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Processing of carbon-fiber reinforced (SiC + ZrC) mini-composites by soft-solution approach and their characterization

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Abstract

Carbon-fiber reinforced (SiC + ZrC) mini-composites have been prepared via soft-solution process using inorganic precursors. In this process, water-soluble compounds have been used to act as precursor materials to impregnate the fiber tow. Thermal analysis provided the temperature range for the pyrolysis to convert the precursors into the desired (SiC + ZrC) matrix. X-ray diffraction of the composites confirmed the phase formation and the crystallite size of these phases were in the range of 25–40 nm. Cross-sectional microstructures of the composites have shown the matrix formation around each individual fiber. The mechanical properties revealed that the tensile strength and fracture energy of the composites pyrolyzed at 1600 °C were significantly higher with typical composite failure behavior, as compared to those pyrolyzed at 1700 °C. The statistical size effects of the tensile strength were investigated on the basis of the Weibull statistics.

Keywords: A. Composites; B. Fibres; C. Mechanical properties; D. Carbon; E. Soft-solution approach

1. Introduction

The interest in ceramic matrix composites (CMCs) is continually growing due to the great flexibility in designing and tailoring of properties of these multi-component systems. CMCs, reinforced with high strength continuous ceramic fibers, have attracted much attention for high temperature structural applications such as gas turbine and power generation systems, because of their superior high temperature strength, reduced weight and improved damage tolerance [1–3]. Particularly, carbon-fiber reinforced silicon carbide ceramic matrix composites (C_f-SiC) are promising candidates for many applications due to their high strength-to-weight ratio which makes them potential candidates for highly demanding engineering applications such as heat shields and structural components for re-entry space vehicles, high performance brake discs, and ultra-high temperature heat exchanger tubes [4].

Improvements in the elevated temperature mechanical properties and oxidation resistance of C_f-SiC composites are the key issues that attracted much attention in the recent past. The matrix phase in the C_f-SiC composites can be strengthened by the addition of refractory carbides like ZrC. Zirconium carbide (ZrC) is of particular interest because of the unique combination of properties like high melting point and the ability to form refractory oxide scales at high temperature [5,6]. ZrC has good high temperature strength, high elastic modulus, and low thermal conductivity and capability to withstand temperatures in the 1900–2500 °C [7,8]. Table 1 summarizes the typical properties of SiC and ZrC ceramics. ZrC addition to the SiC matrix in C_f-SiC composites should improve the properties of the composite. Mini-composites or short-fiber-reinforced composites are more widely used because of their easy adaptability to conventional manufacturing techniques and low cost of fabrication. In present mini-composite approach, the single tows are impregnated with matrix to get the composite. The benefits with the mini-composite approach are better utilization of the expensive fiber material. They bear basic information about fiber/matrix interactions and can be easily modeled owing to their extremely simple fiber configuration and morphology. The increasing number of

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Table 1
Material properties of β-SiC and ZrC [5,6].

Property	SiC	ZrC
Melting point (°C)	2545	3250
Density (kg/m^3)	3220	6730
Young's modulus (GPa)	475	350–440
Hardness (GPa)	25–28	24–27
Thermal expansion Coefficient (ppm/K)	3.8	7.3

Table 2
Preferred chemical compositions of matrix materials in moles.

Composition (wt%)	Colloidal silica (M)	Sucrose (M)	Zirconium oxy chloride (M)
SiC + 5%ZrC	2.37	0.85	0.048
SiC + 10%ZrC	2.25	0.82	0.097
SiC + 15%ZrC	2.12	0.80	0.150
SiC + 20%ZrC	1.99	0.77	0.190

applications of mini-composites makes it more important to understand their mechanical properties, which depend strongly on the interfacial bonding between fiber and matrix.

C_f-SiC composites can be fabricated by chemical vapour infiltration (CVI) process, yet their high performance is attained at prohibitive costs for many applications [9]. Polymer impregnation and pyrolysis (PIP) derived SiC matrix contains free carbon and oxygen [10,11]. The liquid silicon infiltration process, which is a common fabrication route, offers some cost advantage, but produces SiC matrix along with free silicon [12]. Each processing method mentioned above has disadvantages pertaining to reproducibility, cost and performance of the composite. The soft-solution approach using low cost materials like colloidal silica, zirconium oxy-chloride and sucrose are presented to yield carbon-fiber reinforced (SiC + ZrC) matrix composite. The processing conditions are selected to promote nanometer-scale mixing of different phases which can subsequently produce homogeneous ceramic powders as well as composites with any selected reinforcement; that matrix is formed in situ. The present method to synthesize mini-composites is simple and economical compared to the generally used sol–gel methods; it is a quite environmental friendly approach, as it involves neither extremely low or high temperatures, nor toxic reagents. The process is flexible in terms of possible chemical compositions of the matrix [13,14].

