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A novel microwave route for the preparation of ZrC–SiC composites

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Abstract

A novel microwave-assisted carbothermal reduction and carburization route has been used to prepare ZrC–SiC composite powders. Both zircon and mixtures of ZrO_2 and SiO_2 were used as starting materials along with amorphous carbon. Carbothermal reduction and carburization were examined in both argon and nitrogen atmospheres. Reaction kinetics in microwave field was found to exhibit notable differences for the two different starting materials. However, a complete oxide to carbide conversion was achieved in less than 30 min in both cases when argon was used as an ambient gas. The possible structural mechanism involved in the reactions has been discussed.

Keywords: Ceramics; Carbides; Composites; X-ray diffraction

1. Introduction

Zirconium carbide (ZrC) and silicon carbide (SiC) are ceramics of great importance to technology. ZrC has a melting temperature of 3420°C, which makes it an excellent candidate for application in rocket engines in order to achieve cleaner burning of rocket fuel. ZrC is already in use for making field emission arrays and for providing diffusion barrier coating on UO_2 particles in nuclear industry. ZrC also has high hardness, high fracture toughness and high strength [1], which makes it a potentially good material for use in cutting tools. SiC is already a widely used ceramic particularly as an abrasive and in composites used for high-temperature structural applications [1,2]. A composite based on ZrC and SiC is therefore a priced refractory ceramic. But literature reports on ZrC–SiC composites are rather scanty.

The presently used approach to prepare ZrC and SiC is to start with the respective oxides and subject them to carbothermal reduction (to remove oxygen) and carburization (CTR/C) using carbon as a reactant at very high temperatures ($>1700°C$ for reacting zirconia, ZrO_2) [2]. SiC is formed at lower temperatures ($\sim1200°C$). Another approach is to pyrolyze metalorganics in which metal–carbon bonds are already built in [3–5]. ZrO_2 itself is generally obtained from zircon sand, which is mainly zirconium silicate, $ZrSiO_4$. $ZrSiO_4$ decomposes [6] around 1500°C to ZrO_2 and SiO_2 both of which can be made to react with carbon to obtain respective carbides, ZrC and SiC. Thus zircon mixed with SiO_2 or ZrO_2 can be used as a starting material for the preparation of carbide composites of desired composition.

Microwave reactions generally occur at lower temperatures and are completed in extraordinarily short durations of time [7–9]. Microwave route has been used earlier very successfully for carrying out carburization, nitridation and silicidation reactions starting with metal oxides [10–13]. It is therefore thought possible to develop a novel microwave route for the synthesis of ZrC–SiC composites. Further, ZrO_2 and ZrC exhibit significant differences in their bonding and structural aspects, and therefore we consider it as interesting to examine the role of microwave irradiation in such $ZrO_2 \rightarrow ZrC$ conversion.

2. Experimental

Zircon (sand) powder was obtained from BHEL, India and the composition is given in Table 1. It was not

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Table 1
Chemical composition of zircon sand

Compound	Composition (wt%)
ZrO_2	62.0
HfO_2	8.0
SiO_2	28.0
TiO_2	0.2
Al_2O_3	1.2
Fe_2O_3	0.2
CaO	0.4

