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Investigating mechanochemical behavior of Cr_2O_3–B_2O_3–Mg–C quaternary system

Omid Torabi *, Mohammad Hossein Golabgir, Hamid Tajizadegan, Amin Jamshidi

Young Researchers and Elite Club, Najafabad Branch, Islamic Azad University, Najafabad, Iran

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ABSTRACT

Fundamental aspects of reaction behavior and formation path in the Cr_2O_3–B_2O_3–Mg–C quaternary system have been studied to synthesize chromium boride–chromium carbide nanocomposite. In order to find the influence of simultaneous presence of magnesium and carbon on final products, various powder mixtures were chosen according to following reaction: $B_2O_3 + Cr_2O_3 + (9 - x)\,Mg + x\,C$. The value of x varied from 0 to 4. In the absence of carbon ($x = 0$), CrB_2 was synthesize through mechanically induced self-propagating reaction (MSR). In the presence of 8 mol Mg and 1 mol C ($x = 1$), the dominant boride phase was CrB while no chromium carbide was detected. By increasing C content ($x = 2$), the magnesiothermic reduction occurred in MSR mode; whereas, the synthesis of Cr_3C_2 initiated after combustion reaction and completed gradually during milling for 6 h. Further increase in C amount ($x = 3$) resulted in formation of $Mg_3(BO_3)_2$ as unwanted phases as well as CrB and Cr_3C_2. In the presence of 6 mol Mg and 4 mol ($x = 4$), no mechanical reaction was observed even after 8 h of milling. Optimum value of x for the formation of CrB–Cr_3C_2 nanocomposite was 2. Based on the morphological evolutions, it is evident that the mechanosynthesized powder is made up of nanometric particles.

1. Introduction

Borides and carbides of transition metals are well known due to their combinations of outstanding properties such as high mechanical properties (excellent strength and hardness, high elastic modulus), good electrical and thermal conductivity, chemical inertness, and excellent wear and corrosion resistance [1,2]. Thus, these compounds have found their applications including extreme temperature and pressure, e.g., rocket nozzles, drill bits, cutting tools, golf shoe spikes and snow tires [3].

Of these compounds, chromium boride shows potential not only as refractory nature, but also as a hard coating or a protective layer on tools and materials [4,5]. Chromium carbide (Cr_3C_2) is a good reinforcement material for ceramics due to their high melting point, high hardness, high Young's modulus, and wear resistance [6,7]. Matsushita et al. [8] proved that CrB_2 containing 5 to 20 mass % Cr_3C_2 shows a significant improvement in mechanical properties involving hardness and elastic modulus compared with CrB_2 sintering body.

So far, many techniques are available for the synthesis of chromium boride and carbide powders, separately. Chromium boride has been prepared by various methods, such as the direct combination of Cr metal with boron [9], self-propagating high-temperature reaction [10], field-activated pressure-assisted synthesis [1], autoclave by using $CrCl_3$, Mg and MgB_2 [11], reduction-boronation [12] and mechanically induced self-propagating reaction [13]. On the other hand, many techniques have been reported for the production of chromium carbide powder such as solid-state reaction between Cr and carbon [14], carbonization of methane [15], SHS [16], mechanical–thermal synthesis [17] and chemical vapor deposition method (CVD) [18]. However, it has been lack of an extensive study on the simultaneous synthesis of chromium boride and carbide.

Mechanochemical activation as a type of in-situ method is a solid-state powder process which involves inducing chemical reactions in a mixture of as-received powders at room temperature or at least much lower than synthesis temperature. An increase in the kinetics of reactions during high energy milling can be resulted from microstructural refinement, repeated cold deformation and fracture of particles [19,20]. The simplicity, reproducibility, time and energy savings, and high-purity products are the main advantages of this method. Therefore, the mechanochemical technique can be utilized, when the mass production of nanopowders is required.

In our previous paper [13], the fundamental aspects of reaction path in the $Cr_2O_3 + B_2O_3 + Mg$ system to synthesize chromium diboride have been investigated. According to results, the mechanosynthesis of CrB_2 was occurred through mechanically induced self-sustaining reactions (MSR) mode with an ignition time of approximately 2.5 h.

In present work, the simultaneous mechanosynthesis of nano-crystalline chromium boride and carbide nanocomposites was studied in Cr_2O_3–B_2O_3–Mg–C quaternary system. The main purpose of our work

* Corresponding author.
E-mail address: omid_trb@yahoo.com (O. Torabi).

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is to predict the reaction mechanism during milling process based on the results from thermodynamic calculations, phase transformations and morphological evaluations.

2. Experimental

The precursor materials were magnesium (Mg, Merck Co., 99.7% purity, average particles size 40 ± 5 μm), boron oxide (B_2O_3, Merck Co., 99.95% purity, mean particles size 30 ± 5 μm), chromium oxide (Cr_2O_3, Sigma-Aldrich Co., 99.8% purity, mean particles size 50 ± 5 μm) and graphite (C, Sigma-Aldrich Co., 99.5% purity, mean particles size 50 μm). In order to investigate the influence simultaneous presence of Mg and C as reducing agents on the mechanochemical behavior of Cr_2O_3–B_2O_3–Mg–C quaternary system, the various samples with different amounts of reductant were prepared according to the following reaction: $B_2O_3 + Cr_2O_3 + (9 - x)\,Mg + x\,C$. The specifications of the samples and reductant contents are presented in Table 1.