Thermogravimetric studies of (SiC + ZrC) mixed powders lead to the selection of pyrolysis temperature and the nature of the phase formation. Then, unidirectional carbon-fiber reinforced (SiC + ZrC) matrix composites were prepared by soft-solution approach by impregnating the solution phase into a carbon fiber tow, drying, converting sucrose into carbon phase and finally reducing oxides with carbon to form silicon carbide and zirconium carbide. Processing, microstructure and mechanical properties of the mini-composites were mainly discussed.

2. Experimental procedure

2.1. Raw materials

Carbon fiber tow was of T-300 grade (fiber volume%, 45) with 12,000 filaments in a tow; the filament diameter was about 6 μm. Commercial colloidal silica (SiO_2, 40 wt%, Bee Chem. Chemicals Company, Kanpur, India), zirconium oxy-chloride ($ZrOCl_2 \cdot 8H_2O$, AR, Loba Chemicals, India) and sucrose ($C_{12}H_{22}O_{11}$), AR, Qualigens Fine Chemicals, India), were used as source materials for silica (SiO_2), zirconium dioxide (ZrO_2) and carbon respectively to prepare the powders as well as the mini-composites.

2.2. Processing of mini-composites

(SiC + ZrC) matrix forms via carbothermal reduction of silica and zirconia at high temperatures. The amounts of the ingredients were usually expressed in terms of molarity. Typical calculations for the amounts of raw materials in molarities required for the preparation were summarized in Table 2. The amounts of the ingredients were calculated considering the following stoichiometric reactions involved for the preparation of mini-composites consisting of (SiC + ZrC) as a matrix.

$$(1)C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O\uparrow$$

$$(2)ZrOCl_2 \cdot 8H_2O \rightarrow ZrO_2 + 2HCl\uparrow + 7H_2O\uparrow$$

$$(3)SiO_2 + 3C \rightarrow SiC + 2CO\uparrow$$

$$(4)ZrO_2 + + 3C \rightarrow ZrC + 2CO\uparrow$$

The precursor solutions with varying amount of colloidal silica, sucrose and zirconium oxy-chloride were prepared. The precursor powders were prepared using the following three major steps: (1) the prepared precursor solutions were first dried at room temperature for at least 2 days, then dried at 65 ± 5 °C for 12 h, (2) the dried powders were ground and carbonized at 500 °C in argon atmosphere to convert sucrose into carbon, and finally (3) the carbonized powders were pyrolyzed at 1600 °C in argon atmosphere to reduce silica to SiC and zirconia to ZrC by the carbothermal reduction. Initially, thermogravimetric analyses (Setsys 24 TG-DTA thermal analyser SETARAM, France) of dried green precursor powders were carried out to study the mass changes with the temperature for the evaluation of the pyrolysis temperature.

The desired nominal compositions of the mini-composites were SiC: 5 wt% ZrC, SiC: 10 wt% ZrC, SiC: 15 wt% ZrC and SiC: 20 wt% ZrC. Initially, carbon fiber tow was washed with acetone to remove surface impurities and sizing. Then the fiber tows were vacuum impregnated with precursor solutions of SiC + ZrC (Table 2). Impregnated tows were dried carefully at room temperature and at 65 ± 5 °C for 12 h. Dried tows were carbonized at 500 ± 10 °C under argon atmosphere for 1 h for converting sucrose into carbon. Evaporation of bonded water of zirconium oxy-chloride also occurs during carbonization of sucrose. These steps were repeated for 5–6 cycles (further cycles were not recommended due to the rapidly decreasing effectiveness of further impregnations). After the desired

