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In-situ formation of SiC, ZrB₂-SiC and ZrB₂-SiC-B₄C-YAG coatings for high temperature oxidation protection of C/C composites

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ABSTRACT

Si₃N₄, (ZrO₂ + B₄C + Si) and (ZrB₂ + SiC + B₄C + Y₂O₃ + Al₂O₃) were used as precursors for in-situ formation of SiC, ZrB₂-SiC and ZrB₂-SiC-B₄C-YAG coatings respectively. The oxidation behavior of coated C/C composites was studied by cyclic oxidation in air at temperatures between 1500 °C and 1700 °C. The SiC coating exhibited the lowest weight loss at 1500 °C and 1600 °C. After initial mass loss for two cycles of oxidation at 1500 °C, the ZrB₂-SiC coating was found to provide the best protection by the precipitated ZrO₂ in SiO₂ glass at 1700 °C. The ZrB₂-SiC-B₄C-YAG coating performed well at 1700 °C with the formation of a complex YAG glass containing ZrB₂/ZrO₂.

1. Introduction

Carbon fibre reinforced carbon matrix composites (C/C composite) are attractive materials due to their unique properties: low density, high strength to weight ratio, good thermal shock resistance and retention of mechanical properties at elevated temperatures [1–4]. C/C composites are used in thermal structural applications in aerospace and nuclear reactors [5,6]. With low coefficient of thermal expansion, low ablation and unique property of increase in strength with increase in temperature (1000 °C–2300 °C) they are considered as suitable materials in aeronautical and aerospace applications. The wide applications of C/C composites are hampered due to oxygen sensitivity of carbon above 723 K. The rapid oxidation of C/C composites above 723 K will degrade their mechanical properties.

Among high temperature ceramics Si based ceramic (SiC) coatings have been considered efficient to improve the oxidation resistance of the C/C composites. SiC has good compatibility with carbon and the oxygen permeability in the passive layer of SiO₂ glass film is low at elevated temperature [7–9]. For aerospace applications above 1650 °C SiC coating has inherent limit due to the transition from passive to active oxidation that occurs around 1700 °C [10,11]. Formation of bubbles and micro cracks in the SiO₂ glass layer will weaken the oxidation protective property of Si based ceramic coatings.

Ultra high temperature ceramics (UHTS) like TaB₂ and ZrB₂ have high melting point, high hardness, high strength at high temperature, good thermal shock resistance, moderate thermal expansion are potential candidate materials for extreme environments associated with

hypersonic flight and rocket propulsion. The combination of ZrB₂-SiC improves the oxidation resistance at 1000–1800 °C due to the formation of less volatile borosilicate glass with low permeability for oxygen [12–14]. Further, the oxidation resistance and ablation resistance of ZrB₂-SiC based composites can be improved by adding B₄C, Y₂O₃, and Al₂O₃. Pressure less sintering of (ZrB₂-SiC-B₄C) composites with (Y₂O₃ + Al₂O₃) additions has been reported earlier [15]. A complex yttria-alumina-silicate (YAG) glass layer was shown to protect the (ZrB₂-SiC-B₄C) composite from oxidation at high temperature of 1700 °C. The (ZrB₂-SiC-B₄C) composites exhibited good dimensional stability and thermal shock resistance at 2200 °C in oxy-acetylene flame and at 2700 °C in plasma flame.

Among various techniques, pack cementation (PC) and chemical vapor deposition (CVD) are the most common techniques employed to prepare SiC coating on C/C composites. In-situ reaction method can reduce the production cost and results in improved oxidation protection of ZrB₂-SiC coating for the SiC-coated C/C composites [16]. Si and C powders can be used to produce SiC in-situ coating. The ZrB₂ phase can be formed through carbo-thermal reduction using ZrO₂, B₂O₃, and C powders. Instead of costly ZrB₂ powder, inexpensive B₂O₃, ZrO₂, Si and C powders were used as raw materials to prepare the outer ZrB₂-SiC coating by in-situ reaction on SiC-coated C/C composites [17,18].

