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R. V. KRISHNARAO

*Defence Metallurgical Research Laboratory, Kanchanbagh, Hyderabad-500058, India*

R. SANKARASUBRAMANIAN

*Defence Metallurgical Research Laboratory, Kanchanbagh, Hyderabad-500058, India*

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# Thermite assisted synthesis of $ZrB_2$ and $ZrB_2$ -SiC through $B_4C$ reduction of $ZrO_2$ and $ZrSiO_4$ in air

R. V. KRISHNARAO\*, R. SANKARASUBRAMANIAN

*Defence Metallurgical Research Laboratory, Kanchanbagh, Hyderabad-500058, India*

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**Abstract:**  $ZrB_2$  and  $ZrB_2$ -SiC powders have been produced by reducing  $ZrO_2$  and  $ZrSiO_4$  with  $B_4C$  without using any furnace. Magnesium was added to the mixtures of ( $ZrO_2+B_4C$ ) and ( $ZrSiO_4+B_4C$ ). The reaction has been assisted by a floral thermite packed around the compacts. By introducing elemental Si into ( $ZrO_2+B_4C$ ) mixture, composite powders of  $ZrB_2$ -SiC formed. After leaching out MgO with suitable HCl water solution, the product was analysed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The effect of Si,  $B_4C$ , and Mg on the extent of formation of  $ZrB_2$ ,  $ZrB_2$ -SiC, and other phases has been studied. Formation of nano-sized  $ZrB_2$  and  $ZrB_2$ -SiC composite powders was identified. The adaptability of the process for bulk production was examined.

**Keywords:**  $ZrB_2$ ;  $ZrO_2$ ; zircon ( $ZrSiO_4$ ); composites; synthesis

## 1 Introduction

Zirconium diboride ( $ZrB_2$ ) and its oxidation property are well known since 1969. It has unique combination of properties such as high melting point, high chemical stability, high hardness and strength, and high thermal and electrical conductivities. It is suitable for extreme thermal and chemical environments associated with hypersonic flight, rocket propulsion, and atmospheric re-entry [1–3]. Recently, the research on synthesis and sintering of  $ZrB_2$ -based composites has been accelerated because it is being considered for high speed air craft leading edges, as well as for structural parts in high temperature environments. The usage of  $ZrB_2$ -SiC-based composites is hampered due to the cost of  $ZrB_2$  powders and difficulty in fabricating large sizes or complex shapes.

A variety of synthesis routes [4–8] are practiced to

prepare  $ZrB_2$  powders: (i) reduction processes, (ii) chemical routes, and (iii) reactive processes. The reduction route using  $ZrO_2$  as a source of zirconium is much cheaper than other processes. The common reduction reactions include: reduction of  $ZrO_2$  with ( $B_2O_3+C$ ), ( $B_4C+C$ ), or boron. In the final powders, ZrC, C, and B are typical impurities. Commercial  $ZrB_2$  powders are produced by carbothermal reduction of  $ZrO_2$  and  $B_2O_3$ . The as-produced  $ZrB_2$  is agglomerated and requires extensive pulverization to improve the sinterability by decreasing the particle size. But impurities introduced during pulverization and oxygen from surface oxidation of fine size particles deteriorate the densification behavior and properties of final  $ZrB_2$ -based composites [9,10].

The preparation of  $ZrB_2$  powders by reducing  $ZrO_2$  with  $B_4C$  is studied extensively [11]. Synthesis temperature and morphology of  $ZrB_2$  are shown to be altered with change in source of carbon and reaction atmosphere [12]. In our previous work, the formation of pure  $ZrB_2$  by reducing  $ZrO_2$  with  $B_4C$  was reported [13].

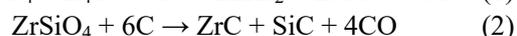
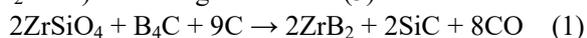
\* Corresponding author.  
E-mail: rvkr4534@yahoo.com

Further, by adding silicon to the reaction mixture of ( $ZrO_2+B_4C$ ), composite powders of  $ZrB_2-SiC$  with particle sizes from sub-micron to nanometer have been produced by rapid heating in air furnace. Self-propagating high temperature synthesis (SHS) is used as an alternative technique to produce ultra-fine powders of zirconium-based composites [14–16]. Khanra *et al.* [14] reported the synthesis of  $ZrB_2$  fine powders using double combustion of  $ZrO_2-Mg-H_3BO_3$  mixture. Using NaCl as diluent to control the particle size,  $ZrB_2$  powders of 75–125 nm in size was produced. Akkas *et al.* [17] studied the production of  $ZrB_2$  powders by SHS method using  $ZrO_2-B_2O_3-Mg$  powder mixture.

By employing simple and economical synthesis route,  $ZrB_2$ -based ceramics can be fabricated at low cost. Zircon sand ( $ZrSiO_4$ ) is more abundant and much cheaper than  $ZrO_2$ . Zircon sand is used to prepare  $ZrO_2$  through caustic fusion, dissolution, solvent extraction, precipitation, and calcination. Zircon can be used instead of  $ZrO_2$  to synthesize pure  $ZrB_2$  and  $ZrB_2-SiC$  powders [18]. If Zr and Si in  $ZrSiO_4$  are fully converted into  $ZrB_2$  and SiC, the resultant powder mixture will contain about 25 wt% of SiC. Consequently, highly homogeneous and ultra-fine  $ZrB_2-SiC$  composite powders are expected from zircon.

Ryu *et al.* [19] prepared ultra-fine powders of  $ZrB_2$  and  $ZrB_2-SiC$  via combustion synthesis using  $ZrSiO_4$ , Mg, C, B, and NaCl as raw materials. Impurities like Si, ZrSi, ZrC, or their combination have been noticed. Jalaly *et al.* [20] reported mechano-synthesis of nano composite of  $ZrB_2-SiC-ZrC$  by magnesiothermic self-sustaining reaction using  $Mg/B_2O_3/ZrSiO_4/C$  system. Recently, preparation of  $ZrB_2-SiC$  composite powders from zircon ( $ZrSiO_4$ ), activated carbon (C), and boron oxide ( $B_2O_3$ ) via microwave-assisted reduction was reported [21].

