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Short communication

Reaction chemistry during self-propagating high-temperature synthesis (SHS) of H₃BO₃–ZrO₂–Mg system

A.K. Khanra*

Department of Metallurgical and Materials Engineering, IIT Kharagpur 721302, India Received 12 August 2006; received in revised form 24 December 2006; accepted 24 January 2007 Available online 30 January 2007

Abstract

In the present investigation, the ZrB_2 powder is produced by SHS of mixture containing H_3BO_3 , ZrO_2 and Mg. The thermal analysis and XRD study reveal the reaction mechanism of ZrB_2 formation by SHS process. Synthesis of H_3BO_3 –Mg system results in formation of $Mg_3(BO_3)_2$ and MgB_4 phases, whereas ZrO_2 is partially reduced to Zr_3O and Zr during synthesis of ZrO_2 –Mg system. The reaction between elemental Zr and MgB_4 results in ZrB_2 formation. The particle size of ZrB_2 is found to decrease with the addition of SHS diluent.

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1. Introduction

The ZrB_2 is an excellent high-temperature ceramic material due to its high melting point, high wear and oxidation resistance. It has several applications such as in hypersonic re-entry vehicles, nose caps, rocket nozzle inserts, air-augmented propulsion system compounds, evaporation boats, cutting tools, cathode material for Al extraction, etc. [1,2]. The ZrB₂ can be prepared by borothermic reduction, carbothermal synthesis, SHS, gas-phase combustion synthesis, etc. [3–6]. Last one decade the SHS becomes a suitable process for production of several ceramic materials. The essential feature of SHS process is that the heat required to drive the chemical reaction is supplied from the reaction itself. Once ignited, extremely high temperature (adiabatic temperature) can be achieved due to the highly exothermic reaction proceeding in a short time. Preparation of boride powder from elemental powder mixture results in high purity powder but makes process costly. Preparation of boride powder from the mixture of boric acid, metal oxide and reducing agent is an alternative processing route and save the cost of the starting materials. The SHS reactions are limited by kinetic considerations related to the rate of reactions and rate of heat transfer ahead of the reaction front, which often results incomplete conversion. The details study of SHS is useful to control the composition of product [7-9]. In the present investigation, the reaction mechanism of ZrB₂ formation by SHS process from mixture containing H₃BO₃, ZrO₂ and Mg is studied with the help of individual reactant mixture system. Present investigations also focus the effect of NaCl as a SHS diluent on ZrB2 particle size.

* Tel.: +91 3222 283264; fax: +91 3222 282280.

E-mail address: asit_iitkgp@yahoo.com.

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2. Experimental procedure

In the present study, the ZrO₂ powder (99.8% pure, and particle size $<44 \mu m$, S.D. Fine chemicals, Mumbai, India), H_3BO_3 (99.5% pure and particle size <44 μ m, Loba-Chemie, Mumbai, India) and Mg (99.9% pure, and particle size $<44 \mu$ m, Loba-Chemie, Mumbai, India) were used as raw materials. First the H₃BO₃ and Mg (molar ratio of 2:3) were dry mixed in a polythelene bottle for 3 h and small quantity of (~ 10 mg) mixture was used for differential thermal analysis and thermogravimetry analysis (DTA/TG). The DTA/TG was carried at different rates of heating of 10 and 20 °C/min with continuous flowing of high pure (XL grade) argon gas. The H₃BO₃-Mg mixture was also heated in a tubular furnace with resistance heating up to 1000 °C. After cooling the MgO was leached out by boiling in dilute HCl solution. The phase analysis of product was characterized by X-ray diffraction (XRD) [Philips 1840, The Netherlands]. Another mixture of ZrO₂ and Mg (molar ratio of 1:2) was similarly tested by DTA/TG. The mixture was heated in a furnace up to 1000 °C and MgO (reaction product) was removed. Then the product was analyzed by XRD technique. The H₃BO₃, ZrO₂ and Mg (molar ratio of 2:1:5) were dry mixed, which was used for DTA/TG study and heated in a furnace up to 1000 °C. Similarly the synthesized product was characterized by XRD technique. The experiment was also carried out by adding 20 wt% NaCl as a SHS diluent to the reactant mixture. These all experiments were performed in high pure argon atmosphere and rate of heating was 20 °C/min. The morphology of leached and dried product from H₃BO₃-ZrO₂-Mg system was studied by scanning electron microscope (SEM) [JEOL, JSM 840A, Japan] and transmission electron microscope (TEM) studies [CM 200, The Netherlands].