Si₃N₄ coating is also used for long term oxidation protection of C/C composites up to 600 °C [19]. Si₃N₄ can be converted into SiC by pyrolysis at high temperatures with or with addition of carbon [20,21]. Similarly, the formation of ZrB₂-SiC composite powders by reaction of ZrO₂, B₄C and Si is reported [22,23]. The ZrB₂-SiC composite powders

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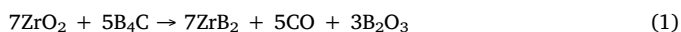
were used for air plasma coating on C/C composites. Due to coating in air the surfaces of ZrB₂ particulates exposed to high temperature are oxidized and resulted in the formation of ZrO₂ in ZrB₂-SiC composite coating. In the present work in-situ formation of three different coatings viz., SiC, ZrB₂-SiC, and ZrB₂-SiC-B₄C-YAG was carried out in a single step on C/C composites using Si₃N₄, (ZrO₂+B₄C+Si) and (ZrB₂+SiC+B₄C+Y₂O₃+Al₂O₃) respectively. The oxidation of in-situ coated C/C composites up to temperature of 1700 °C was studied.

2. Experimental

2.1. Preparation of in-situ coatings on C/C composite

Two dimensional bulk C/C composites with a density of 1.72 g cm⁻³ were used in the present study. Small test coupons of approximate size 12 mm × 10 mm × 4 mm were cut from the C/C composite block. The cut coupons were manually abraded on 400 grit SiC abrasive paper and cleaned ultrasonically in ethanol. The ground and cleaned coupons were dried in an oven at 373 K for 2 h.

Si₃N₄ powder of grade LC12 from H C Starck Germany was used for making SiC coating. ZrO₂ powder supplied by Nuclear Fuel Complex, Hyderabad, India, B₄C powder supplied by China Abrasives, Zing Zhou, China and Si powder of mesh size -325# obtained from Metal Powder Company Ltd., Thirumangalam India were used to make ZrB₂-SiC coating. The weights of Si, B₄C, and ZrO₂ are 20 g, 40 g and 100 g respectively to get weight ratio of ZrO₂/B₄C = 2.5 and B₄C/Si = 2.0. The self made ZrB₂ powder used in the third coating was synthesized by reacting ZrO₂ with B₄C according to reaction:



To obtain a single phase ZrB₂ without impurities like un-reacted ZrC, ZrO₂, and free C, the excess of B₄C was taken in wt. ratio of ZrO₂/B₄C = 2.5 against the stoichiometric wt. ratio ~3.0 according to reaction (1). The details of synthesis of ZrB₂ and ZrB₂-SiC powders are reported elsewhere [22]. The ZrB₂ with average particle size < 1 μm, SiC powder with particle size (d₅₀ ~ 0.8 μm) supplied by H.C. Starck, Germany, Al₂O₃ of super fine size (d₅₀ ~ 0.7 μm) obtained from Alcan and sub micron sized Y₂O₃ were taken in a wt. % of 50, 20, 12, 9 and 9 respectively.

The mixing of powders was done for 24 h in a polythene bottle with alumina balls. A water solution with 2–4 wt.% polyvinyl alcohol (PVA) binder was added to three types of powders and blended for 1 h. After slurry coating the C/C composite coupons are dried in an oven at 373 K for 2 h. The dried slurry coated samples are placed in separate graphite crucibles with minimum contact with grafol sheet pre-coated with BN water solution to avoid reaction of the coatings with crucible. The crucibles were placed in the resistance heating furnace (ASTRO, USA, Model 1000-3060-FP20). The furnace was initially evacuated to a moderate vacuum (5 × 10⁻² torr) before inletting the argon at 1 atm. Temperature was monitored with a radiation pyrometer Model 939A3 of Honeywell. Heating rate employed was ≈ 15 °C min⁻¹. The in-situ formation of coatings was carried out at 1550 °C / 1 h.