The conventional carbo-borothermal reduction (reaction (1)) process using  $ZrSiO_4$ ,  $B_4C$ , and C generally forms  $B_2O_3$  or borosilicate glass. The liquid phases promote the rapid grain growth of  $ZrB_2$  particles and suppress the formation of SiC. Oh *et al.* [22] synthesized  $ZrB_2-SiC$  powders in a two-step process following reactions (2) and (3) without forming borosilicate glass. Initially ZrC and SiC are formed by carbothermal reduction of zircon by reaction (2). The resultant ( $ZrC+SiC$ ) is heated with  $B_4C$ , to form ( $ZrB_2+SiC$ ) according to reaction (3).

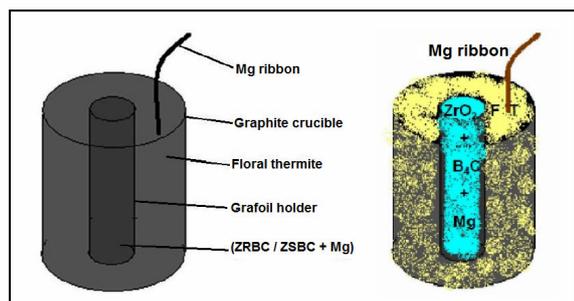


There is a necessity to develop a simple and economical process to produce pure powders of  $ZrB_2$  and  $ZrB_2-SiC$ , free from impurities like  $ZrO_2$ , ZrC, C, and borosilicate using relatively cheaper and abundantly available raw material zircon. Krishnarao [18] studied the formation of  $ZrB_2$  or  $ZrB_2-SiC$  free from impurities in a single step by reacting zircon with excess  $B_4C$  and without adding free carbon. However, there is no literature on SHS of  $ZrB_2$  or  $ZrB_2-SiC$  using ( $ZrO_2+B_4C+Mg$ ) or ( $ZrSiO_4+B_4C+Mg$ ) as raw materials. In the present work, the possibility of preparing pure powders of  $ZrB_2$  or  $ZrB_2-SiC$  by reacting  $ZrO_2/ZrSiO_4-B_4C-Mg$  with the assistance of floral thermite (FT) has been explored.

## 2 Experimental

$ZrO_2$  powders were supplied by Nuclear Fuel Complex, Hyderabad, India. Milled zircon of -325# was supplied by Remet UK Ltd.  $B_4C$  powders were supplied by China Abrasives, Zingzhou, China. Elemental Si of -325# and Mg of 100–500  $\mu m$  in size were supplied by the Metal Powder Company Ltd., Thirumangalam, India.

Initially,  $ZrO_2$  and  $B_4C$  were taken in two weight ratios of  $ZrO_2/B_4C=2.5$  and 1.6 to obtain single phase  $ZrB_2$  and  $ZrB_2$  with excess  $B_4C$  after the reaction [13]. Using agate pot and  $Al_2O_3$  balls, dry mixing was carried out for 8 h. These mixtures are designated as ZRBC2.5 and ZRBC1.6, respectively. 30 wt% of Mg was added to ZRBC2.5 and ZRBC1.6 to examine the possibility of self-sustaining reaction. Further, elemental Si of 15 wt% and 20 wt% was added to ZRBC2.5 and ZRBC1.6 respectively to obtain  $ZrB_2-SiC$  and  $ZrB_2-SiC-B_4C$  composite powders. The powder mixtures were taken in cylindrical holder of grafoil of 12 mm in diameter. The samples taken in grafoil holder were placed in graphite crucible of 50 mm in inner diameter and 2.5 mm in wall thickness, as shown in Fig. 1. The annular gap between the graphite crucible and grafoil sample holder was filled with FT used in domestic fireworks. Thermite containing potassium nitrate, sulphur, 3–9 mm aluminium flakes, and charcoal is known to burn with white bright sparkles. A magnesium ribbon was placed to ignite the FT. Without using floral thermite, the ZRBC samples with Mg, Si, or Mg+Si were also tried to react by igniting with Mg ribbon.



**Fig. 1** Schematic diagram showing the arrangement of ZRBC powder samples for FT assisted reaction.

Further, the Mg content was increased to 50 and 60 wt% with and without Si. Compacts of 30 mm in diameter and 10 mm in thickness were made by manual pressing with hammer on the top punch in steel die. Poly vinyl alcohol (PVA) in water solution was used as binder. The green compacts were dried in oven at 100 °C for 6 h. The dried compacts were placed on FT kept in graphite crucible. Approximately 7 g of FT was used to cover the samples and ignited with Mg ribbon.

In the case of zircon,  $ZrSiO_4$  and  $B_4C$  were taken in two weight ratios of  $ZrSiO_4/B_4C=3.3$  and 2.5, designated as ZSBC3.3 and ZSBC2.5 respectively.  $ZrSiO_4$  and  $B_4C$  reacted in above ratios were shown to form pure  $ZrB_2$  and  $ZrB_2-SiC$  composite powders [18]. Two kinds of quantity of Mg (24 and 40 wt%) were added to ZSBC samples.

After studying the formation of different phases in ZRBC, 1 kg bulk sample of ZRBC2.5 with 15 wt% Si and 30 wt% Mg was made. The compact was placed on FT spread on an alumina insulation brick kept in a stainless steel tray. The sample was totally covered with FT, and Mg ribbon was inserted into FT on four sides. After reacting by igniting the Mg ribbon, sand was thrown on the red hot mass to avoid oxidation of sample during cooling to room temperature.

