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ScienceDirect

Ceramics International 42 (2016) 351–356

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Fabrication and mechanical properties of multi-walled carbon nanotube reinforced reaction bonded silicon carbide composites

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Received 29 June 2015; received in revised form 18 August 2015; accepted 18 August 2015
Available online 2 September 2015

Abstract

Different amounts (0, 1, 3, 5, 10 or 15 wt%) of multi-walled carbon nanotubes (MWCNT)–reinforced reaction bonded silicon carbide (RBSC) composites were fabricated by epoxy resin curing and liquid infiltration of molten silicon at 1600 °C for 90 min. First, the MWCNTs were coated by phenolic resin, which could decompose into amorphous carbon. The in situ formation of the SiC coating via the reaction of amorphous carbon and silicon on the surface of MWCNTs could prevent siliconization. The influence of incorporated MWCNTs on the micro-structure and mechanical properties of RBSC composites was researched. The composites show a higher bending strength of 365 MPa and a fracture toughness of 6.9 MPa $m^{1/2}$, which are higher than those of monolithic RBSC (a bending strength of 236 MPa and a fracture toughness of 3.8 MPa $m^{1/2}$). Based on micro-structural measurements, the improved mechanical properties of the MWCNTs/RBSC composite compared with those of the as-fabricated RBSC can be ascribed to three mechanisms: MWCNT pullout, MWCNT bridging and crack deflection.

Keywords: C. Mechanical properties; Multi-walled carbon nanotubes; Silicon carbide; Coating; Reactive sintering

1. Introduction

Due to their excellent mechanical properties, high chemical stability, high thermal conductivity and machinability, silicon carbide (SiC) ceramics can be used in an aerospace environment for combustion turbines, cowling mounts and reflector scopes [1,2]. Since 1950s, an increasing number of researchers have focused on RBSC-based ceramics because of their unique predominance in reactive sintering. During sintering, molten silicon or silicon alloy infiltrates into the porous C/SiC green-body by capillary force, and then densification is completed by the in situ formation of SiC and residual silicon. Compared with other technologies, reactive sintering has the advantages of low reaction temperatures, less sintering time, low cost, and near-net shape production [3-5].

However, the resistance ability to crack propagation of RBSC is lower than that of common sintered SiC because of the presence of residual silicon. Therefore, the brittleness of RBSC limits its application in some formidable fields. To enhance the strength and the toughness of RBSC, some methods have been investigated, such as the elimination of residual silicon and second-phase (particle, whiskers and fibers) reinforcing [6–8].

Wilhelm et al. [9] have fabricated RBSC composites using different particle sizes of the original materials and investigated their influence on the mechanical properties of the final form. Although there was a low content of free silicon within the composites, the fracture toughness was limited to only 3.8 MPa $m^{1/2}$. Aroati et al. [10] chose boron carbide (B_4C) and SiC with multimodal particle-sizes to increase the density of the green-body and to reduce the residual silicon. However, the flexural strength of the composite was only enhanced from 180 to 280 MPa. Many researchers [11,12] have attempted to decrease the fraction of free silicon and increase the toughness of the composites by incorporating molten alloyed silicon. However, the mechanical properties of these composites could not be markedly improved.

Since carbon nanotubes (CNTs) first appeared, many efforts have been made to fabricate this material and explore its properties. CNTs have been considered as a substitute for

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http://dx.doi.org/10.1016/j.ceramint.2015.08.117
0272-8842/

carbon fibers in the reinforcement of the ceramics because of their outstanding mechanical properties and good chemical stability [13,14]. In the same manner, CNT reinforcement can minimize the debilitating brittle failure of RBSC and expend energy by CNT pull-out, bridging, debonding and crack deflection [15,16].

However, there are three main problems associated with the reinforcement of RBSC by MWCNTs: First, the dispersion of MWCNTs is a critical issue because their nano-size and large aspect ratio lead to agglomeration. Second, it is difficult to obtain moderate interface-bonding between MWCNTs and SiC. Third, the MWCNTs could be attacked by molten silicon at high temperatures [17–19].

Furthermore, there have been few studies on methods to protect the MWCNTs from damage by molten silicon [18]. Our present work focuses not only on enhancing the mechanical properties of RBSC but also on avoiding the attack of MWCNTs by silicon at high temperatures. Before their addition to the matrix, MWCNTs were modified with phenolic resin (PF), which can decompose into amorphous carbon. In situ formation of SiC on the surface of MWCNTs via a chemical reaction between silicon and amorphous carbon could protect MWCNTs and offer a means to bond with the original SiC grains, both of which can improve the toughness of composites [20]. The SiC/C slurry with modified MWCNTs was molded by epoxy resin curing. The achieved green-body completed the densification via infiltrating molten silicon. The variations in the micro-morphologies of MWCNTs and the mechanical properties of MWCNTs/SiC with different mass fractions of MWCNTs (1 wt%, 3 wt%, 5 wt%, 10 wt% and 15 wt%) were studied. Finally, the strengthening and toughening mechanisms were also investigated.