3. Results and discussion

The typical DTA/TG plots of H_3BO_3 -Mg system at different heating rates are shown in Fig. 1. The thermograms show two endothermic peaks to appear at 139 and 169 °C, respectively. These two peaks are due to melting and dissociation of boric acid. This is confirmed from individual DTA of boric acid and relevant thermodynamic data. The endothermic peak due to melting of B_2O_3 is not detected here. The thermograms reveal an endothermic peak at 650 °C due to melting of Mg and then a sharp exothermic peak appears at 853 °C. The exothermic peak appearing at 853 °C could be the reaction initiation temperature of H_3BO_3 -Mg system. The rate of heating has insignificant effect on the reaction initiation temperature. The TG plot shows the corresponding weight change taking place during the thermal analysis. Initial sharp weight loss is due to removal of water from boric acid and then slight weight gain is found. This small weight gain may be oxidation of unreacted Mg. The XRD pattern of H_3BO_3 -Mg system shows presence of MgO as a major phase with Mg-borate in the as synthesized powder (Fig. 2). The XRD pattern of leached powder shows Mg-borate as major phase and MgB₄ as a minor phase, respectively. The chemical reactions of H_3BO_3 -Mg system may be written as

$$2H_3BO_3 \rightarrow 3H_2O + B_2O_3 \tag{1}$$

$$4B_2O_3 + 7Mg \rightarrow MgB_4 + 2Mg_3(BO_3)_2 \tag{2}$$



Fig. 1. Typical DTA/TG plot of H₃BO₃-Mg system: D₁, D₂-DTA at 10 and 20 °C rate of heating and T₁, T₂--TG at 10 and 20 °C rate of heating.



Fig. 2. XRD patterns for H₃BO₃–Mg system: (a) and (b) are unleached and leached powder.

During synthesis of H_3BO_3 -Mg system the elemental boron may form, which is not detected by XRD analysis due to amorphous in nature. The reaction between B_2O_3 and Mg can be written as

$$B_2O_3 + 3Mg \rightarrow 2B + 3MgO \tag{3}$$

The DTA/TG plot of ZrO_2 –Mg system shows only an exothermic peak at 645 °C (Fig. 3). The endothermic peak due to melting of Mg is not detected, which indicates overlapping of the solid state reaction between Mg and ZrO_2 on melting reaction. The rate of heating has no effect on the exothermic peak position. The TG plot shows initial small decrease in weight and then a rapid weight increase at a constant rate for both rates of heating. The weight gain during thermal analysis however indicates MgO formation through reaction with adsorbed gases and residual oxygen in the atmosphere. The XRD pattern of ZrO_2 –Mg system is shown in Fig. 4. The unleached powder mainly contains MgO and ZrO_2 phase, whereas the leached powder shows ZrO_2 as a major phase with Zr_3O and elemental Zr as minor phases. Presence of $ZrO_2 \rightarrow Zr_3O \rightarrow Zr$. It has been also seen that addition of extra Mg has no effect on XRD pattern of synthesized product from ZrO_2 –Mg mixture.

A typical DTA/TG plot for H_3BO_3 –ZrO₂–Mg system is shown in Fig. 5. The DTA plot shows two endothermic peaks at 139 and 169 °C and then an endothermic peak at 650 °C. Similar endothermic peaks are also found during H_3BO_3 –Mg system. After endothermic peak at 650 °C, a massive exothermic peak is found at 794 °C. The exothermic peak at 794 °C for H_3BO_3 –ZrO₂–Mg system may be the ignition temperature of exothermic reaction. The exothermic peak at 650 °C, which is found during DTA of ZrO₂–Mg system, is not observed here. This is an unexpected matter and further investigation is under progress. The rate of heating and NaCl addition seem to have no effect on ignition



Fig. 3. Typical DTA/TG plot of ZrO₂-Mg system: D₁, D₂-DTA at 10 and 20 °C rate of heating and T₁, T₂-TG at 10 and 20 °C rate of heating.



Fig. 4. XRD patterns of ZrO₂-Mg system: (a) and (b) are unleached and leached powder.

temperature. It has been also seen that addition of NaCl as SHS diluent to reactant mixture has insignificant effect on ignition temperature, which indicates that it does not affect the mechanism of the present SHS process and the NaCl is remaining neutral. TG plot shows initial rapid decrease of weight due to loss of H_2O and then there is no weight change observed till exothermic reaction. The weight decrease during exothermic reaction may be due to flying away of some particles from the crucible during DTA/TG analysis and the vigorous exothermic reaction could be the cause for this. The XRD pattern of H_3BO_3 –ZrO₂–Mg system is shown in Fig. 6. The XRD pattern of the powder (unleached) shows presence of MgO as a major phase along with ZrB₂ and ZrO₂ phases. The leached powder shows presence of ZrB₂ as a major phase along with ZrO₂ and B_{51} Zr phases (Fig. 6B). The sequence of chemical reactions of H_3BO_3 –ZrO₂–Mg system can be written as

$$MgB_4 + Zr \to MgB_2 + ZrB_2 \tag{4}$$

$$MgB_2 + Zr \to ZrB_2 + Mg \tag{5}$$

$$\operatorname{Zr} + 2\operatorname{B} \to \operatorname{Zr}\operatorname{B}_2$$
 (6)