purified any further since the behavior of HfO_2 which is the major impurity is very similar to that of ZrO_2. Commercial ZrO_2 (LOBA chime, India), amorphous SiO_2 powder (Acme synthetic chemicals, India) and amorphous carbon were used in these studies. Microwave-assisted CTR/C reactions were performed with two different starting materials; (i) stoichiometric mixture of zircon and amorphous carbon and (ii) stiochiometric mixture of ZrO_2, amorphous SiO_2 and amorphous carbon. The weights of required reactants were calculated on the assumption that the overall reaction corresponds to $ZrSiO_4(\equiv ZrO_2 + SiO_2) + 6C \rightarrow ZrC + SiC + 4CO\uparrow$. Various other molar ratios of oxides and amorphous carbon were tried out and it was found that oxide: carbon ratio of 1:6 (stoichiometric) was the most adequate for the preparation of composite powders. The reactants were ground together and the powder mixtures were pelletized and embedded in an insulated thin SiC pit. The pit and the pellet were together placed inside a quartz setup having a facility for passing gasses. Pellets were irradiated with 2.45 GHz microwaves in a multimode microwave oven (LG, India) with a maximum operating powder of 700 W. Initially, pellet was exposed to 40% of maximum power (a duty cycle of 10 s ON and 14 s OFF) for 5 min and for next 5 min at 60% power (a duty cycle of 15 s ON and 5 s OFF) and switched to maximum power after 10 min. Such a protocol was followed in order to maintain the physical integrity of the pellet. Pellet was found to disintegrate if exposed to 100% power at once and it took longer time for the reaction to complete. Reactions were performed in the ambience of flowing argon and nitrogen using a flow rate of $50\,cm^3/min$. Temperature was measured using a shielded Pt/Rh thermocouple kept in close proximity to the sample and bringing it into contact with the pellet immediately (in under 2 s) after interrupting the microwave irradiation. Since the thermocouple which was placed close to the pellet was already heated to nearly the temperature of the pellet itself, the error in temperature measurement was very minimum and no more than $-10^{\circ}C$ to $-15^{\circ}C$. Pellets were irradiated with microwaves for various durations of time and the products formed were examined using X-ray diffraction (XRD, Siemens D-5005, Germany). Morphology of the composite powder and its composition was examined using scanning electron microscopy (SEM) and energy dispersive analysis of X ray (EDAX), respectively (JEOL JSM-5600LV, Japan, with EDAX facility). Different pellets were used to follow the reaction for different durations of time but with common heating protocol.

3. Results and discussion

In Figs. 1 and 2 the XRD patterns of the products of the reactions in (i) (zircon + carbon) and (ii) (ZrO_2 + SiO_2 + carbon) powders, respectively, are shown for different reaction times. These reactions were carried out in argon atmosphere. The variation of temperature of the pellets as a function of time for the same irradiation protocol is shown in Fig. 3. XRD patterns of zircon (Fig. 1) and of ZrO_2 + amorphous SiO_2 (Fig. 2) are also included for comparison.

It is seen from Fig. 1 that during the first 10 min there is no reaction between zircon and carbon although the

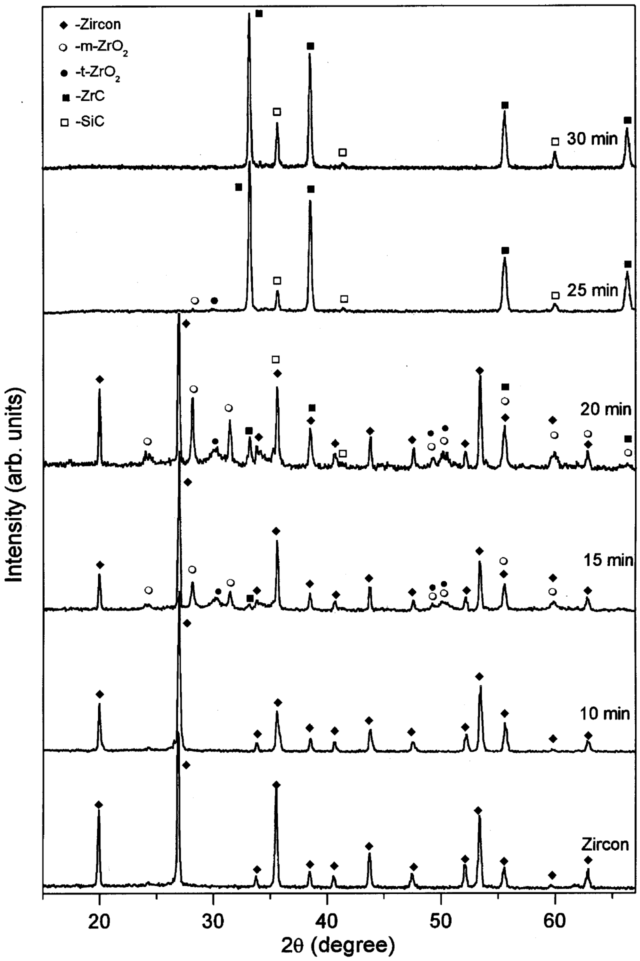

Fig. 1. XRD patterns of zircon and carbon mixture under microwave irradiation at different intervals of time in argon atmosphere.