2. Experimental process

2.1. Raw materials and preparation

MWCNTs (Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences) with dimensions of 50–100 nm in diameter and 6–15 μm in length were chosen. The mixed SiC powders (Shuitian Material Technology Co., Ltd., Shanghai, China) were choosen with sizes of 0.5 μm, 1 μm, 3.5 μm, and 7 μm (at a mass ratio of 2:2:3:3). Carbon black (Artech Specialty Graphite Co., Ltd, Chengdu, China) with size of 1 μm was introduced.

To remove the catalyst and impurities from the MWCNTs, the MWCNTs were first oxidized by nitric acid at 120 °C for 4 h. Then, the purified MWCNTs were dispersed in the phenolic resin (PF) (Mingyang adhesive material Co., Ltd., Wuxi, China), mixed with ethyl alcohol and ultrasonicated. The PF-modified MWCNTs were pretreated at 60 °C and were then combined with the uniform SiC/C slurry, which was prepared using the mixed SiC powders and carbon black (at a mass fraction of 0.5 wt%) in epoxy resin (E-51, Mingyang adhesive material Co., Ltd., Wuxi, China) by ultrasonication and continuous ball milling for 16 h, with the ethanol as solvent and diethyl phthalate as dispersant. The final suspension was solidified into a green-body by the curing agent for the epoxy resin at room temperature. Then, the obtained green-body was carbonized under vacuum at 1000 °C for 8 h. Lastly, the preformed body was sintered at 1600 °C for 90 min by infiltrating with liquid silicon.

2.2. Characterization

After reactive bonding, the samples were analyzed by X-ray diffraction (Rigaku XRD, MiniFlex 600). Each sintered sample was cut into eight parallelepipeds with dimensions of 3 mm × 4 mm × 40 mm and 2 mm × 4 mm × 36 mm on the inside diameter slicer, respectively, mechanically polished and chamfered with boron nitride pastes. The physical properties of composites were investigated using a universal testing machine (AG-IC-50KN, SHIMADZU) using the three-points bending test with loading speeds of 0.5 mm/min and 0.05 mm/min for bending strength and fracture toughness, respectively. The bending strength was tested using 3 mm × 4 mm × 40 mm bars with a span of 30 mm at room temperature. The fracture toughness was tested on 2 mm × 4mm × 36 mm bars using a single notched beam (2 mm in depth and 0.02 mm in width). The micro-morphologies of the MWCNTs and fractured surfaces of the composites were investigated by scanning electron microscopy (SEM, FEIINSPECT). The densities of samples were tested in distilled water using Archimedes method. The crack propagation was determined using a hardness tester (HV-101S). To remove the free silicon, the fracture surface was etched by saturated sodium hydroxide.

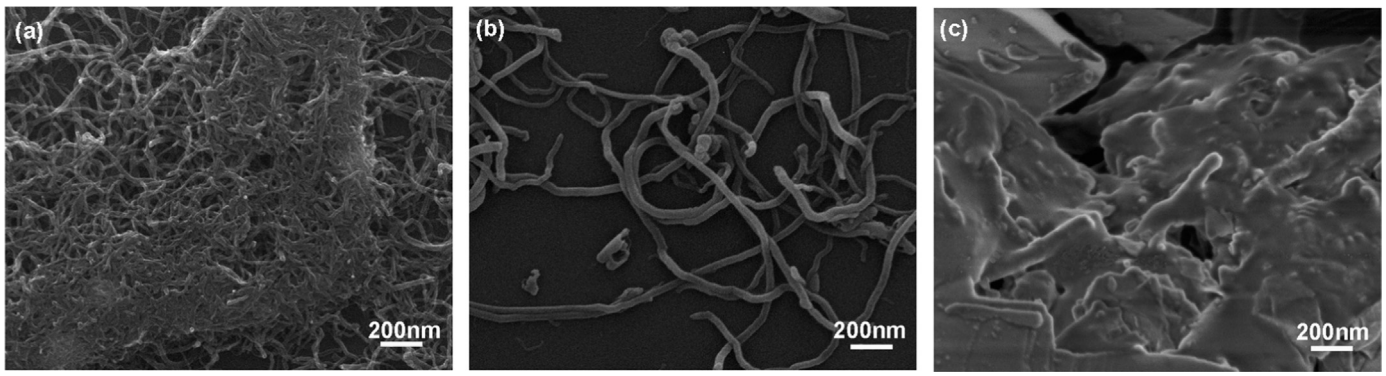

Fig. 1. SEM of MWCNTs on a silicon wafer: (a) original MWCNTs, (b) nitric acid-treated MWCNTs, and (c) MWCNTs coated by PF.