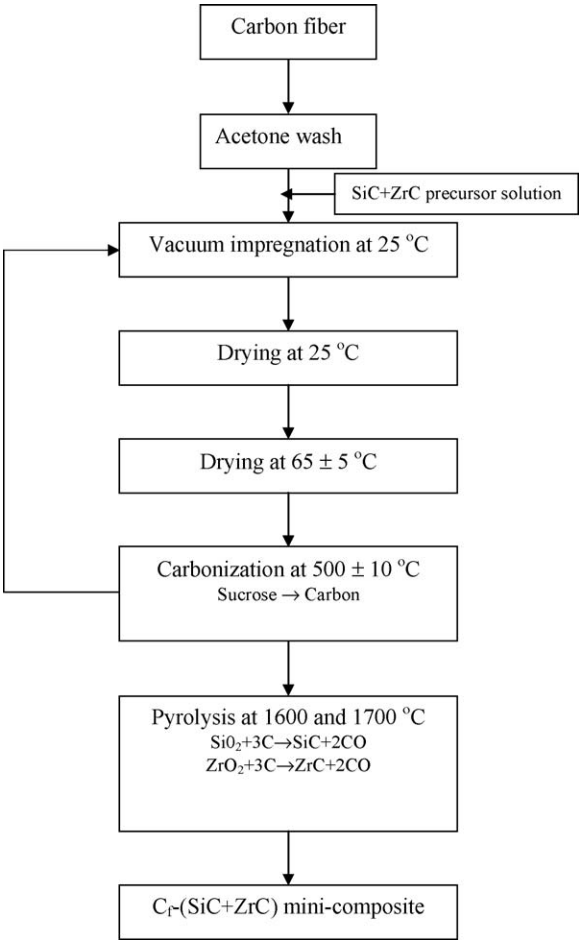

Fig. 1. Flow chart for the synthesis of carbon fiber reinforced (SiC + ZrC) mini-composites using soft-solution approach.

impregnation/carbonization cycles carbonized tows were pyrolyzed at 1600 and 1700 °C for 3 h under flowing argon to obtain the (SiC + ZrC) matrix. Flow sheet for the process was shown in Fig. 1. Bulk densities and open porosity of the samples were determined by the Archimedes principle and theoretical density was based on the rule of mixture. The density of the composites increases with the number of impregnation cycles.

2.3. Microstructural evolution

Pyrolysis products in powder form as well as the mini-composites were subjected to X-ray diffraction (Philips Model No. PW 320) to identify the phases formed as well as the crystallite size of the individual phases. The crystallite size (D_{hkl}) corresponding to the full-width-half-maximum (FWHM) was calculated by using Scherer formula given as:

$$D_{hkl} = \frac{K\lambda}{\beta \cos\theta} \tag{5}$$

where K is a constant (0.931), λ is the X-ray wavelength, β is the half-width of the peak in degrees of 2θ at half of maximum intensity and θ is the Bragg angle. The FWHM was calculated by fitting of Pseudo-Voight profile function [15,16]. The fitting of Pseudo-Voight profile function was done by using an X-ray line profile fitting programme, XFIT [15,16]. The strain independent crystallite size was calculated by extrapolating the plot between breadths corresponding to the FWHM ($1/D$) and $\sin\theta$ equal to zero.

It was difficult to prepare cross-sectional polished samples from the mini-composites. During the preparation porous and brittle matrix of mini-composite was severely damaged. During dry cutting using a diamond saw without coolant, the brittle fibers were torn and pulled out. When cut in wet condition, the removed carbon residue and fiber remnants were smeared on the surface, making further observations difficult. It was possible to view the microstructure of the composites by filling the porosity with a low-viscosity resin and careful polishing. The polished sections were studied to highlight the microstructural features. Environmental Scanning electron microscopy (ESEM, FEI, and QUANTA 400) was used to study the microstructure of the mini-composites.

2.4. Mechanical properties

The prepared mini-composites are in the form of tows or cylindrical thin wires (diameter: 0.657 mm and length: 100 mm) after processing. For each type of mini-composite, 10 tensile tests were carried out directly on these wires having constant gauge length of 50 mm and average cross-sectional area of 0.43 mm^2. The required length of a composite was first pasted on a paper tab with a suitable adhesive (commercial Fevi quick), this was held in the machine grip and then the paper tab was cut open just prior to loading the specimen for the test [17]. Tensile tests were conducted using a servo-hydraulic testing machine (Model 8801; Instron Corp., UK) at room temperature under a displacement rate of 0.5 mm/min. The load was measured using a 1 kN load cell. Once the mini-composite sample was mounted on the machine, the cardboard tab supporting the fiber was cut and testing carried out. Relatively simple bend testing (flexure testing) is generally used for ceramic samples. However it is not suitable for ceramic matrix composites due to non-uniform stress state and brittle nature of composite matrix [18]. The mini-tow composite tensile sample has uniaxial tensile stress condition, which gives more appropriate data, compared to flexure testing [19]. Weibull statistical analysis of the tensile data was carried out to get an idea of the scatter in data [20]. The tensile strength and fracture energy obtained from the area under the tensile curves were calculated from the average values of 10 tests for each composition.

