Synthesis of carbon fibre-reinforced, silicon carbide composites by soft-solution approach

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Abstract. The aim of the present work centers on synthesizing and characterizing carbon fibre (C_f) reinforced, silicon carbide matrix composites which are considered to have potential applications in aerospace and automobile industry. A series of composites, namely the C_f-SiC, C_f-(SiC+ZrC), C_f-(SiC+ZrB$_2$), and C_f-(SiC+ZrO$_2$), have been prepared by a proposed soft-solution approach. This approach involves the use of water-soluble precursors of colloidal silica, sucrose, zirconium oxychloride, and boric acid as sources of silica, carbon, zirconia, and boron oxide, respectively to achieve the desired matrices through drying, carbonization and carbothermal reduction. The prepared powders and the composites were characterized by thermal analysis, X-ray diffraction (XRD), optical microscopy, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analyses to assess the phase formation and microstructure of the materials, apart from assessment of their tensile properties. The study shows that the soft-solution process yields matrices with finer crystallite sizes, having homogeneous distribution of the constituent phases of either the powders or of the composite matrices. The role of the additional phases on the tensile properties of the composites has been discussed using consideration of thermal stresses at fibre-matrix interface; whereas the role of the carbothermal reduction temperature in determining these properties has been explained using the interfacial characteristics of the fibre-matrix. Addition of ZrO$_2$ in the matrix of SiC has shown to improve the properties of C_f-SiC composites considerably. The results of this investigation unambiguously demonstrate that aqueous solution-based processing can be used for fabrication of these composites in relatively shorter time in an environmental friendly manner without using any expensive equipment. The approach is capable

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of yielding composites with different phases in the matrix by simple variation of precursor materials and solutions. The small crystallite sizes, fine particle distribution and low carbothermal reduction temperatures are some of the specific merits of the proposed method.

Keywords. Carbon fibre, silicon carbide composites; soft-solution approach; carbothermal reduction; tensile strength; interfaces.

1. Introduction

Significant progress has been made in the field of continuous carbon fibre reinforced silicon carbide matrix (C_f-SiC) composites which are potential candidates for applications where high specific strength with suitable fracture toughness at elevated temperatures are required in several applications, such as automotive brakes, high-efficiency engine systems, chemical reactors and re-entry space vehicles (Rak 2001; Deo *et al* 2003; Naslain 2005; Zhang *et al* 2008; Zhang & Li 2009). But these applications using these composites are limited by the numerous processing difficulties, inadequate material data base, high cost of precursors, expensive equipments for synthesis (Evans & Zok 1994). Though C_f-SiC composites can be synthesized by several methods, each of the existing processing methods is usually associated with limitations specifically pertaining to reproducibility, cost, and environment. Hence, new processing techniques are required to meet the demands to synthesize high performance and cost-effective C_f-SiC composite materials in simple, rapid and environmental friendly manner. This investigation is an attempt to meet such challenges for preparing C_f-SiC as well as C_f-SiC with different additional phases in the matrix of these composites.
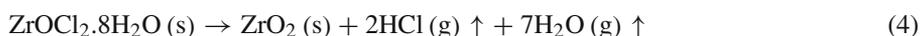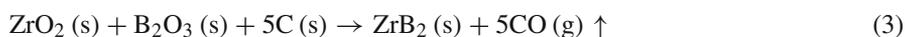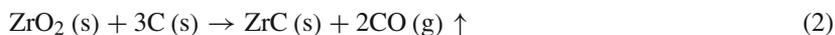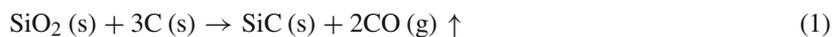
A variety of methods, such as chemical vapor infiltration (CVI), polymer impregnation and pyrolysis (PIP), liquid silicon infiltration (LSI), sol–gel, reaction hot-pressing, have been used for the fabrication of C_f-SiC composites (Reed 1995). The description of these processes together with their merits and demerits are available in the open literature. In the CVI method, the matrix is prepared by infiltrating the preforms via reaction of gaseous precursors, but this is expensive (Naslain 2004). The PIP method is based on the use of organo metallic pre-ceramic precursors (Mentz *et al* 2006); higher number of cycles for 'impregnation/pyrolysis' steps are required for manufacturing relatively dense materials by this method which makes it expensive and time-consuming (Lee *et al* 2007). In LSI method, porous C_f-C is produced by pyrolysis of carbon-rich resin matrix and is then infiltrated with molten silicon (Krenkel 2001); but the presence of free silicon may act as a source of failure. The hot pressing method used for the manufacture of C_f-SiC composites is limited by its capacity to form only simple shapes, but often degrades the fibre reinforcement. The sol–gel processing for ceramic composites inherits the merits of fine scale mixing and low densification temperature, which leads to improved properties (Liedtke *et al* 2007), but is limited due to relatively higher shrinkage during processing. However, there is scanty knowledge about the mechanical property, morphological evolutions, and damage behaviour of C_f-SiC composites under tensile loads. Evaluation of the role of environment on damage mechanisms and the service life of these materials under different types of mechanical loading are needed to assess the applicability of C_f-SiC composites (Verrilli *et al* 2004).

