Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Journal of the European Ceramic Society xxx (2015) xxx–xxx
www.elsevier.com/locate/jeurceramsoc

CNT and PDCs: A fruitful association? Study of a polycarbosilane–MWCNT composite

Federico Dalcanale[a,b,*], Jonas Grossenbacher[c], Gurdial Blugan[a], Maurizio R. Gullo[c], Jürgen Brugger[c], Hendrik Tevaearai[d], Thomas Graule[a], Jakob Kuebler[a]

[a] *Empa, Laboratory for High Performance Ceramics, Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, Duebendorf, Switzerland*
[b] *Laboratory for Multifunctional Materials, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland*
[c] *Microsystems Laboratory, EPFL, Station 17, CH-1015 Lausanne, Switzerland*
[d] *Clinic for Cardiovascular Surgery, Inselspital Berne, Berne University Hospital and University of Berne, Berne, Switzerland*

Received 5 January 2015; received in revised form 11 February 2015; accepted 14 February 2015

Abstract

The effect of MWCNT introduction in a polycarbosilane based ceramic on its electrical properties is presented. The electrical conductivity of two MWCNT powders was measured under dynamic compaction up to 20 MPa when it reached 3–5 S/cm. The compaction behavior was also analyzed and modeled. A composite was then realized using allylhydridopolycarbosilane SMP10® and divinylbenzene as matrix. Intact 10 mm MWCNT-SiC ceramic discs samples with 2 wt.% filler load were produced pressure-less via liquid route despite the linear shrinkage of about 30%. Nanotubes microstructure and distribution in the matrix were confirmed after pyrolysis with TEM and SEM analysis. Anyhow similar electrical conductivity values after pyrolysis between the loaded and unloaded samples were measured. The microstructure analysis via XRD and TEM revealed that the percolative carbon network formed through the use of divinylbenzene improves the electric conductivity more than that of MWCNT addition and also simplifies the whole process.

Keywords: Carbon nanotubes; Polymer derived ceramics; Electrical properties; MWCNT–SiC composite; MEMS

---

1. Introduction

The development of composites addresses the need to improve one or few particular properties of a base material, the matrix, in order to meet the requirements of the specific application. In the case of ceramics their lightweight and chemical resistance are attractive for sensors, electrodes and energy harvesting. The limits of their use related to the extremely low electric conductivity can be overcome with the use of silicides and borides that leads to a metallic-like behavior [1,2]. On the other side the processing of these involves sintering temperatures up to 2200 °C and high pressures to improve the density. In addition the shaping freedom is constrained to the powder-processing techniques. For these reasons among ceramic classes, polymer derived ceramics (PDCs) are unique in its genre because they offer an alternative to the traditional powder process. PDCs use silicon based polymers as precursors that are first cured and subsequently pyrolyzed resulting in a ceramic. Some examples are siloxanes, silazanes and polycarbosilanes that are respectively used to obtain Si–O–C, Si–C–N and Si–C based ceramics. Being liquid, the precursors can be easily molded in the micro-scale with a high degree of complexity and then used for the fabrication of micro electric mechanic systems (MEMS). As opposed to conventional powder methods (i.e. micromachining, pressing or powder injection molding) where simple shaping and a poor resolution is achievable [3]. One of the main challenges for MEMS processing via a liquid route is the formation of microbubble during curing that leads to crack

---

* Corresponding author at: Empa, Laboratory for High Performance Ceramics, Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, Duebendorf, Switzerland. Tel.: +41 587654967.
E-mail address: federico.dalcanale@empa.ch (F. Dalcanale).

http://dx.doi.org/10.1016/j.jeurceramsoc.2015.02.016
0955-2219/

Please cite this article in press as: Dalcanale F, et al. CNT and PDCs: A fruitful association? Study of a polycarbosilane–MWCNT composite. *J Eur Ceram Soc* (2015), http://dx.doi.org/10.1016/j.jeurceramsoc.2015.02.016

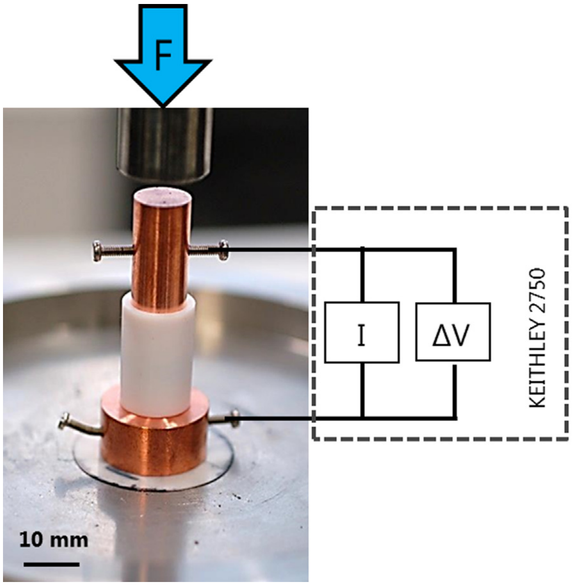

Fig. 1. Device used for the measurement of the MWCNT powder conductivity under pressure. One of the Al_2O_3 discs is placed under it. Above, the terminal part of the load cell can be noticed. A schematic representation of the electric connection to the multimeter is also shown.

