

Self-propagating high-temperature synthesis of ZrB_2 in the system ZrO_2 - B_2O_3 - Fe_2O_3 -Al

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Self-propagating high-temperature synthesis (SHS) has been used to prepare many refractory materials such as carbides, borides, silicides, oxides, hydrides, intermetallics and complex composites [1, 2]. Zirconium diboride (ZrB_2), because of its high melting point, superior hardness, low electrical resistance, and inertness to many molten metals and slags, is a strong candidate material for wear parts, cutting tools, nozzles and electrodes [3, 4]. Previous work on SHS production of ZrB_2 has been based on the synthesis directly from its elements [5, 6]. However, the main disadvantage of SHS is that the products are porous because of the large pores in the original mixture of reactants and because of the large volume change resulting from the transformation of the reactants to the products. Also, volatilization of impurities at elevated combustion temperature can increase the degree of porosity of the final products. Synthesis concurrent with densification can improve the situation some extent. Recently, Feng *et al.* [7] prepared ZrB_2 - Al_2O_3 -Al ceramic metal composites with an improved density and toughness by combustion synthesis. They used an excess amount of Al in a mixture of ZrO_2 , B_2O_3 and Al in order to infiltrate simultaneously molten Al into the pores of the ZrB_2 - Al_2O_3 matrix formed by the SHS reaction. Dense ceramic alloy or casting materials may be obtained when the processing temperature exceeds the melting points of the final products. Combustion synthesis is expected to melt at least a portion of constituents due to the highly exothermic reaction and with selection of an appropriate reaction system [8]. The objective of this study was to investigate the possibility of producing molten phases of ZrB_2 , during SHS reaction by adding Fe_2O_3 and excess Al to a stoichiometric mixture of ZrO_2 , B_2O_3 and Al.

The reactant powders of ZrO_2 ($\sim 1 \mu m$), B_2O_3 ($\sim 5 \mu m$), Fe_2O_3 ($\sim 5 \mu m$) and Al ($\sim 7 \mu m$) were mixed and homogenized by ball milling in ethyl alcohol for 10 h using a polyethylene bottle with zirconia ball media. After drying, the mixed powders were shaped into compacts (55 mm in diameter \times 30 mm in height). The compacts were charged in a graphite crucible, and then placed into a reaction chamber. The reaction chamber was vacuum treated and preheated to the ignition temperature (800–900 °C) with a heating rate of 10 °C/min under 2 atm. Ar atmosphere. After the combustion reaction was completed, samples were cooled in the chamber to room temperature. The synthesized products

were investigated using X-ray diffraction (XRD) for phase analysis, scanning electron microscopy (SEM) for microstructure observation, and a pycnometer was employed for density measurement.

The calculated variations of adiabatic combustion temperature with initial temperature for two reactant systems of ZrO_2 - B_2O_3 -Al and ZrO_2 - B_2O_3 - Fe_2O_3 -Al are shown in Fig. 1. During the combustion, the adiabatic temperature (T_{ad}) in the latter system reaches a higher level than that of the former system with ignition temperature. This result indicates that in coupling the forming reactions of ZrB_2 and Al_2O_3 with another, i.e., thermite reaction of iron(III) oxide and aluminum, a higher adiabatic temperature is achieved. Also, in assuming that the ignition temperature (T_{ig}) is 1000 K and the system is operating under adiabatic conditions, the adiabatic combustion temperatures of ZrO_2 - B_2O_3 -Al and ZrO_2 - B_2O_3 - Fe_2O_3 -Al systems were 2840 K and 3320 K, respectively. At these temperatures, in the former case the adiabatic temperature is lower than the melting point of ZrB_2 (3300 K), but in the latter case it is slightly above. Thus, in latter case the final products may at least be partially molten. However, it is expected that the actual reaction system will deviate