The state-of-the-art of preparation and characterization of C_f-SiC composites indicates that (i) the existing methodologies to fabricate these composites have several limitations and (ii) characterization techniques for the microstructural constituents are established, but estimation of the mechanical properties needs careful attention and more emphasis. Based on this background, an

attempt has been made in this investigation to prepare C_f-SiC composites by a new approach with an emphasis on understanding the possible role of additives on the matrix material. The primary goal has been supplemented by characterization of the tensile properties. The main objective of this investigation is to develop a simple and rapid process to fabricate C_f-SiC composite which is capable of overcoming a major part of the limitations associated with the existing processes. The steps to fulfill the objectives are: (i) to study the feasibility of soft-solution approach to prepare matrix materials, (ii) to prepare C_f-SiC composites without/with additional phases of varying amounts and (iii) microstructural characterization and evaluation of tensile behaviour of the composites. To achieve the objectives, the present work has been divided into following sections: section 2 deals with the preparation of powder/powder mixtures of SiC, ZrC, ZrB$_2$ and ZrO$_2$ using soft solution approach. Preparation of C_f-SiC composites as well as C_f-SiC composites with additional phases like ZrC, ZrB$_2$ and ZrO$_2$, are given in section 3. Microstructural characterization of the composites is given in section 4. Tensile behaviour of the C_f-SiC composites followed by their statistical analysis are given in section 5. The summary and conclusions are provided in section 6.

2. Processing of ceramic powders by soft-solution approach

Water-soluble colloidal silica (silica, 40 wt.%), sucrose ($C_{12}H_{22}O_{11}$), boric acid (H_3BO_3) and zirconium oxychloride ($ZrOCl_2.8H_2O$) have been used as raw materials for achieving silica, carbon, boron oxide (B_2O_3) and zirconium dioxide (ZrO_2), respectively. The following stoichiometric reactions are involved with the preparation of the different types of powder mixtures consisting of SiC, ZrC, ZrB$_2$ and ZrO$_2$.

$$SiO_2 \, (s) + 3C \, (s) \rightarrow SiC \, (s) + 2CO \, (g) \uparrow \tag{1}$$

$$ZrO_2 \, (s) + 3C \, (s) \rightarrow ZrC \, (s) + 2CO \, (g) \uparrow \tag{2}$$

$$ZrO_2 \, (s) + B_2O_3 \, (s) + 5C \, (s) \rightarrow ZrB_2 \, (s) + 5CO \, (g) \uparrow \tag{3}$$

$$ZrOCl_2.8H_2O \, (s) \rightarrow ZrO_2 \, (s) + 2HCl \, (g) \uparrow + 7H_2O \, (g) \uparrow \tag{4}$$

The soft-solution approach involves the following steps to prepare the composite powder/powder mixtures: (i) preparation of green precursor solutions by dissolution of the raw materials, (ii) drying of precursor solutions at room temperature at least for 2 days followed by heating at 338 K for 12 h, (iii) carbonization of dried powders at 773 K/1 h for the conversion of sucrose to carbon as well as decomposition of zirconium oxychloride to zirconia and boric acid to boria and (iv) finally carbothermal reduction of oxides to carbides/borides at 1873 and 1973 K for 3 h as shown by the reactions (1), (2) and (3).