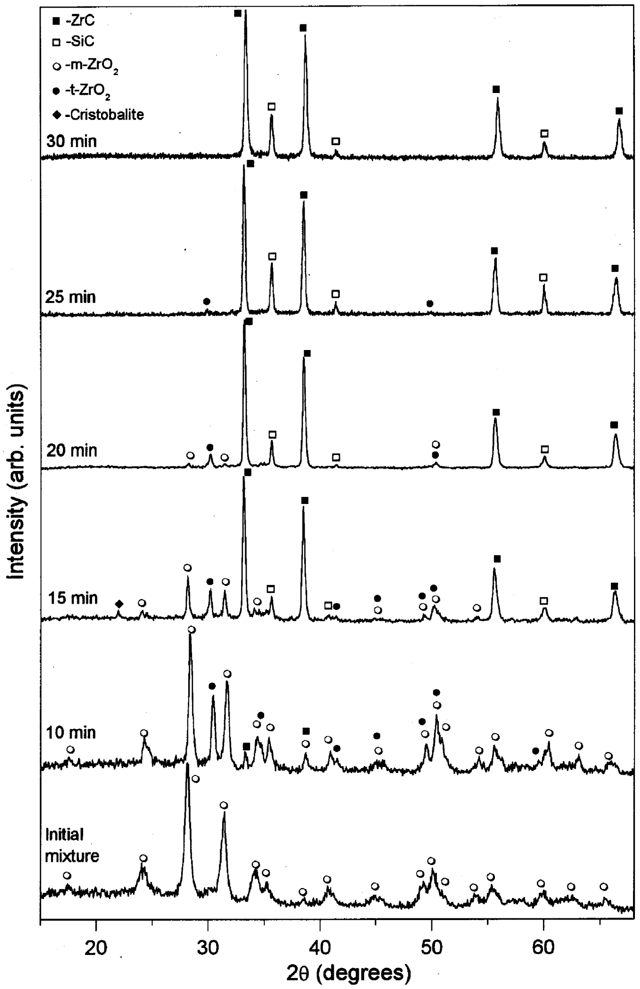

Fig. 2. XRD patterns of ZrO_2, SiO_2 and carbon mixture under microwave irradiation at different intervals of time in argon atmosphere.

