Chapter 1

Introduction

1.1. General

In recent years, there is world wide interest for the development of materials for use in the automotive, aerospace and other industrial components, operating at elevated temperatures under adverse environmental conditions. Weight reduction, improved service performance and significant decrease in the manufacturing cost of components are the major driving forces for the development of the new generation of materials, particularly composites. In the field of ceramic-matrix composites (CMCs), which are potential candidates for engineering applications where in low density, high strength, and high toughness are required, significant progress has been made over the last two decades (Lubin, 1982; Peters, 1998). These CMCs are candidate materials for applications at high-temperatures often as substitutes for conventional ferrous materials and light alloys like those in re-entry space vehicles, thermal protection system, automotive brake disks, heat exchangers, gas turbines, and chemical reactors (Flegel, 2001; Gadow and Speicher, 2001; Luthra and Corman, 2001; Naslain, 2005; Zhang and Li, 2009). The present investigation encompasses this regime of research direction.

Ceramic-matrix composites in which continuous C or SiC fibers are embedded in a non oxide ceramic matrix have allowed significant breakthrough in improving fracture toughness of ceramic with composites (Mallick, 1997; Rak, 2001a). For example, considerable emphasis has been laid on the developments of fiber-reinforced ceramic matrix composites (CMC) for various applications at elevated temperatures as stated in the preceding paragraph. In addition, use of composite materials in commercial transport aircraft is attractive because reduced airframe weight enables better fuel economy and therefore lowers operating costs (Deo, 2003).

Carbon-fiber-reinforced carbon (C/C) is one of the most important CMCs, which has been under development since the 1960s (Buckley, 1988; Kimura, 1976; Savage, 1993; Shindo, 1961). These composites have been initially designed and produced for use in rocket engines and re-entry heat shields, which require components to withstand extremely severe service conditions but short lifetimes (Sheehan, 1994). In the second stage of development, carbon-silicon carbide (C_f-SiC) and silicon carbide-silicon carbide (SiC_f-SiC*)* composites are being developed in order to have composites with improved oxidation resistance and hence enhanced lifetime in oxidizing atmospheres. C_f-SiC composites are being considered for high temperature structural applications due to their low specific weight, high temperature strength, thermal shock resistance, low coefficient of thermal expansion (CTE), good thermal conductivity (TC), abrasion resistance and high fracture toughness (Besmann, 1991; Naslain, 2004; Toshihiro, 1998).

However, C_f-SiC composites have low durability except in inert atmospheres. At higher temperatures ($\geq$1973 K), the oxidation of the fiber, matrix and the interface simultaneously influence the overall oxidation behaviour of C_f-SiC composites (Glime and Cawley, 1995; Luan, 2007). Improvement of oxidation resistance of these materials at higher temperatures is thus a burning issue to the material scientists. One of the approaches to overcome this problem is to provide oxidation/evaporation resistant coatings (Upadhya, 1997). But researchers are also looking for newer solutions to provide oxidation/ablation protection for C_f-SiC composites at ultra-high temperatures. Possible use of zirconium and zirconium-based ceramics like zirconium carbide (ZrC), zirconium boride (ZrB_2) and zirconium oxide (ZrO_2) have attracted considerable attention for this purpose (Opeka, 2004). These ceramics have melting points over 3273 K, relatively low densities, and the ability to form refractory oxide of zirconium (melting point 3043 K). The addition of SiC has been shown to effectively improve the oxidation resistance of ZrB_2 and ZrC (Fahrenholtz, 2004; Wang, 2008a; Yang, 2008; Zhou, 2008a). The present investigation has taken into account the above-mentioned information for the development of C_f-SiC composites with an aim to modify the matrix of these CMCs with zirconium based ceramics.

A variety of methods such as chemical vapor infiltration (CVI)**,** polymer impregnation and pyrolysis (PIP), liquid silicon infiltration (LSI), sol-gel, slurry infiltration, reaction forming / bonding etc. have been used for the fabrication of ceramic matrix composites (Mazdiyasni, 1990; Reed, 1995). In the CVI method the matrix is prepared by infiltrating three-dimensional preforms via reaction of gaseous precursors (Ohzawa, 1997). The isothermal CVI process yields materials with good mechanical properties but requires long manufacturing time and sophisticated equipment and is, therefore, very expensive (Naslain, 2004). An alternate to isothermal CVI is the thermal gradient CVI; it is faster, but limited in producing complex shapes (Stinton, 1988).