The dried green powders have been first subjected to thermogravimetric analyses to understand the changes in the reactants during heating. The onset temperature of carbothermal reductions for these powders prepared by the soft-solution process is $\leq$1673 K. But the temperatures for carbothermal reductions of silica, zirconia and zirconia+boria are found to be 1788, 1930 and 1770 K, respectively from thermodynamic data. The lowering of temperature for the onset of carbothermal reduction of green precursors has been attributed to the amorphous nature of the obtained carbon.

XRD patterns of the processed SiC powders in figure 1 primarily indicate the characteristic peaks of cubic β-SiC. The estimated crystallite sizes of β-SiC processed at 1873 and 1973 K are 23.6 nm and 27.8 nm, respectively. The observed higher crystallite size at 1973 K can be
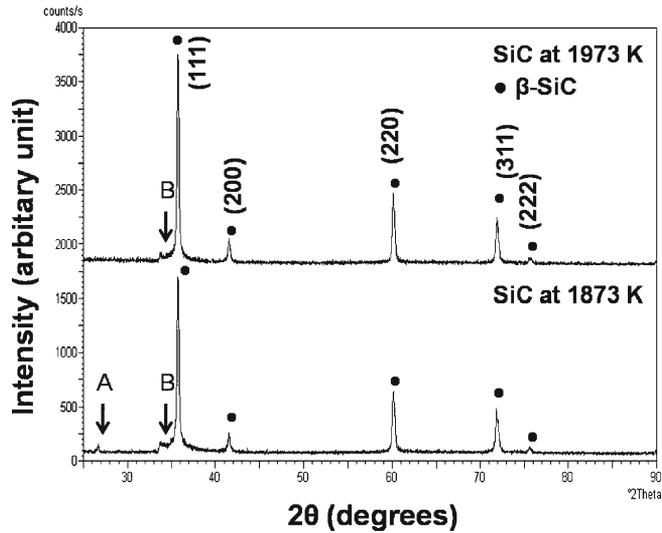
Figure 1. XRD patterns of SiC powder obtained after carbothermal reduction of silica at 1873 and 1973 K. Peaks at A and B are attributed due to unreacted silica and stacking fault in β-SiC, respectively.

attributed to the grain growth of β-SiC. The XRD patterns of the powder/powder mixtures of ZrC, ZrB_2, (SiC+ZrC) and (SiC+ZrB_2) show only the characteristic peaks of β-SiC, ZrC and ZrB_2 free from any un-reacted carbon, silica and zirconia. The XRD of ZrB_2 and (SiC+ZrB_2) powders prepared using stoichiometric proportions of the reactants as given by Eq. (3) show
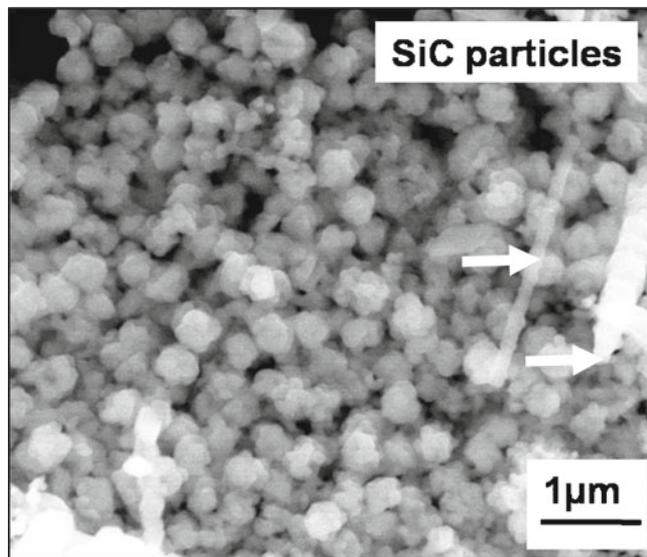

Figure 2. SEM image of SiC powder obtained by carbothermal reduction of silica showing nearly spherical particle morphology. Arrow indicates formation of whiskers.

additional peaks of ZrC. The estimated crystallite sizes of the obtained phases are in the range of 20–100 nm. The estimated crystallite sizes of β-SiC and ZrB_2 in (SiC+ZrB_2) powder are found to be 23.3 and 21.7 nm, respectively, suggesting that SiC can reduce grain growth of ZrB_2. Typical SEM image of SiC powder, processed at 1873 K, is shown in figure 2. The synthesized SiC powder appears to be agglomerate of a large number of individual crystallites; a few SiC whiskers are also found to form as shown in the same image. The particle size of SiC is of the order of 200 nm. The carbothermal reduction of silica through soft-solution approach thus generates a composite consisting of β-SiC particles and SiC whiskers in the absence of any metal catalysts from outside.

