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Synthesis of boron-rich solids of light metals in mechanochemical reactors

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The possibility of mechanochemical synthesis and influence of mechanical activation on the thermal synthesis of boron-rich solids of light metals are investigated. The synthesis of such compounds as AlB_2 and CaC_2B_2 in the mill AGO-2 is established. Influence of mechanical activation (using the mill SPEX 8000) on the synthesis of $Mg_{0.5}Al_{0.5}B_2$ is shown.

1. Introduction

The discovery of high-temperature superconductivity in magnesium diboride (MgB_2, 39 K [1]) and ferromagnetism in calcium borocarbide (CaB_2C_2, 77 K [2]) has stimulated interest in boron and carbon compounds [3–14]. However, traditional technology of preparation of nanocrystalline or magnetic boron-containing materials is rather complicated and includes several steps [5]: Melt synthesis followed by ultra-rapid quenching of the melt, crystallization of an amorphous product in a high-vacuum furnace, grinding, etc. Therefore, the attempts have been made to synthesize the transition- and heavy-metal borides by mechanochemical route [5–8]. Mechanochemical synthesis of light borides (containing e.g., Mg, Al, C, Si, N, P, S) has hitherto been virtually untouched. Heats of formation of some light borides from elements are, for example, 22.0 kcal/mol for MgB_2, 48.0 kcal/mol for AlB_{12}, and 60.3 kcal/mol for NB and S_2B_3 [9], and their range coincides with the heat of classical combustion reactions in the Al-Ni system (28.3–67.5 kcal/mol) [6]. Therefore, it is hoped that light borides can be synthesized by mechanically stimulated combustion reactions [7, 8].

In the present work, the effect of mechanical activation on the synthesis of Mg, Al, and Ca borides and borocarbides is studied. These materials are routinely obtained by a conventional ceramic method in the course of a long-term and multiple-stage heating of a metal and amorphous boron mixture at sufficiently high temperatures ($T \sim 1000^\circ$C) and pressures ($p \sim 200$ MPa) [1–3]. Our calculations [15] showed that the p-T conditions in mechanochemical reactors are close to those involved in a conventional ceramic synthesis.

2. Experimental

As a mechanochemical reactor, an AGO-2 steel two-vial water-cooled planetary ball mill with the relative impact velocity of milling tools $W_a = 11$ m/s was used [8, 16]. The following conditions were used for the milling: the volume of the vial was $V = 140$ cm^3, the number of steel balls of radius $R = 0.2$ cm was $N = 400$, the water flow rate was 1 cm^3/s; the water temperature was monitored at the outlet. To compare the effect of the intensity of the mechanical treatment, a SPEX 8000 Mixer/Mill with tungsten carbide ball was also used. The milling process in the SPEX 8000 Mixer/Mill was characterized by the following parameters: $V = 160$ cm^3, $N = 1$, $R = 0.55$ cm, and the relative impact velocity of milling tools $W_s = 4$ m/s [17].

The B-Mg/Al and B-C-Mg/Ca systems containing 1 g of boron were mechanically treated; the duration of the mechanical treatment varied from 1.5 to 21 h. The initial compounds were the same as in [1–3], except for the fact that the mixtures contained excess amounts of magnesium and aluminum (∼3%) and calcium (∼5%) relative to the stoichiometric amounts. For the milling experiment using the AGO-2 mill, only crystalline boron was used (fraction >80 μm), whereas for the milling using the SPEX 8000 mill, amorphous boron was loaded. The products of mechanical activation were studied by X-ray powder diffraction (XRD) and conventional methods of thermal analysis (TA). The TA measurements were carried out in an argon atmosphere in the temperature range 20–900°C at a heating rate of 10 K/min. The mechanically treated samples were annealed at ∼1000°C in an argon flow (∼1 cm^3/s) in tantalum crucibles with titanium sponge placed upstream from the crucibles in the heated zone of a quartz tube in order to purify argon from a possible admixture of oxygen.

