Acta Materialia 100 (2015) 118–125

Contents lists available at ScienceDirect

Acta Materialia

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

Stiffness, strength and interwall sliding in aligned and continuous multi-walled carbon nanotube/glass composite microcantilevers

Geoffrey Otieno, Antal Koos [1], Frank Dillon, Noor Azlin Yahya, Claire E.J. Dancer, Gareth M. Hughes, Nicole Grobert, Richard I. Todd *

Department of Materials, University of Oxford, Oxford OX1 3PH, UK

ARTICLE INFO

Article history:
Received 2 May 2015
Revised 7 August 2015
Accepted 20 August 2015
Available online 29 August 2015

Keywords:
Carbon nanotubes
Glass matrix composites
Mechanical properties
Microcantilevers

ABSTRACT

Individual perfect multi-wall carbon nanotubes (MWCNT) can exhibit exceptional properties, such as an elastic modulus of ~1 TPa. However, integration of carbon nanotubes (CNTs) in bulk ceramic composites has not yet resulted in the significant improvements in mechanical properties that such data suggest to be achievable. Composites with aligned and continuous CNTs and with high CNT volume fractions might be expected to maximise the improvements. We have produced aligned MWCNT preforms by chemical vapour deposition and fabricated dense, aligned and continuous 20% MWCNT/glass composites. This was achieved by infiltration of a ceramic precursor sol into the interstices of a MWCNT preform and consolidation by hot-pressing. The elastic modulus was measured using microcantilever tests and showed a 32% improvement over that of glass. The Young's modulus inferred for the MWCNTs in the composite was 200 ± 20 GPa. The load–displacement curves showed a non-linear and hysteretic behaviour which was attributed to interwall sliding within the MWCNTs. Apparent bridging of the cracks by the MWCNTs and a load maximum preceding failure were observed in the composite, indicating progressive toughening with crack growth. The results are discussed in terms of the microstructures of the MWCNTs and composites.

1. Introduction

There have been many attempts during the last 20 years to take advantage of the excellent properties offered by individual carbon nanotubes (CNT) by incorporating them in composites [1]. With glass or ceramic matrices, improvements in properties such as wear resistance [2,3] and electrical and thermal conductivity [4,5] have been reported but most attention has been focused on mechanical properties. Most studies have investigated randomly orientated CNTs within a matrix [6,7] but these composites have shown only modest improvements in stiffness and toughness [8,9]. From the experience with advanced fibre composites, aligning the CNTs would be expected to result in enhanced mechanical properties in the direction of alignment. It should also enable higher volume fractions of CNTs to be incorporated.

Two general methods of fabricating aligned CNT ceramic composites have been reported: (i) alignment of CNTs during composite processing e.g. by extrusion [10] or electrophoretic deposition [11,12] and (ii) infiltration of an aligned CNT preform with a ceramic precursor [4,13]. The first method suffers from the susceptibility of CNTs to agglomeration during processing and the CNTs are not continuous within the final composite. The second method (infiltration) results not only in aligned CNTs, but also the CNTs are continuous within the matrix. We have previously reported the use of aligned CNT preforms for infiltration with a sol precursor [4] whilst Chandrashekar et al. [13] used chemical vapour infiltration (CVI). Both of these routes produced porous composites, however, and their mechanical properties have not been investigated.

In the present study, dense glass matrix composites containing continuous and aligned multiwalled CNTs (MWCNTs) have been produced based on our previous infiltration-based route [4] but using hot pressing rather than pressureless sintering during densification. The alignment allows significantly higher volume fractions of MWCNTs to be incorporated than has been achieved with unaligned composites. The microstructure, elastic properties and fracture behaviour of the composites are reported. The mechanical properties are investigated using microcantilever beams loaded using a nanoindenter. This recently developed technique has two significant advantages in the present case. Firstly, it enables the limited volumes of material available with present pro-

* Corresponding author.
E-mail address: richard.todd@materials.ox.ac.uk (R.I. Todd).
[1] Present address: Institute for Technical Physics and Materials Science, Centre for Energy Research, Konkoly-Thege ut 29-33, Budapest 1121, Hungary.

http://dx.doi.org/10.1016/j.actamat.2015.08.045
1359-6454/

cessing technology to be assessed before expending the considerable resources required to scale up production of these complex and expensive materials. This extends a previous approach using conventional nanoindentation of surfaces to characterise very limited amounts of ordered ceramic/CNT composites [14]. Secondly, microcantilever beams enable testing on the scale of the microstructure, enabling fundamental processes such as interwall sliding which underpin the macroscopic behaviour, to be studied in isolation, thus leading to a deeper understanding of the factors ultimately responsible for the mechanical properties of such composites.

