Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 34 (2014) 1053–1061

www.elsevier.com/locate/jeurceramsoc

Effects of multi-walled carbon nanotubes on the crystallization behavior of PDCs-SiBCN and their improved dielectric and EM absorbing properties

Yajun Zhang, Xiaowei Yin *, Fang Ye, Luo Kong

Science and Technology on Thermostructure Composite Materials Laboratory, Northwestern Polytechnical University, West Youyi Road, No. 127, Xi'an, Shaanxi 710072, PR China

Received 28 October 2013; received in revised form 19 November 2013; accepted 22 November 2013
Available online 25 December 2013

Abstract

Polymer derived siliconboron carbonitride ceramics (PDCs-SiBCN) containing multi-walled carbon nanotubes (MWCNTs-SiBCN) were fabricated and heat treated at 1350 °C and 1500 °C in nitrogen atmosphere. XRD patterns show the characteristic peaks of SiC appeared in MWCNTs-SiBCN treated at 1500 °C, which is 300 °C lower than the crystallization temperature of SiC in PDCs-SiBCN. The decrease of temperature can be ascribed to the heterogeneous nucleation promoted by MWCNTs as nucleating agent. Energy change during heterogeneous nucleation is analyzed to explain the acceleration of crystallization. The dielectric and electromagnetic (EM) absorbing properties of the as-prepared MWCNTs-SiBCN are investigated, which show a better wave-absorbing ability than PDCs-SiBCN treated at the same temperature, owing to a distinctive $A+B+C$ microstructure in MWCNTs-SiBCN. This work makes it possible to fabricate the PDCs-SiBCN with good EM absorbing property at a lower temperature, granting them potential as a matrix material candidate in ceramic matrix composite field.

Keywords: Multi-walled carbon nanotubes; Polymer derived ceramics; Crystallization temperature; Electromagnetic absorbing property

1. Introduction

During the last decades, polymer derived ceramics (PDCs) have triggered great interest among researchers because of their remarkable properties over conventional ceramics, such as excellent thermal stability,[1] high-temperature mechanical properties,[2] oxidation and corrosion resistances.[3–6] Additionally, the polymer-to-ceramic conversion process makes PDCs an attractive candidate for the matrix of ceramic matrix composite (CMC), the starting materials for fabrication of ceramic fiber, coating, film, powder and so on.[7–12] Among a variety of PDCs, polymer derived siliconboron carbonitride ceramics (PDCs-SiBCN) are distinguished from others for their supreme ultra-high temperature stability up to 2200 °C, good resistance to oxidation and creep, and high strength and modulus,[13,14] endowing them potential in the field of high-temperature structural materials.

Besides the structural performance, the functional performance of PDCs is desired at the same time with the development of materials science. In some advanced electronic devices and telecommunication applications, electromagnetic (EM) absorbing property is needed to prevent microwave interference, which makes the microwave absorbing materials irreplaceable. It is reported that heat treatment can improve the conductivity of PDCs,[15] indicating an improvement of EM absorbing property. In our previous work,[16] it was proved that SiC nanocrystals as a dielectric lossy phase were generated in PDCs-SiBCN after the heat treatment at 1650 °C, resulting in an increased EM absorbing property of PDCs-SiBCN. However, such a high heat-treatment temperature can influence the application of PDCs-SiBCN in CMC considering the performance degradation of fibers and other reinforcing phases at higher temperatures. Therefore, in this work, it is expected to lower the crystallization temperature of SiC in ceramics and consequently attain a good EM absorbing property at a lower preparation temperature.

It is reported that multi-walled carbon nanotubes (MWCNTs) as a nucleating agent can increase the crystallization rate of polymer matrix and ceramics matrix due to heterogeneous nucleation effect.[17–20] This effect enlightens our idea of

* Corresponding author. Tel.: +86 029 88494947; fax: +86 029 88494620.
E-mail addresses: yinxw@nwpu.edu.cn, yinxiaowei@yahoo.com (X. Yin).

0955-2219/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jeurceramsoc.2013.11.044

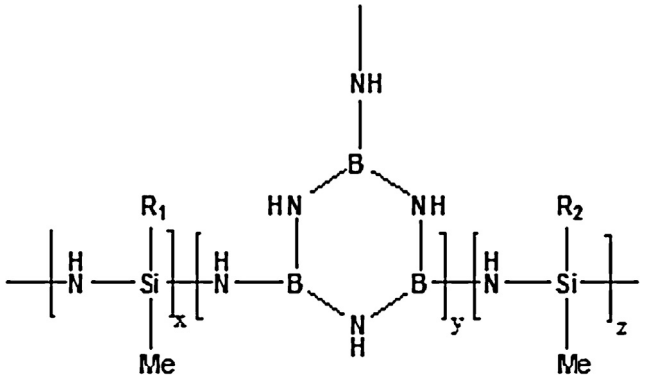

Fig. 1. The molecule structural formula of L-PBSZ.

introducing MWCNTs into PDCs-SiBCN to promote the formation of SiC nuclei and further accelerate the crystallization of SiC, leading to the decrease of the preparation temperature. Additionally, MWCNTs have good electrical conductivity,[21–23] which means the introduction of MWCNTs may enhance the electrical property of ceramics. Based on the above, it is predicted that PDCs-SiBCN containing MWCNTs (MWCNTs-SiBCN) with an excellent EM absorbing property can be prepared at a lower heat treatment temperature compared with PDCs-SiBCN.