3. Results and discussion

Fig. 1 compares the X-ray diffraction patterns of (a) the 2B-Al mixture mechanically activated for 1.5 h followed by a thermal treatment, (b) the 2B-Al mixture

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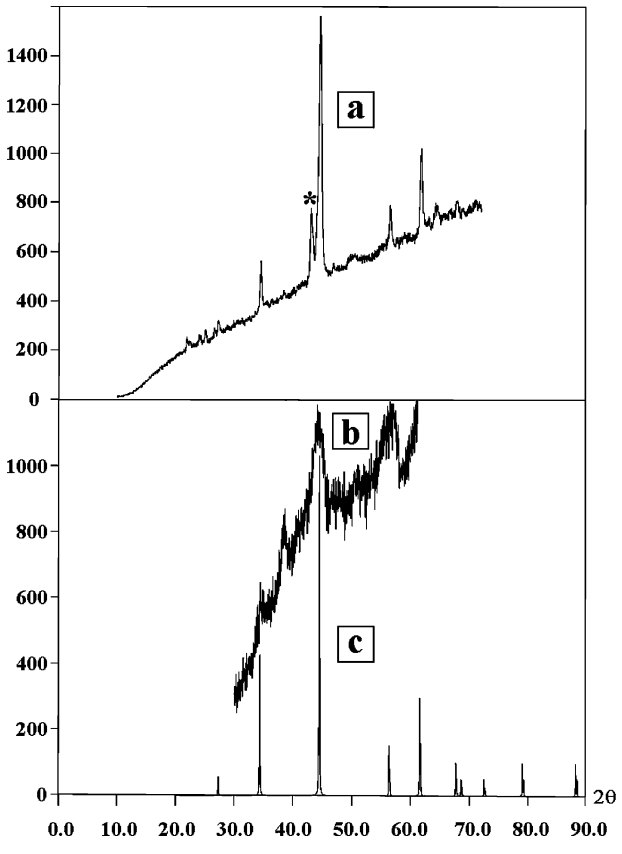

Figure 1 X-ray diffraction patterns of (a) the 2B-Al mixture mechanically activated for 1.5 h (in an AGO-2 mill) followed by a thermal treatment in an atmosphere of argon up to 900°C; the symbol * corresponds to the most intensive reflexation of Al_xFe_y, where the attitude $x/y > 2.5$, (b) the 2B-Al mixture milled for 1.5 h in an AGO-2 mill, and (c) the crystalline AlB_2 (PDF 39-1483).

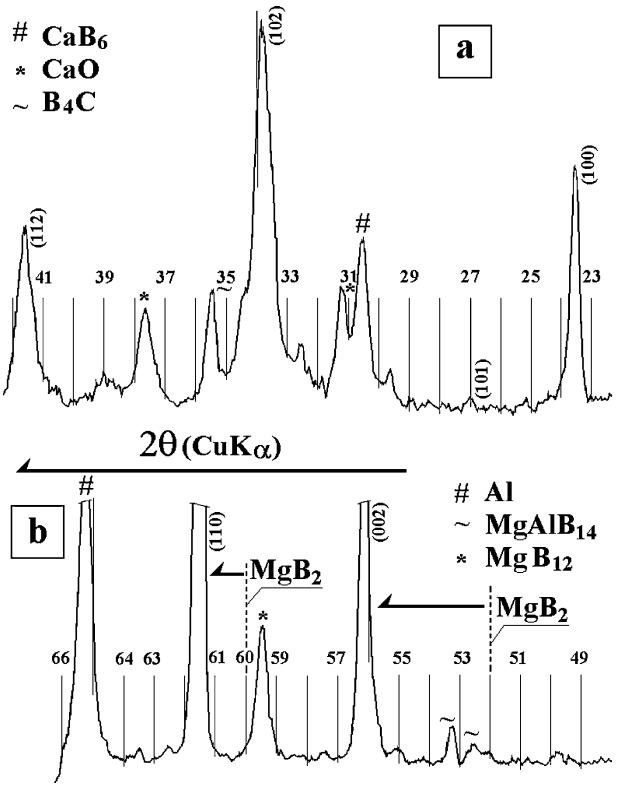

Figure 2 X-ray diffraction patterns of (a) the 2B-2C-Ca mixture milled for 21 h (in an AGO-2) followed by annealing for 2 h in an atmosphere of argon at ~1000°C; see PDF 34-952, 83-515, 82-1691, 74-2136, (b) the 4B-Mg-Al mixture milled for 2 h (in a SPEX 8000 mill) followed by annealing for 2 h in an atmosphere of argon at ~1000°C; see PDF 8-263, 3-939, 12-539.

milled for 1.5 h, and (c) the crystalline AlB_2 (PDF 39-1483). It has been found that mechanical treatment of the 2B-Al mixture for 1.5 h (in the AGO-2 mill) results in the formation of a compound with the composition close to aluminum diboride, see Fig. 1b.