3. Results and discussion

3.1. Selection of processing temperature

Thermogravimetric and differential thermogravimetric (DTG) analysis curves of dried precursor powders are shown in Fig. 2. Fig. 2a is for the precursor for the formation of pure ZrC and Fig. 2b is for the formation of SiC + 20%ZrC. The mass loss peaks were observed at low temperatures could be due to the loss of moisture and decomposition of zirconium

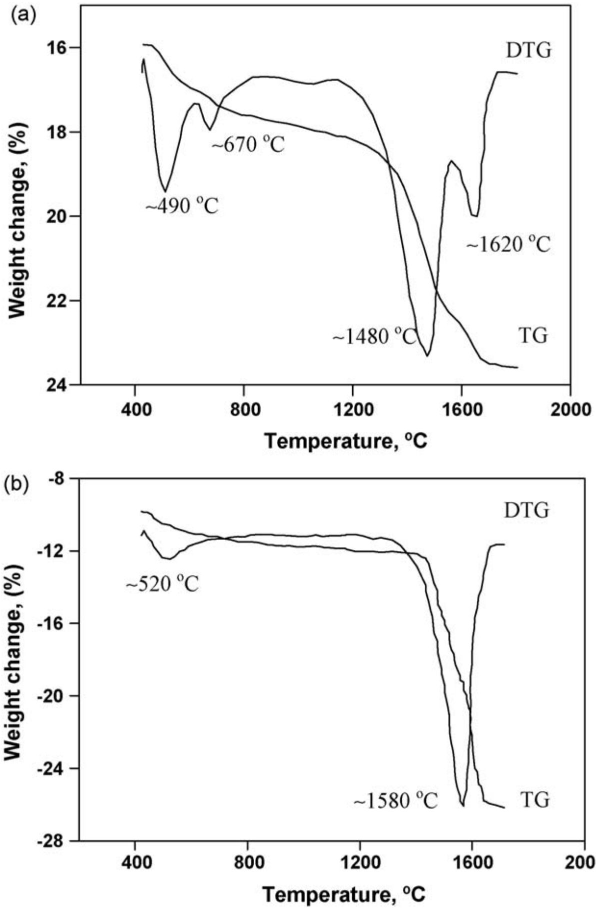

Fig. 2. Thermogravimetric and differential thermogravimetric (DTG) curves of the precursor powders. (a) pure ZrC and (b) SiC + 20%ZrC.

oxy-chloride as well as sucrose [21]. The peaks at high temperature were due to the carbothermal reduction of ZrO_2 to form ZrC (Fig. 2a) and reduction of ($SiO_2 + ZrO_2$) to form (SiC + ZrC) (Fig. 2b). In case of pure ZrC formation two peaks were observed for the carbothermal reduction, indicative of two-step reductions. However, in case of (SiC + ZrC) only one peak was observed indicating that both oxides are simultaneously reduced to form combined carbides. The TG curve of (SiC + ZrC) precursor shows that temperature of formation of carbides is shifted towards the higher temperature relative to the pure ZrC precursor. It shows that carbothermal reduction of SiO_2 occurs at lower temperature compared to reduction of ZrO_2 to give ZrC. Second peak is absent in Fig. 2b probably because of low amount of ZrO_2 in the precursor powder compared to pure ZrC precursor. Based on the thermogravimetric studies, two temperatures 1600 and 1700 °C were selected for the pyrolysis.

3.2. X-ray diffraction studies

Fig. 3 shows the XRD patterns of powder samples obtained by pyrolyzing the precursor powders, which confirms the formation of β-SiC and ZrC phases. XRD patterns of the C_f-(SiC + ZrC) mini-composites processed at 1600 and 1700 °C are shown in Figs. 4 and 5 respectively. The composite mainly

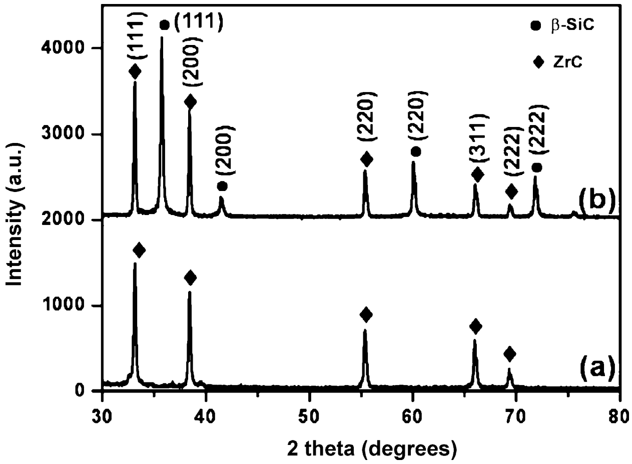

Fig. 3. XRD patterns of powders (a) ZrC at 1700 °C and (b) (SiC + ZrC) at 1700 °C.

