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Solution based processing and properties of carbon fiber reinforced SiC + ZrO_2 composites

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ABSTRACT

Uni-directional carbon fiber (C_f) reinforced SiC + ZrO_2 composites were prepared by a solution approach in which the matrix was prepared using water-soluble precursors of colloidal silica, sucrose and zirconium oxychloride as sources of silica, carbon and zirconia respectively. After suitable heat treatment, the precursors convert into fine SiC + ZrO_2 particles with a uniform dispersion. In C_f/SiC + ZrO_2 composites, in situ formation of SiC + ZrO_2 provides an effective way for uniform dispersion of SiC and ZrO_2 in the matrix. Analysis indicates complete reaction of the precursors to yield SiC + ZrO_2 as the composite matrix. The room temperature mechanical properties and the fracture behaviour of the composites were examined. A tensile strength of 617 ± 54 MPa and fracture energy of 2.69 ± 0.9 MJ/m^3 were obtained. The tensile strength of C_f/SiC + ZrO_2 composites was twice that of C_f/SiC composites produced by same approach. This is attributed to stabilization of the zirconia phase in the presence of the SiC phase by tailoring the starting materials and their composition.

1. Introduction

The development of new classes of structural materials is a renewed emphasis area to use in the extreme environments like maneuverable hypersonic vehicle. These materials research studies a broad range of material properties such as strength, toughness, fatigue resistance, and corrosion resistance [1]. During the last three decades, research in the discovery of new classes of materials and development of processing methods for ultra high temperature materials has been erratic [2]. As a result, there is a scarcity of fundamental research data available on the mechanical performance and manufacturability of ultra high temperature materials [3]. As well known, zirconia-based ceramics have demonstrated a wide range of attributes, including high melting point ($Tm \approx 2700\ ^\circ C$) and stability, high strength and toughness, good heat resistance, unique wear resistance, interesting electronic properties such as fast ionic conductivity for structural and functional applications [4]. In advance, the problem of the low fracture toughness of ceramics can be overcome by designing and preparing composite materials reinforced with fibers, whiskers and particles. Up to now, surprisingly there are a few researches on ZrO_2-matrix composites reinforced with fibers. The interest in ceramic matrix composites (CMCs) is continually growing due to their great flexibility in designing and tailoring of properties for multi-component systems. Especially, CMCs reinforced with high strength continuous ceramic fibers, have attracted much attention for high temperature structural applications because of their superior high temperature strength, reduced weight and improved damage tolerance [5,6]. Particularly, carbon fiber reinforced CMCs 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 [7]. The aim of the present work was to explore the potential of continuous carbon fibers reinforced SiC + ZrO_2 matrix composites by in-situ development for structural applications.

Several processing methods, such as chemical vapor infiltration (CVI), polymer impregnation and pyrolysis (PIP), sol–gel method, slurry infiltration followed by hot pressing, and in situ chemical reaction techniques, have been employed for fabricating continuous fiber-reinforced CMCs [8]. Each processing method has its advantages and disadvantages pertaining to reproducibility, cost, and performance of the composite. New processing techniques are desirable to meet the demands of high performance and low

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cost. The solution approach is using low-cost materials such as colloidal silica, zirconium oxychloride, boric acid and sucrose [9]. The processing conditions are so selected as to promote nanometer-scale mixing of different phases which can subsequently produce homogeneous composites with any selected reinforcement; the matrix is formed in situ. The present method to synthesize 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 [9–11].

Unidirectional carbon–fiber reinforced SiC + ZrO_2 matrix composites are prepared by solution approach by impregnating the solution phase into a carbon fiber tow, drying, converting sucrose into carbon phase, and finally reducing silica with carbon to form silicon carbide and zirconium oxide. Processing, microstructure and mechanical properties of the composites are mainly studied.

2. Experimental procedure

2.1. Materials

Carbon fiber tow was of T-300 grade (fiber vol%, 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 oxychloride ($ZrOCl_2{\cdot}8H_2O$, 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 composites.

2.2. Processing of composites

SiC + ZrO_2 matrix forms by the decomposition of zirconium oxychloride and carbothermal reduction of silica at high temperatures. The precursor solutions with varying amounts of colloidal silica, sucrose, and zirconium oxychloride were prepared. The amounts of the ingredients were calculated considering the following stoichiometric reactions involved for the preparation of composites consisting of SiC + ZrO_2 as the matrix.

