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Research Article

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

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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].

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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 bee 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).

$$2ZrSiO_4 + B_4C + 9C \rightarrow 2ZrB_2 + 2SiC + 8CO \quad (1)$$

$$ZrSiO_4 + 6C \rightarrow ZrC + SiC + 4CO \quad (2)$$

$$2ZrC + B_4C \rightarrow 2ZrB_2 + 3C \quad (3)$$

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 μm 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.

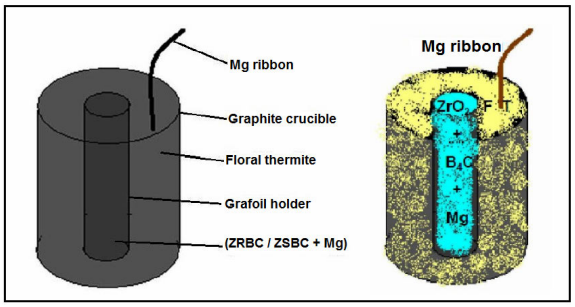

Fig. 1 Schematic diagram showing the arrangement of ZRBC powder samples for FT assisted reaction.

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 ℃ 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 ℃. The dried acid treated sample was subjected to X-ray diffraction (XRD) analysis. A Philips X-ray diffractometer, model PW3710, with Cu Kα 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 ℃ [13]. The change in standard Gibbs free energy (ΔG°) 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

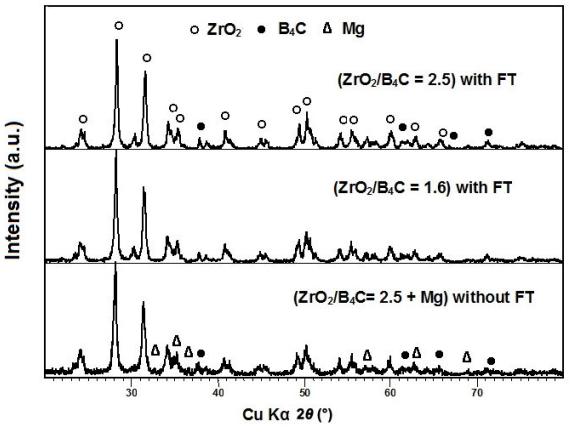

Fig. 2 XRD patterns of ZRBC unreacted samples.

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 ℃ 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 ℃ (1523 K). Since the thermal conductivity of ZrO_2 is very low, FT reaction alone cannot raise the temperature of the total ZRBC sample to 1250 ℃ (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_2 and B_4C.

$$7ZrO_2 + 5B_4C \rightarrow 7ZrB_2 + 3B_2O_3 + 5CO \quad (4)$$

$$\Delta G^\circ_{298} = +1000.0\ \text{kJ/g},\ \ \Delta H^\circ_{298} = +1239.2\ \text{kJ/g}$$

$$7ZrSiO_4 + 5B_4C \rightarrow 7ZrB_2 + 3B_2O_3 + 5CO + 7SiO_2 \quad (5)$$

$$\Delta G^\circ_{298} = +789.4\ \text{kJ/g},\ \ \Delta H^\circ_{298} = +974.5\ \text{kJ/g}$$

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_{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 $T_{ad} \geqslant 1800$ K, the SHS reaction is possible according to Merzhanov criterion. The reaction (6) is highly exothermic and its adiabatic temperature ($T_{ad} = 3148$ 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_{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_2 and B_4C is feasible without a furnace.

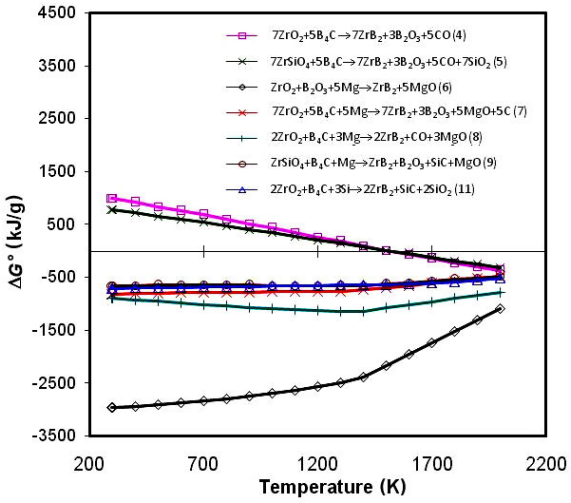

Fig. 3 Gibbs free energy of different reactions as a function of temperature.