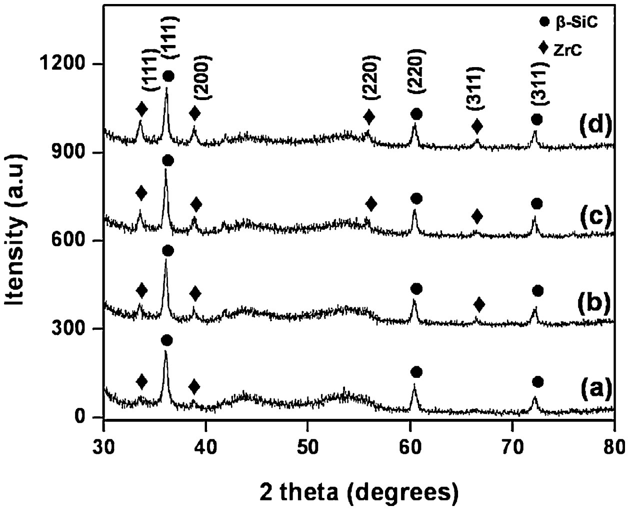

Fig. 4. XRD of C_f-SiC mini-composites with (a) 5%ZrC, (b) 10%ZrC, (c) 15%ZrC and (d) 20%ZrC processed at 1600 °C.

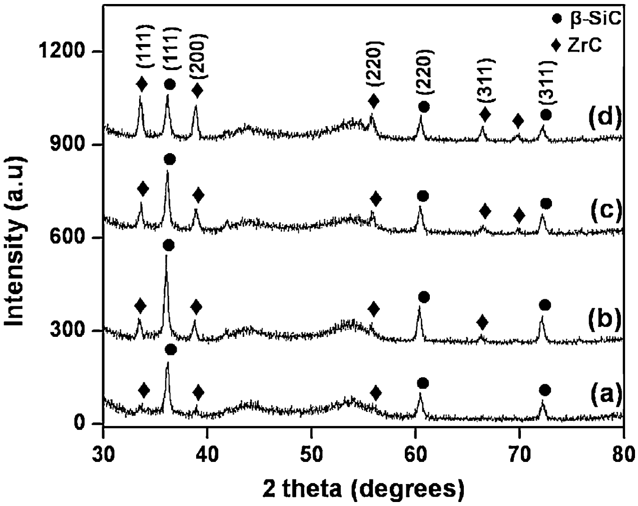

Fig. 5. XRD of C_f-SiC mini composites with (a) 5%ZrC, (b) 10%ZrC, (c) 15%ZrC and (d) 20%ZrC processed at 1700 °C.

Table 3
Crystallite sizes of SiC and ZrC of C_f-(SiC + ZrC) mini-composites.

Composition (wt%)	Crystallite size (nm)			
	Pyrolysis temperature			
	1600 °C		1700 °C	
	SiC	ZrC	SiC	ZrC
SiC + 5%ZrC	27	–	34	–
SiC + 10%ZrC	27	38	33	38
SiC + 15%ZrC	29	32	25	36
SiC + 20%ZrC	29	28	25	30

consists of β-SiC, ZrC and minor graphite peaks originating from the carbon fiber tow. There was no trace of unreacted SiO_2 and ZrO_2 in the diffraction patterns. The peak intensities for ZrC increased with increasing ZrC content in the matrix. The crystallite sizes of SiC and ZrC in the mini-composites synthesized at different pyrolysis temperatures are presented in Table 3. The crystallite sizes of SiC and ZrC in the mini-composites were in the range of 25–40 nm at both the processing temperatures. The presence of fibers and the second phase in the matrix might not allow the growth of crystallites in the composites. The small crystallite sizes and low pyrolysis temperature to complete carbothermal reduction were indicative of the fine scale mixing of the reactants in the precursors. The initial solution phase allows homogeneous molecular level mixing of the different compounds and the crystallites of the product phases nucleate from an amorphous phase.

3.3. Microstructure of mini-composites

Fig. 6 illustrates a typical polished section of the composite showing individual fibers clearly separated by the (SiC + ZrC) matrix. EDAX analysis of the mini-composite (Fig. 6a) shows the presence of C and Si with minor peaks for zirconium and oxygen. This was due to the predominance of carbon fibers in this area. Fig. 6b shows a back scattered image of the matrix phase. The bright phase was ZrC, while the darker phase SiC indicates the uniform distribution of both the phases. The EDAX analysis of the matrix clearly shows the predominance of SiC in this matrix with a minor zirconium peak.

