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Effect of the aluminum content on the mechanochemical behavior in ternary system Al–B_2O_3–C

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ABSTRACT

The effect of aluminum content on the mechanochemical behavior of ternary system Al–B_2O_3–C to fabricate Al_2O_3/B_4C composite was investigated. A mixture of boron oxide powders along with different amounts of aluminum and graphite was activated in a ball mill. The value of Al content varied from 2 mol to 7 mol compared to the stoichiometric mole ratios (4 mol). Thermodynamics evaluation indicates that the value of Al content in the mixture plays a key role and overall reaction enthalpy and adiabatic temperature altered by variation of aluminum and carbon content. Experimental findings revealed that at low aluminum content (2 mol Al), aluminothermic reaction proceeded in gradual mode and no carbothermal reduction took place. Increase in Al content up to 3 mol led to a change in the mode of aluminothermic reaction to MSR (mechanically induced self-propagating reaction) and gradual occurrence of carbothermic reaction. By increasing the amount of Al (10/3–4 mol Al), aluminothermic reaction provided sufficient heat for activating endothermic carbothermic reduction; hence, both reducing reactions happened simultaneously. Further increase in Al content (7 mol Al) led to gradual aluminothermic reaction and excess Al acted as inert matrix.

1. Introduction

Due to high melting point, excellent hardness, low specific density (2.52 g/cm^3), high elastic modulus and high chemical stability, boron carbide (B_4C) is a well suited choice as reinforcement to improve mechanical and thermal properties of alumina (Al_2O_3) base composites [1]. Previous studies have shown that the addition of 10–20 vol% B_4C whiskers to alumina matrix increased fracture toughness up to 6.2 MPa [2]. Also, Jung et al. proved that the addition of B_4C particles to monolithic Al_2O_3 increased the micro-hardness and decreased the grain size of the composites, therefore, its cutting performance improved compared to the inserts prepared from monolithic pressureless sintered Al_2O_3 [3].

Hot-pressing and Self-propagating High Temperature Synthesis (SHS) techniques were investigated to fabricate Al_2O_3/B_4C ceramic base composite [3,4]. To overcome restrictions of these methods such as necessity of high temperature and formation of by-products like aluminum borate ($9Al_2O_3 . 2B_2O_3$), in previous work [5], mechanochemical method was used to synthesize Al_2O_3/B_4C composite powder by using commercial pure materials Al, H_3BO_3 and C. Mechanochemical process is a solid state powder processing method which involves inducing chemical reactions in a mixture of reaction powders at room temperature or at much lower temperatures compared to the temperature of conventionally mixed powders [6,7]. According to previous work results [5], aluminum plays the role of a reducing agent to reduce B_2O_3. Afterwards, the elemental boron B reacts with C to form B_4C.

Recently, reduction of many metallic oxides by solid aluminum reducing agents (aluminothermic reduction) has been significantly investigated. Having studied the effect of metallic aluminum powder on the production of boron carbide–alumina composite [8], Atasoy reported that liquid–solid reaction mechanism, which occurred during the aluminothermic process, had a specific influence on the formation of boron carbide. The aluminothermic reduction of boron oxide induced by the high-energy ball milling attracts the attention of researchers due to the potential applications like the synthesis of microcrystalline and nanocrystalline composites. According to the research carried out by Sharifi et al., by increasing milling process up to 40 h, the B_2O_3–Al reacted with a combustion mode producing Al_2O_3–AlB_{12} nanocomposite [9].

In addition to aluminothermic reaction, solid state carbothermal reduction of B_2O_3 was examined in many researches. Alizadeh et al. and Jung et al. investigated carbothermal reduction of B_2O_3 to fabricate B_4C by heating process [10]. Moreover, synthesis of boron carbides by reducing boron oxides with carbon and magnesium in mechanochemical process was investigated [11,12].

Aluminothermic reduction of B_2O_3 is a highly exothermic reaction. Thus, it is logical to presume that the extreme heat generated by the aluminothermic reaction during milling can provide sufficient energy to activate reduction of boron oxide by carbon. It means that B_2O_3 may be reduced by both Al and C during high energy ball-milling of ternary

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mixture Al–B_2O_3–C, simultaneously. Activation of carbothermic reduction by aluminothermic reaction during mechanochemical method has been reported in several researches [13,14].

The main purpose of the present work is to investigate the effect of Al amount in Al–B_2O_3–C mixture on the Al_2O_3/B_4C composite formation and mechanism of reactions during ball milling process. Also, influence of aluminothermic reaction on carbothermic reduction during simultaneous reduction of B_2O_3 was studied.

