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ScienceDirect
Journal of the European Ceramic Society 30 (2010) 2357–2364
www.elsevier.com/locate/jeurceramsoc

Improved ablation resistance of C–C composites using zirconium diboride and boron carbide☆

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Available online 13 April 2010

Abstract

Zirconium diboride and boron carbide particles were used to improve the ablation resistance of carbon–carbon (C–C) composites at high temperature (1500 °C). Our approach combines using a precursor to ZrB_2 and processing them with B_4C particles as filler material within the C–C composite. An oxyacetylene torch test facility was used to determine ablation rates for carbon black, B_4C, and ZrB_2–B_4C filled C–C composites from 800 to 1500 °C. Ablation rates decreased by 30% when C–C composites were filled with a combination of ZrB_2–B_4C particles over carbon black and B_4C filled C–C composites. We also investigated using a sol–gel precursor method as an alternative processing route to incorporate ZrB_2 particles within C–C composites. We successfully converted ZrB_2 particles within C–C composites at relatively low temperatures (1200 °C). Our ablation results suggest that a combination of ZrB_2–B_4C particles is effective in inhibiting the oxidation of C–C composites at temperatures greater than 1500 °C.

Keywords: High-temperature materials; Precursors–organic; Sol–gel processes; Thermal properties; Composites

1. Introduction

Advanced thermal protection systems are needed to mitigate effects of aerothermal heating that otherwise limit the performance of aerospace vehicles.[1] C–C composites are a family of materials that possess extraordinary and unique characteristics that make them attractive for use in a wide range of applications especially when low density materials are desirable, such as in aerospace applications.[2–4] C–C composites have very low densities in the range of 1.5–2.2 g/cm^3 while maintaining their high mechanical strengths, >3000 MPa, at elevated temperatures in non-oxidizing environments.[4] They also have high toughness values and exhibit fracture behavior that allows them to deform gracefully under load and avoid catastrophic failure when their ultimate strengths are exceeded. They can operate in severe chemically aggressive environments but require protection from oxidation and usually use coatings or oxygen inhibitor systems[5] for continuous use above 500 °C.

Extensive research has been performed on diboride based UHTCs, such as ZrB_2 due to their extremely high melting temperatures, >3245 °C, and excellent mechanical properties at high temperature. ZrB_2 has been studied due to its low density (6.09 g/cc) and low cost. In terms of oxidation mechanisms, it has been shown that ZrB_2 oxidizes to ZrO_2 and liquid B_2O_3, which evaporates at higher temperatures (>1200 °C) as B_2O_3 (g).[6] B_4C is also one of the most stable compounds with a melting temperature of 2350 °C and very low density (2.52 g/cc).[7] Densified B_4C slowly oxidizes at 600 °C and results in the formation of a thin transparent B_2O_3 film, which cracks after cooling. Up to 1200 °C the oxidation process is limited by the diffusion of reagents through the oxide layer.[8]

Low cost and reliable testing methods for evaluating oxidation resistant materials are needed in order to investigate fundamental material oxidation mechanisms at temperature. Unfortunately, there are only a couple of test facilities that can test high-temperature materials over a wide range of temperatures, 500–2600 °C, in a controlled environment.[17] Conventional box furnaces use $MoSi_2$ heating elements that operate in air up to 1700 °C. Graphite element furnaces operate up to 2300 °C but are not capable of operating under oxidizing environments. Therefore, alternative high-temperature facilities that can operate up to 2600 °C, such oxyacetylene torches are

☆ Presented at the Air Force Office of Scientific Research Workshop on Aerospace Materials for Extreme Environments, St. Louis, MO, August 3–5, 2009.

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0955-2219/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2010.02.025

critical in studying ablation and oxidation resistance of UHTCs at high-temperatures.[19]

Ablation is an erosive phenomenon with a removal of material by the combination of thermo-mechanical, thermo-chemical, and thermo-physical factors from high temperature, pressure, and velocity of combustion flame.[18] Oxidation and ablation resistance are very important properties in evaluating the utility of UHTC coatings for use in aerospace applications. The ablation behavior of diboride and carbide coatings on C–C composites and oxidation resistance of bulk UHTC composites have been successfully studied using oxyacetylene torch testing.[19]

Our approach is to use ZrB_2 and B_4C particles as inhibitors to the oxidation process of bulk C–C composites using liquid precursors and powder filled phenolic resins that are incorporated into the C–C composite fabrication steps. The liquid precursor method involves coating the C–C composite with precursors prior to composite lamination and densification. Although, there has been significant work on developing UHTC coatings for oxidation protection of carbon fibers and C–C composites[9–16] there has been limited work on developing ZrB_2 and B_4C inhibited C–C composites. The goal of this research is to investigate alternative C–C composite inhibition processing methods using precursors to ZrB_2 and investigate high-temperature oxidation and ablation testing methods using oxyacetylene torch testing on commercially available B_4C filled C–C composites.

