Ceramics International (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

In situ fabrication and characterization of laminated C/ZrC ceramic via filter papers and zirconia powders

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ARTICLE INFO

Keywords:
C/ZrC ceramic
Hot pressing sintering
ZrO_2
Filter paper
In-situ reaction

ABSTRACT

Capillary infiltration and an in situ reaction between filter papers and zirconia powders were employed to synthesize laminated C/ZrC composite via vacuum impregnation and hot-pressing sintering at 1700 °C for 90 min under a pressure of 30 MPa. The microstructures and mechanical properties of the laminated C/ZrC composite were characterized via XRD, SEM, TEM analyses and the three-point bending test. The results indicated that the obtained composite exhibited a distinct laminar structure with alternating carbon and zirconium carbide layers. The composite had a bulk density of 1.89 g/m^3, an open porosity of 21.6%, and a bending strength of 128 MPa. Typical non-brittle fracture behaviors are observed, and the composites show an elastic deformation at the beginning of the test, exhibiting a zigzagging rise until the maximum stress is reached.

1. Introduction

Laminated composites are a novel class of materials applied in high-temperature filters, porous ceramics, and acoustic and heat insulation structures. These composites can broaden the application of structural ceramics owing to the reliability of their mechanical properties [1]. Laminated composites exhibit a non-catastrophic fracture behaviour because of their increased fracture toughness and fracture energy, which has been demonstrated in our previous studies [2–4]. So far, several systems, including Ti/Al_2O_3 [5], ZrC/SiC [2,3], ZrB_2/SiC [4,6–8], HfC/SiC [9], ZrO-Zr_2CN/Si_3N_4 [10–12], SiCw/SiC [13], Ni/Cu [14], Ti-TiBw/Ti [15], TiB_2-SiC/graphite flake [16], HfC-SiC/BN [17], TiB_2-TiC laminated Ti composite [18], laminated ZrB_2-SiC/graphite ceramics [19], Al_2O_3/Ni laminar ceramics [20], and laminated ZrB_2-SiC/BN ceramic [21], have been reported. Most of studies focused on the mechanical performances and microstructures of the obtained ceramics. Compared with the previous studies, we pay more attention to high temperature oxidation and ablation resistance of laminated composites besides their mechanical performances and microstructures. However, the cost of raw materials used for the laminated ceramics, such as HfC, ZrC, and ZrB_2, limits their large-scale production. To reduce preparation costs, considerable efforts have been concentrated on improving the preparation process and optimizing the preparation conditions. In addition, lower-cost raw materials have taken the place of the expensive raw materials. In our previous studies, a low-cost zirconium salt has been used to fabricate C_f/UHTCs matrix composites [22]. In this work, zirconium and carbon source are provided by zirconia powders and filter papers, respectively.

In recent years, naturally regenerating resources, such as woods and bamboos, have been used to fabricate biomorphic composites. The application of the derived biomorphic ceramics is still restricted because of their poor mechanical properties. However, in contrast to natural products such as woods, paper preforms are products technically manufactured from wood. Their composition, porosity and density are highly regular due to the reproducibility of the filter papers making processing [23]. More importantly, waste papers can also be used, which provides an environmental benefit. Furthermore, filter papers and zirconia powders are not only abundant from natural resources but are moderate in price.

In this study, C/ZrC multilayer composites were fabricated through hot-pressing technology. The filter paper pyrolysis, microstructure and mechanical properties of the laminated C/ZrC composite are presented. The interface bonding states and structure research of the laminated C/ZrC composite were studied in detail.

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http://dx.doi.org/10.1016/j.ceramint.2017.01.093
Received 21 November 2016; Received in revised form 18 January 2017; Accepted 18 January 2017

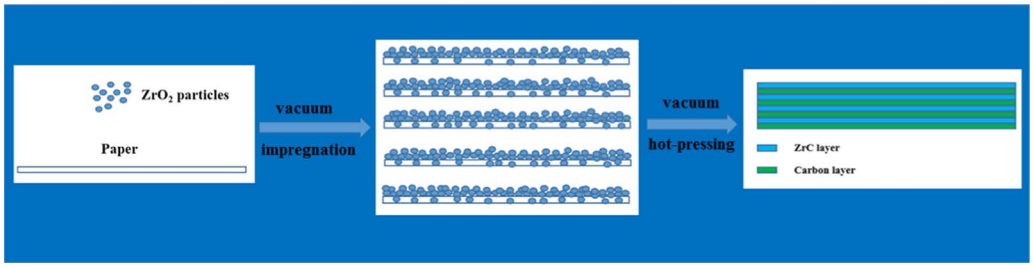

Fig. 1. Processing scheme of laminated C/ZrC ceramics.

2. Experimental procedure

Fig. 1 shows a flow chart of the process for laminated C/ZrC ceramics using zirconia powders and filter papers.

2.1. Sample preparation

Filter papers (Shanghai Bestest Biological Technology Co., Ltd, China) with an average thickness of 220 μm and an approximate weight of 100 g/cm^2 were used as the carbon sources. Commercially available zirconia powders (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China, 99.99% purity) with a mean particle size of 20 nm were used as the zirconium source. A thermosetting phenolic resin (Shanghai Qinan Adhesive Material Factory, Shanghai, China) was acted as the adhesive between the filter paper sheets and zirconia powders. Commercially available graphite powders (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China, 99.99% purity) were used to modify filter papers.