$$ZrO_2 + B_2O_3 + 5Mg \rightarrow ZrB_2 + 5MgO \quad (6)$$

$$\Delta G^\circ_{298} = -2959.8\ \text{kJ/g},\ \Delta H^\circ_{298} = -3052.0\ \text{kJ/g},\ T_{ad} \approx 3148\ \text{K}$$

$$7ZrO_2 + 5B_4C + 5Mg \rightarrow 7ZrB_2 + 3B_2O_3 + 5MgO + 5C \quad (7)$$

$$\Delta G^\circ_{298} = -809.2\ \text{kJ/g},\ \Delta H^\circ_{298} = -826.9\ \text{kJ/g},\ T_{ad} \approx 1162\ \text{K}$$

$$2ZrO_2 + B_4C + 3Mg \rightarrow 2ZrB_2 + CO + 3MgO \quad (8)$$

$$\Delta G^\circ_{298} = -882.2\ \text{kJ/g},\ \Delta H^\circ_{298} = -783.2\ \text{kJ/g},\ T_{ad} \approx 1183\ \text{K}$$

$$ZrSiO_4 + B_4C + Mg \rightarrow ZrB_2 + B_2O_3 + SiC + MgO \quad (9)$$

$$\Delta G^\circ_{298} = -650.3\ \text{kJ/g},\ \ \Delta H^\circ_{298} = -662.1\ \text{kJ/g},\ \ T_{ad} \approx 896\ \text{K}$$

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_2 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_2–SiC. In ZRBC1.6, a small peak of unreacted or excess B_4C 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_2 and ZrC are observed. According to reaction (7), the required weight ratio of ZrO_2/B_4C is ~3. During the reduction of ZrO_2 with B_4C (reaction (4)) by heating in furnace, excess B_4C ($ZrO_2/B_4C = 2.5$) is required to compensate the loss of B_2O_3 and to form a single phase ZrB_2 [13]. In FT assisted reaction, the B_4C content in ZRBC2.5 is not adequate to complete the

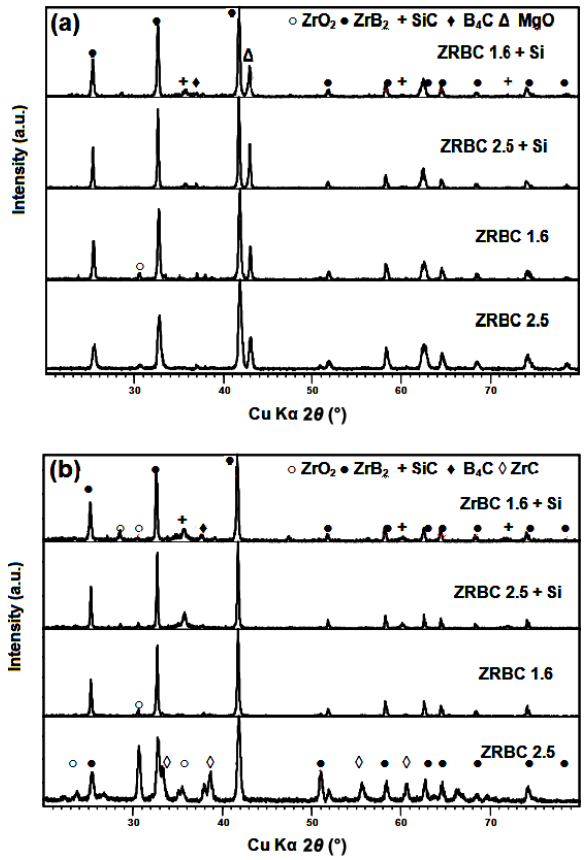

Fig. 4 XRD patterns of ZRBC samples (a) after FT assisted reaction and (b) after leaching with HCl acid.

