Int. Journal of Refractory Metals and Hard Materials 31 (2012) 89–95

Contents lists available at SciVerse ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

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

Combustion and formation behavior of hybrid ZrB_2 and ZrC particles in Al–Zr–B_4C system during self-propagation high temperature synthesis

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ARTICLE INFO

Article history:
Received 7 April 2011
Accepted 8 September 2011

Keywords:
Self-propagation high temperature synthesis (SHS)
ZrB_2
ZrC
Reaction behavior

ABSTRACT

Hybrid ZrB_2 and ZrC particles were prepared by self-propagation high temperature synthesis (SHS) using Al, Zr and B_4C powders as starting reactants. As effective diluents, Al play an important role in the SHS reactions, during which the solid Al and Zr reacted in the first instance followed by melting of Al that reacted with Zr to generate $ZrAl_3$. Meanwhile, due to the heat generated by the reactions, C and B atoms were dissolved into the Zr–Al liquid, leading to the precipitation of ZrB_2 and ZrC out of the supersaturated liquid phases. In the case of samples with Al content of 30 wt.%, ZrB_2 particles exhibit typical hexagonal and rectangular shapes, whilst a spherical shape was displayed with ZrC particles. The synthesized structure of the ZrB_2 and ZrC can be as fine as nanoscale. Not only prevented the synthesized products from growing, the Al addition also promoted the SHS reaction.

1. Introduction

Boride and carbide of zirconium (ZrB_2 and ZrC) possess good combination of ultra-high hardness, high melting point, low density, and excellent wear resistance, which make them attractive candidates for aerospace applications [1, 2], In comparisons, the use of any single-phase (either ZrB_2 or ZrC) for high-temperature structural applications is quite limited due to its relatively poor oxidation and ablation resistance, as well as the poor damage tolerance [3]. Therefore, research efforts have now turned to the development of double or multiple phase ceramics [4, 5]. Conventional synthesis and fabrication methods of multiple phase ceramics include pressureless sintering (PLS) [6], hot pressing (HP) [7], hot isostatic pressing (HIP) [8], spark plasma sintering (SPS) [9]. Another viable method to produce ceramic composite is through self-propagation high temperature synthesis (SHS) [10], which is an energy-efficient technique for the fabrication of ceramics and intermetallics. With this technique, heterogeneous and self-sustained chemical reactions can be ignited due to sufficient exothermic effect of an external heating pulse applied to the surfaces of reactant pellets, and the reactions then propagate in the forms of both chemical and thermal waves [11].The major advantages of the SHS technique are its very high reaction rate and the elimination high temperature furnaces used in conventional sintering owing to the existence of SHS induced self-generation of energy. However, to date, the report about ZrB_2–ZrC synthesized by SHS is relatively limited. A few works include a ZrB_2 platelet-reinforced ZrC ceramic composite prepared by Breval and Johnson [12] through the reaction between powders of zirconium and boron carbide, and the synthesis of ZrC and ZrB_2 by the combination of mechanical alloying and SHS in air taking Zr–B–C powders as starting materials (Tsuchida and Yamamoto [13]). In our previous studies, it was proved that the addition of metal with low melting point decreases the combustion temperature by forming a liquid at a low temperature and improves the surface reaction rate during SHS process, which helps to obtain ultrafine even nano-scale ceramic particles [14,15]. However, limited works on the SHS reaction of the addition of metals to Zr–B_4C system have been reported. Therefore, the present study attempts to investigate the feasibility of SHS reaction in Al–Zr–B_4C system and clarify the reaction mechanism with the Al addition.

2. Experimental

The ZrB_2 and ZrC particulates were prepared starting from powders of Al, Zr and B_4C according to the following reaction equation:

$$3Zr + B_4C + xAl = 2ZrB_2\ ZrC + xAl \quad (1)$$

where x is the stoichiometric content of Al equal to 0 and 30 wt.%, respectively. Compositions of the samples are shown in Table 1. Fig. 1 shows the SEM images of the raw materials, i.e. commercial purity powders of Al (~ 99% purity, ~25–40 μm), Zr (~99% purity, ~25–40 μm) and B_4C (~95% purity, ~45–60 μm). The powders were dry-mixed in a mechanical shaker for 4 h (Fig. 1d), followed by a cold-compacting in a cylindrical die 20 mm in diameter and 15 mm in height to obtain a relative density of 60±0.5%. Ignition was accomplished by a tungsten heating coil placed near one end of the green compact. The SHS experiment was carried out inside a steel chamber with an argon atmosphere

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doi:10.1016/j.ijrmhm.2011.09.011

Table 1
Compositions of the two mixed powders.

Samples	Elements contents (wt.%)		
	Al	Zr	B_4C
Zr–B_4C	0	89.06	10.94
30wt.%Al–Zr–B_4C	30	58.08	11.92

by applying a pressure of 0.1 mPa. The copper-mold-aided combustion front quenching experiment with 30 wt.% Al in the compact was conducted. The SHS reaction apparatus and the experimental procedure were detailed in ref [16].