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

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

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

The amounts of the ingredients are usually expressed in terms of molarity (a measure of concentration of a solution in number of moles of the solute per liter of solution). Typical calculations for the amounts of raw materials in molarities (mol/L, M) required for the preparation is summarized in Table 1. The desired nominal compositions of the composites were SiC: 5 wt% ZrO_2, SiC: 10 wt% ZrO_2, SiC: 15 wt% ZrO_2, and SiC: 20 wt% ZrO_2. 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 + ZrO_2 as presented in Table 1.

Impregnated tows were dried carefully at room temperature and at 60–70 °C for 12 h. The dried tows were carbonized at 500 °C under argon atmosphere for 1 h for converting sucrose into carbon. Evaporation of bonded water of zirconium oxychloride also occurs during carbonization of sucrose. These steps were repeated for 5–6 cycles (further cycles were not required after completion of six cycles due to the rapidly decreasing effectiveness of further impregnation). After the desired impregnation/carbonization cycles, green composites were carbothermally reduced at 1600 °C for 3 h under flowing argon to obtain the SiC + ZrO_2 matrix. Flow sheet for the employed process is shown in Fig. 1.

2.3. Characterization of composites

The prepared composites were subjected to X-ray diffraction (XRD, Philips Model No. PW 320) to identify the phases formed and to determine the crystallite size of the individual phases. It was difficult to prepare cross-sectional polished samples from the composites. It was possible to view the microstructure of the composites by filling the porosity with a low-viscosity resin and polished using fine ceria powder as a media. Environmental scanning electron microscopy (ESEM, FEI, and QUANTA 400, The Netherlands) was used to study the microstructure of the composites.

In this approach, single tows were impregnated along the fiber direction to get the composite. One of the benefits with the mini-composite approach was the better utilization of the expensive fiber material. The tow composite samples can be stressed in uni-axial direction in tension, which gives more appropriate data, compared to flexure testing [12,13]. Tensile tests were conducted

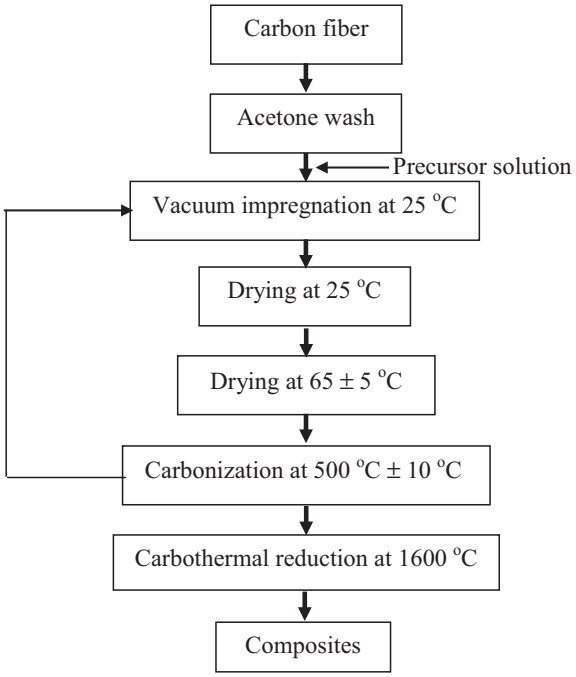

Fig. 1. Flow chart for the synthesis of C_f/SiC + ZrO_2 composites using solution approach.

Table 1
Estimated amounts of the reactants and corresponding raw materials.

Composition	Colloidal silica (ml) → silica (g)	Sucrose (g) → carbon (g)	Zirconium oxychloride (g) → zirconia (g)
SiC + 5%ZrO_2	355.90 → 142.36	285.50 → 85.66	13.07 → 5.00
SiC + 10%ZrO_2	337.16 → 134.87	271.74 → 81.53	26.14 → 10.0
SiC + 15%ZrO_2	318.43 → 127.37	254.54 → 76.37	39.21 → 15.0
SiC + 20%ZrO_2	299.70 → 119.88	240.78 → 72.24	52.28 → 20.0