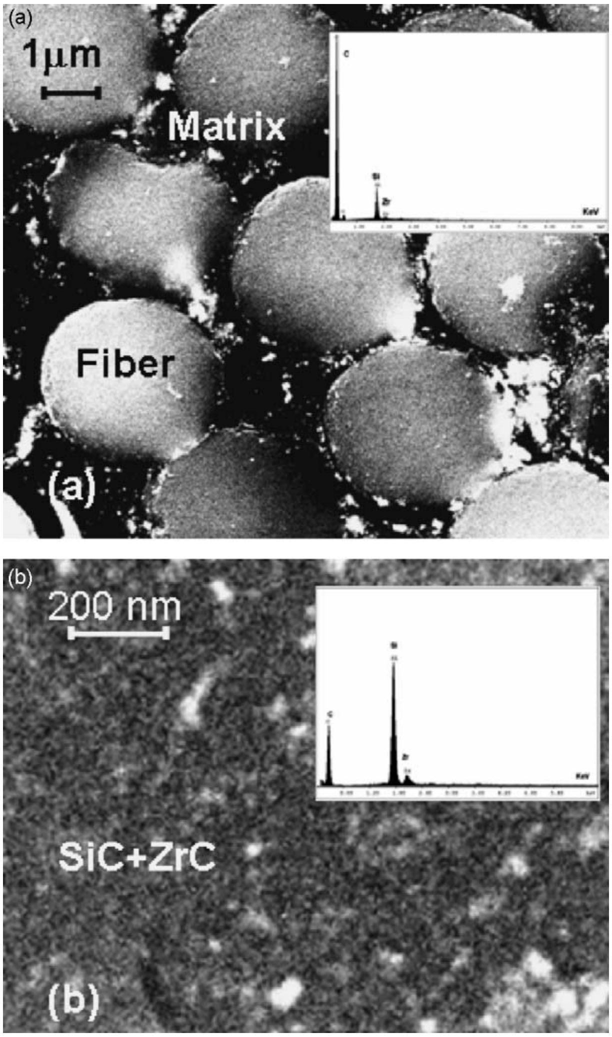

Fig. 6. (a) ESEM image of carbon-fiber reinforced (SiC + ZrC) composite pyrolyzed at 1600 °C for 3 h and (b) selected area of matrix from the composite (corresponding their EDAX analysis inserted in figures).

3.4. Evaluation of tensile properties

Table 4
Mechanical properties of C_f-(SiC + ZrC) mini-composites.

Composition	Theoretical density (kg/m^3)	Bulk density (kg/m^3)	Tensile strength (MPa)	Fracture energy (MJ/m^3)	Weibull modulus (m)
Processed at 1600 °C					
SiC + 5%ZrC	1950	1680	201 ± 31	0.23	6.20
SiC + 10%ZrC	1980	1710	242 ± 26	0.36	14.5
SiC + 15%ZrC	2080	1730	251 ± 23	0.33	17.9
SiC + 20%ZrC	2350	1790	263 ± 23	0.34	10.3
Processed at 1700 °C					
SiC + 5%ZrC	1950	1740	191 ± 10	0.17	3.2
SiC + 10%ZrC	1980	1760	192 ± 34	0.33	5.5
SiC + 15%ZrC	2080	1760	197 ± 24	0.20	7.8
SiC + 20%ZrC	2350	1780	213 ± 26	0.29	7.9

Mechanical properties of the C_f-(SiC + ZrC) mini-composites prepared in the present work are listed in Table 4. Examination of the density data presented in the table indicates that the density of the composites increases with the increase in the volume fraction of ZrC which is expected, because these phases possess higher density than SiC. It can be further observed that the mini-composites, pyrolyzed at 1700 °C exhibited comparatively poorer densification. The tensile strength and fracture energy were 263 ± 23 MPa and 0.34 MJ/m^3, respectively for C_f-(SiC + 20%ZrC) mini-composites pyrolyzed at 1600 °C. While, tensile strength and fracture energy of the mini-composites were 213 ± 26 MPa and 0.29 MJ/m^3, respectively for the mini-composites pyrolyzed at 1700 °C. However, the strength reduction was observed with increasing temperatures.

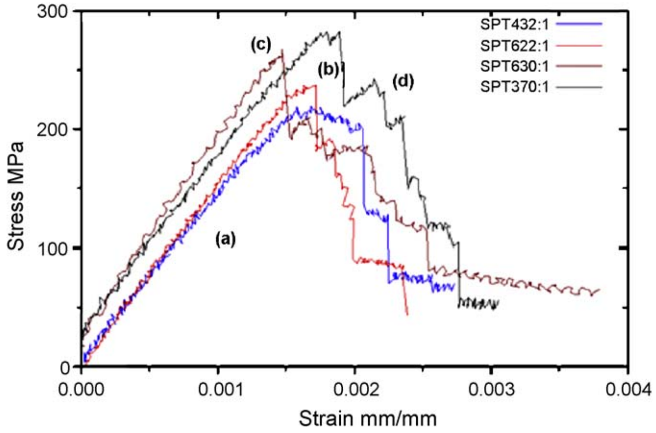

Fig. 7. Typical room temperature tensile stress–strain curves of C_f-SiC mini composites with (a) 5%ZrC, (b) 10%ZrC, (c)15%ZrC and (d) 20%ZrC processed at 1600 °C.