Combustion temperature was measured by a two-color optical pyrometer (Incon Modline R) with a response time of 10 ms. The velocity of combustion wave was determined by timing of the reaction propagation from one end of the sample to the other. Furthermore, ignition process of reactant mixtures was studied by differential thermal analysis (DTA) (model Rigaku-8150, Rigaku, Tokyo, Japan) using a heating rate of 30 K/min under an argon atmosphere (99.00 pct). Composition of the combustion sample was determined after quenching by X-ray micro-diffraction (D8 Discovery with GADDS, Bruker AXS, Karlsruhe, Germany) using an 800 μm beam in diameter. The as-product and DTA sample were identified by X-ray diffraction (D/Max 2500PC Rigaku, Japan) with Cu-K_α radiation using a scanning speed of 4°/min with an angle (2θ) step of 0.05°. The microstructure of the product was inspected by scanning electron microscopy (SEM; FEI-Sirion 200, USA). Moreover, after washing by 18 vol.% HCl solution, absolute alcohol and distilled water for several times and drying, the extracted powders were characterized by transmission electron microscopy (TEM; JEM-2010, Japan) and selected area electron diffraction (SAED) with an accelerating voltage of 160 kV.

3. Results and discussions

3.1. Thermodynamic analysis

All possible chemical reactions during the SHS experiment of Al, Zr and B_4C powders are listed as follows:

$$Zr + 3Al = ZrAl_3 \quad (2)$$

$$2Zr + B_4C\ 2ZrB_2\ C \quad (3)$$

$$Zr + B_4C\ ZrC\ 4B \quad (4)$$

$$3Zr + B_4C\ 2ZrB_2\ ZrC \quad (5)$$

$$10Al + 3B_4C = 6AlB_2 + Al_4C_3 \quad (6)$$

$$AlB_2 + Zr = ZrB_2\ Al \quad (7)$$

$$Al_4C_3 + 3Zr = 3ZrC + 4Al \quad (8)$$

Using the thermodynamic data from the Ref. [17], the Gibbs free energies (ΔG) and the reaction enthalpies (ΔH) of the above reactions were calculated to determine the phases of synthesized products, as shown in Fig. 2, from which it can be seen that all above reactions are thermodynamically favorable ($\Delta G<0$) and exothermic ($\Delta H<0$) over the calculated temperature ranges. It should be noted that ZrB_2 and ZrC are the most stable phases because the negativity of Gibbs free energy with reaction between Zr and B_4C leading to them [Eq. (5)] is the largest among all the above reactions.

Another important thermodynamic parameter of SHS process, the adiabatic combustion temperature, T_{ad}, represents the highest temperature a

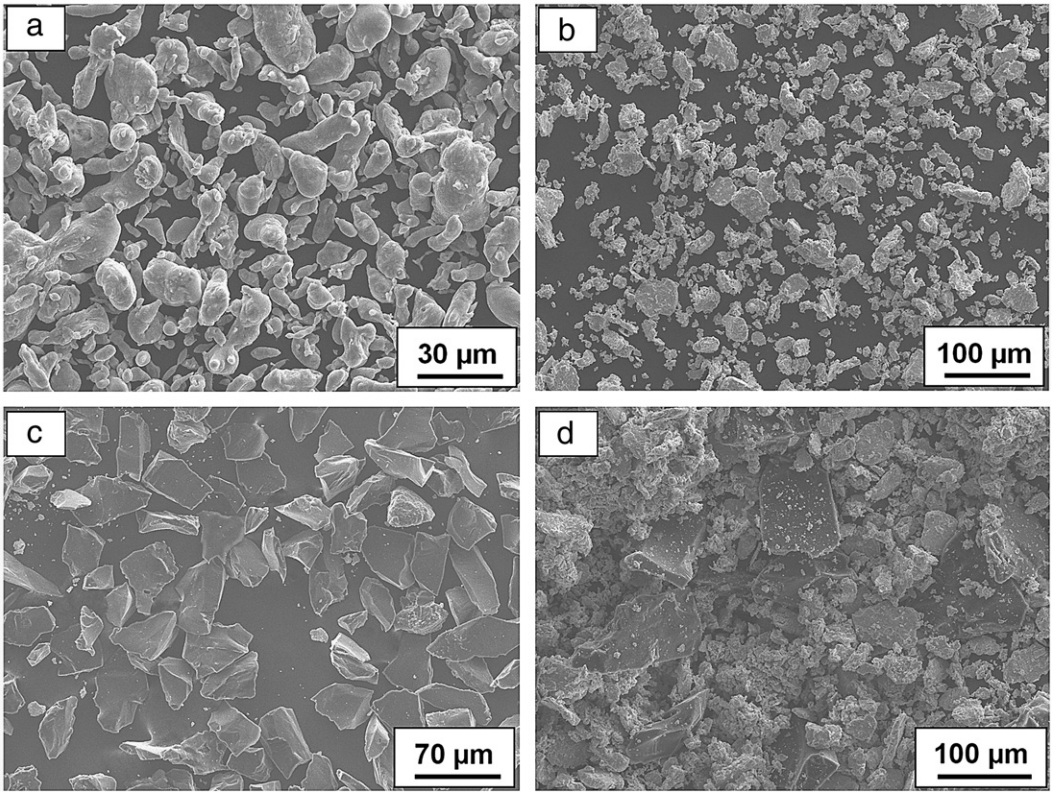

Fig. 1. SEM images of raw materials: (a) Aluminum, (b) Zirconium, (c) Boron Carbide and (d) mixed powders.