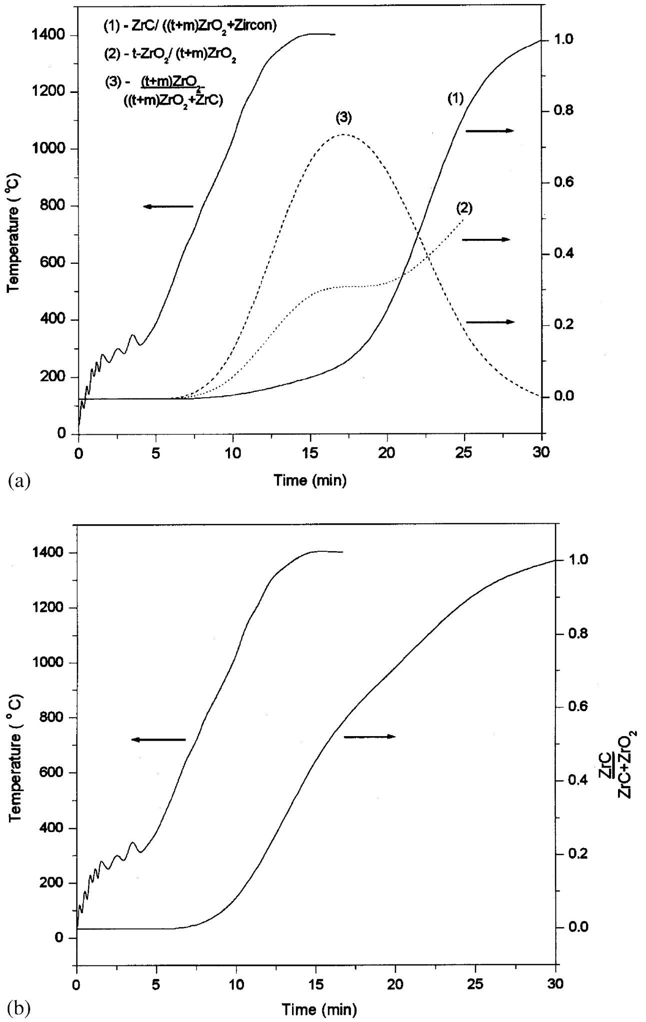

Fig. 3. Kinetics of ZrC formation from the reactants (a) zircon and carbon mixture and (b) ZrO_2, SiO_2 and carbon mixture.

temperature has reached ~950°C. At the end of 15 min zircon undergoes decomposition giving rise to both monoclinic and tetragonal ZrO_2 (m and t-ZrO_2 as indicated). Formation of ZrC [14] has just begun as indicated by the appearance of its (111) reflection at $2\theta = 33.15°$. However, no SiO_2 related reflection is observed suggesting that SiO_2 has either got converted into SiC or has remained amorphous. Since, the highest intensity (111) reflection of SiC [15] gets merged into (112) reflection of zircon ($2\theta = 35.6°$) [16] and it is hard to confirm the formation of SiC at the end of 15 min. However, at the end of 30 min complete conversion of zircon into ZrC and SiC is observed and no peak attributable to any other compound is present in the XRD pattern. The highest intensity peaks corresponding to ZrC and SiC are in the ratio of ($I_{ZrC}/I_{SiC} = 2.80$) which is nearly equal to the ratio of the number of electrons in Zr and Si (2.85) suggesting that no SiO_2 is lost by evaporation as SiO because of any partial reduction by carbon ($SiO_2 + C \rightarrow SiO + CO$). This was independently confirmed using EDAX analysis (element % of Zr/Si ~1). EDAX results did not indicate the presence of oxygen in the final product.

The reaction of the mixture of ZrO_2 and SiO_2 with carbon in argon atmosphere exhibits some differences. XRD of the starting mixture is shown in Fig. 2. The peaks in XRD are all due to m-ZrO_2. There is a broad hump extending up to $2\theta = 20°$ which may be attributed to amorphous SiO_2 used in the mixture. However, formation of amorphous phase was not further confirmed, as it was not essential for the following discussion. There are already changes in the XRD pattern at the end of 10 min. There is evolution of t-ZrO_2 peak (101) at $2\theta = 29.98°$. But at the end of 15 min there is evolution of both SiC and ZrC peaks. This is also associated with crystallization of SiO_2 to cristobalite and further transformation of m-$ZrO_2 \rightarrow$ t-ZrO_2. At the end of 20 min there is complete conversion of $SiO_2 \rightarrow \beta$-SiC and nearly complete conversion of $ZrO_2 \rightarrow ZrC$ with only a small retention of ZrO_2. The maximum intensity peaks of ZrC and SiC at the end of 25 min are still in the ratio (2.72) which is lower than that observed when (zircon + carbon) mixture was used as starting material. Low intensity peaks at $2\theta = 29.98^\circ$ and 49.88° indicate that unreacted t-ZrO_2 is still present in the pellet. At the end of 30 min, however, the reaction was found to be complete and no trace of t-ZrO_2 peaks could be identified. The intensity ratio of I_{ZrC}/I_{SiC} reaches a higher value of 2.83 compared to the 25 min product.