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

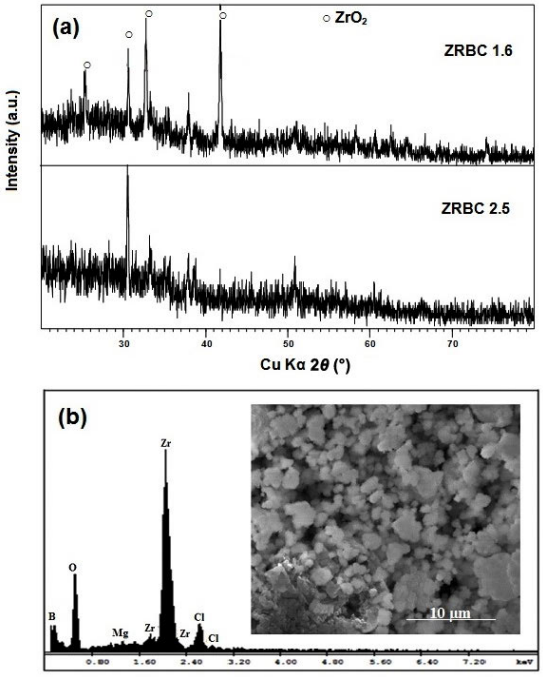

Fig. 5 (a) XRD patterns and (b) SEM image and EDS analysis of ZRBC after FT assisted reaction and leaching with concentrated HCl acid.

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).

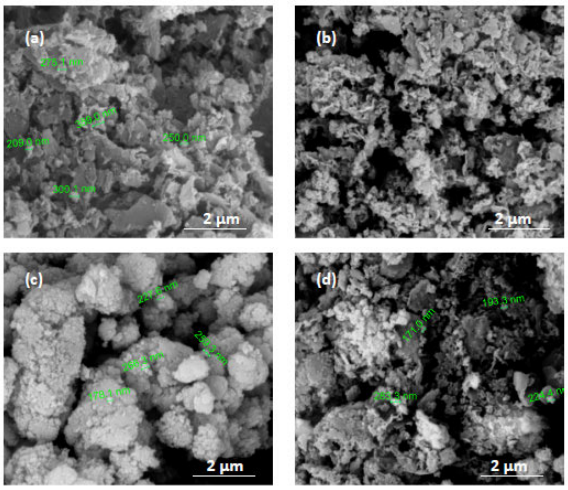

Fig. 6 SEM images after FT assisted synthesis and leaching with 1.5 M HCl: (a) and (c) ZrB_2 from ZRBC2.5 and ZRBC1.6 respectively, (b) and (d) (ZrB_2+SiC) from ZRBC2.5+Si and ZRBC1.6+Si respectively.

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]:

$$\mathrm{Si + C \rightarrow SiC + 73\ kJ/mol} \qquad (10)$$

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

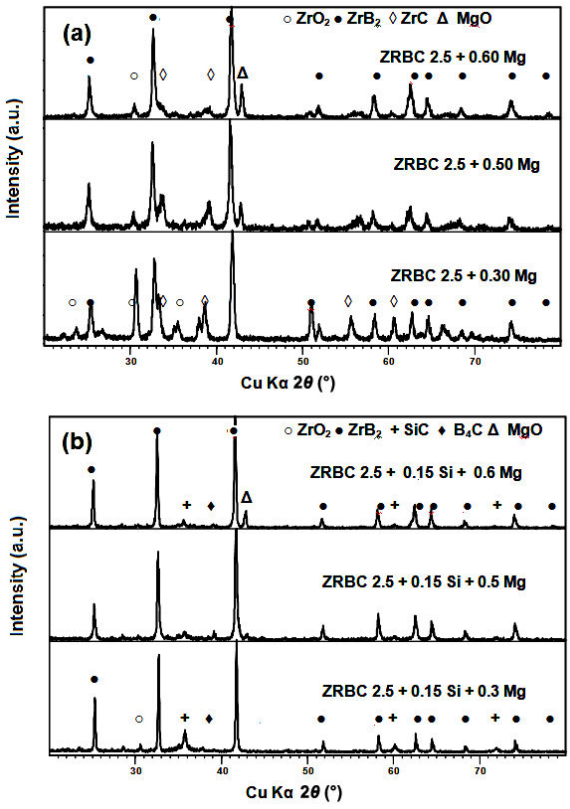

Fig. 7 Effect of Mg content on (a) ZRBC2.5 and (b) ZRBC2.5+Si. XRD patterns are after FT assisted reaction and leaching with HCl acid.