It has been revealed that under the same milling conditions, mechanical treatment of the 2B-Mg system leads to the formation of a roughly amorphous, very hard and monodisperse grains with the size of about 1 mm. The mechanical activation of the 2B-2C-Mg and 2B-2C-Ca systems for 21 h results in the formation of fully amorphized powders.

The intensity of the SPEX 8000 mill is considerably lower (about eightfold) than that of the AGO-2 mill, as judged by the ratio $(W_a/W_s)^2$. Therefore, the efficiency of the SPEX 8000 mill (in a time comparable with that for AGO-2) appeared to be insufficient to induce the synthesis in all the systems under consideration (2B-Mg, 2B-Al, 4B-Mg-Al, 4B-4C-Mg-Al, 2B-2C-Mg, 2B-2C-Ca, 4B-4C-Mg-Ca). The X-ray diffraction patterns of mixtures milled in the SPEX 800 mill show the reflections of the starting materials. Moreover, these reflections are observed, in addition to the reflections of target products, even after annealing of these samples for 2 h at 1000°C (as it can be seen in Fig. 2b for the case of the 4B-Mg-Al system).

It has been found that the thermal treatment of the milled mixtures results in the crystallization of only aluminum diboride AlB_2 (Fig. 1a). Annealing for 2 h at 1000°C of the 2B-2C-Ca mixture (activated using the AGO-2 mill) leads to the formation of CaC_2B_2 (Fig. 2a). This is also supported by the change in color from black (for the initial powder) to reddish-brown (after annealing). Similarly, annealing for 2 h at 1000°C of the 4B-Mg-Al mixture (activated using the SPEX 8000 mill) leads to the formation of $Mg_{0.5}Al_{0.5}B_2$ (Fig. 2b). Thus, the boron-rich solids are obtained using combined method of the mechanical and thermal activations. It should be noted that these materials cannot be prepared by the conventional synthesis under the same conditions of the thermal treatment.

The X-ray data for the annealed 4B-Mg-Al system, obtained from the analysis of the diffraction pattern (shown in Fig. 2b), correlate with those reported in [3]. Formation of $Mg_{1-x}Al_xB_2$ up to $x = 0.4$ was demonstrated in [3] based on the shifts of (002) and (110) reflections of MgB_2 toward larger angles. The analysis of the corresponding diffraction lines revealed that the material prepared in the present case is characterized by the value of $x = 0.5$. As expected, the value of the shift of these reflections (Fig. 2b) exceeds those measured in [3].

Note some specific features of the syntheses of compounds in the systems containing metallic magnesium. These features are caused by the high volatility of magnesium at elevated temperatures. The DTA curve for the 2B-Mg system (activated in the AGO-2 mill) shows endothermic peaks at 620 and 700°C, which coincide with the onset of the gradual weight loss of the sample on the TG curve (Fig. 3).

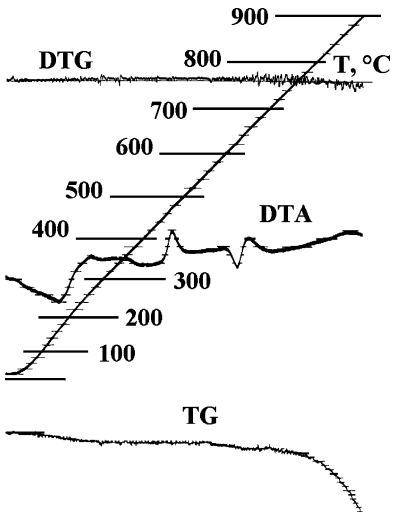

Figure 3 Thermal analysis of the 2B-Mg mixture mechanically activated for 1.5 h in an AGO-2 mill.

Annealing of Mg-containing systems is accompanied by the appearance of a gray deposit on the cold portion of the quartz tube; chemical analysis identifies this deposit as Mg. Therefore, synthesis in magnesium-containing systems can be carried out only under a high pressure [1, 3].

4. Conclusions

The results presented point out the possibility of the direct mechanochemical synthesis of amorphized borides and borocarbides of light metals. AlB_2 and CaC_2B_2 were obtained by mechanochemical route using the AGO-2 mill. It was found that crystalline boron can be used for the synthesis of light-metal borides and borocarbides, which was impossible in [1–3] (see [3] for details).

Acknowledgments

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