Fig. 3a summarizes the kinetic data of microwave-assisted CTR/C reaction of zircon in argon atmosphere. Variation of the ratio, [ZrC/(ZrC + zircon + ZrO_2)] as a function of time shows that virtually no ZrC is formed till about 10 min at which time the temperature has reached 1020°C. By 20 min it forms about 15% ZrC. Between 20 and 25 min the formation of ZrC is very rapid and at 25 min ZrC constitutes 90% of all the zirconium compounds in the reaction mixture. The conversion is complete by about 30 min. In the region of 10–20 min the crucial reaction is the decomposition of zircon to ZrO_2 and SiO_2. It is also the region dominated by the exothermic reaction of (SiO_2 + C) leading to the formation of SiC. Exothermic formation of SiC provides the additional local heating for initiating (ZrO_2 + C) reaction. It should be noted that ZrO_2 and SiO_2 are formed simultaneously but initially $SiO_2 \rightarrow SiC$ reaction dominates. Subsequently the exothermicity of both $SiO_2 \rightarrow SiC$ ($\Delta H = -145.6\,\mathrm{k\,cal\,mol^{-1}}$) and $ZrO_2 \rightarrow ZrC$ ($\Delta H = -162.5\,\mathrm{k\,cal\,mol^{-1}}$) reactions render the rate so fast that it is hard to distinguish their kinetics. Curve 2 in Fig. 3a represents (t-ZrO_2/(t-ZrO_2 + m-ZrO_2)) vs. t variation and it indicates that as-formed ZrO_2 is largely monoclinic. But as $ZrO_2 \rightarrow ZrC$ conversion progresses rapidly the rise in the local temperature lead to partial conversion of m-ZrO_2 to t-ZrO_2. However, the total quantity of ZrO_2 present in the reactant mixture itself decreases rapidly with time (curve 3 in Fig. 3a) but the temperature in this region attains a plateau of ~1400°C. The complementary kinetics of the formation of SiC could not be followed because, as mentioned earlier, the 100% peak of SiC (the most sensitive) merges with one of zircon peaks.

In the case of ZrO_2–SiO_2 mixtures, formation of ZrC (Fig. 3b) is noticed even at 10 min. This is because SiO_2 is present as such in the mixture and the $SiO_2 \rightarrow SiC$ conversion gets initiated readily at 10 min (1020°C). The enthalpy of this exothermic reaction increases the local temperature of ZrO_2 particles to a level required for the formation of ZrC. The formation rate slows down after about 50% of ZrO_2 is converted to ZrC which indicates completion of the $SiO_2 \rightarrow SiC$ reaction by this time. The heat required to sustain $ZrO_2 \rightarrow ZrC$ conversion rate is provided by its own exothermicity in this time regime. Nevertheless, complete conversion of $ZrO_2 \rightarrow ZrC$ is observed at the end of 30 min.

The reaction between zircon and carbon was performed in N_2 atmosphere also. Essentially similar features were noted except that the reactions were slow in the sense that even at the end of 30 min presence of ZrO_2 is observed in XRD (Fig. 4) along with small amount of crystallized SiO_2. One of the reasons could be the oxygen impurity present in N_2 gas could have burnt away a part of carbon thereby reducing the available carbon. This leads to unreacted ZrO_2.

It is interesting to dwell on the structural aspects of the above microwave-induced reactions. Zircon has a tetragonal structure in which Zr is coordinated to eight oxygen atoms in a triangular dodecahedron. Si is coordinated to four oxygen atoms in a regular tetrahedron. ZrO_8 dodecahedra share edges both with SiO_4 tetrahedra and among themselves. All oxygen atoms are chemically identical and are three coordinated (2 to Zr and 1 to Si). The valence sum rule [17] shows that the oxygen atom in $Zr^{VIII}Si^{IV}O_4^{III}$ has an effective valency of $(2 \times \frac{4}{8} + 1 \times \frac{4}{4}) = 2$. But the sharing of oxygen by Zr and Si in the structure is unequal. In terms of the component polyhedral units, $ZrSiO_4$ is equivalently represented as $\{[ZrO_{8/3}]^{4/3-}[SiO_{4/3}]^{4/3+}\}$. Thus, Zr dodecahedron is oxygen rich (negative charge) and silicon tetrahedron is oxygen deficient (positive charge) reflecting the inequality in oxygen sharing. At temperatures greater than 1000°C the structure becomes unstable and decomposes to component oxides ZrO_2 and SiO_2. Microwave may also effectively assist the decomposition of these large and charged units. The decomposition involves an effective charge transfer from $[ZrO_{8/3}]^{4/3-}$ units to $[SiO_{4/3}]^{4/3+}$ units. The connectivity of the edge