The polymer impregnation and pyrolysis (PIP) method is based on the use of organo metallic pre-ceramic precursors such as silazanes or carbosilazanes (Mentz, 2006); complex shaped components can be manufactured by this method. However, high number of iterative cycles for 'impregnation/pyrolysis' steps are required for manufacturing relatively dense materials by this method which makes it expensive and time-consuming (Ziegler, 1999). The residual porosity in the materials fabricated by PIP significantly affects the mechanical properties of the resulting composites. One of the options of the PIP process is fabrication of ceramic composites using inert and reactive fillers to limit excessive shrinkage of the ceramic matrix (Lee, 2007). Complex shapes of C_f-SiC composites are already being manufactured by the infiltration of carbon preforms using molten silicon at 1973 K; this process leads to dense C_f-SiC material using liquid silicon infiltration process (LSI) (Bhatt, 2000; Krenkel, 2001). The method may leave residual free silicon in the product, which impairs strength at elevated temperatures.

The potential advantages of sol-gel processing for ceramic composites are fine scale mixing and low densification temperature, leading ultimately to improved properties (Liedtke, 2007), but shrinkage in the composites while processing by this method require special techniques to avoid cracking (Lutz and Swain, 1991). The hot pressing method used for the manufacture of C_f-SiC composites is limited by its capacity to form only simple plate shapes. Additionally, this method can considerably degrade the fiber reinforcement through treatment at high temperatures and pressures. However, there is scanty knowledge about the mechanical property, microstructure evolution and its influence on mechanical property and damage behavior 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, 2004).

1.2 Motivation of the work

The applications of ceramic matrix composites are still limited by the lack of suitable reinforcements, processing difficulties, sound material data bases, lifetime and cost. Continued research and development are essential to understand the issues pertaining to problems of structure-property relations in C_f-SiC materials and thereby reduce the costs of precursors (i.e., fibers and interface coatings), and to develop new cost-effective methods for a wide variety of applications. Recent processing routes using gaseous or liquid phase methods in vacuum can produce shaped material in a single step, but require considerably higher energy than standard high-temperature processes. Each of these techniques usually requires high temperature and long production period, which are not economical and environmental friendly. Environmental pollution and energy consumption are two of the key issues in all manufacturing sectors around the world. Thus, industrial processes which do not require high energy and are practiced under environmentally benign conditions bear potential for longer survival. Each of the existing processing methods for C_f-SiC has several advantages associated with limitations pertaining to reproducibility, cost, and high-temperature properties. Thus new processing techniques are required to meet the demands for challenging high performance and low cost of precursors to process advanced composite materials for elevated temperature applications.

A process, called here as soft-solution processing, can be examined to fabricate advanced composite materials in an economical, environmental friendly and energy efficient way. Yoshimura and Suchanek (1997), Yoshimura (1998), Yoshimura et al. (1999) and Yoshimura (2006) have introduced solution processing route to synthesize double oxide films (ex. coating of $CaTiO_3$ on TiAl) under hydrothermal conditions at lower temperatures; this route possesses the potential to prepare several desired materials with unique properties. Moreover, chemical composition and microstructure of the synthesized ceramics can be controlled by adjusting its processing conditions. This method involves use of only aqueous solution and as a consequence it is environmental friendly and energy efficient apart from the fact that it does not require any expensive equipment.

1.3 The major objective

The main objective of this study is to examine the possibility of developing an approach based on aqueous solution processing for the preparation of carbon fiber reinforced composites, which is flexible in terms of generating various matrix microstructures. Necessary supplement to the primary goal is to carry out pertinent characterization of the developed structures and their tensile properties.

1.4 Lay out of the work

Chapter 1 presents an outline related to the scope of the present work and the primary objective of this investigation.

Chapter 2 provides a critical review on the developments of C_f-SiC composites and addresses the issue of developing an environmental friendly methodology for preparing C_f-SiC composites with or without additives; an area which needs exhaustive investigation.

Chapter 3 incorporates information related to selection of raw materials and subsequent processing of ceramic matrix constituents followed by their characterization. These details are a-priori required for the preparation of C_f-SiC and C_f-(SiC+ additive) composites; the additives considered are ZrC, ZrB_2 and ZrO_2.

Chapter 4 presents the detailed descriptions of the experimental steps for preparing C_f-SiC composites without and with additives, and their subsequent characterization by XRD and SEM.

Chapter 5 elucidates the procedure for generating tensile stress-strain data for the fabricated composites and then describes their tensile behaviour and incorporates information on fracture surface examinations. Statistical analyses of the tensile strength and tensile fracture energy using Weibull statistics form a considerable part of this chapter.

Chapter 6 deals with the role of additional phase on the tensile and fracture behaviour of C_f-SiC composites. Some preliminary measurements on oxidation resistance are included here.

Chapter 7 presents the highlights of the inferences drawn in the preceding chapters and attempts to provide a unified view related to the contributions of the present investigation. It also incorporates suggestions for future work in this direction, which are essential to consolidate the results for exploring the commercial viability of C_f-SiC composites for the next generation.