2. Experimental

2.1. Explanation

The general form of the total reactions taking place in ternary system Al–B_2O_3–C is represented in reaction (1).

$$4Al + 2B_2O_3 + C = 2Al_2O_3 + B_4C \quad (1)$$

It is believed that this reaction includes two stages: first, reduction of $2B_2O_3$ with 4Al which is a highly exothermic reaction and second, the reaction of elemental B with C leads to B_4C formation [5]. In order to investigate the effect of Al value on mechanochemical behavior of this system, powders were mixed according to the following desired stoichiometric compositions:

A. *Stoichiometric Al content*: in this case, distinct amounts of precursors were mixed according to reaction (1).
B. *Under-stoichiometric Al content*: the powders were mixed to give the following desired under-stoichiometric composition:

$$2B_2O_3 + (1+x)C + \left(4-2\left(\frac{x}{3}\right)\right)Al = B_4C + xCO + \left(2-\left(\frac{x}{3}\right)\right)Al_2O_3 \quad (2)$$

In the above reaction, x is a variable which gradually influences the primary carbon and aluminum amount (mole). Value of x varied from 0.5 to 3.

C. *Over-stoichiometric Al content*: the higher value of stoichiometric Al powder was mixed with boron oxide and carbon according to reaction (3) to investigate the effect of excess Al as matrix on the Al–B_2O_3–C system.

$$7Al + 2B_2O_3 + C = 3Al + 2Al_2O_3 + B_4C \quad (3)$$

2.2. Procedure

The precursor materials were aluminum (Merck, 99.7% purity, particles size 40 ± 5 μm), boron oxide (Merck, 99.95% purity, mean particles size 30 ± 5 μm) and graphite (Merck, 99.5% purity, mean particles size 50 μm).

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 1. To prevent the oxidation process, the container vessel of milling was filled with high purity argon gas before ball milling.

Table 1
Details of ball mill machine and milling conditions.

Rotation speed of container vessel (rpm)	500
Diameter of container vessel (mm)	100
Container vessel 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

For determination of remaining boron oxide content, at first, the obtained powder was weighed and taken as W_1. It was then washed by hot water (60–70°C) for 1 h with magnetic stirrer and then the solution was filtered and the residue on the filter was dried at 90°C for 2 h and weighed as W_2. The different $W_1 - W_2 = W_3$ is the amount of remaining B_2O_3. The resulting powder oxidized at 700°C for 30 min in the air then was weighed as W_4. Therefore, the different $W_3 - W_4 = W_5$ 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]. In an attempt to reduce errors, the reported data are averages of three experimental values.

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 $10° < 2\theta < 90°$. "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 reaction process and features were also investigated by Thermal Gravimeter (TG model BÄHR 503). A small amount of reactants weighing about 50 ± 5 mg was held in an alumina crucible and heated under argon flow (flow rate: 50 ml/min) at a heating rate of 10°C/min up to 1100°C.

3. Results and discussion

3.1. Thermodynamics evaluation

Although the interpretation of thermodynamic behavior of in situ solid state reactions such as mechanical activation is not completely studied, using some usual thermodynamic relations could help to know the basic information about reactions and to estimate their behavior during the process. Fig. 1 shows the ΔG°, ΔH° and T_{ad} curves plotted by the value of Al. The value of T_{ad}, the maximum temperature which could be attained as a result of reaction heat, would be calculated using the equation below [15]:

$$\Delta Q = -\Delta H^0_{298} + \int_{298}^{Tm} \sum C_p(Solid).dT + \Delta H_m + \int_{Tm}^{Tad} \sum C_p(Liquid).dT = 0 \quad (4)$$

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

Thermodynamic calculations were carried out based on two assumptions: (a) milling container vessel was sealed and isolated

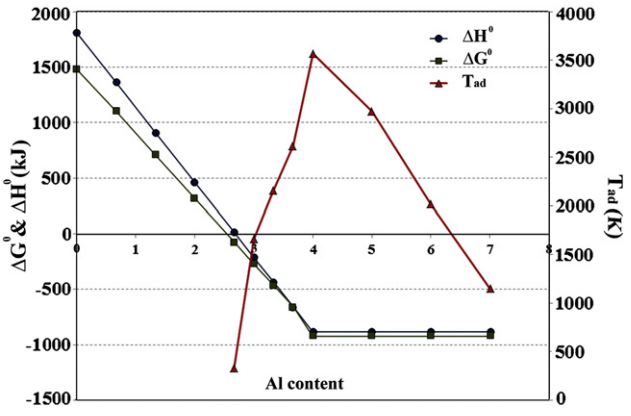

Fig. 1. The ΔG°, ΔH° and T_{ad} curves plotted by value of Al.