2. Experimental procedure

2.1. C–C composite materials and processing

The C–C composite supplier (HITCO Carbon Composites Inc., Gardenia, CA) performed multiple variations of C–C processing and post-processing heat treatments per our request. Composite compositions were varied based on the whether or not the phenolic resin was filled with 30 wt.% B_4C particles, conventional carbon black, or ZrB_2–B_4C particles. A list of the processing conditions and properties measured at HITCO for the samples they supplied are shown in Table 1. The carbon black and B_4C filled C–C composite discs were a 2D C–C composite comprising T300-3K fibers in an 8-harness satin weave, densified to ~1.5–1.6 g cm^{-3} by chemical vapor infiltration.

The ZrB_2 inhibited C–C composites followed a slightly different processing procedure as described herein. The T300-3K 8-harness satin weave fabric (TPI Style 4243) was dimensionally stabilized by heat-setting at high temperature in an inert atmosphere. Square fabrics (25.4 cm) were used for coating with precursor solution to zirconium diboride. Coated fabric was impregnated with a boron carbide filled phenolic resin, laminated, and autoclave cured. The cured panel was then processed first in an oven, then in a vacuum furnace, to convert the resin to carbon, and subsequently chemical vapor infiltrated to fill the voids with pyrolytic carbon. The finished panel had a thickness of 0.6 cm, a fiber volume of 47%, and a bulk density of 1.69 g cm^{-3}. The panel was cut into 1.6 cm diameter flat discs, which were used for further coating development and testing. All samples were cut at an angle to the plies to simulate a shingle lay-up.

Table 1
C–C composite compositions and physical properties.

Filler type	CC139C C-black	CCZrBC ZrB_2–B_4C	CC137E B_4C
CVD time (h)	150	150	150
Final density (g/cc)	1.593	1.637	1.695
Final voids (%)	16.7	16.3	16.2

The processing variables and purpose for pre-treatment are as follows: (1) filling the phenolic resin with B_4C particles will allow for the creation of a more oxidation resistant bulk C–C composites when an oxygen inhibitor, such as boron, is present within the composite. Inhibition of oxygen using B_4C particles increases the oxidation resistance of graphite.[5,20] The addition of ZrB_2 is believed to increase the high-temperature oxidation resistance above 1500 °C due to the more refractory oxide formations at temperature. The presence of B_4C inside the C–C weave also serves as a reservoir for boron that favorably interacts at high temperatures with carbon[5]; (2) chemical vapor infiltration (CVI) times of 150 were used in order to achieve high density materials.

2.2. ZrB_2 organometallic precursor

ZrB_2 precursor synthesis was conducted in the exclusion of air and water using standard glove box techniques under argon atmosphere. In order to synthesize precursors to ZrB_2 powders the following chemicals $ZrCl_4$, $NaBH_4$, and 1,2-dimethoxyethane (dme) were used. The appropriate concentration of $ZrCl_4$ was added to dme and stirred under an argon atmosphere. Then $NaBH_4$ was slowly added to the mixture followed by stirring for 12 h to allow for the simple exchange reaction to take place according to the following equation.[21]

$$ZrCl + 4NaBH_4 \xrightarrow{dme} NaCl + (Zr(BH_4))_4$$

At which point NaCl precipitated out of solution and was centrifuged for removal from the precursor suspension. The decanted $(Zr(BH_4)_4)$(dme) solution was then removed and underwent thermal treatment in order to confirm the formation of ZrB_2. Thermal heat treatments were performed under argon, using a 5 °C/min heating rate up to 1150 °C, hold for 1 h, and ramp down to room temperature at 20 °C/min. The formation of ZrB_2 nanoparticles was then confirmed using TEM and EDS analysis. This precursor synthesis has also been used to create ZrB_2 coated C–C composites.[22]

2.3. ZrB_2 sol–gel precursor processing

ZrB_2 synthesis was conducted in open-air environment inside a chemical hood. The following chemicals were used: zirconium oxychloride–hydrate, triethyl borate, and phenolic resin (~57% char yield) in anhydrous ethanol. A 30 wt.% solution of zirconium-oxychloride was prepared in ethanol by stirring overnight to fully dissolve the system. Triethyl borate (10 wt.% excess) and phenolic resin were then added to the solution and sonicated to fully dissolve the phenolic resin. The precursor