Chapter 17

C/C–ZrB_2–ZrC–SiC Composites Derived from Polymeric Precursor Infiltration and Pyrolysis Part I:

Preparation and Microstructures

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ABSTRACT

Two-dimensional C/C-ZrB_2-ZrC-SiC composites with three phases of ultra high temperature ceramics (UHTCs) are fabricated for the first time using blending pre-ceramic polymeric precursors through the traditional polymer infiltration and pyrolysis (PIP) technique, in which a porous carbon fiber reinforced pyrolytic carbon (C/C) with a porosity of about 60% is prepared as preforms. The fabricated composite possesses a matrix of 20ZrB_2-30ZrC-50SiC, which is obtained by co-pyrolysis of three pre-ceramic polymers solution in xylene with certain molar ratios. Pyrolysis of these ZrB_2-ZrC-SiC pre-ceramic precursors is studied with XRD characterization of the residual solids. The gas phase products are analysized with an on-line GC-MS-FTIR coupling technique, which confirms the formation of crystalline ZrC and ZrB_2 from these precursors at temperatures above 1400°C. Possible mechanisms of pyrolysis and formation of pure ZrB_2 from the precursors with various B/Zr molar ratios are suggested. The densification process and microstructures of the fabricated composite are studied. It is found that a composite with a bulk density of 2.06 g/cm^3 and open porosity of 9.6% can be obtained after 16 PIP cycles. The formed matrix exhibits homogeneous dispersion of three matrix ceramics without any oxide impurities, i.e., the nano

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sized ZrB_2 and ZrC particles dispersed in a continuous SiC ceramic with clean crystalline boundaries and particle dimensions less than 200 nm. No erosion or interface reaction occurs upon the carbon fiber reinforcement, which therefore avoids a dramatic deterioration of mechanical strength of carbon fiber and the composite. Improvement of PIP benefits from two aspects; firstly, the dense pyrolytic carbon interphase deposited on fiber surface by CVI serves as barrier coating and secondly, pyrolysis of the novel organic polymeric precursors does not release corrosive by-products such as hydrogen chloride.

INTRODUCTION

Carbon fiber reinforced carbon matrix composite (C/C) has been used as nose tips, leading edges, re-entry heat shields etc, in aerospace vehicles and nozzles/throat of solid fuel engines for several decades, in which the material may experience ultra high temperature environment above 3000 ºC and detention time varies from instantaneous to thousands of seconds (Chapman & Hall, 1993; Fitzer & Manocha, 1998; Thomas, 1993). But these applications are generally proceeding at a non- or weak oxidized atmosphere, a certain degree of carbon ablation and vaporization is permitted, which results in a great deal of heat being adsorbed and subsequent cooling effect on the surface of material. However, even in these cases a lowest ablation rate was also highly expected, because a minute mass and dimension recession of the composite can also have dramatic changes on the fluid dynamic features of the high speed vehicles during flying, re-entering or propulsion (Thomas, 1993; Cui, Su, R. Li, H. Li, & Kang, 2000; Wang, Li, Ao, Xu, Liu, & Hu, 2006). Adding some refractory carbide and boride particles (now known as ultra-high temperature ceramics, UHTCs), such as ZrC, ZrB_2,TaC and HfC, or some dispersed/fibrous metals with high melting points (W, Ta) into C/C have been studied to decrease its ablation rate (Cui et al., 2000; Wang et al., 2006; Gao, Liu, Guo, Shi, & Zhai, 2007; He, Zhou, Ziong, & Huang, 2006). These dispersed additives do not change the mechanical properties of the C/C composite significantly, but decrease its ablation and denudation rates. This benefit should contribute to higher hardness, lower oxidation and vaporization rates of these UHTCs and their derived oxides than the carbon fiber and the matrix.

This kind of modification by adding dispersed UHTCs into C/C with small volume fractions does not assure the composite to be used in an oxidizing atmosphere at ultra high temperature for a reasonable duration of time, which is especially required recently from the developing of advanced air-breathing propulsion technologies, such as subsonic and hypersonic ramjet, turbo engines and combined turbo-ramjet engines with very high propulsion/weight ratios (Jackson, Eklund, & Fink, 2004; van Wie, Drewry Jr., King, & Hudson, 2004; Opeka, Talmy, & Zaykoski, 2004). In these applications, composites with low density and very low ablation rates working at air or oxygen-rich combustion gas atmosphere are highly required. Traditional C/C, ceramic particle dispersed C/C, multi-layer coated C/C, SiC matrix CMC and any monolithic ceramics cannot accomplish these kinds of applications, which has promoted great challenges to the science and engineering of ultra-high temperature materials (Jackson et al., 2004; van Wie, 2004).

UHTCs composites, especially diboride based UHTCs, such as ZrB_2-SiC and HfB_2-SiC have been studied intensively for this purpose because of their outstanding oxidation and ablation resistance at temperatures above 2000 ºC in a hypersonic oxidizing gas flow [see Ref. 11 and its cited references]. ZrB_2 exhibits extremely high melting point of 3245 °C with excellent high temperature mechanical properties, low cost and relative lower density (6.09 g/cm^3) compared to HfB_2, which exhibits an even higher melting point,