Zirconia powders and the thermosetting phenolic resin were first ball milled at room temperature with an appropriate volume ratio using ethyl alcohol as the solvent to form a homogenously dispersed slurry. Filter papers were shaped into rounded specimens with a diameter of 45 mm. Subsequently, the shear-free filter papers were then impregnated with the slurry under vacuum. The specimens were then dried in a vacuum oven at 120 °C for 12 h and stacked together, as shown in Fig. 1. The stacked bodies were pyrolysed at 900 °C for 30 min at a heating rate of 10 °C/min. The process was applied to decompose the papers and thermosetting phenolic resin into charcoal and pyrolysis carbon. Finally, the laminated sample was sintered in a vacuum hot-pressing furnace (VVPgr-80–2300, Shanghai Chenhua Electric Furnace co., Ltd, China) at 1700 °C for 90 min under an applied pressure of 30 MPa to transform it into a composite ceramic.

2.2. Sample modification and characterizations

Density of specimens was measured by the Archimedes' method using distilled water as a wetting agent. The distribution of the particle size was characterized via Laser Diffraction Particle Size Analyzer (FAM13320, United States). The phase formation of the samples was analyzed by X-ray diffraction (D8-ADVANCE, Germany). TG/DSC (METTER TOLEDO TGA/DSC 1, Switzerland) was utilized to determine the decomposition and reaction temperature range. Vickers hardness were measured by means of the Vickers indentation method (Model HV-1000IS, Shanghai Jvjing Precision Instrument Manufacturing Co., Ltd.) using a load of 5 kg and a dwell time of 10 s. The structures of laminated C/ZrC composite were observed by an optical metalloscope (BA310MET, China). The microstructures of the samples were detected by scanning electron microscopy (SEM) (FEI QUANTA FEG 250, United States) equipped with energy dispersive X-ray analysis (EDX). The nanostructure was observed on 200 kV Field Emission transmission electron microscope (FEI Tecnai G2 F20, United States). The samples were cut into 3 mm×4 mm×36 mm specimens and polished for the three-point bending test in an electromechanical universal testing machine (CMT5504, MTS SYSTEMS, co., LTD, China) with a cross-head speed of 0.5 mm/min and a span of 30 mm. Tests were conducted at room temperature with five specimens of each group. The final value is the average of the three results.

$$\sigma_f = \frac{3PL}{2bh^2}$$

Where σ_f is flexural strength, MPa; P is load, N; L is span, 30 mm; and b, h are the width and thickness of the sample, mm.

3. Results and discussion

The filter paper and zirconia powders were observed via SEM (in Fig. 2). Each paper fibre retains its initial structure (circular or tabular shape), and the pore channel diameter is approximately 5 μm, as shown in Fig. 2**(a** and **c)**. Meanwhile, the filter paper surface has hollow channels with diameters of approximately 10 μm or more. Moreover, fibres are linked by crisscrossing within the pulp. In Fig. 2**(b** and **d)**, the particle sizes of zirconia powders with different morphologies are approximately 20 nm. However, some agglomerations exist. The grain sizes of zirconia powders are smaller than the fibre diameter and the gaps between the fibres, which provide the tunnel for the infiltration of the slurry in the next stage. These conditions enable the zirconia powders to traverse the fibres and the gaps between the fibres during the impregnation process. The distribution curve of ZrO_2 particle size is shown in Fig. 3. The median of ZrO_2 particle size is about 87 nm (> 75%) due to the agglomerations of nano ZrO_2. Obviously, zirconia powders were nanoparticles through Fig. 3.

The TG/DSC curves for filter papers and filter papers impregnated by the slurry involving zirconia powders are plotted in Fig. 4. Obvious weight loss occurred between 330 °C and 400 °C during pyrolysis, while a minimal mass loss occurred after 900 °C. A slight initial mass loss occurred up to 120 °C because of water loss from the sample. The mass residue of filter papers (4.1 wt%) is lower than that of filter papers impregnated with the slurry (12.8 wt%). Meanwhile, the DSC curves show a prominent exothermic peak. Three exothermic peaks and one endothermic peak appear during the thermal analysis process, indicating the carbonization of filter papers and the reaction between the carbon and zirconia powders. Of course, the pyrolysis of filter papers plays an important role on the properties of the composites. Details on the pyrolysis reaction can be found in the literature [16]. After the pyrolysis of the filter papers, the main phase is carbon (Fig. 4**b**), which suggests that the filter papers carbonized completely. The XRD analysis (Fig. 4**d**) reveals that the final products consist of ZrC, ZrO_2 and C phases. The crystalline ZrC phase is clearly present after the carbothermal reduction between C and ZrO_2, and there is also residual ZrO_2. The volume percentages calculated from the XRD pattern among the three phases ZrC, ZrO_2 and C is 63.4%, 31.6% and 5.0%, respectively. C originates from the carbonization of filter papers or carbon spraying during the observation of the sample. Residual ZrO_2 is present in the sample, indicating that the reaction cannot be completed under such conditions and that the carbon obtained from filter papers and phenolic resin is not sufficient. To transform the remaining ZrO_2 into ZrC, further carbon sources are introduced. The possible reactions during the pyrolysis and the heat-treatment process are as follows: