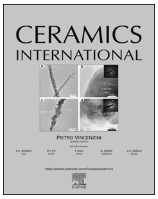
Ceramics International 42 (2016) 11217–11223

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint



Ignition and chemical mechanisms of volume combustion synthesis of titanium diboride

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ARTICLE INFO

Article history:
Received 6 March 2016
Received in revised form
3 April 2016
Accepted 7 April 2016
Available online 8 April 2016

Keywords:
A. Powders: solid state reaction
A. Combustion synthesis
B. Thermal Analysis
D. Borides

ABSTRACT

Reaction ignition and chemical mechanisms in volume combustion synthesis of TiB_2 via TiO_2–B_2O_3–Mg precursors were studied using in-situ differential thermal analysis, X-ray diffraction, scanning electron microscopy and thermochemical modeling. Mg–TiO_2 samples ignited at 607 °C through a sudden single step solid-solid reaction while Mg–B_2O_3 samples ignited at 810 °C after melting of magnesium. X-ray diffraction analysis revealed that reduction of TiO_2 occurs in multiple steps and forms intermediate compounds. Results showed that heat released from the first reaction between TiO_2 and Mg ignites the reactions between Mg, Ti and B_2O_3 resulting in the formation of TiB_2. Samples with larger TiO_2 particle size or a higher sample surface to volume ratio showed a two-step reaction behavior and the released heat in the first solid state reaction was insufficient for the propagation of the reaction throughout the sample. In addition, $Mg_3B_2O_6$ undesired by-product was formed as a result of this two-step reaction.

1. Introduction

In recent years, boride ceramics have been extensively developed due to their specific properties. Titanium diboride, one of the most stable boron compounds has high hardness and melting temperature, good thermal and electrical conductivity as well as resistance to oxidation up to 1000 °C [1–5]. Because of these properties titanium diboride based ceramics have found applications in cutting tools, wear components, impact-resistant armor, heating elements and as the cathodes in Hall–Heroult process for production of aluminum [6–8].

Combustion synthesis is known as a rapid, facile and cost-effective method for the production of fine titanium diboride particles using low-cost materials [1,9–11]. Volume Combustion Synthesis (VCS), or thermal explosion, is a synthesis method, where all the reactants are uniformly heated up to an ignition temperature by an external heat source and then a sudden exothermic reaction takes place throughout the sample volume [12–15]. This is in contrast to the Self-propagating High-temperature Synthesis (SHS), where a local heat source ignites the reaction and the hot combustion wave passes through the mixture and completes the reaction [9,12,16]. However, in both methods, the reactants are usually well mixed fine powders, which are pressed into a pellet. Intimate contact between the particles is essential in order to initiate the reaction and conduct the heat wave during the synthesis [9,12,17].

Physical and chemical properties of the product such as particle and crystalline size, product yield and formation of undesirable by-products depends on various variables, such as reactants type, particle size and stoichiometric ratio [18–21], heating rate [22–24], addition of inert diluent [11,25–27], sample size and aspect ratio, sample green density [9] and mechanical activation [28,29]. Understanding the effects of these parameters on combustion synthesis needs the identification of the mechanisms of the reactions; in the case of VCS this identification can shed more light on ignition phenomena.

Several attempts have been made to clarify the mechanisms of the reaction in the combustion synthesis of TiB_2 or TiB_2 composites [30–33]. In this work, the reaction ignition and chemical mechanisms in volume combustion synthesis of TiB_2 via TiO_2–B_2O_3–Mg precursors were evaluated. A combination of thermodynamic reaction simulation, in-situ thermal analysis of pellet samples, sample quenching, X-ray diffraction and SEM analysis were applied.

2. Experimental

TiO_2 (≥ 99.0% purity Merck Chemicals 10080) and Mg powders (≥ 98.5% purity Merck Chemicals 105815) were used with average particle sizes of 0.3 μm and 250 μm, respectively. B_2O_3 was prepared by calcination of H_3BO_3 (≥ 99.5% purity Surechem B5102) at 450 °C and the calcined product was ground to an average particle size of 100 μm.

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http://dx.doi.org/10.1016/j.ceramint.2016.04.032
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Two binary mixtures, $Mg:B_2O_3$ with a molar ratio of 4.2:1 and $Mg:TiO_2$ with a molar ratio of 2.8:1, and a ternary mixture of $Mg:TiO_2:B_2O_3$ with a molar ratio of 7:1:1 were prepared. The excess amount of magnesium from the stoichiometric proportion required for conversion of the oxides was used to compensate the loss of magnesium due to evaporation. The precursor powders were dry mixed for 1 h and then pressed in a form of 16.4 mm diameter and 16.7 mm height cylindrical pellets with an average compact density equal to 70% of the theoretical maximum density of the mixture.

The pellets were suspended in the middle of a 5 cm ID, 100 cm long sealed quartz reaction chamber. The tubular reactor was placed in an electrical furnace and heated to 220 °C for half an hour under an argon atmosphere to remove moisture from the pellet. Samples were then heated at the rate of 15 °C/min to the ignition temperature under the argon atmosphere. In-situ thermal analysis was performed using two K-type thermocouples, one on top and one at the bottom, in contact with the pellet sample to measure the ignition temperature and other thermal effects before the ignition. Thermocouples also acted to suspend the samples in the middle of the furnace as shown in Fig. 1. Suspension of the samples ensured thermal homogeneity of the samples. A third thermocouple was used to measure the temperature of the furnace as the reference temperature. An Advantech USB-4817 data acquisition system was used to acquire the temperature measurements.