The successfully reacted sample was collected and crushed using pestle and mortar. The hand ground powders were subjected to leaching with HCl water solution of 0.6–2.0 M concentrations for 0.5 h to eliminate MgO. The filtrate was thoroughly washed with water before drying in an oven at 100 °C. The dried acid treated sample was subjected to X-ray diffraction (XRD) analysis. A Philips X-ray diffractometer, model PW3710, with Cu  $K\alpha$  radiation through Ni filter, was used. A scanning electron microscope (SEM) supplied by FEI Quanta 400, the Netherlands, was used to study the morphology of the reacted powders.

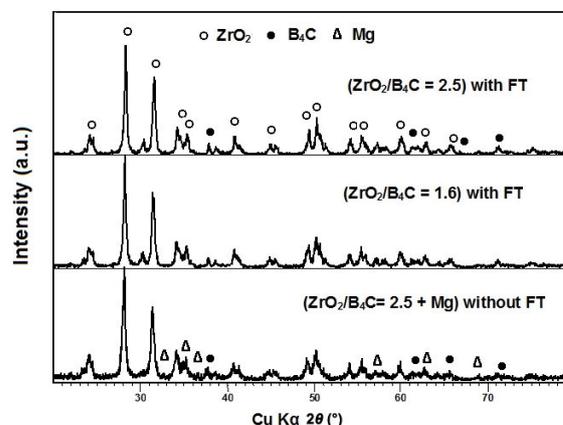
Further, 100 g reacted bulk ZRBC2.5 with 15 wt% Si

and 30 wt% Mg was taken in an agate pot, and grinding was carried out using  $Al_2O_3$  balls for 8 h. 10 g fine ground powder sample was collected and leached with 1.48 M HCl water solution for 1.5 h to eliminate MgO. The filtrate was thoroughly washed with water and dried in an oven. The carbon and oxygen analysis was carried out with an LECO, model CS444, USA. The dried leached sample was fused with 3:1 ( $Na_2CO_3:K_2CO_3$ ) and dissolved in 1:1 ( $HCl:H_2O$ ), followed by 1:5 ( $H_2SO_4:HNO_3$ ) and 1–2 drops of HF. Elemental analysis of Zr, B, Si, and Mg has been carried out on inductively coupled plasma optical emission spectrometer (ICPOES), model Ultima expert of Hariba, France.

### 3 Results and discussion

#### 3.1 Necessity of FT and Mg

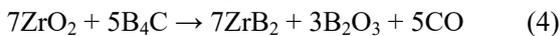
The XRD patterns of ZRBC2.5 and ZRBC1.6 ignited with Mg ribbon are shown in Fig. 2. No new phases have been observed in the XRD patterns. In both samples, there is no reaction even after completion of FT reaction. The FT reaction alone could not raise the temperature of the samples to bring the reaction between  $ZrO_2$  and  $B_4C$ . During the  $B_4C$  reduction of  $ZrO_2$ , the formation of  $ZrB_2$  is reported at and above a temperature of 1250 °C [13]. The change in standard Gibbs free energy ( $\Delta G^\circ$ ) at elevated temperatures can offer information about the feasibility of reactions. Gibbs free energies for the reactions at various temperatures were calculated using the data of energy of formation of the substances listed in Ref. [23] by subtracting the total free energy of the reactants from



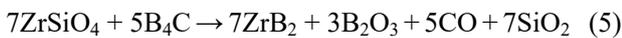
**Fig. 2** XRD patterns of ZRBC unreacted samples.

that of the products, at the respective temperatures. Adiabatic temperatures of reactions were calculated using the enthalpy data in the same reference by equating the total enthalpy of the reactants at 25 °C to that of the products at the adiabatic temperature using linear interpolation method.

Thermodynamic calculations in Fig. 3 show that the reactions (4) and (5) are feasible at and above a temperature of 1250 °C (1523 K). Since the thermal conductivity of ZrO<sub>2</sub> is very low, FT reaction alone cannot raise the temperature of the total ZRBC sample to 1250 °C (1523 K). For the similar reason without FT assistance, Mg in ZRBC sample was not ignited/oxidized (Fig. 2) to form MgO. With the assistance of FT, Mg in ZRBC sample can ignite/oxidize and favor the reaction between ZrO<sub>2</sub> and B<sub>4</sub>C.



$$\Delta G_{298}^\circ = +1000.0 \text{ kJ/g}, \Delta H_{298}^\circ = +1239.2 \text{ kJ/g}$$



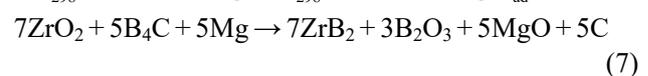
$$\Delta G_{298}^\circ = +789.4 \text{ kJ/g}, \Delta H_{298}^\circ = +974.5 \text{ kJ/g}$$

When both oxides of Zr and B are used as raw materials, the reduction with Mg (reaction (6)) is feasible at all temperatures (Fig. 3). Since this reaction satisfies the Merzhanov criterion [24], it can progress in self-sustaining manner. The adiabatic combustion temperature ( $T_{\text{ad}}$ ), the maximum temperature that can be attained for a given reaction system, is broadly used to determine the feasibility of an SHS reaction. If the adiabatic temperature  $T_{\text{ad}} \geq 1800 \text{ K}$ , the SHS reaction is possible according to Merzhanov criterion. The reaction (6) is highly exothermic and its adiabatic

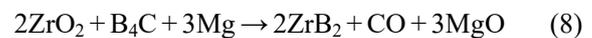
temperature ( $T_{\text{ad}} = 3148 \text{ K}$ ) is much higher than 1800 K. Although the reactions (7)–(9) are exothermic at all temperatures, they do not satisfy the Merzhanov criterion. The  $T_{\text{ad}}$  of reactions (7)–(9) (1162, 1183, and 896 K, respectively) are very much lower than 1800 K. They are considered as ordinary reactions. The experimental results and thermodynamic calculations clearly show that the reactions (7)–(9) cannot progress in a self-sustaining manner and require external heating source. With the assistance of external heating by FT and *in situ* heating by Mg, the reaction between ZrO<sub>2</sub> and B<sub>4</sub>C is feasible without a furnace.