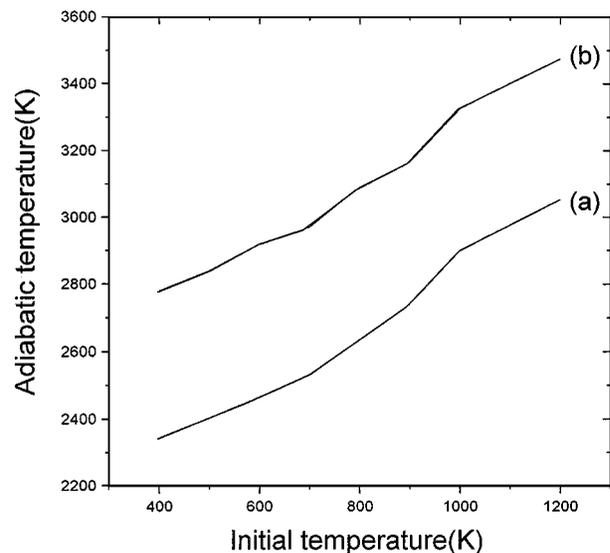


Figure 1 Calculated variation in adiabatic temperature with initial reactant temperature for the combustion product. (a) $ZrO_2 + B_2O_3 + 3.33Al$ system; (b) $ZrO_2 + B_2O_3 + xFe_2O_3 + (3.33 + y)Al$ system ($x : y = 1 : 2$).

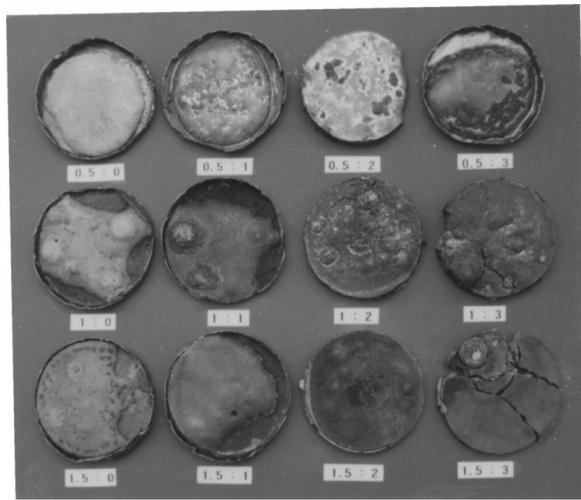


Figure 2 Photograph of the combustion products with Fe_2O_3 and Al additives.

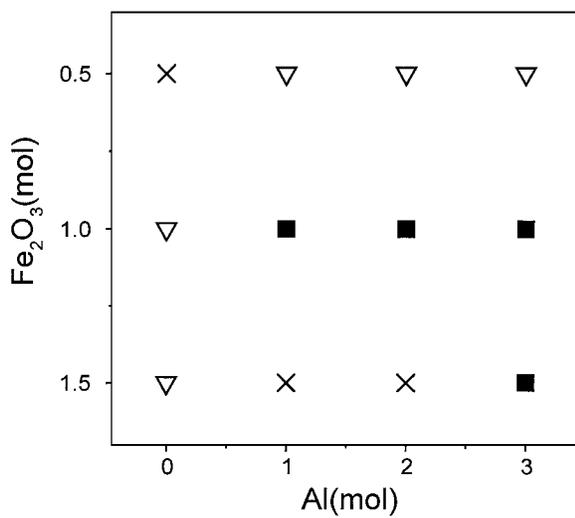


Figure 3 The degree phase separation of the combustion products in $\text{ZrO}_2 + \text{B}_2\text{O}_3 + x\text{Fe}_2\text{O}_3 + (3.33 + y)\text{Al}$ system (molar ratio). ■ : Phase separation in many parts. ▽ : Phase separation in a few parts. × : No phase separation.

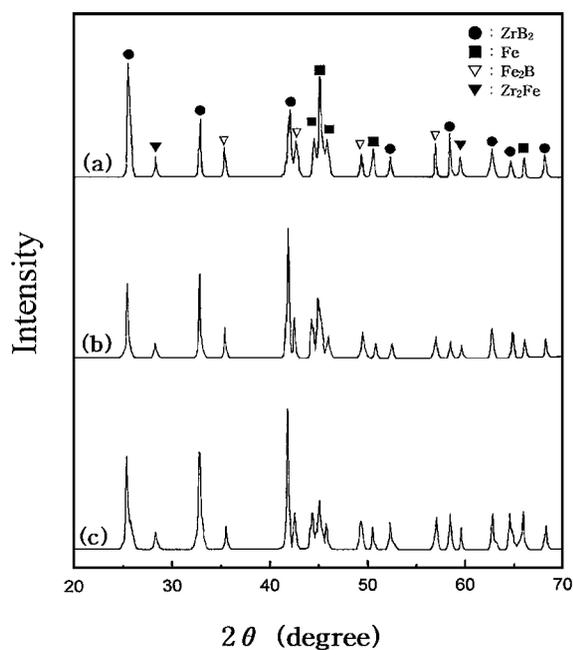


Figure 4 XRD patterns of the molten phase separated from the slag phases to Fe_2O_3 : Al (molar ratio) additives. (a) 1 : 1; (b) 1 : 2; (c) 1 : 3.