2.2. Oxidation and characterization of in-situ coated C/C composites

Isothermal oxidation was carried out for 15 min for each cycle at different temperatures: 1500 °C, 1600 °C and 1700 °C. The oxidation in air was studied using a raising hearth furnace of Nasker & Co, Kolkata, India. The specimens taken in alumina crucibles are placed on the furnace hearth and directly introduced into the hot zone of the furnace by raising the hearth. After holding for 15 min at oxidation temperature the furnace hearth was lowered and specimens in alumina crucible are allowed to cool down to room temperature. After measuring the weight of each specimen the oxidation cycle is repeated for four times at 1500 °C and 1600 °C, and two times at 1700 °C.

The oxidation behavior of the samples was studied by measuring weight loss using an electronic balance with 0.1 mg sensitivity. The surface area of each specimen was measured before coating. The specific weight change per unit surface area for each cycle was plotted against the duration of oxidation

$$\Delta W = (W_i - W_o) / SA \quad (2)$$

Where ΔW specific weight change, W_i = weight of the specimen after oxidation cycle, and W_o = weight of the specimen before oxidation and SA = surface area of the specimen. The as coated and oxidized specimens were cut using diamond cutting wheel or CNC wire cut EDM. The cut samples were mounted in epoxy and polished to mirror finish using fine diamond (0.25 μm) abrasive. A Philips X-ray diffractometer, Model PW3710, with Cu K_α radiation through Ni filter was used to identify different phases in the coatings. The surface morphology and cross sections of polished samples were analyzed for microstructure with a scanning electron microscope (SEM of FEI Quanta 400, Netherlands) equipped with energy dispersive spectroscopy (EDS). Electron probe micro analyser (EPMA) was used for elemental analysis of the coatings.

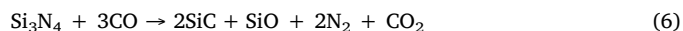
3. Results and discussion

3.1. Formation, microstructure and morphology of in-situ coatings

XRD patterns of in-situ coatings formed after heat treatment at 1500 °C in argon are shown in Fig. 1. Three different coatings viz., SiC, ZrB₂-SiC, and ZrB₂-SiC-B₄C-YAG are identified with their corresponding phases. In SiC coating, peaks of either unreacted Si₃N₄ or Si formed from decomposition of Si₃N₄ were not detected. Si₃N₄ can be converted into SiC by reacting with carbon in argon [24,25], by decomposing in nitrogen [26] and in vacuum [20,27]. Upon heating to high temperature in presence of carbon the SiO₂ passive layers on Si₃N₄ powder particles react with carbon to form SiC.



Si₃N₄ subsequently react with CO to form SiC



Under the low partial pressure of N₂ or vacuum conditions Si₃N₄ decomposes and silicon react with CO to form SiC without the need for the addition of extraneous carbon [20].

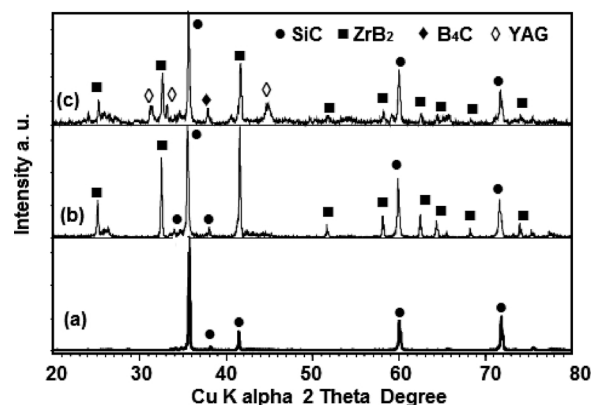


Fig. 1. XRD patterns of in-situ coatings formed on C/C composites (a) SiC, (b) ZrB₂-SiC and (c) ZrB₂-SiC-B₄C-YAG.

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