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Full Length Article

Thermal properties of C_f/HfC and C_f/HfC-SiC composites prepared by precursor infiltration and pyrolysis

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ABSTRACT

Ultra-high temperature ceramic infiltrated carbon-fibre composites were prepared by precursor infiltration and pyrolysis (PIP) using a laboratory synthesized precursor. Microstructures and thermal properties including thermal expansion, thermal diffusivity, specific heat capacity and oxidative stability are correlated. XRD reveals the presence of C_f-HfC and C_f-HfC-SiC phases without formation of oxides. The CTE observed at 1200 °C is slightly higher for C_f-HfC ($3.36 \times 10^{-6}\,K^{-1}$) compared to C_f-HfC-SiC ($2.95 \times 10^{-6}\,K^{-1}$) composites. Lower thermal diffusivity of the C_f-HfC-SiC compared to C_f-HfC composites is attributed to a thermal barrier effect and cracks in the composites which formed due to the CTE mismatch between carbon fibre and the matrix as well as CO generated during graphitization. The thermal conductivity of C_f-HfC ($4.18 \pm 0.14\,Wm^{-1}\,K^{-1}$) is higher than that of C_f-HfC-SiC composite ($3.33 \pm 0.42\,Wm^{-1}\,K^{-1}$). Composites microstructures were coarse with some protruding particles (5 µm) with a homogeneous dense (~70%) matrix (HfC and HfC-SiC) for both composites.

1. Introduction

Hypersonic re-entry vehicles, and propulsion applications require materials that can withstand extreme temperatures > 2000 °C in corrosive/oxidative atmospheres with high thermal gradient, as well as mechanical stresses, thermal or shock wave loading [1] as experienced by these vehicles during flight. Although carbon/carbon (C/C) composites meet the requirements of high-temperature strength and have low CTE, good thermal shock and ablation resistance [2], their poor oxidation resistance restricts applications in air at high temperature. Therefore, development of new materials with the ability to operate at extreme temperature in air is needed.

Ultra-high temperature ceramics (UHTCs) of group IV transition metal carbides, nitrides and borides have been studied extensively for nuclear and hypersonic aerospace structural components like inert matrix and accident tolerant nuclear fuels and thermal protection system (TPS), engine cowl inlets, turbopump rotors, nose caps, nozzle exit ramps, re-entry heat shields, rocket nozzles, and wing leading edges because of their ability to withstand temperatures above 3000 °C along with high thermal and electrical conductivities, chemical inertness and excellent ablation/oxidation resistance [3–6]. Among the different transition metal carbides, hafnium carbide (HfC) possesses the highest melting point ~3950 °C and also exhibits good ablation resistance, low vapour pressure as well as chemical inertness [7]. In addition, the oxide of HfC (HfO_2) has a high melting point and low vapour pressure [6] which makes it an attractive candidate for hypersonic aerospace structural applications.

Silicon carbide (SiC) is a common additive used to promote densification and oxidation/ablation resistance of UHTCs effectively [7–10]. It is frequently used in powder form or as thin (5–50 µm) coatings in many industrial applications such as wear-resistant coatings, corrosion or oxidation protection (silica) barriers [11–14]. Hafnium-containing silicates have been observed to limit the oxygen diffusion more than pure silica [15].

Several methods have been developed to introduce UHTCs phases into or coatings onto C/C composites in order to improve the C/C oxidation resistance. Chemical vapour deposition (CVD) of HfC coating was reported by Wang et al. [16]. Li et al. [17,18] studied ablation resistance and thermophysical properties of C/C composites by immersing carbon felt in a hafnium oxychloride aqueous solution forming different wt% of HfC by varying impregnation time and cycles. Tan et al. [19] studied the ablation behaviour and its mechanism of C/C-HfC-SiC composites prepared by CVI and PIP. Shu-Ping et al. [20] studied the effect of HfC on the ablation and mechanical properties of C/C prepared by infiltration of hafnium metallic salt. Recently, Xue et al. [21] studied the microstructure and ablation behaviour Cf-HfC