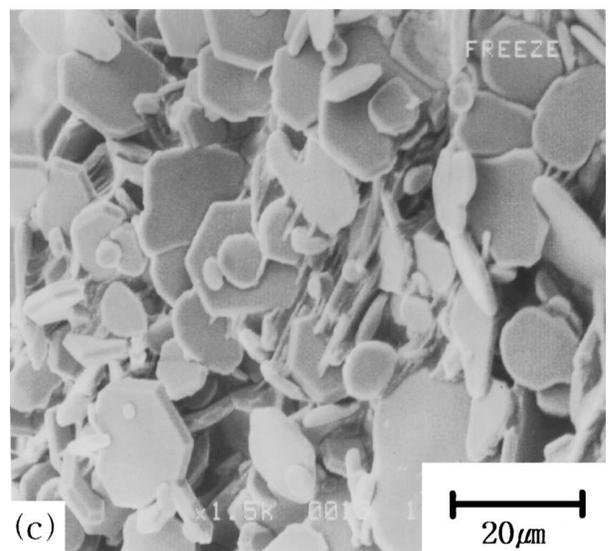
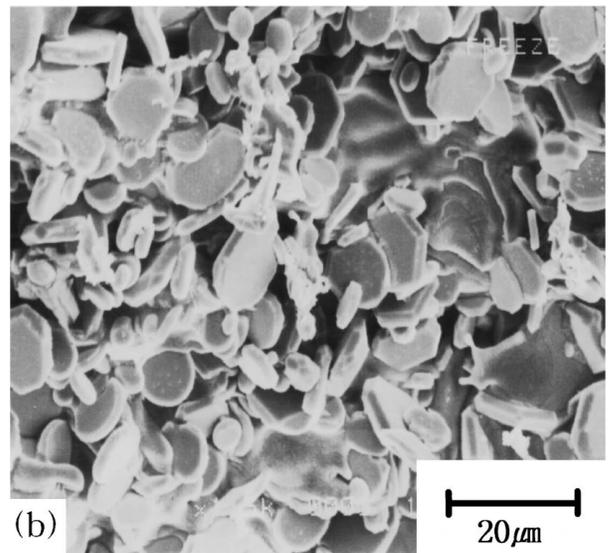
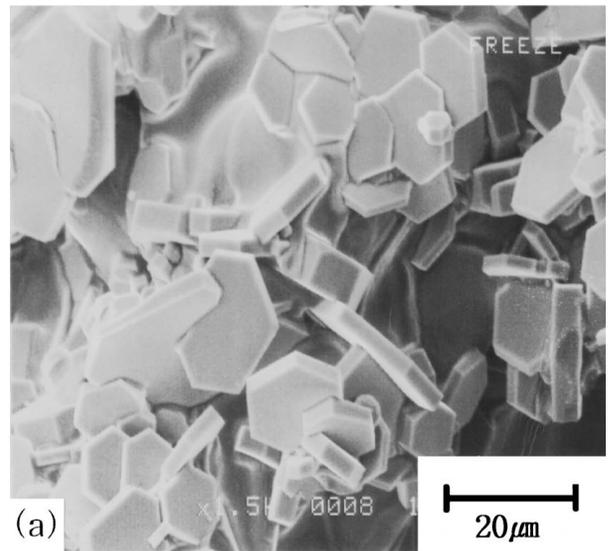


Figure 5 SEM photograph of fracture surface of the molten phase separated for Fe_2O_3 : Al (molar ratio) additives. (a) 1 : 1; (b) 1 : 2; (c) 1 : 3.