formation in pyrolysis. Curing under isostatic pressing or tight sealing of the mold is used to avoid microbubble formation [4]. This method is not suitable for MEMS fabrication and pressure-less alternatives have to be found. In the case of Si–C–N, micro-gears were first reported by Liew et al. [5]. The same authors also investigated it further as possible material for electrostatic actuators, pressure transducers, combustion chambers, thermal actuators and micro-grippers for moving chip-sized objects [6,7]. Another advantage offered by the use of PDCs is the relative simple incorporation of fillers [8] using polymer processing technology. These can be mixed with the liquid precursors and embedded in the preceramic resin before pyrolysis. In this context carbon nanotubes (CNT) have attracted tremendous interest for their superior mechanical [9] and electrical properties [10] associated with their high aspect-ratio. Percolation can be reached with the introduction of a small quantity of CNT, usually lower than 2 wt.%, depending upon CNT quality, type and dispersion method. Despite the advantages their use as filler in PDCs is recent [11] and mainly restricted to Si–C–N ceramics. Processing and mechanical properties have been investigated [11–16] showing the positive effect of CNT on fracture toughness while there are contradictory results about Young modulus and hardness. On the other hand only a few papers report the effect on the electrical properties. Ionescu et al. [17] improved the electrical conductivity of Si–C–N ceramic from 1×10^{-9} to 4×10^{-2} S/cm adding 2 vol.% of MWCNT. Similarly Shopova et al. achieved 2×10^{-2} S/cm with 1 wt.% of SWCNT while 1.58×10^{-6} was reported for polyaluminasilazane fibers produced starting from polysilazane containing 1.2 wt.% MWCNT [18]. Even fewer investigations are available, to the best of our knowledge, concerning the electrical properties of Si–C/CNT and Si–C–O/CNT composites. For example 2.5 vol.% CNTs were in situ grown via ethanol injection during pyrolysis increasing the conductivity up to 1.8×10^{-1} S/cm. In the case of Si–C/CNT composites only processing and mechanical properties are reported [18–20]. The use of CNT is not the only method to improve the electrical properties of PDCs. It is possible to reach values in the order of 1×10^{-2} to 1×10^{-1} S/cm through the formation of a carbon percolative network during pyrolysis. This can be promoted using carbon-rich precursors [21,22], divinylbenzene (DVB) as cross-linker [23] or also introducing metal catalysts [24]. Our aim is to study the use of CNT as filler material for PDC and in particular for polycarbosilane. The electrical conductivity of two commercial MWCNT powders is examined in a continuous compression test while also analyzing its compaction behavior. Starting from a carbon enriched matrix, a SiC/CNT 2 wt.% composite was then produced via liquid route and without applied pressure. The microstructure as well as the presence and dispersion of CNT were investigated via SEM and TEM. XRD analysis was used to determine the crystalline phase formation during pyrolysis. Electrical properties of the matrix and the composite were compared to study the effect on the MWCNT introduction.

2. Materials and methods

2.1. Carbon nanotubes

Two different types of commercially available MWCNT were used without any purification. Baytubes C150P (Bayer Material-Science AG, Leverkusen, Germany) that possess purity >95 wt.%, tube length >1 µm and agglomerates bulk density of 120–150 kg/m^3. NanocylTM NC7000 (Nanocyl S.A., Sambreville, Belgium) that possess purity >90 wt.%, average tube length of 1.5 µm and agglomerates bulk density of 66 kg/m^3. Both are produced via catalytic chemical vapor deposition (CVD) method. More information can be found in the respective datasheets.

2.2. Preceramic polymer

Commercially available allylhydridopolycarbosilane SMP10® (batch J20867, viscosity 51 cps Starfire Systems Inc., USA) with nominal formula $[SiH(CH_2CH{=}CH_2)CH_2]_{0.1}[SiH_2CH_2]_{0.9}$ was used as preceramic polymer. Divinylbenzene (DVB, technical 80%, mixed isomers) and 1,1′-azobis(cyclohexanecarbonitrile) (ACHCN), as a carbon source and radical initiator respectively, were purchased from Sigma–Aldrich Switzerland and used as received.

2.3. Measurement of CNT-powder DC conductivity under pressure

The conductivity of the two CNT powder were determined using a device manufactured based on the scheme reported in the paper of Marinho et al. [25] and visible in Fig. 1. We choose to use a polytetrafluoroethylene PTFE die instead of ceramic one to reduce the friction with the copper piston during compression. In addition four removable screws were installed on the piston and base to facilitate the fixation of copper wires used for

Please cite this article in press as: Dalcanale F, et al. CNT and PDCs: A fruitful association? Study of a polycarbosilane–MWCNT composite. *J Eur Ceram Soc* (2015), http://dx.doi.org/10.1016/j.jeurceramsoc.2015.02.016