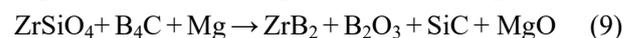
$$\Delta G_{298}^\circ = -2959.8 \text{ kJ/g}, \Delta H_{298}^\circ = -3052.0 \text{ kJ/g}, T_{\text{ad}} \approx 3148 \text{ K}$$



$$\Delta G_{298}^\circ = -809.2 \text{ kJ/g}, \Delta H_{298}^\circ = -826.9 \text{ kJ/g}, T_{\text{ad}} \approx 1162 \text{ K}$$



$$\Delta G_{298}^\circ = -882.2 \text{ kJ/g}, \Delta H_{298}^\circ = -783.2 \text{ kJ/g}, T_{\text{ad}} \approx 1183 \text{ K}$$



$$\Delta G_{298}^\circ = -650.3 \text{ kJ/g}, \Delta H_{298}^\circ = -662.1 \text{ kJ/g}, T_{\text{ad}} \approx 896 \text{ K}$$

### 3.2 Effect of addition of silicon

Above results confirm the necessity of external heat source for the feasibility of reaction of Mg added ZRBS sample. With the assistance of FT, formation of ZrB<sub>2</sub> has been observed in XRD patterns of ZRBC2.5 and ZRBC1.6 containing 30 wt% Mg (Fig. 4(a)). This is evident from the presence of MgO peak in XRD patterns. Addition of elemental Si to ZRBC2.5 and ZRBC1.6 results in the formation of ZrB<sub>2</sub>-SiC. In ZRBC1.6, a small peak of unreacted or excess B<sub>4</sub>C has also been observed. The reacted samples were leached with HCl water solution of 0.6–2.0 M concentrations. Even after repeated leaching for three times with low concentrated (0.6 M) HCl solution, MgO in reacted ZRBC samples could not be eliminated. MgO in reacted samples could be eliminated by leaching with 1.5 M HCl (Fig. 4(b)).

In the XRD pattern of acid treated ZRBC2.5 (Fig. 4(b)), peaks of ZrO<sub>2</sub> and ZrC are observed. According to reaction (7), the required weight ratio of ZrO<sub>2</sub>/B<sub>4</sub>C is ~3. During the reduction of ZrO<sub>2</sub> with B<sub>4</sub>C (reaction (4)) by heating in furnace, excess B<sub>4</sub>C (ZrO<sub>2</sub>/B<sub>4</sub>C = 2.5) is required to compensate the loss of B<sub>2</sub>O<sub>3</sub> and to form a single phase ZrB<sub>2</sub> [13]. In FT assisted reaction, the B<sub>4</sub>C content in ZRBC2.5 is not adequate to complete the

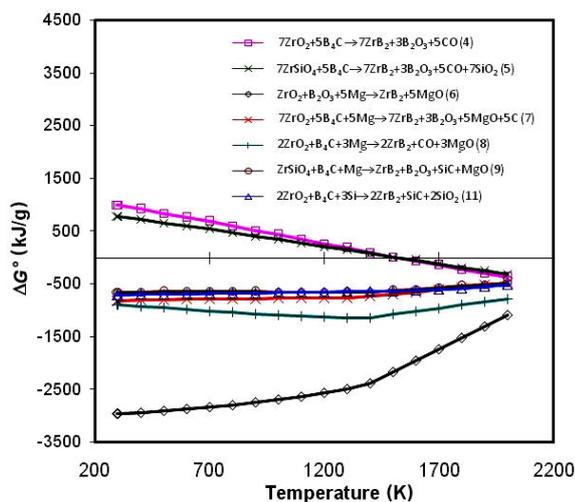


Fig. 3 Gibbs free energy of different reactions as a function of temperature.

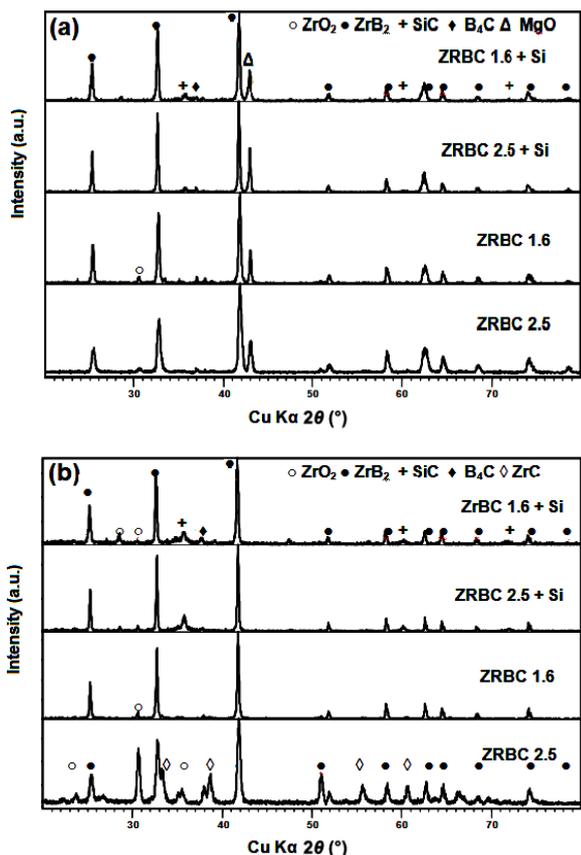


Fig. 4 XRD patterns of ZRBC samples (a) after FT assisted reaction and (b) after leaching with HCl acid.

reduction of  $ZrO_2$ . This conclusion is further supported with the absence of ZrC peak in acid treated ZRBC1.6 containing excess  $B_4C$ . It is interesting to notice the absence of ZrC peak in ZRBC2.5 with addition of 15 wt% Si. Compared to furnace heating, the FT assisted synthesis (with Mg in ZRBC) requires more quantity of  $B_4C$ . This is due to dilution effect of Mg present in ZRBC or higher loss of  $B_2O_3$  due to rapid heating to very high temperature. When Si is also present in the ZRBC system, the reduction of  $ZrO_2$  has led to completion by decreasing the dilution effect of Mg or loss of  $B_2O_3$ . This could be due to the reaction of Si with  $B_4C$  to form SiC and B. B reduces  $ZrO_2$  to form  $ZrB_2$ . With Si addition,  $ZrB_2$ -SiC and  $ZrB_2$ -SiC- $B_4C$  are identified as the major phases in ZRBC2.5 and ZRBC1.6 respectively after treatment with HCl acid.