In other sets of experiments the effect of heat loss from the samples to the surroundings and TiO_2 particle size was studied. In the first set smaller samples, 6.6 mm height and 16.4 mm diameter, were prepared and subjected to the same thermal regime as the samples with 16.7 mm height. Identical samples were quenched at different time intervals to determine phase formations after each exothermic reaction. Quenching was performed by quickly removing the quartz tube from the thermal zone of the furnace under a constant flow of argon. Second set of experiment was conducted with relatively larger TiO_2 particles (≥ 99.0% purity Sigma Aldrich 248576 with particles size smaller than 44 μm).

The phase composition and morphology of the products were examined by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM), respectively. The phase formations during the synthesis were calculated using FactSage [34] thermochemical software.

3. Results and discussion

3.1. Mg-TiO_2 reacting system

Fig. 2 shows the XRD pattern of the CVS product of Mg–TiO_2 sample. Table 1 compares the XRD results with the equilibrium phase composition calculated with FactSage. Results show MgO as the main reaction product as well as Ti_2O and Mg_2TiO_4 non-equilibrium phases indicating that equilibrium was not reached.

Fig. 3 shows the reaction proceeding of TiO_2 with progressive addition of magnesium predicted using FactSage. Results show that TiO_2 converts to Ti_2O_3 and complex Mg–Ti–O compounds ($MgTi_2O_5$ and Mg_2TiO_4). The formation of Mg_2TiO_4 as an intermediate by-product was only possible at temperatures higher than 1000 °C. Further addition of magnesium, between the TiO_2:Mg molar ratio of 0.5 and 1, leads to the decomposition of these Mg–Ti–O compounds and formation of TiO. More addition magnesium, results in the production of metallic titanium together with MgO. Formation of MgO and other Mg–Ti–O compounds can act as a barrier for the diffusion of Mg to the reaction surfaces.

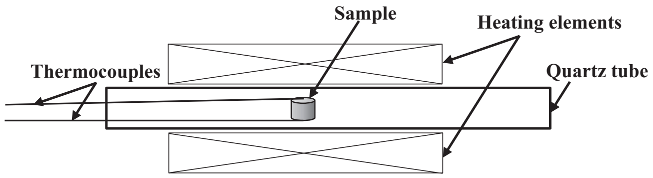

Fig. 1. Schematic synthesis apparatus and in-situ thermal analysis setup.

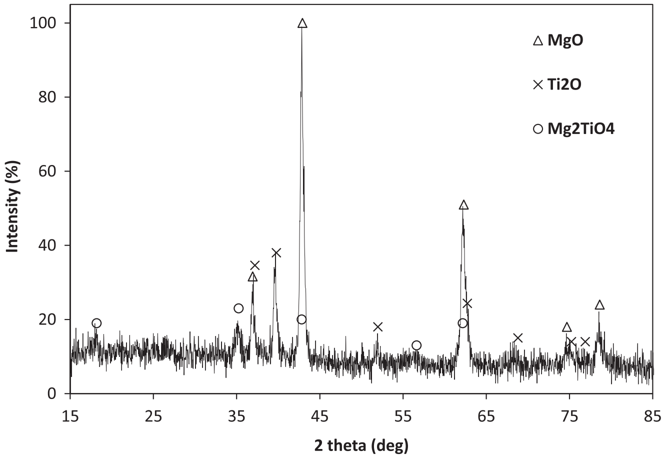

Fig. 2. XRD pattern of Mg–TiO_2 synthesis. MgO, Ti_2O and Mg_2TiO_4 were detected.

Table 1
Equilibrium phases calculated using FactSage [34] thermochemical software and XRD analysis of the synthesis products in TiO_2–Mg system.

System	Equilibrium condition	XRD results
TiO_2–Mg	Ti, MgO	Ti_2O, Mg_2TiO_4, MgO

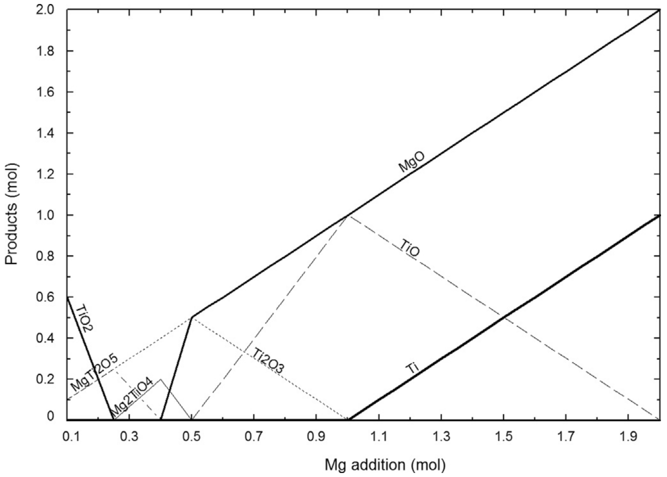

Fig. 3. Phase formations in Mg–TiO_2 system calculated with FactSage [34] thermochemical software.

Fig. 4 shows the in-situ differential thermal analysis of the 2.8Mg–1TiO_2 pellet samples. A small change in the slope of the differential temperature line was observed at 440 °C indicating a slow exothermic reaction. The reaction initiated at 607 °C and a sudden temperature increase equal to 330 °C was measured. Ignition is below the melting point of magnesium, 650 °C, which means the combustion initiated in the solid state. TiO_2 particles covered magnesium particles since they are smaller than magnesium particles by two orders of magnitude. A good contact between the two solid particles and short diffusion distance enhanced the solid state reaction.

Theoretical adiabatic combustion temperature of 1TiO_2–2.8 Mg