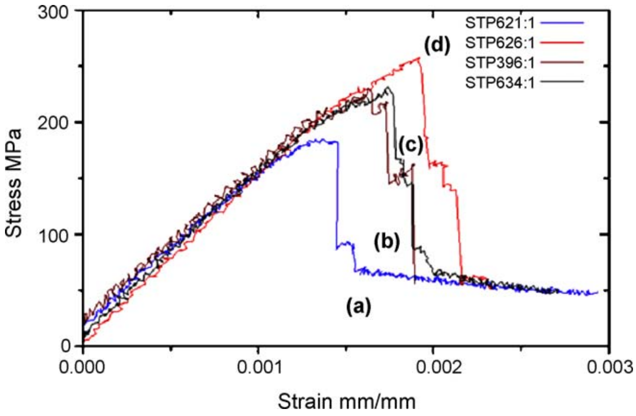

Fig. 8. Typical room temperature tensile stress–strain curves of C_f-SiC mini composites with (a) 5%ZrC, (b) 10%ZrC, (c) 15%ZrC and (d) 20%ZrC processed at 1700 °C.

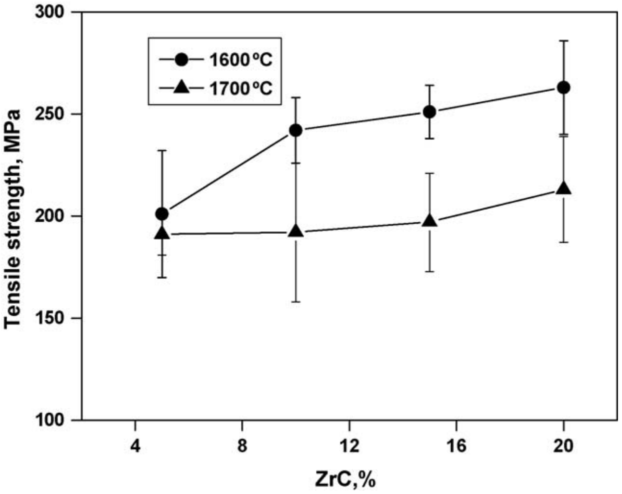

Fig. 9. Variation of tensile strength of mini-composites as a function of temperature and % of ZrC.

Fig. 7 shows the stress–strain behavior of mini-composites pyrolyzed at 1600 °C. The mini-composite pyrolyzed at 1600 °C shows a linear region, which was reflecting the elastic deformation of the composites and a gradual decrease in load after the point of maximum load, due to the individual fiber breakage. Mini-composites exhibited the non-brittle fracture characteristics, displaying a step-like path and the failure of individual fibers showing multi-step fiber fracture with matrix cracks. Fig. 8 shows the tensile behavior of mini-composites pyrolyzed at 1700 °C. In case of mini-composites pyrolyzed at 1700 °C stress decreased rapidly after the point of maximum load due to the brittle nature of the composite. Fig. 9 shows the variation of tensile strength with the addition of ZrC from 5 to 20% as well as with pyrolysis temperature.

In order to quantify these results, several mini-composite samples were prepared and tensile tests were carried out. Weibull statistical analysis was carried out on this data to obtain the Weibull modulus. Weibull modulus gives an idea about the scatter in the data and higher the value lower is the scatter. Fig. 10 presents a typical Weibull plot for the carbon-fiber reinforced SiC + 20%ZrC composites processed at 1600 and 1700 °C. Weibull shape parameters in axial direction shows different values of m, respective of the carbon fiber, matrix and the strength level. This result supports that the tensile strength obtained for a constant gauge length can be generalized as a measure of the fiber strength depending on the matrix microstructure.