Treatment of ZRBC samples after FT assisted reaction with concentrated HCl, has been found to oxidize the  $ZrB_2$  (Fig. 5(a)). The EDS analysis in Fig. 5(b) also reveals the oxidation of  $ZrB_2$  upon treatment with concentrated HCl acid. This could be due to very fine size of  $ZrB_2$  formed in FT assisted synthesis. SEM images of typical FT assisted synthesized  $ZrB_2$  (from

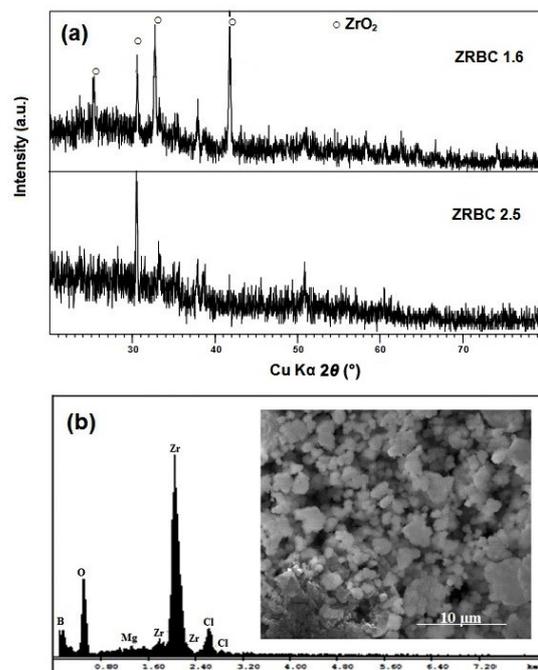


Fig. 5 (a) XRD patterns and (b) SEM image and EDS analysis of ZRBC after FT assisted reaction and leaching with concentrated HCl acid.

ZRBC2.5 and ZRBC1.6) and ( $ZrB_2$ +SiC) (from ZRBC2.5 with silicon and ZRBC1.6 with silicon), are shown in Fig. 6. The particle sizes in all samples are very fine on the order of nanometer. Rapid heating of compacts of ( $ZrO_2$ + $B_4C$ +Si) in furnace is shown to form fine sub-micron-sized  $ZrB_2$ -SiC [13]. Under the influence of Mg and FT, the rate of reaction is very high and leads to the formation of nanoparticles of  $ZrB_2$  and ( $ZrB_2$ +SiC).

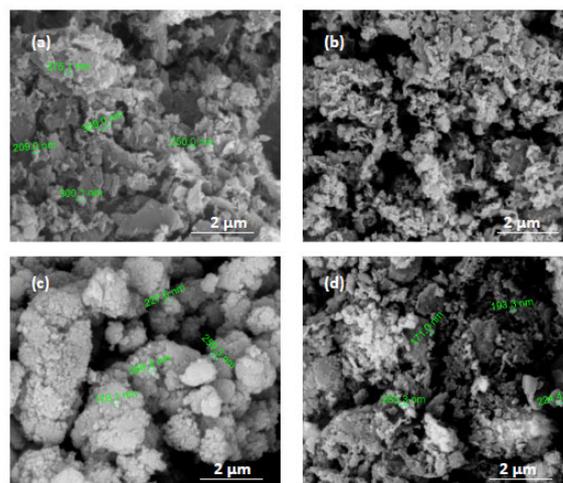


Fig. 6 SEM images after FT assisted synthesis and leaching with 1.5 M HCl: (a) and (c)  $ZrB_2$  from ZRBC2.5 and ZRBC1.6 respectively, (b) and (d) ( $ZrB_2$ +SiC) from ZRBC2.5+Si and ZRBC1.6+Si respectively.

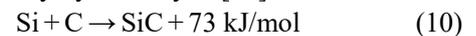
### 3.3 Effect of Mg content

FT assisted reaction has been carried out by increasing the Mg content from 30 to 50 and 60 wt% in ZRBC2.5 and ZRBC1.6 with and without silicon. The intensities of peaks of  $ZrO_2$  and ZrC are found to decrease with increase in Mg content in ZRBC2.5 (Fig. 7(a)). The maximum attainable temperature of ZRBC sample can increase with increase in the Mg content and favour the extent of completion of reaction. But the residual MgO after acid treatment has increased with increase in initial Mg content. Since all the samples are subjected to similar acid treatment, the MgO in samples with high initial Mg content is not totally eliminated. Total elimination of MgO appears to be possible by using sufficient quantity of acid solution and appropriate duration of acid treatment.

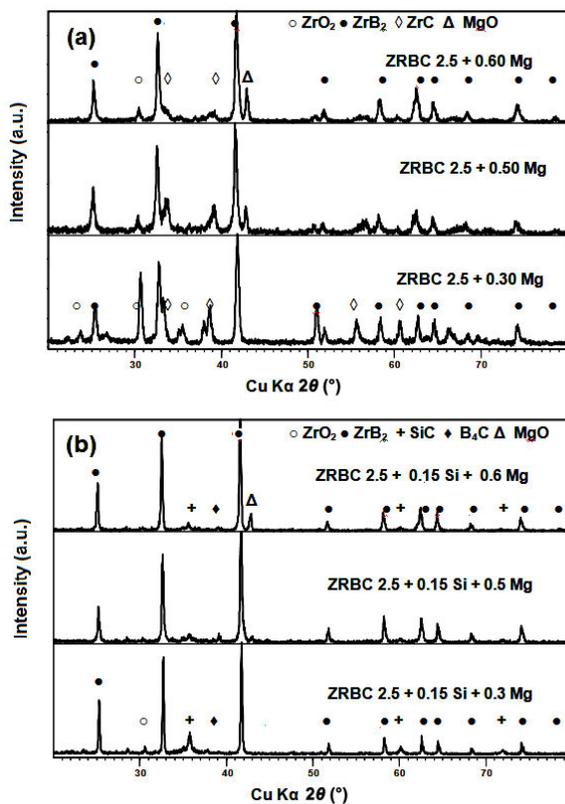
With the addition of 15 wt% Si to ZRBC2.5, appearance of SiC and absence of ZrC are observed in XRD patterns (Fig. 7(b)). Further, increase in Mg content has led to the increase in residual MgO. This is a clear evidence for addition of silicon favouring the completion of reaction. Similarly, by increasing the  $B_4C$  content in ZRBC1.6, the reaction is completed with