However, presence of $Mg_3(BO_3)_2$ is not detected during XRD of H_3BO_3 – ZrO_2 –Mg system. The presence of $Mg_3(BO_3)_2$ phase in H_3BO_3 –Mg system and absence of $Mg_3(BO_3)_2$ phase in ZrO_2 – H_3BO_3 –Mg system is also observed by Weimin et al. during combustion synthesis of TiB₂[9]. This indicates it may not form or even if it forms, it may subsequently dissociate to form other species. The detail of investigation is under progress.



Fig. 5. Typical DTA/TG plot of ZrO_2 -H₃BO₃-Mg system: D₁, D₂-DTA at 10 and 20 °C rate of heating and T₁, T₂--TG at 10 and 20 °C rate of heating.



Fig. 6. XRD patterns of different powders of H_3BO_3 -Zr O_2 -Mg system: (a) unleach powder, (b) leached powder (without NaCl addition) and (c) leached powder (20 wt% NaCl addition).

In the present investigation presence of unreacted ZrO_2 in the product indicates an incomplete conversion. Addition of extra Mg (molar ration of H₃BO₃:ZrO₂ and Mg 2:1:8) also has no effect of XRD result. A similar phenomenon is also found during synthesis of ZrO_2 –Mg system. In case of production of TiB₂ production from mixture of H₃BO₃, TiO₂ and Mg, the unreacted TiO₂ is not found, which may indicates complete conversion [10]. The ZrO₂ may be much more stable oxide than TiO₂, which always leads to incomplete conversion. The XRD pattern in case of NaCl addition shows presence of extra ZrO_2 peak. The appearance of extra peak may indicate decrease of conversion, which results from loss of heat due to NaCl addition. The XRD patterns indicate line broadening of highest intensity peak (1 0 1) for NaCl added sample as compared to without NaCl added sample, which is due to diluent addition. Applying Scherrer formulae, the crystallite size of ZrB_2 are found to be ~75 and 43 nm for without NaCl and 20 wt% NaCl added samples, respectively. The TEM images of SHS powders are shown in Fig. 7. It also shows presence of agglomeration of spherical particles and the particle size decreases with the NaCl addition. During synthesis NaCl melts and vaporizes and deposit on ZrB₂ particle, which reduces the grain growth of particle. The corresponding selected area diffraction pattern (SAD) shows presence of mirror images of dots (inset of Fig. 7a and b), which indicates twin formation in the particle.



Fig. 7. TEM images of leached ZrB₂ powder: (a) without NaCl addition and (b) 20 wt% NaCl addition.

4. Conclusions

An attempt has been made here to study the reaction mechanism during production of ZrB_2 by SHS technique. During SHS, the H_3BO_3 is reduced to $Mg_3(BO_3)_2$ and MgB_4 , whereas ZrO_2 is partially reduced to Zr_3O , Zr. Then elemental Zr reacts with MgB_4 for ZrB_2 formation. Incomplete reduction of ZrO_2 results in presence of unreacted ZrO₂ in the product. Addition of diluent to the reactant mixture helps in decrease of ZrB_2 particle size.

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References

- [1] I.M. Low, R. Mcpherson, J. Mater. Sci. Lett. 8 (1989) 1281.
- [2] A.K. Khanra, L.C. Pathak, S.K. Mishra, M.M. Godkhindi, Adv. Appl. Ceram. 104 (2005) 1.
- [3] P. Millet, T. Hwang, J. Mater. Sci. 31 (1996) 351.
- [4] H. Zhao, Y. He, Z. Jee, J. Am. Ceram. Soc. 78 (1995) 2534.
- [5] D.D. Radev, M. Marinov, J. Alloys Compd. 244 (1996) 48.
- [6] L. Chen, Y. Gu, Z. Yang, L. Shi, J. Ma, Y. Qian, Scrip. Mater. 50 (2004) 959.
- [7] K.V. Logan, J.D. Walton, Ceram. Eng. Sci. Proc. 5 (1984) 712.
- [8] J.B. Holt, D.D. Kingman, G.M. Bianchini, Mater. Sci. Eng. 71 (1985) 321.
- [9] W. Weiman, F. Zhengyi, W. Hao, Y. Runzhnag, J. Mater. Proc. Tech. 128 (2002) 162.
- [10] A.K. Khanra, L.C. Pathak, S.K. Mishra, M.M. Godkhindi, Mater. Lett. 58 (2004) 733.