3. Processing of ceramic composites by soft-solution approach

The selected carbon fibre is of T-300 grade (PAN type, Volume: 45%, Tae Kwang Ind. Co. Ltd, Japan) with 12,000 filaments in a tow having filament diameter of about 6 μm. The details of the precursor solutions for obtaining the desired matrices are similar to that used for preparing the ceramic powder or powder mixtures as described in the preceding section. The preparation of the carbon fibre reinforced composites consisted of the following steps: (i) as-received carbon fibre tow was washed with acetone, (ii) these were vacuum-impregnated with precursor solutions of interest to achieve different matrices like SiC, (SiC+ZrC), (SiC+ZrB_2) and (SiC+ZrO_2), (iii) dried at room temperature for 6 h and at 338 K for 2 h for removal of any excess water. The dried samples were then carbonized at 773 K for 1 h in order to convert sucrose to carbon. The sequence involving 'vacuum impregnation, drying and carbonization' was repeated for 6 cycles to improve the density of the composites. Samples were reduced at 1873 K and 1973 K for 3 h in argon atmosphere. The density of the prepared composites has been measured using Archimedes principle. The estimated bulk densities of C_f-SiC composites processed at 1873 and 1973 K are 1870 and 1830 kg/m^3, respectively. The density of the composites increases with increasing amount of the additional phases like ZrC, ZrB_2 and ZrO_2.

4. Microstructure of the composites

The nature and crystallite sizes of the matrix phases in the microstructures of the prepared composites have been estimated by XRD and SEM. The XRD patterns of processed composites are shown in figure 3. The C_f-SiC composite shows peaks of β-SiC and graphite originating from carbon fibre, while composites with additional phases also exhibit peaks of the corresponding additional constituents like ZrC, ZrB_2 and ZrO_2. The crystallite sizes of the matrix phases have been estimated by Scherrer analyses and these are found to be in the range of 10–40 nm. The crystallite sizes of the matrix phases of the composites are smaller than that of the corresponding phases in the concerned powders, suggesting hindrance to grain growth in the composites by the fibres and additional phases. For example, the presence of SiC inhibits the grain growth of ZrB_2 in C_f-(SiC+ZrB_2) composites and vice versa. Grain growth of the matrix phases is observed with increase in processing temperature; for example the crystallite sizes of β-SiC, processed at 1873 and 1973 K are 23.7 nm and 28.3 nm, respectively.

Typical cross-sectional images of C_f-SiC composites, processed at 1873 and 1973 K are shown in figure 4. The fibres are embedded in a densified matrix with original shapes and are having nearly homogeneous distribution within the matrix, indicating almost no damage to the fibres during the fabrication of the composites. However, fine cracks (marked with arrows in figure 4b)
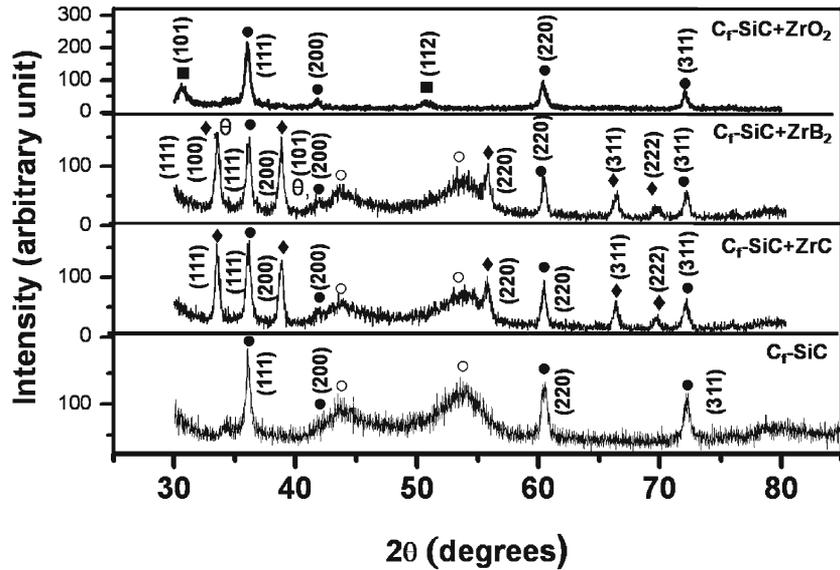
Figure 3. XRD patterns of C_f-SiC composites with/without additional phases. The symbols used for the diffraction peaks of the different phases are: ●-β-SiC, ◆-ZrC, θ-ZrB$_2$, ■-ZrO$_2$ and ○-graphite.