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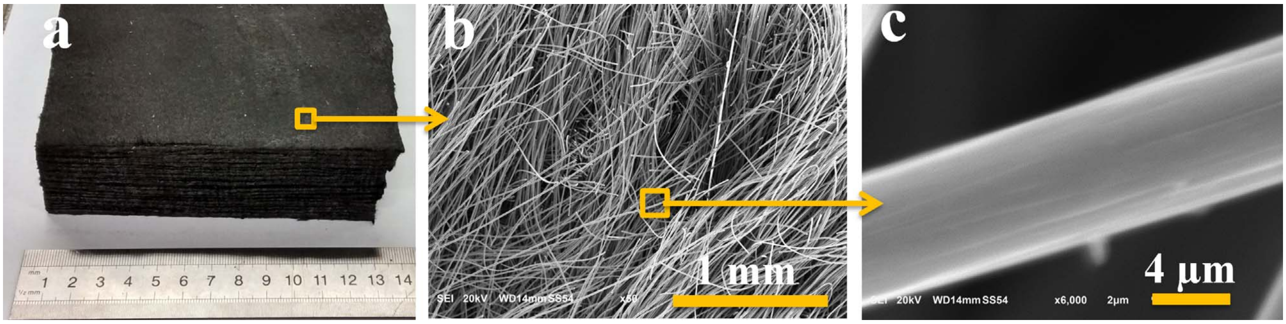

Fig. 1. (a) Optical macrograph and (b, c) SEM images of carbon fibre from the felt.

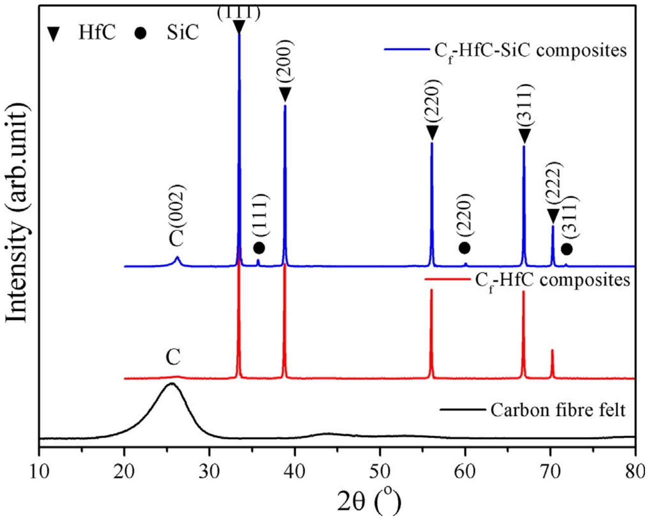

Fig. 2. XRD of as-received carbon fibre felt, C_f-HfC and C_f-HfC-SiC sintered composites.

composites by PIP. Hafnium and SiC multilayer coatings for the protection of carbon composites by low pressure LPCVD was prepared by Verdon et al. [22]. Jayaseelan et al. [23] employed a reactive infiltration process (RIP) by combining polymer infiltration (PIP) and slurry impregnation to incorporate ZrB_2 into C/C hollow tube. Paul et al. [24] prepared carbon fibre-UHTC powder composites by slurry impregnation and pyrolysis. However, there are serious problems in transition metal salt aqueous solution impregnation since it reacts with the carbon fibre surface leading to decrease in mechanical strength along with lower loading of the final matrix. In slurry impregnation the UHTC phases cannot be distributed homogeneously in the composites. The depth and impregnation efficiency is limited due to the slurry suspension. To our knowledge, little research has focused on the detailed thermophysical properties of C_f-HfC and C_f-HfC-SiC composites using PIP process which has the advantage of preparing near net shape composites with uniform phase dispersion.