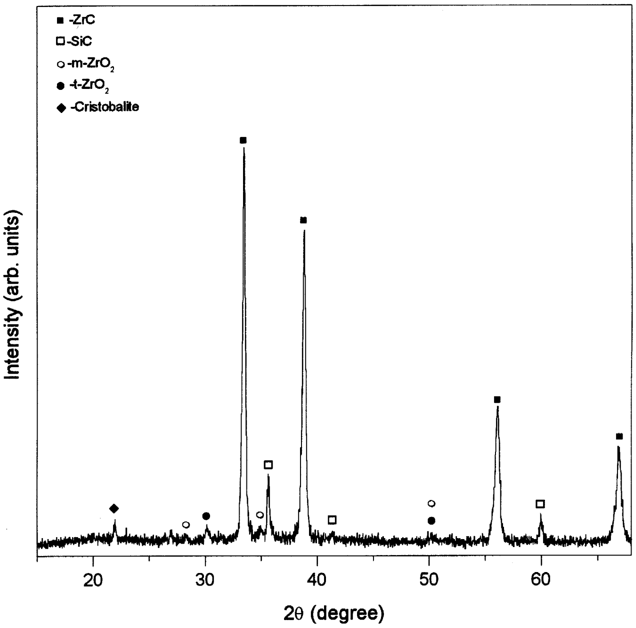

Fig. 4. XRD pattern of zircon and carbon mixture after 30 min of microwave exposure in N_2 atmosphere.

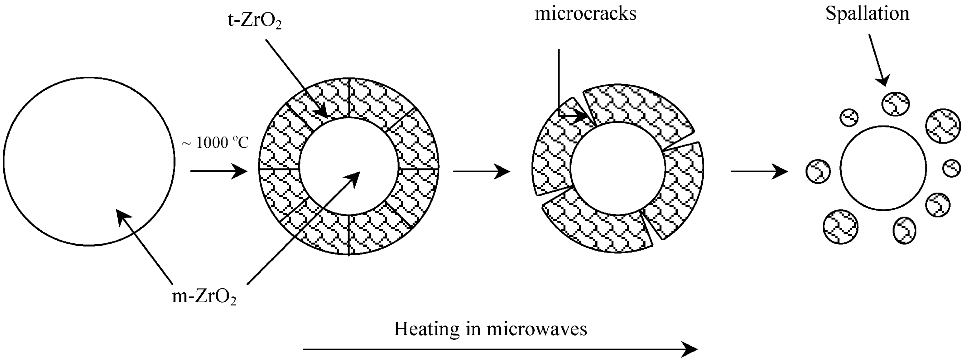

Fig. 5. A schematic representation of m→t conversion of ZrO_2 and spallation of t-ZrO_2.

sharing [ZrO_8] triangular dodecahedra helps them to reorganize into t-ZrO_2 very readily. The stability of t-ZrO_2 is also helped both by the extreme fineness of as-formed ZrO_2 particles and the temperature. The [SiO_4] tetrahedra, on the other hand are structurally disconnected and the "exsolved" SiO_2 is therefore amorphous. This is consistent with the absence of any XRD features attributable to crystalline SiO_2 after the decomposition of zircon (Fig. 1). The as-formed SiO_2 is highly reactive towards carbon and forms SiC. This is responsible for creating runaway type heating of the sample (Fig. 3). The heating also initiates the $ZrO_2 \rightarrow ZrC$ reaction in its neighborhood. We note here that zircon itself is not a good susceptor of microwaves [18] and the initial heating is entirely due to microwave susceptibility of amorphous carbon. However, at the reaction temperatures of about 1000°C, ZrO_2 is also known to become microwave active [19].

