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Fabrication and microstructure of 3D C_f /ZrC-SiC composites: through RMI method with ZrO_2 powders as pore-making agent

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Received 8 October 2015; received in revised form 4 January 2016; accepted 5 January 2016

Abstract

3D C_f/ZrC–SiC composites were prepared by a combination process of slurry infiltration and reactive melt infiltration. ZrO_2 powders and $ZrSi_2$ alloy, both of which reacted with amorphous carbon, were used as pore-making agent and infiltrator, respectively. After carbothermal reduction at 1650 °C, X-ray diffraction analysis revealed that ZrO_2 powders were completely converted into ZrC by reacting with amorphous carbon, and an in-situ formed submicron porous configuration was observed at the areas containing ZrO_2. Results showed that the matrix in composites mainly consisted of SiC, ZrC and a small quantity of residual metal. SEM and TEM images revealed the formation of ZrC or SiC intergranular particles in the matrix and the characteristic around the residual resin carbon. The composites had a bending strength of 94.89 ± 16.7 MPa, fracture toughness of 11.0 ± 0.98 MPa $m^{1/2}$, bulk density of 3.36 ± 0.01 g/cm^3, and open porosity of $4.64 \pm 0.40\%$. The formation mechanisms of ZrC–SiC dual matrix and intrabundles' structure were discussed in the article.

Keywords: B. Composites; B. Microstructure-final; D. Carbides; Carbothermal reduction

1. Introduction

Carbon fiber reinforced silicon carbide matrix composites (C_f/SiC) have caused the extensive concern due to their excellent high-temperature strength, high thermal conductivity, low coefficient of thermal expansion (CTE), good thermal shock and oxidation resistance [1,2]. At present, C_f/SiC composites are widely used as thermal structure materials and friction materials in aerospace industries, such as advanced jet vanes, nose caps and leading edges [3]. However, when the temperature is higher than 1650 °C, the application of C_f/SiC composites in hypersonic aircrafts are limited because of the active oxidation of SiC and rapid evaporation of the low viscosity glasses formation. The development of hypersonic flight vehicles needs new composites to meet the requirements of high ablation resistance in ultrahigh temperatures and oxidizing atmosphere.

As one of the ultrahigh-temperature ceramics (UHTCs), zirconium carbide (ZrC) is widely known due to its high melting point (3540 °C), relative low density (6.47 g/cm^3) and high ablation resistance [4]. In addition, the as formed refractory oxide, i.e. zirconia, possesses high melting point and viscosity without being peeled by airflow. Numerous studies [5,6] have shown that introducing ZrC into C_f/SiC composites to form C_f/SiC–ZrC composites can significantly increase the ablation resistance to 2000 °C.

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http://dx.doi.org/10.1016/j.ceramint.2016.01.041
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Please cite this article as: D. Wang, et al., Fabrication and microstructure of 3D C_f /ZrC-SiC composites: through RMI method with ZrO_2 powders as pore-making agent, Ceramics International (2016), http://dx.doi.org/10.1016/j.ceramint.2016.01.041

ZrC powders slurry infiltration [7], polymeric Zr-containing precursor conversion [8–10] and reactive melt infiltration (RMI) with Zr-containing metal [11–13] are the most common methods to introduce ZrC into C_f/SiC composites. Compared with the former two methods, RMI is more suitable for high relative density product fabrication. Molten metal penetrates into the porous matrix with additives dispersed in skeleton of fibers, then reacts with active additives in RMI process. As the liquid phase cools, it expends to fill all void space [14]. Infiltration depth can be influenced by pore radius, the viscosity of melt, contact angle and so on. According to the Washburn formula, appropriate pore size is beneficial to the improvement of the infiltration depth. The contact angle for Zr/ceramic interface is in the range of 37–60° [15] and that for Si/C interface is in the range of 0–20° [16]. The element Si can be used to increase the wettability between Zr and C and decrease the porosity of composites. In our previous study [12], a porous nano-configuration could be formed via the reaction between ZrO_2 and carbon, finally a compact matrix was obtained by infiltrating $ZrSi_2$ alloy.

In the present work, nano-ZrO_2 powders were added into C_f/C fabrics to reform pore texture after carbothermal reduction process. Another goal of present work is to improve the content of ZrC in composites by infiltrating ZrO_2 slurry and molten $ZrSi_2$ alloy. The microstructure of obtained C_f/ZrC–SiC composites was characterized and the evolution mechanism was discussed in details.