The precursors milled in a planetary ball mill for various durations at room temperature. Also, the details of the ball mill machine and milling conditions are given in Table 2. To prevent oxidation, the milling vial was filled with high purity argon gas before ball milling.

In this study, the amounts of the remaining B_2O_3 and C were calculated to understand reaction mechanism. For calculating the remaining B_2O_3 value, firstly, the powder obtained from milling was weighed and considered as W_1. Then, the powder was washed with hot water (60–70 °C) for 1 h with a magnetic stirrer and then the solution was filtered and the residue on the filter was dried at 90 °C for 2 h, and then weighed as W_2. The difference $W_1 - W_2 = W_3$ is the amount of remaining B_2O_3. For removing probable Mg and MgO, the obtained powder leached with 10% hydrochloric acid for 1 h. The solution was filtered after leaching and the purified products were washed by distilled water for several times to eliminate extra HCl acid until the pH value is about 7. Again, the residue on the filter was dried at the 90 °C for 2 h and weighed as W_4. At the end, the obtained powder oxidized at 700 °C for 30 min in the air was then weighed as W_5. Therefore, the difference $W_4 - W_5 = W_6$ yields the amount of free carbon. 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 as well as the mechanically alloyed powders. The diffractometer (Philips X'Pert-MPD X) was operated at 40 kV and 30 mA. Scanning was performed between $10° < 2\theta < 90°$. "PANalytical X'Pert HighScore" software was also used for the analysis of different peaks. The diffraction patterns of the products were compared to the standards proposed by the Joint Committee on Powder Diffraction and Standards (JCPDS).

The morphology and the agglomerate size distribution of the powders were studied by field emission scanning electron microscopy (FE-SEM, Hitachi 4160, 15 kV). X-ray energy dispersion spectroscopy (EDS) and elemental mapping analysis attached to the SEM were utilized for determining the elemental composition and finding the elements in the image. In addition, the size and morphology of the powders were thoroughly studied by transmission electron microscopy, TEM (Philips CM10, Eindhoven) operated at 100 kV.

Table 2
The details of the ball mill machine and the 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

The reported values of the adiabatic temperature (T_{ad}) for systems would be calculated by using the equation below [19,20]:

$$\Delta Q = -\Delta H^0_{298} + \int_{298}^{Tm} \sum C_p(\text{Solid}).dT + \Delta H_m + \int_{Tm}^{Tad} \sum C_p(\text{Liquid}).dT = 0 \quad (1)$$

where C_p, ΔH^0_{298} and ΔQ are specific heat capacity, standard enthalpy changes of formation at 298 K and the heat of reaction, respectively.

3. Results and discussion

3.1. Phase evolution and structural features (XRD analysis)

Fig. 1 displays the X-ray diffraction patterns of all samples ($S_1 - S_5$) before acid leaching. In the absence of graphite (S_1), the mechanosynthesis reactions were occurred after about 3 h of milling. According to the figure, final products after the combustion time included MgO and CrB_2. In sample S_2 with 8 mol Mg and 1 mol C, the combustion time was 3 h and 20 min. In this sample, MgO, and CrB_2 as well as CrB were obtained during milling. With increasing carbon content in sample S_3, chromium carbide was formed beside MgO and CrB without any trace of CrB_2. For this sample, the sharpest peak of graphite was still detected after 4 h of milling. In XRD pattern of sample S_4 with higher C amount in the mixture (Fig. 1), the weak peaks of reactants (including Cr_2O_3 and C) as well as the sharp peaks of MgO and CrB are observed. In addition, several peaks corresponding to $Mg_3(BO_3)_2$ were detected after 5 h of milling. Magnesium borate appears as a major by-product the in systems containing Mg–B_2O_3 [13,21]. With increasing graphite content (S_5), the chemical reactions slightly progressed even after 8 h of milling. The presence of sharp peaks belonging to Cr_2O_3 and weak peaks of MgO and $Mg_3(BO_3)_2$ support this fact.

In order to have better recognition, all samples except S_5 were leached with HCl according to the mentioned procedure (experimental section). XRD patterns of samples after leaching (Fig. 2) reveal that the by-products including MgO and/or $Mg_3(BO_3)_2$ were completely eliminated from the final products. In agreement with Fig. 1(before

Table 1
The specifications of the samples.

x	Samples	Reactions	Combustion time (h)	Remaining C after combustion reaction (%)	Remaining B_2O_3 after combustion reaction (%)
$x = 0$	S_1	$B_2O_3 + Cr_2O_3 + 9\,Mg$	~3	–	Trace
$x = 1$	S_2	$B_2O_3 + Cr_2O_3 + 8\,Mg + C$	~3.3	Trace	
$x = 2$	S_3	$B_2O_3 + Cr_2O_3 + 7\,Mg + 2C$	~4	~19	Trace
$x = 3$	S_4	$B_2O_3 + Cr_2O_3 + 6\,Mg + 3C$	~5	~42	~27
$x = 4$	S_5	$B_2O_3 + Cr_2O_3 + 5\,Mg + 4C$	~8 milling (no combustion)	~98	~86

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