are observed at fibre–matrix interface of the composites, processed at 1973 K; formation of these fine cracks has been attributed to thermal mismatch at fibre–matrix interface at higher processing temperature. Uniform distribution of fibres within the matrix as well as that of the constituent phases is observed in all the composites, processed at 1873 and 1973 K. A thin layer of ZrC around the carbon fibres in C_f-(SiC+ZrC) and C_f-(SiC+ZrB$_2$) composite, processed at 1973 K is observed and this is attributed to possible reaction between carbon fibre and ZrO$_2$ at the fibre–matrix interface.
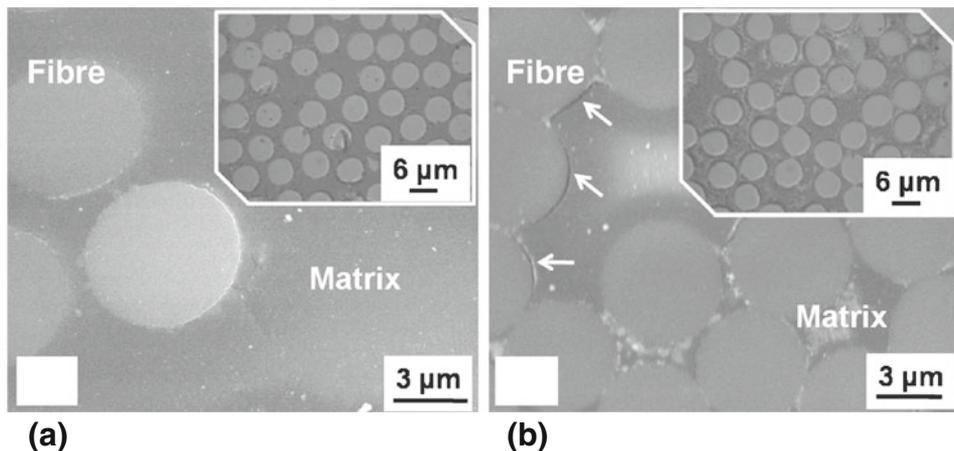

Figure 4. SEM images of C_f-SiC composites, processed at (**a**) 1873 K and (**b**) at 1973 K. The inserts are optical images at lower magnification. The arrows indicate cracks at fibre–matrix interface.

5. Tensile behaviour of composites

Tensile tests were carried out on specimens having 50 mm gauge length and 0.657 mm gauge diameter using paper tabs with suitable adhesive for gripping following ASTM standards (ASTM D4018, 2001). These tests were carried out at a cross head speed of 0.5 mm/min using an Instron machine (Model 8801, UK) fitted with 1 kN load cell. For each type of composite, 10 tensile tests were made to estimate average tensile strength and tensile fracture energy, and the results were subjected to Weibull statistical analysis following Lamon (2001).

Typical stress–strain plots of the C_f-tow and C_f-SiC composites are shown in figure 5. The stress–strain plots of C_f-tow exhibit that stress first increases linearly followed by a non-linear regime up to the maximum stress and then it decreases gradually in a jerky manner till fracture. The jerks after maximum load are attributed to the breakage of individual fibre or bunch of fibres in the fibre tow bundle (figure 5a). The stress–strain behaviour of C_f-SiC composites, processed at 1873 K, also exhibits the three different regimes till fracture of C_f-tow. The nonlinear domain of the stress–strain curve for C_f-SiC unlike C_f-tow is considered to originate from matrix micro-cracking while the step-wise failure is indicative of fibre de-bonding and pullout (figure 5b). The stress–strain behaviour of C_f-SiC composites, processed at 1973 K, exhibits catastrophic failure which is presumed to be governed by the strengthening of fibre-matrix interfacial bonding (Padmavathi *et al* 2008).