The details of the reaction in (ZrO_2+amorphous SiO_2) mixture is however different in several ways. Although the initial heating of the mixture is due to amorphous carbon and the second stage of runaway heating is provided by the exothermic $SiO_2 + 3C \rightarrow SiC + 2CO$ reaction, $SiO_2 \rightarrow SiC$ and $ZrO_2 \rightarrow ZrC$ conversions are not coupled in the same way as in the case of zircon. Enthalpy of the $SiO_2 \rightarrow SiC$ reaction heats ZrO_2 particles in the mixture. In comparison to ZrO_2 formed in situ when zircon is used, the ZrO_2 particles in $ZrO_2 + SiO_2 + C$ mixture are much bigger. Since ZrO_2 particles are very poor thermal conductors only the outer shell of the particles get transformed to t-ZrO_2. The transformed shells of t-ZrO_2 are under severe tensile stress as they have lower molar volume (change in volume for m→t transformation of ZrO_2 is ~6%) [20], and therefore there is break down of outer layer into small particles (spallation). This is also a type of thermal shearing process briefly discussed in an earlier publication from this laboratory [21]. The process is visualized in Fig. 5. This is consistent with the observation that as the reaction proceeds, m-ZrO_2 is converted to t-ZrO_2 to a significant extent. This step renders $ZrO_2 \rightarrow ZrC$ conversion lag behind the $SiO_2 \rightarrow SiC$ conversion and as a consequence the latter reaction proceeds rapidly towards completion. Therefore, $ZrO_2 \rightarrow ZrC$ conversion proceeds rapidly till about 50% and the rate slows down thereafter as seen in Fig. 3b.

$ZrO_2 \rightarrow ZrC$ conversion itself has interesting chemical and structural features. At the temperature of the reaction (1400°C) ZrO_2 is in tetragonal form and Zr is therefore eight coordinated to oxygen atoms. The product ZrC on the other hand has *Fm*3*m* structure in which both Zr and C are six coordinated. While Zr–O bonding is 67% ionic, Zr–C bonding is only 31% ionic (Pauling ionicity) (the metallic behavior [22] of ZrC is consistent with this bonding behavior; $\rho_{(300\,K)} = 78 \times 10^{-6}\,\Omega\,cm$). Therefore, during the formation of ZrC from ZrO_2, the partial charge on Zr decreases form +0.65 (in ZrO_2) to +0.28 (in ZrC) (calculated using Sanderson's procedure [23]). Carbon, therefore, behaves as an electron donor. Correspondingly during the formation of CO from C, the partial charge on C changes from 0 to +0.165 which is again a process of oxidation of carbon. Reaction mechanism is visualized as follows. Carburization of Zr and elimination of CO occur simultaneously (concerted reactions). It is likely to be a consequence of the structure of carbon used in the reaction. The amorphous carbon used in the reaction consists of small bits of graphene sheets [24]. Zr^{4+} strongly polarizes the π electron cloud on graphene sheet towards itself on one end and therefore enables the carbon atoms at the other end of the graphene sheet (which is polarized positively) to react with the oxygen atoms simultaneously. Since the more ionic ZrO_2 couples to microwaves at this temperature, microwaves may also induce large amplitude vibrations, which increase Zr^{4+}–O^{2-} separations and assist the reaction [25].

SEM images of zircon powder used as a reactant and the composite powders obtained by the two procedures are shown together in Fig. 6. Zircon particles (Fig. 6a) possess faceted morphology and a broad distribution of sizes. But the composite powders appear (Fig. 6b and c) to be agglomerates of SiC and ZrC particles of almost similar sizes. The high temperature and the significant