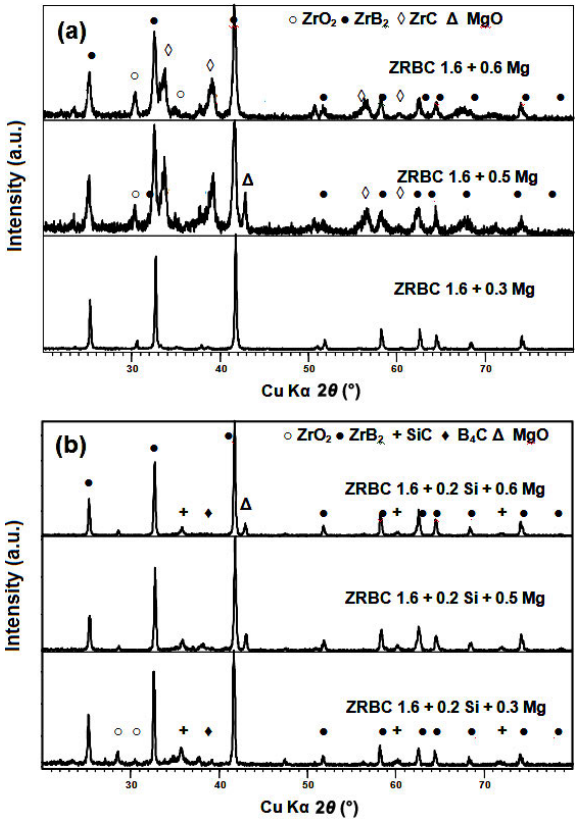

Fig. 8 Effect of Mg content on (a) ZRBC1.6 and (b) ZRBC1.6+Si. XRD patterns are after FT assisted reaction and leaching with HCl acid.

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 ℃ with formation of β-SiC powders. Even by rapid heating of (ZrO_2+B_4C+Si) compact by suddenly introducing into the furnace, formation of ZrB_2 and SiC was observed at and above a temperature of 1300 ℃ only [13].

$$2ZrO_2 + B_4C + 3Si \rightarrow 2ZrB_2 + SiC + 2SiO_2 \quad (11)$$

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

Thermodynamic calculations in Fig. 3 and T_{ad} = 1175 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_4C at about 1300 ℃ to form SiC (reaction (12)). The boron released from B_4C reacts with ZrO_2 to form ZrB_2 according to reaction (13). The reactions (12) and (13) require high temperatures for completion of reaction. The borothermal reaction to synthesize ZrB_2 powders has already been used by many researchers. Braton and Nicholls [27] used reaction (13) and obtained ZrB_2+BO gas at 1150 ℃. Peshev and Bliznakov [4] reported that a temperature of 1600 ℃ is needed for the completion of reaction of ZrO_2 with boron. Ran *et al.* [28] studied the borothermal reduction of nanometric ZrO_2 powders (reaction (13)) to synthesize sub-micron-sized ZrB_2 powders in vacuum. ZrO_2 was completely converted into ZrB_2 when thermally treated at a temperature of 1000 ℃ for 2 h in a vacuum.

$$B_4C + Si \rightarrow SiC + 4B \quad (12)$$

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

$$ZrO_2 + 4B \rightarrow ZrB_2 + 2BO \quad (13)$$

$$3ZrO_2 + 10B \rightarrow 3ZrB_2 + 2B_2O_3 \quad (14)$$

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

Recently Guo *et al.* [29] reported the formation of fine ZrB_2 through borothermal reduction of coarse ZrO_2 (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:

$$7ZrO_2 + 5B_4C + 5Mg + 5Si \rightarrow 7ZrB_2 + 3B_2O_3 + 5MgO + 5SiC \quad (15)$$

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

$$2ZrO_2 + B_4C + 4Mg + Si \rightarrow 2ZrB_2 + 4MgO + SiC \quad (16)$$

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

The reaction (15) is exothermic but does not satisfy the Merzhanov criterion. T_{ad} of reaction (15) is much lower than 1800 K. Reaction (16) is highly exothermic and T_{ad} is much above 1800 K. But in this reaction, the quantities of B_4C and Si are very low. Since the rate of heating during FT and Mg assisted reaction is very high, large excess of B_4C is required to compensate the loss of B_2O_3 (by sublimation) and to complete the reduction of ZrO_2. The weight ratio of ZrO_2 /B_4C required according to reaction (4) is ~3.0. Normal furnace heating requires a weight ratio of ZrO_2 /B_4C=2.5 to compensate the loss of B_2O_3 and to form single phase ZrB_2. In FT and Mg assisted reaction (7) the weight ratio of ZrO_2 /B_4C=2.5 is not adequate to complete the reduction of ZrO_2. By increasing the B_4C content as in ZRBC1.6 (Fig. 8(a)) or by adding Si to ZRBC2.5 (Fig. 7(b)), the reduction of ZrO_2 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_2/B_4C = 4.4. It is equal to increasing the Mg content without providing sufficient B_4C or Si (Fig. 7(a)). Therefore, through reaction (16), it is not possible to obtain single phase ZrB_2 without impurities like ZrC and ZrO_2. 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_2 and B_4C 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_2–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_2 and SiC (Fig. 10). The chemical