The variations of tensile strength of C_f-SiC with processing temperature as well as that of composites with additional phases are illustrated in figure 6. The average tensile strength values of C_f-SiC composites processed at 1873 and 1973 K are 316 ± 48 MPa and 149 ± 38 MPa, respectively. Addition of ZrC and ZrB_2 to the matrix of C_f-SiC composites degrades their tensile strength and fracture energy, while addition of ZrO_2 improves their tensile properties. The degradation of tensile strength owing to the addition of ZrC and ZrB_2 to the matrix of C_f-SiC composites is attributed to the presence of considerable thermal stresses at fibre-matrix interfaces developed due to chemical reaction between the fibres and the matrix. The improvement in tensile strength of C_f-SiC composites by the addition of ZrO_2, has been explained due to the presence of finer crystallite sizes of SiC and t-ZrO_2 in the matrix and due to the transformation toughening of t-ZrO_2.

Typical fracture surfaces of the composites, processed at 1873 and 1973 K are shown in figure 7. The former one (figure 7a) is associated with longer fibre pull-out while the latter one (figure 7b) exhibits shorter fibre pull-out. Since identical fibres and processing conditions except different carbothermal reduction temperatures are used for the preparation of all the composites,
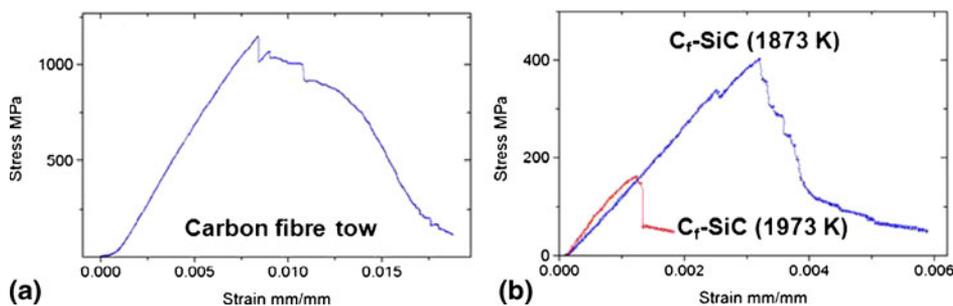

Figure 5. Stress–strain plots of (**a**) carbon fibre tow and (**b**) C_f-SiC composites. The processing temperatures are shown in parentheses.
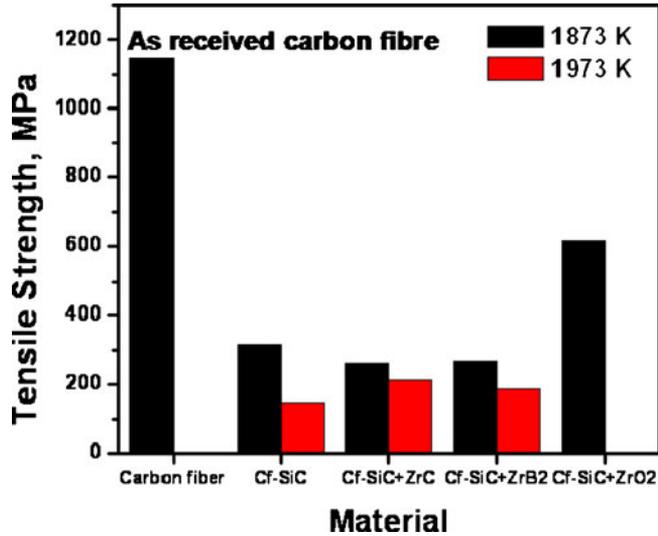
Figure 6. Variation of tensile properties.