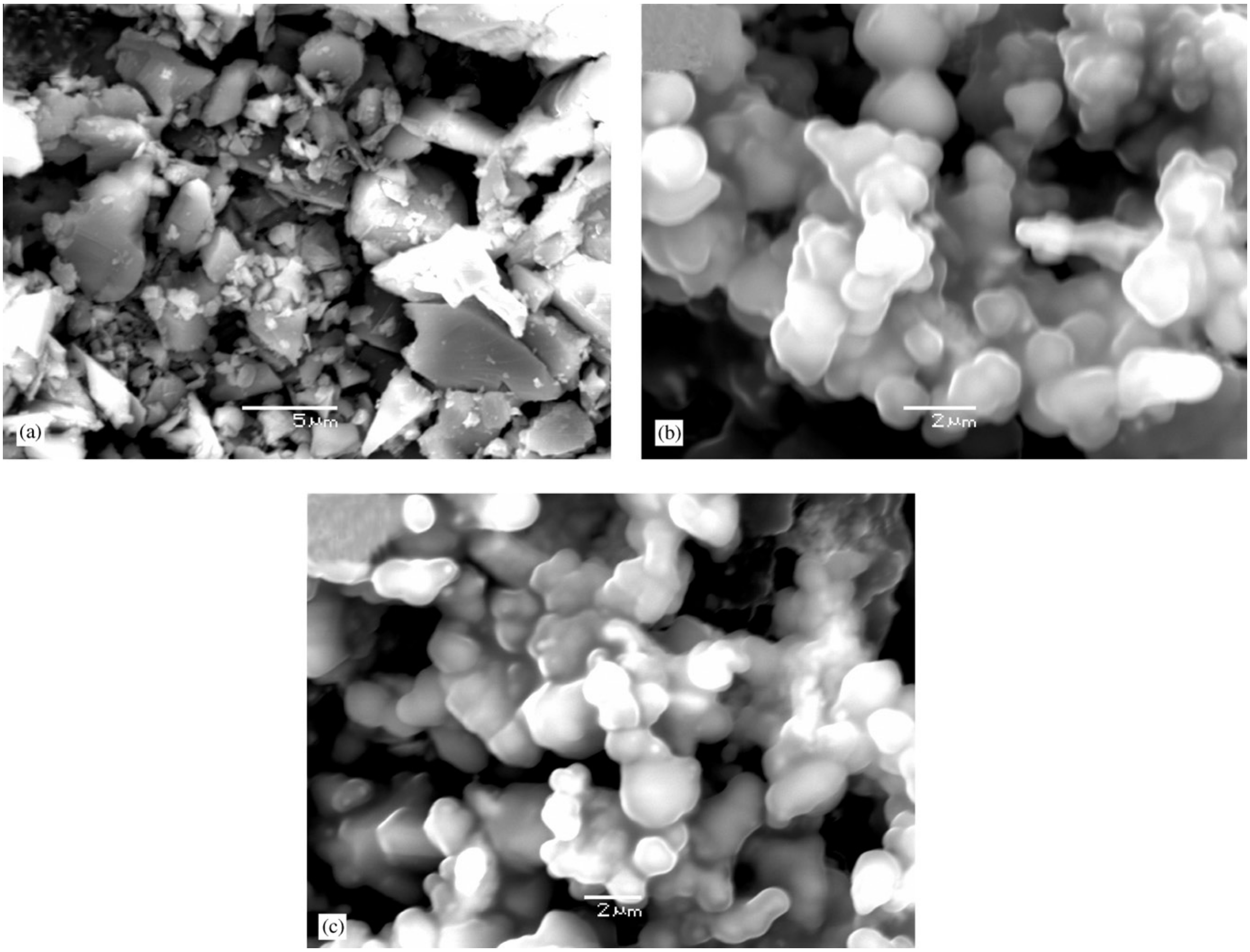

Fig. 6. SEM images of (a) zircon and ZrC–SiC powder obtained from (b) zircon + carbon and (c) $ZrO_2 + SiO_2$ + carbon mixtures after 30 min of microwave exposure in argon atmosphere.

residence time of the products in microwaves have lead to local sintering as evidenced by the necking of the particles. The densities of the products are higher than the effective ρ_{average} of the initial pellet ($ZrSiO_4 + C$) and therefore the product appears very porous. Studies related to sintering of the composites and their mechanical properties are in progress.

4. Conclusions

A novel microwave route has been developed in which ZrC–SiC composites are formed at much lower temperatures and in extraordinarily short durations of time. The formation of carbides is found to be facile, both either zircon or a mixture of ZrO_2 and SiO_2 are subjected to microwave-assisted CTR/C in argon atmosphere thus establishing the feasibility of making ZrC–SiC composites of any desired combination. The structural chemistry aspect of the reduction of both zircon and ZrO_2 to ZrC by carbon have also been discussed.

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