peaks of negligible intensity for  $ZrO_2$  and ZrC (Fig. 8(a)). But additional increase in Mg content has led to the incomplete reaction and reappearance of peaks for  $ZrO_2$  and ZrC. The increased quantity of Mg causes increase in loss of  $B_2O_3$  and dilution for reaction between main reactants  $ZrO_2$  and  $B_4C$ . The intimacy between  $ZrO_2$  and  $B_4C$  will decrease and lead to incomplete reaction. This dilution effect or loss of  $B_2O_3$  is nullified with the addition of 20 wt% Si to ZRBC1.6 (Fig. 8(b)). Formation of SiC and peak for excess  $B_4C$  have been noticed. However, the residual MgO content increases with increase in initial Mg in the sample.

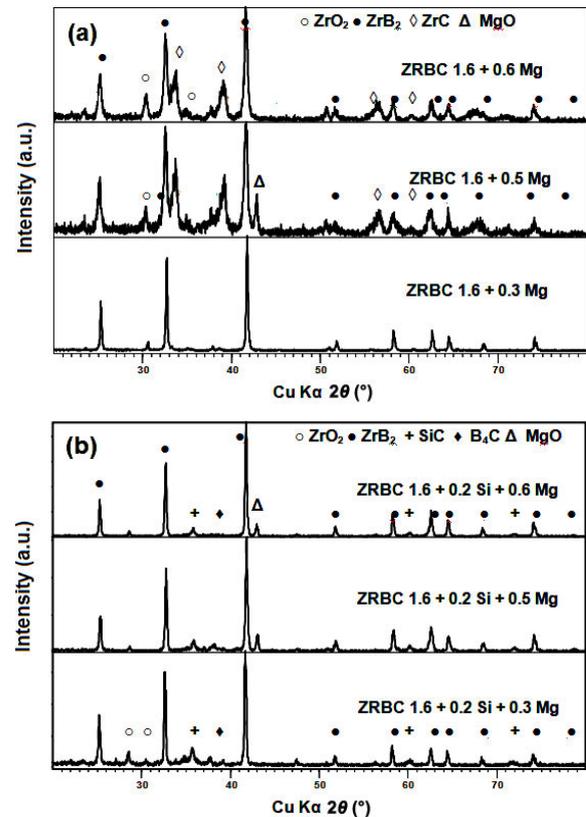
From above results, the role of Si is found to be very critical and important. To examine the possibility of self-sustained reaction, a compact of (ZRBC2.5+15 wt% Si+30 wt% Mg) was ignited with Mg ribbon without the assistance of FT. But the sample was not reacted. The reaction (10) between Si and C has been studied extensively by Mukasyan [25]:



Reaction (10) has a moderate enthalpy of product formation and thus has relatively border line adiabatic combustion temperature ( $T_{ad} = 1860 \text{ K}$ ) for SHS mode.



**Fig. 7** Effect of Mg content on (a) ZRBC2.5 and (b) ZRBC2.5+Si. XRD patterns are after FT assisted reaction and leaching with HCl acid.



**Fig. 8** Effect of Mg content on (a) ZRBC1.6 and (b) ZRBC1.6+Si. XRD patterns are after FT assisted reaction and leaching with HCl acid.

It is not easy to accomplish a self-sustained reaction in this system. To enhance the reactivity of Si–C system in SHS mode, several approaches have been developed: (i) preheating of the reactive media, (ii) addition of electrical field, (iii) chemical activation, (iv) synthesis in air/nitrogen systems, and (v) mechanical activation. Pampuch *et al.* [26] showed that preheating of the stoichiometric mixture of Si+C in the flow of argon gas, leads to the self-ignition mode at a temperature of ~1300 °C with formation of β-SiC powders. Even by rapid heating of (ZrO<sub>2</sub>+B<sub>4</sub>C+Si) compact by suddenly introducing into the furnace, formation of ZrB<sub>2</sub> and SiC was observed at and above a temperature of 1300 °C only [13].

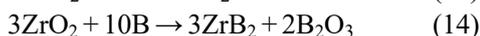
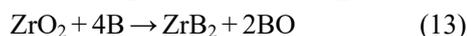


$$\Delta G_{298}^\circ = -700.1 \text{ kJ/g}, \Delta H_{298}^\circ = -710.1 \text{ kJ/g}, T_{\text{ad}} \approx 1175 \text{ K}$$

Thermodynamic calculations in Fig. 3 and  $T_{\text{ad}} = 1175 \text{ K}$  also suggest that reaction (11) is an ordinary reaction and cannot progress in self-sustaining manner. In ZRBC samples when Si is present, during FT assisted reaction, Si reacts with C in B<sub>4</sub>C at about 1300 °C to form SiC (reaction (12)). The boron released from B<sub>4</sub>C reacts with ZrO<sub>2</sub> to form ZrB<sub>2</sub> according to reaction (13). The reactions (12) and (13) require high temperatures for completion of reaction. The borothermal reaction to synthesize ZrB<sub>2</sub> powders has already been used by many researchers. Braton and Nicholls [27] used reaction (13) and obtained ZrB<sub>2</sub>+BO gas at 1150 °C. Peshev and Bliznakov [4] reported that a temperature of 1600 °C is needed for the completion of reaction of ZrO<sub>2</sub> with boron. Ran *et al.* [28] studied the borothermal reduction of nanometric ZrO<sub>2</sub> powders (reaction (13)) to synthesize sub-micron-sized ZrB<sub>2</sub> powders in vacuum. ZrO<sub>2</sub> was completely converted into ZrB<sub>2</sub> when thermally treated at a temperature of 1000 °C for 2 h in a vacuum.