it is reasonable to assume that the discrepancy in the mechanism of fracture and hence in tensile properties is due to variation of interfacial characteristics of the fibre and the matrices (Padmavathi *et al* 2009a & 2009b). The magnitudes of Weibull shape parameter (m) associated with tensile strength values of C_f-SiC composites having additional phases like ZrC, ZrB_2 and ZrO_2 indicate, in general, relatively lower scatter whereas the estimated values of Weibull shape parameter associated with fracture energy usually exhibit larger scatter. Limited oxidation tests
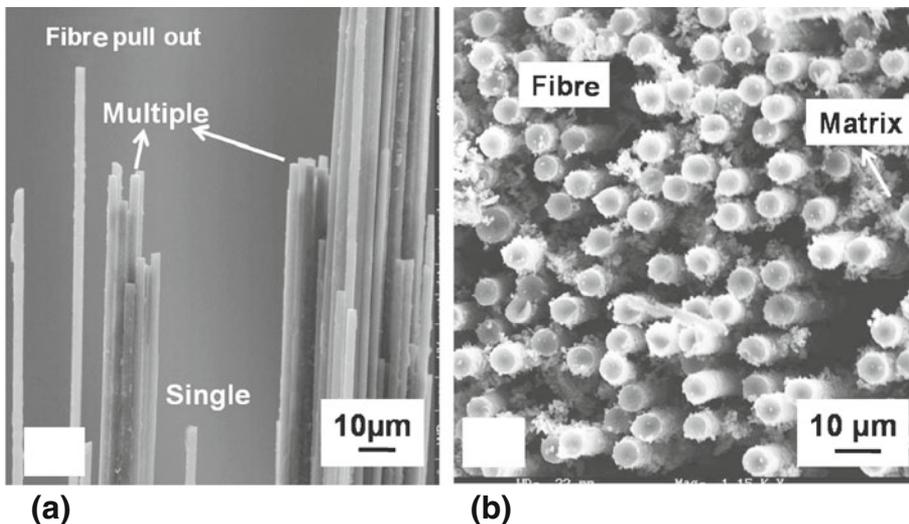

(a)   **(b)**

Figure 7. Fracture surfaces of C_f-SiC composites processed at: (**a**) 1873 K and (**b**) 1973 K.

indicate that the composites with additional phases, i.e., ZrB_2 or ZrC are more resistant to oxidation than their monolithic forms (i.e., ZrB_2 or ZrC) due to the formation of surface oxide products like SiO_2 and ZrO_2, which protect the composites against complete degradation by oxidation.

6. Summary and conclusions

The feasibility of an aqueous solution-based method to prepare SiC, SiC+ZrC, SiC+ZrB$_2$ and SiC+ZrO$_2$ powders and their composites with carbon fibre reinforcement has been established, this effort is supplemented by suitable characterization of the prepared powders and composites. The methodology has the advantage to prepare the powders and the composites in a relatively shorter time and in an environmentally friendly way. This method bears the potential for extension to the synthesis of metal carbides and borides and their composites. The following conclusions have emerged from this study.

(i) A procedure has been developed to prepare ultra-fine SiC powders using aqua-based precursor solutions. This approach has been successfully employed to prepare powder/powder mixtures like SiC, (SiC+ZrC) and (SiC+ZrB$_2$). Small crystallite sizes ($<$100 nm) and uniform distribution of the phases have been obtained due to molecular level mixing of the precursor materials.

(ii) The suggested methodology is capable of preparing C_f-SiC, C_f-(SiC+ZrC), C_f-(SiC+ZrB$_2$) and C_f-(SiC+ZrO$_2$) composites by simple variation of precursor materials and solutions, and are free from un-reacted species.

(iii) The crystallite sizes of all the phases in the synthesized matrices are in the range of 20–40 nm and the fibres are uniformly distributed within the matrix of the composites at both the processing temperatures of 1873 and 1973 K. A few cracks are observed at the fibre-matrix interface of the composites processed at 1973 K.

(iv) Tensile properties of the processed composites are found to be inferior compared to that of carbon fibre tow. The tensile strength and fracture energy of C_f-(SiC+ZrO$_2$) composites are superior compared to that of C_f-SiC composites. The composites processed at 1873 K exhibited superior properties than those of composites processed at 1973 K. The average values of both tensile strength and fracture energy of C_f-SiC composites increase with increasing amounts of additional phases like ZrC, ZrB$_2$ or ZrO$_2$.

(v) The observed phenomena of long and short fibre pull-out of the composites processed at 1873 and 1973 K, respectively, during their fracture indicate weaker and stronger fibre-matrix interfacial bonding, respectively. The nature of the interfacial bonding is governed by generated thermal stresses at the interface, chemical reaction between fibre and matrix and degradation of fibres.

(vi) The magnitudes of Weibull shape parameter (m) associated with the tensile strength values of C_f-SiC composites having additional phases like ZrC, ZrB$_2$ and ZrO$_2$ indicate, in general, that these are associated with lower scatter whereas the estimated values of Weibull shape parameter associated with fracture energy usually exhibit larger scatter.

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