some amounts of calcium and magnesium borates are present in the structure. Consequently, not only elemental boron but also borates contribute to these boron yields due to their resistant nature to hydrochloric acid.

4. CONCLUSIONS

Mechanochemical synthesis of elemental boron was attempted from $\text{B}_2\text{O}_3 + 3\text{Ca}$, $\text{B}_2\text{O}_3 + 3\text{Mg}$ and $\text{B}_2\text{O}_3 + 3\text{Al}$ powder mixtures. The formation of elemental boron, $\text{CaO}$ and $\text{Ca}_3(\text{BO}_3)_2$ phases was accomplished after 1 h milling in Spex 8000 D Mixer/Mill with 10/1 ball-to-powder weight ratio, whereas elemental boron, $\text{MgO}$ and $\text{Mg}_3(\text{BO}_3)_2$ phases were obtained after 6 h milling. Reduction of $\text{B}_2\text{O}_3$ with $\text{Al}$ was not succeeded up to 6 h milling. 30:1 ball-to-powder weight ratio causes almost total amorphization. Maximum 97% conversion yield of boron oxide was provided with the contribution of elemental boron and borates.

REFERENCES