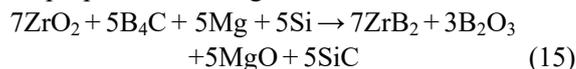
$$\Delta G_{298}^\circ = -3.6 \text{ kJ/g}, \Delta H_{298}^\circ = -25.1 \text{ kJ/g}, T_{\text{ad}} \approx 323 \text{ K}$$



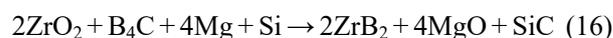
$$\Delta G_{298}^\circ = -221 \text{ kJ}, \Delta H_{298}^\circ = -219 \text{ kJ}, T_{\text{ad}} \approx 770 \text{ K}$$

Recently Guo *et al.* [29] reported the formation of fine ZrB<sub>2</sub> through borothermal reduction of coarse ZrO<sub>2</sub> (reaction (14)). Mg in the ZRBC samples raises the temperature and favours reactions (11)–(14). Thus the addition of silicon is found to favour the reduction reaction to proceed to completion. Reactions (15) and

(16) are proposed when Mg and Si are added to ZRBC:



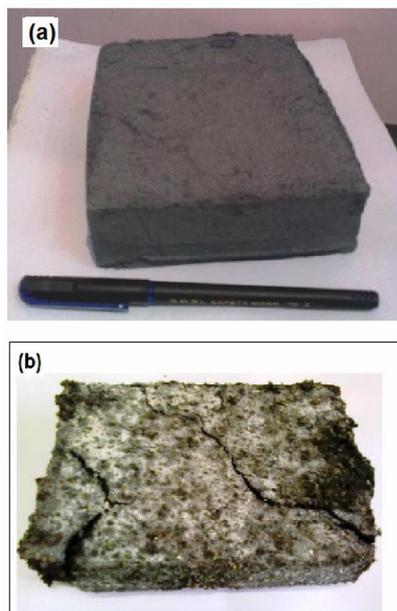
$$\Delta G_{298}^\circ = -981 \text{ kJ}, T_{\text{ad}} \approx 1343 \text{ K}$$



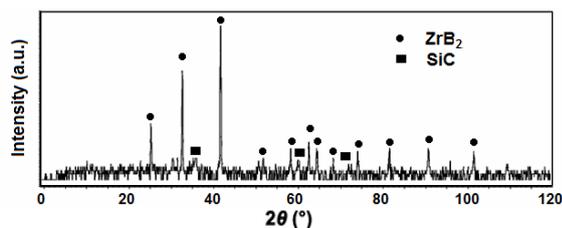
$$\Delta G_{298}^\circ = -1785.2 \text{ kJ}, T_{\text{ad}} \approx 2410 \text{ K}$$

The reaction (15) is exothermic but does not satisfy the Merzhanov criterion.  $T_{\text{ad}}$  of reaction (15) is much lower than 1800 K. Reaction (16) is highly exothermic and  $T_{\text{ad}}$  is much above 1800 K. But in this reaction, the quantities of B<sub>4</sub>C and Si are very low. Since the rate of heating during FT and Mg assisted reaction is very high, large excess of B<sub>4</sub>C is required to compensate the loss of B<sub>2</sub>O<sub>3</sub> (by sublimation) and to complete the reduction of ZrO<sub>2</sub>. The weight ratio of ZrO<sub>2</sub>/B<sub>4</sub>C required according to reaction (4) is ~3.0. Normal furnace heating requires a weight ratio of ZrO<sub>2</sub>/B<sub>4</sub>C=2.5 to compensate the loss of B<sub>2</sub>O<sub>3</sub> and to form single phase ZrB<sub>2</sub>. In FT and Mg assisted reaction (7) the weight ratio of ZrO<sub>2</sub>/B<sub>4</sub>C=2.5 is not adequate to complete the reduction of ZrO<sub>2</sub>. By increasing the B<sub>4</sub>C content as in ZRBC1.6 (Fig. 8(a)) or by adding Si to ZRBC2.5 (Fig. 7(b)), the reduction of ZrO<sub>2</sub> can be completed. In the present work, a weight ratio of Mg/Si = 2 is used whereas in the reaction (16) the weight ratio of Mg/Si = 3.47 and the weight ratio of ZrO<sub>2</sub>/B<sub>4</sub>C = 4.4. It is equal to increasing the Mg content without providing sufficient B<sub>4</sub>C or Si (Fig. 7(a)). Therefore, through reaction (16), it is not possible to obtain single phase ZrB<sub>2</sub> without impurities like ZrC and ZrO<sub>2</sub>. In this FT assisted synthesis, the main role of FT and Mg is generation of heat energy to raise the temperature to favour the reaction between ZrO<sub>2</sub> and B<sub>4</sub>C in ZRBC samples.

Considering the above results, the sample with composition (ZRBC2.5+15 wt% Si+30 wt% Mg) was selected for bulk synthesis of ZrB<sub>2</sub>–SiC. PVA water solution was used as binder and the above mixture was pressed in rectangular steel die by manual pressing with hammer on the top punch. After drying in an oven, the compact (Fig. 9(a)) was placed on FT spread on an alumina insulation brick. The sample was totally covered with FT. The FT was ignited with Mg ribbon. After the reaction, sand was thrown on the red hot mass to avoid the oxidation of sample during cooling to room temperature. The sample before and after FT assisted reaction is shown in Fig. 9. After grinding and leaching with 1.48 M HCl, the XRD pattern reveals the formation of ZrB<sub>2</sub> and SiC (Fig. 10). The chemical



**Fig. 9** Appearance of 1 kg bulk sample of (ZRBC2.5+15 wt% Si+30 wt% Mg): (a) before and (b) after FT assisted reaction.