In the case of C_f-(SiC + ZrC) mini-composites processed at 1700 °C mini-composites have showed the brittle failure with

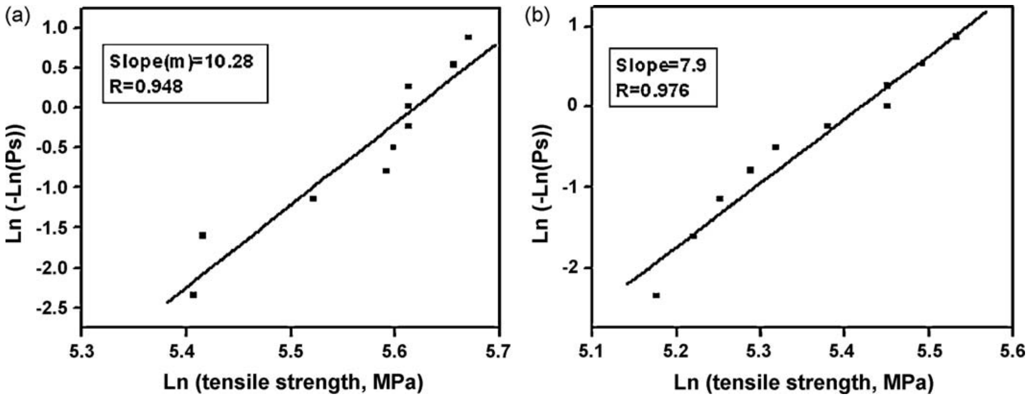

Fig. 10. Plot to obtain the Weibull modulus for C_f-(SiC + ZrC) mini-composites (a) 10.28 for 10 samples pyrolyzed at 1600 °C and (b) 7.9 for 10 samples pyrolyzed at 1700 °C (R = linear regression and Ps = survival probability).

lower strength values. The reason for brittle behavior in the composites pyrolyzed at temperature above 1700 °C is considered to be mainly due to the strong fiber:matrix interfacial bonding and the degradation of the fibers due to the possible reactions between silicon carbide and residual silica as well as reactions between carbon fiber and zirconia at high temperature [22]. Therefore, it can be concluded that the fiber:matrix interfacial bonding in the composite pyrolyzed at 1600 °C is believed to be desirable in comparison with the composite pyrolyzed at higher temperatures, which may be responsible for the good mechanical properties in these composites. There is further evidence that at temperatures above 1650 °C, carbon fiber reacts with ZrO_2 to form a strong interface boding deteriorating the mechanical properties [23].

To the best knowledge of the authors, tensile strength of C_f-(SiC + ZrC) mini-composites has not been reported so far by any earlier investigator. A comparison of the tensile strength values (201–263 MPa) of C_f-(SiC + ZrC) mini-composites with that (316 MPa) of C_f-SiC mini-composites (14) indicates that tensile strength of C_f-SiC mini-composite decreases with the addition of ZrC. This decrease is due to the addition of ZrC, which possesses lower strength than SiC as well as due to increased porosity in C_f-(SiC + ZrC) compared to that in C_f-SiC mini-composites (14). The results in Fig. 9, however, show that tensile strength of C_f-(SiC + ZrC) mini-composites increases with increase amount in %ZrC. This increase in strength with increasing %ZrC is due to the improvement in the density of the mini-composites having higher amount of ZrC, as shown by the results compiled in Table 4.

4. Conclusions

A methodology has been developed and it has been clearly demonstrated the possibility of preparation of the ultra fine (SiC + ZrC) powder as well as unidirectional carbon-fiber reinforced (SiC + ZrC) matrix mini-composites by soft-solution approach. It is possible to change the phase composition of the matrix in the composite by changing the precursor composition. The results are as follows:

X-ray diffraction of the powders and the composites confirms that β-SiC and ZrC form in the matrix phase. The crystallite sizes of SiC and ZrC in the mini-composites are in the range of 25–40 nm for both processing temperatures. Microstructure of the cross-section clearly has shown the matrix formation around each individual fiber in the mini-composite.

The addition of ZrC to the matrix from 5 to 20% improves the room temperature tensile properties of the mini-composites. From the results, the addition of ZrC (10–20%) greatly improves the strength of the mini-composites. Evaluation of room temperature tensile property shows that in the composites processed at 1600 °C, strength increases gradually with the ZrC content. However, in case of composites processed at 1700 °C, strength varies only within 5% with the variation of ZrC content between 5 and 20%. Weibull statistics supports that the tensile strength obtained for a constant gauge length can be generalized as a measure of the fiber strength depending on the matrix microstructure.

This difference may be due to stronger fiber:matrix interface bonding and possible reactions between silicon carbide and residual silica in the matrix at high temperatures. In addition, at higher temperature zirconia can react with carbon fibers forming a strong interface bonding resulting in poor mechanical properties. The present study confirms the fiber:matrix interphase characteristics play a key role in controlling mechanical properties of the fiber-reinforced composites. The mechanical properties of obtained mini-composites at higher temperature are in progress.

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