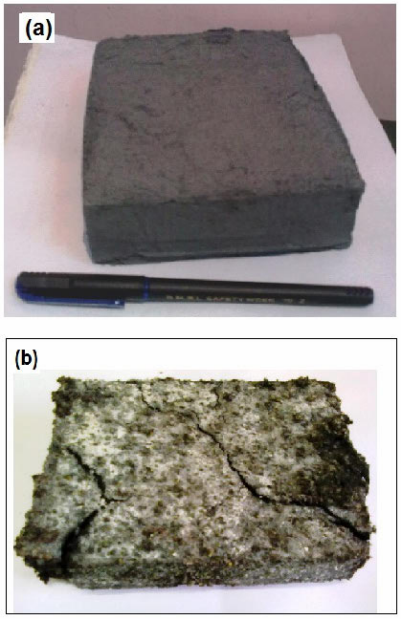

Fig. 9 Appearance of 1 kg bulk sample of (ZRBC2.5+15 wt% Si+30 wt% Mg): (a) before and (b) after FT assisted reaction.

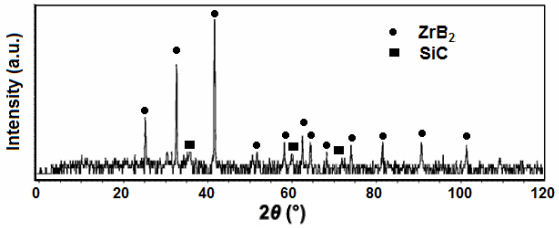

Fig. 10 XRD pattern of 1 kg bulk sample of (ZRBC2.5+15 wt% Si+30 wt% Mg) after FT assisted reaction and leaching with HCl acid.

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 ℃ 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

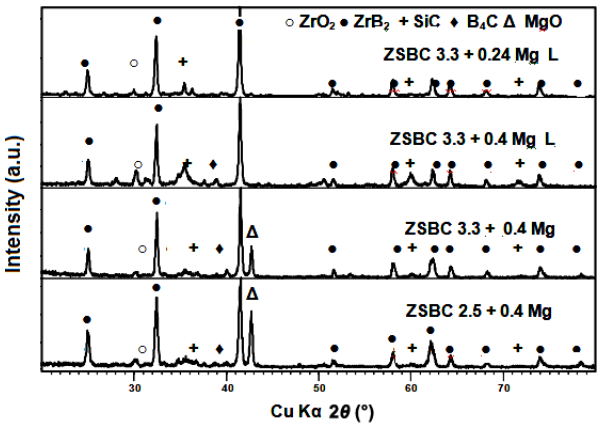

Fig. 11 XRD patterns of ZSBC samples after FT assisted reaction. L means after leaching with HCl acid.

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.

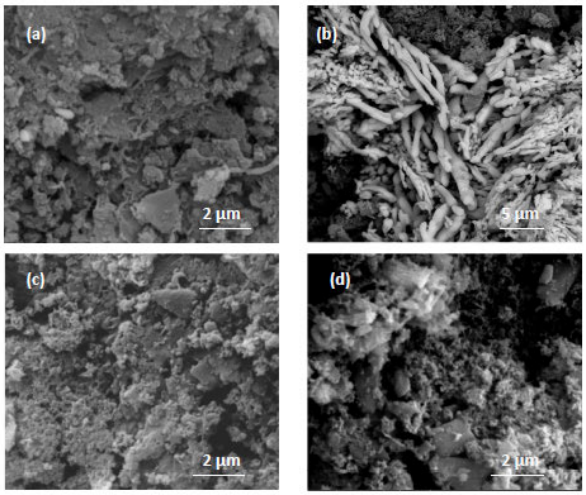

Fig. 12 SEM images of ZrB_2–SiC from (a) and (b) ZSBC3.3+24 wt% Mg, (c) ZSBC3.3+40 wt% Mg, and (d) ZSBC2.5+40 wt% Mg after FT assisted synthesis and leaching with 1.5 M HCl.

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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