2. Experimental procedure

2.1. Material preparation

The carbon fiber reinforced ZrC–SiC composites were prepared by combining reaction melt infiltration with slurry impregnation methods. Carbon fibers (T700; Toray, Tokyo, Japan) with an average diameter of 7 μm were woven into three-dimensional (3D) needle-punched fabrics by Nanjing Fiberglass Research and Design Institute (Nanjing, China). Then the 3D needle-punched fabrics were coated with three layer PyC/SiC interphase by chemical vapor infiltration (CVI). ZrO_2 powders and phenolic resin (Wuxi Mingguang Adhesive Meterial Co. Ltd., Wuxi, China) were mixed with a weight ratio of 2:1 and dispersed in alcohol to form homogeneous slurry by ball-milling for 24 h with ZrO_2 balls. The 3D carbon fiber fabrics were impregnated by this slurry and followed by pyrolysis at 900 °C to form C/ZrO_2–C composites. The porous C/ZrO_2–C composites were densified by two cycles of PIP process with phenolic resin. Next, the carbothermal reduction reaction was operated to convert ZrO_2 into ZrC and to improve the open porosity. Finally, the molten $ZrSi_2$ alloy was infiltrated into as-prepared C_f/ZrC–C composites at 1850 °C by capillary forces.

ZrC that synthesized via carbothermal reduction required more than 1657 °C according to Eq. (1) at standard status. In order to determine the optimal temperature for carbothermal reduction in vacuum, commercial nanoscaled m-ZrO_2 powder and graphite were used in an additional experimental. Zirconia powders and graphite were uniformly mixed with a weight ratio of 1:1 because of the majority of carbon in preforms.

$$ZrO_2(s) + 3C(s) \rightarrow ZrC(s) + 2CO\ (g) \quad (1)$$

2.2. Test and microstructure characterization

The pore diameter distributions of the C_f/ZrO_2–C preform were determined by mercury porosimeter (Autopore IV 9500V1.09, Micromeritics Instrument Ltd. USA) before and after the carbothermal reduction. The size of the tested samples was 5 mm × 5 mm × 8 mm. The bulk densities and open porosities of samples were measured by Archimedes's method with deionized water.

The phase compositions of the different composites were characterized by X-ray diffraction (XRD) with a Cu K_α target. Specimens for microstructure examinations were polished with 0.3 μm diamond suspension. The microstructure characterization was observed by scanning electron microscope (SEM, FEI Quanta 250, Hillsboro, America; FE-SEM, HITACHI S-4800, Tokyo, Japan), transmission electron microscopy (TEM, Tecnai G2 F20) and the elemental analysis was conducted by energy dispersive spectroscopy (EDS, Aztec X-Max 20, Oxford, Britain). TEM studies were conducted on an ultrathin sectioning that had been ion milled and coated a thin layer of amorphous carbon to prevent the accumulation of charge.

To remove the residual $ZrSi_2$ alloy in composites, polished samples were immersed into hydrofluoric acid at room temperature for 48 h. The morphology of the etched cross-sectional samples was studied by FE-SEM.

The flexural strength was measured using a three-point-bending test (Instron-5566, Instron Corp., Canton, MA) with a 50 mm span and a loading rate of 0.5 mm/min. At least five samples with a dimension of 5 mm × 4 mm × 60 mm were used. The edges of all samples were chamfered. The fracture surface of bending was observed by SEM. A single-edge-notched-beam (SENB) test was applied on notched specimen of $4.0 \times 8.0 \times 60\ mm^3$ (notch with 4.0 mm in depth) with 0.05 mm/min crosshead speed and 30 mm span to determine fracture toughness (K_{IC}).

3. Results and discussion

3.1. Carbothermal reduction for ZrO_2 powders

Carbothermal reductions were carried out in vacuum. XRD patterns of the mixed powders of ZrO_2 and graphite heated at different temperatures for 1 h are shown in Fig. 1. It can be seen from Fig. 1 that raw powder of ZrO_2 consisting of monoclinic zirconia phase without impurity peak. At 1550 °C, zircon reacts with graphite incompletely. There are several weak peaks showing the presence of m-ZrO_2. Complete conversion of zircon into ZrC without ZrO_2 peaks is observed at 1600 °C, though the highest intensity (111) reflection of ZrC is still weak. With the temperature increasing from 1600 °C to 1650 °C, peaks of ZrC become more pointed. The

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