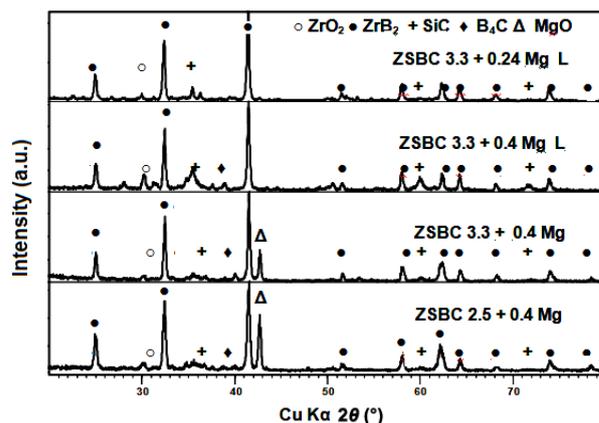


**Fig. 10** XRD pattern of 1 kg bulk sample of (ZRBC2.5+15 wt% Si+30 wt% Mg) after FT assisted reaction and leaching with HCl acid.

analysis of the  $ZrB_2$ -SiC composite powders obtained from 1 kg bulk ZRBC2.5 sample is: Zr 58.88 wt%, B 13.95 wt%, Si 18.68 wt%, C 8.10 wt%, O 0.23 wt%, and Mg 0.16 wt%. This result shows that the bulk production of clean  $ZrB_2$ -SiC powders free from impurities is possible by FT and Mg assisted reaction of  $ZrO_2$  with  $B_4C$  in open air.

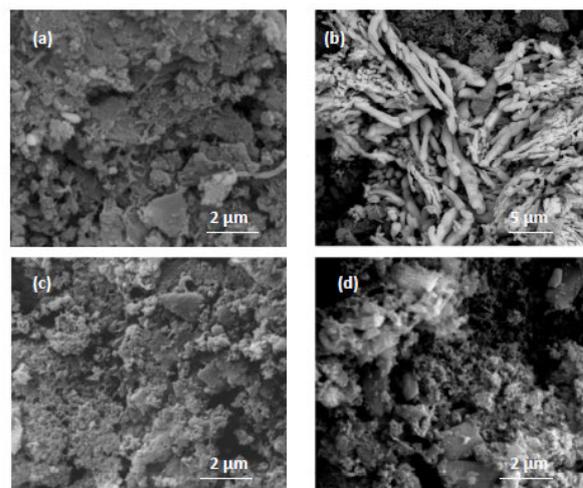
### 3. 4 FT assisted reduction of $ZrSiO_4$ with $B_4C$

Reduction of  $ZrSiO_4$  with  $B_4C$  (reaction (5)) is feasible at and above 1250 °C only. With the addition of Mg to ( $ZrSiO_4+B_4C$ ), reaction (9) is exothermic at all temperatures (Fig. 3). But the reaction cannot proceed in self-sustaining manner due to the  $T_{ad}$  of reaction (896 K) is much lower than 1800 K required for SHS mode. The XRD patterns of ZSBC samples reacted with FT assistance are shown in Fig. 11. In both samples of ZSBC3.3 and ZSBC2.5, formation of  $ZrB_2$  and SiC is



**Fig. 11** XRD patterns of ZSBC samples after FT assisted reaction. L means after leaching with HCl acid.

observed. The peak intensity of MgO in ZSBC2.5 is higher than that of MgO in ZSBC3.3. MgO could be eliminated by leaching with 1.48 M HCl. After elimination of MgO, peaks of low intensity for unreacted  $ZrO_2$  and  $B_4C$  are observed in ZSBC3.3 sample. This could be due to 40 wt% Mg in the sample which causes dilution for reaction between main reactants  $ZrSiO_4$  and  $B_4C$ . By decreasing the Mg content to 24 wt% in ZSBC3.3, the peak of unreacted  $B_4C$  is eliminated.  $ZrB_2$ -SiC composite powders are formed from (ZSBC3.3+24 wt% Mg) sample. The peak of very low intensity for  $ZrO_2$  could be due to oxidation of fine size  $ZrB_2$  during acid treatment. The SEM images in Fig. 12 show that  $ZrB_2$ -SiC composite formed from all ZSBC samples contain sub-micron-to-nanometer-sized particles.



**Fig. 12** SEM images of  $ZrB_2$ -SiC from (a) and (b) ZSBC3.3+24 wt% Mg, (c) ZSBC3.3+40 wt% Mg, and (d) ZSBC2.5+40 wt% Mg after FT assisted synthesis and leaching with 1.5 M HCl.

Thus the present results support the possibility of synthesizing  $ZrB_2$  and  $ZrB_2$ -SiC by reducing  $ZrO_2/ZrSiO_4$  with  $B_4C$  without using any furnace. The combination of floral thermite for external heating and Mg for *in situ* heating of the reactants is the main criterion for the success of the synthesis in air.

#### 4 Conclusions

Synthesis of  $ZrB_2$  and  $ZrB_2$ -SiC by reducing  $ZrO_2$  and  $ZrSiO_4$  with  $B_4C$  without using any furnace has been studied. Magnesium was added to the mixtures of ( $ZrO_2+B_4C$ ) and ( $ZrSiO_4+B_4C$ ), and the reaction has been assisted by a floral thermite packed around the compacts. By introducing elemental Si into ( $ZrO_2+B_4C$ ) mixture, composite powders of  $ZrB_2$ -SiC have been formed. The concentration of HCl water solution was optimised to eliminate the MgO in the synthesized samples. The effect of Si,  $B_4C$ , and Mg on the extent of formation of  $ZrB_2$ ,  $ZrB_2$ -SiC, and other phases has been studied. Formation of nanometer-sized particles in  $ZrB_2$  and  $ZrB_2$ -SiC composite powders was identified. The suitability of the process for bulk production was examined.

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