In the present work, MWCNTs-SiBCN with different weight fractions of MWCNTs were fabricated and heat treated at different temperatures. The TG-DSC, phase composition and microstructure of ceramics were investigated. The dielectric and EM absorbing properties of ceramics were measured. The microstructure evolution process and EM absorbing mechanism of ceramics were discussed in order to correlate the microstructure with performance.

2. Experimental

2.1. Chemicals

A new and commercially available liquid polyborosilazane (L-PBSZ, Institute of Chemistry, Chinese Academy of Science) was used as the polymer precursor. Fig. 1 shows the molecule structural formula of L-PBSZ. R1 and R2 are H and/or vinyl group, and Me represents methyl group. The polymer contains B–N six-membered rings, C exists in Si–CH_3 and Si–CH=CH_2, and –Si–N–B– is the backbone of polymer. The mole ratio of chemical elements in L-PBSZ was n(Si):n(B):n(C):n(N) = 1:0.35:1.02:0.35. MWCNTs (TNM5, Chengdu Organic Chemicals Cooperation) was used as the additive. Paraffin was used as the carrier of MWCNTs. All chemicals were used as received without further purification.

2.2. Synthesis, pyrolysis and heat treatment

The hybrids with paraffin as the matrix and MWCNTs as the additive (MWCNTs-paraffin) were fabricated. Bulk paraffin was cut into slices and mixed with 0.5, 1, 2, 4, 10, 15 wt% of MWCNTs. Drops of normal hexane were added into the mixtures to dissolve the paraffin and help the grind in order to achieve relatively uniform mixtures. The obtained mixtures were filled into a metal mold and cold pressed at 10 MPa to shape them into the size of 22.86 mm × 10.16 mm × 3 mm.

For fabrication of MWCNTs-SiBCN, L-PBSZ was first cross-linked at 170 °C for 2 h in high purity N_2 and then ball-milled at 120 r/min for 2 h to get fine powders. The radius of the powders was controlled by a 80 mesh griddle. The obtained powders were mixed with 2, 4, 8 wt% of MWCNTs, respectively, and ball-milled at 120 r/min for 5 h to get uniform mixture powders. After that, the mixture powders were put into a metal mold and cold pressed at 70 MPa to shape the powders into boxes. The obtained boxes were pyrolyzed at 900 °C for 2 h in high purity N_2 and cooled naturally in the furnace. In this way, the as-pyrolyzed MWCNTs-SiBCN samples were achieved. For abbreviation, the samples were labeled as 2%/4%/8%MWCNTs-SiBCN, respectively. Finally, the as-pyrolyzed samples were heat treated at 1350 °C and 1500 °C, respectively, for 2 h in high purity N_2. The as-prepared MWCNTs-SiBCN samples were cut and grinded into the size of 22.86 mm × 10.16 mm × 3 mm for permittivity test.

2.3. Compositional and microstructural characterization

The TG-DSC curves of cross-linked L-PBSZ with and without MWCNTs were analyzed in high purity N_2 using high temperature simultaneous thermal analyzer (STA429CD/3/7; Geratebau GmbH, Netzsch, Germany). The temperature range is from room temperature to 1450 °C. Phase evolution and crystallization analysis were conducted by X-ray diffraction (XRD, X' Pert Pro, Philips, Netherlands). Transmission electron microscopy (TEM G-20, FEITecnai, Hillsboro, USA) was used to analyze the microstructure of the powder samples. High-resolution transmission electron microscopy (HRTEM) images of the samples were conducted on a 200 kV LaB_6 TEM. To prepare the TEM powder samples, rubbed ceramic powders were dispersed in analytically pure alcohol through ultrasonic bath. Small droplets of the obtained suspensions were placed on Cu TEM grid covered with a holey carbon film and dried under hot bulb.

2.4. Dielectric and EM absorbing properties characterization

The relative complex permittivities of as-prepared samples were tested on a vector network analyzer (VNA; MS4644A, Anritsu, Kanagawa, Japan) using the waveguide method at 8.2–12.4 GHz (X-band).

In this work, the EM absorbing property of materials is measured by RC, which is calculated based on metal back-panel model.[24] RC expresses the ratio of the total reflected EM power against incident EM power. The lower the RC is, the better the absorbing property is. RC is determined by relative