In this work, UHTC infiltrated carbon fibre composites (penetrated by HfC and mixed HfC-SiC) were prepared by wet-chemical synthesised organic-inorganic hybrid PIP. The phase constituents and microstructures along with thermal expansion, thermal diffusivity, specific heat capacity and oxidative stability in air were characterised.

2. Experimental

Two-dimensional needle punched carbon fibre felt (Zoltek, USA) having bulk density of 0.1 g cm^3, was used. Hafnium tetrachloride ($HfCl_4$), acetylacetone ($C_5H_8O_2$), hydroquinone ($C_6H_6O_2$) and tetraethyl orthosilicate ($SiC_8H_{20}O_4$) obtained from Sigma-Aldrich Company Ltd, Gillingham, Dorset, UK were used as the starting materials in the synthesis of HfC and HfC/SiC precursors.

Table 1
Precursor, yield and matrix (HfC and HfC-SiC) loading versus infiltration cycle.

Carbon fibre felt (g)	Precursor loading (g)	HfC yield @1500 °C (g)	Loading (%)
Initial felt (4.90)	14.12 ± 0.2	12.12 ± 0.2	147
2nd infiltration	16.32 ± 0.2	14.06 ± 0.2	186
3rd infiltration	18.34 ± 0.2	16.26 ± 0.2	231
4th infiltration	22.22 ± 0.2	18.10 ± 0.2	269
5th infiltration	21.12 ± 0.2	18.70 ± 0.2	281

Carbon fibre felt (g)	Precursor loading (g)	HfC-SiC yield @ 1500 °C (g)	Loading (%)
Initial felt (8.1)	23.1 ± 0.2	20 ± 0.2	146
2nd infiltration	25.2 ± 0.2	22.6 ± 0.2	180
3rd infiltration	28.3 ± 0.2	26.7 ± 0.2	230
4th infiltration	32 ± 0.2	29.8 ± 0.2	267
5th infiltration	33 ± 0.2	30.8 ± 0.2	280

The HfC and HfC/SiC hybrid precursors were both synthesised in house. First hafnium tetrachloride was functionalized with acetylacetone (Hf/Acac) at 70 °C for 2 h using anhydrous ethanol as solvent to form a hafnium metal diketonate ligand in order to prevent metal ion precipitation during rapid hydrolysis and improve the solubility of metal ions in common organic solvents. Subsequently hydroquinone was added to the Hf/Acac solution and refluxed for 5 h. Similarly, for the silicon carbide, tetraethyl orthosilicate/hydroquinone were reacted at 60 °C for 3 h. The two precursor solutions were then mixed together for another 1 h. A transparent orange solution was obtained and the excess solvent was removed by a rota vapour (R-20 BUCHI Rotavapor, Switzerland).

The precursors prepared (HfC and HfC/SiC) for the fabrication of composites with carbon felt were highly soluble in common organic solvents like acetone, chloroform, methanol and ethanol informing low viscosity making it easy to infiltrate with high UHTCs matrix yield. Before precursor infiltration the carbon fibre felt was cleaned by immersing in acetone followed by ultrasonication and rinsing with deionised water to remove any organic residue and foreign contaminants from carbon fibre spinning/carbonization. Precursor infiltration was carried out in a vacuum chamber by dipping carbon fibre felt into the precursor solution of HfC and HfC-SiC with subsequent evacuation which removed air out of the pores of carbon fibre felt. The samples were kept under vacuum of 10^{-4} m bar for 10 min in the precursor solution and then released to atmospheric pressure that pushed the precursor solution into the pores. The samples were removed from precursor solution and dried in a hot air oven. C_f/HfC and C_f/HfC-SiC composites were fabricated by five cycles of infiltration with the organic-inorganic hybrid precursor into carbon fibre felt. After each infiltration cycle they were dried at 100 °C for 3 h in a hot air oven and pyrolised at 1500 °C under argon for up to 4 infiltration cycles in a horizontal tube furnace. The fifth infiltration cycle involved pyrolysis at 1500 °C with holding time of 1 h. Finally, composites were pressureless