from adiabatic reaction conditions, due to heat losses through various modes. Fig. 2 shows photographs of the surface of combustion products with Fe_2O_3 and further Al additions to a stoichiometric mixture of ZrO_2 , B_2O_3 and Al. The appearance of all combustion products

was observed in the molten state at combustion temperature. In adding $\text{Fe}_2\text{O}_3 : \text{Al} = 0.5 : 0, 1.5 : 1-2$ (molar ratio), only large voids existed in the inner continuous slag, while in $\text{Fe}_2\text{O}_3 : \text{Al} = 0.5 : 1-3, 1.5 : 0$ (molar ratio), small solid particles precipitated or segregated from the slag. However, in combustion products with $\text{Fe}_2\text{O}_3 : \text{Al} = 1 : 1-3, 1.5 : 3$ (molar ratio) additions, the cast structure of the molten state existed in the inner slag, and it could be easily separated from the slag, compared with other mixtures containing added Fe_2O_3 and Al. These results are shown in a semi-quantitative manner in Fig. 3. For the cast materials thoroughly separated from combustion products with $\text{Fe}_2\text{O}_3 : \text{Al} = 1 : 1-3$ (molar ratio) additions, the densities of these casts were 83.2% (1 : 1), 92.3% (1 : 2) and 97.3% (1 : 3) of the theoretical, respectively. The change in crystalline phases on relative molar ratio of Fe_2O_3 and Al was investigated by XRD of the surface of the casts (Fig. 4). In all these casts, ZrB_2 , Fe, FeB_2 and Zr_2Fe diffraction peaks were observed and no Al or $\alpha\text{-Al}_2\text{O}_3$ peaks were detected. From the results, it was confirmed that ZrB_2 based cast materials wholly separated from the slag containing mainly $\alpha\text{-Al}_2\text{O}_3$ could be obtained. This phenomenon may be explained in terms of the differences in specific gravity in the liquid state. The specific gravity of Al_2O_3 (3.9) is significantly lower, compared with ZrB_2 (6.1) and liquid-Fe (7.9). Also, FeB_2 and Zr_2Fe as intermediate phases might be responsible for the prevention of solid solution of Zr into liquid Fe-side and B into liquid Fe-side as a result of the non-equilibrium nature of the combustion process. It has been reported [9, 10] that (i) at 800 °C, intermediate compounds do not exist in the Zr-B-Fe system; (ii) there are solid solution regions of a small amount of Fe in the Zr-side and a minor amount of Zr or B in the Fe-side; and (iii) ZrFe_2 , $\text{Zr}_6\text{Fe}_{23}$, FeB and FeB_2 are known as intermediate phases. Fig. 5 shows the SEM photographs of fracture surfaces of the cast materials. The microstructures were significantly different with different added ratios of Fe_2O_3 and Al in spite of similar combustion condition. At $\text{Fe}_2\text{O}_3 : \text{Al} = 1 : 1$ (molar ratio) addition, the ZrB_2 grains on the surface of molten phases were present as hexagonal platelets with equal length edges (Fig. 5a), while at $\text{Fe}_2\text{O}_3 : \text{Al} = 1 : 2-3$ (molar ratio), disk- and hexagonal-platelets coexisted (Fig. 5b and c). In addition, their grain sizes were

different according to the added ratio of Fe_2O_3 and Al. In particular, the average grain size ($\sim 20 \mu\text{m}$) for the addition of $\text{Fe}_2\text{O}_3 : \text{Al} = 1 : 3$ (molar ratio) (Fig. 5c) was remarkably large compared to that ($\sim 12 \mu\text{m}$) of $\text{Fe}_2\text{O}_3 : \text{Al} = 1 : 2$ (molar ratio) (Fig. 5b). These differences in grain size are attributed to the difference in the extent of liquid phase formation during the combustion reaction [11]. An increase in adiabatic combustion temperature due to higher exothermic reaction will result in the formation of larger amounts of liquid. The influence of the amount of liquid phase formation during combustion reaction on the grain growth of casting materials may be considered in two contrary viewpoints: (i) an increase in the amount of liquid phase may inhibit grain growth of ZrB_2 by Ostwald ripening [12]; and (ii) it may lead to the grain growth due to the prolonged duration for releasing more latent heat during rapid cooling process.

In conclusions, on adding Fe_2O_3 and additional Al (1 : 1-3, 1.5 : 3 (molar ratio)), ZrB_2 based cast materials, which separated easily from the slag, could be produced from a stoichiometric mixture of ZrB_2 , B_2O_3 and Al by SHS reaction. The resulting ZrB_2 particles exhibited hexagonal or disk plate-like shapes on solidification.

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