2. Experimental

2.1. Synthesis of aligned MWCNT preforms

Aligned MWCNTs were grown on quartz substrates (10×20 mm^2) using an aerosol CVD setup consisting of a piezoelectric generator, a quartz tube (2.2 cm inner diameter), a 50 cm long horizontal tube furnace, gas flow controller and acetone gas trap [15]. A solution of 5 wt% ferrocene ($Fe[C_5H_5]_2$, Aldrich 98%, the iron catalyst precursor) in toluene ($[C_6H_5CH_3]$, Aldrich, the carbon source) was used for the synthesis of aligned MWCNTs. The synthesis temperature was 800 °C with Ar as carrier gas at a flow rate of 1.7×10^{-5} m^3/s. The resulting nanotubes could be mechanically stripped from the substrate to produce freestanding preforms of aligned MWCNTs with length 3–5 mm.

2.2. Preparation of the sol

The sol was prepared using a method we have reported previously [4,8]. Briefly, an initial solution was prepared by mixing 4.7 ml tetraethyl orthosilicate ($Si[OC_2H_5]_2$, Aldrich >98%) with 2.25 ml of 4 M aluminium trisecbutoxide ($Al[OCH(CH_3)C_2H_5]_3$, Aldrich, >98%). A second solution was prepared by mixing 4.7 ml ethanol with 1 ml of 2 M sodium acetate (NaO_2CH_3, BDH, UK, 99%), 0.7 ml of trimethyl borate ($B[OCH_3]_3$, Aldrich, >98%), 0.5 ml 67% nitric acid (Aldrich) and 0.5 ml of distilled water. The two solutions were mixed to produce a sol that would yield aluminoborosilicate glass of 63 wt% SiO_2, 24 wt% Al_2O_3, 10 wt% B_2O_3 and 3 wt% Na_2O.

2.3. Infiltration of the MWCNT preforms with ABS sol and hot-pressing

Vacuum infiltration was used to introduce the sol into the interstices of the aligned MWCNT preforms. The sol was left to gel and dry within the interstices of the aligned MWCNT preforms at room temperature for 12 h. The gel infiltrated aligned MWCNT performs were further dried at 350 °C in air for 3 h to remove unreacted organic material. Five infiltrations were performed to increase the amount of matrix precursor introduced in the interstices of the preform. The infiltrated and dried aligned MWCNT preforms were loaded typically 3 at a time directly in a 15 mm diameter graphite die and the gaps between the preforms were then filled with calcined glass precursor. These compacts were then hot pressed under Ar. The loading of the preforms was such that the pressure was applied normal to the direction of alignment of the MWCNT as shown schematically in Fig. 1 so that densification could take place in the pressing direction without excessive bending of the CNTs.

The hot-pressing conditions were: pressure 25 MPa, peak temperature 1100 °C, heating rate 25 °C/min, holding time at peak temperature 10 min and natural cooling rate. After hot pressing, regions containing a single aligned MWCNT preform were identified and excised by diamond sawing and grinding to produce specimens with MWCNT aligned over thicknesses of several millimetres. For comparison, pure ABS glass was also produced by hot pressing under the same conditions.

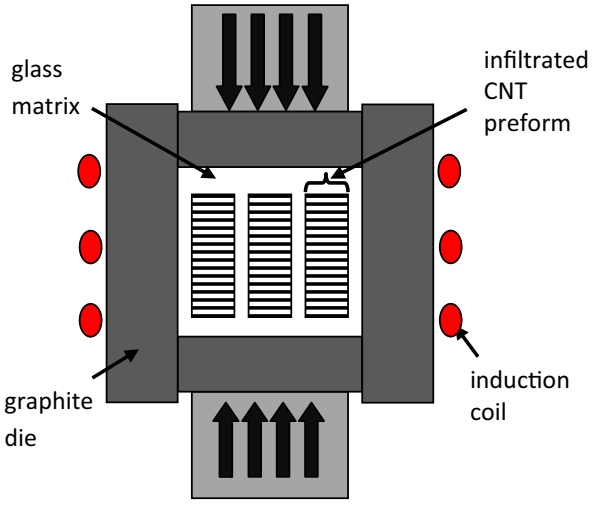

Fig. 1. Schematic showing the orientation of the CNTs during hot-pressing (arrows show the direction of applied pressure). The CNT alignment orientation is horizontal.

2.4. Analysis

The densities of the hot-pressed composite specimens were measured according to the Archimedes method with deionized water as the immersion medium. For the MWCNT preforms, the density was obtained from the measured mass and dimensions. Optical microscopy, scanning electron microscopy (SEM, JEOL 6500F) and transmission electron microscopy (TEM, JEOL 2000FX, 200 kV and JEOL 4000, 400 kV) were used to examine the microstructures of the composites. Both the unreinforced glass and the composites were polished using diamond slurries from 25 μm to 1 μm before microstructural studies using SEM. Also, focused ion beam (FIB) milling was used to produce polished cross-sectional surfaces (FEI FIB200, 30 kV) and to perform FIB tomography (Zeiss NVision 40, 30 kV). The tomographic reconstruction was done using Avizo software (Mercury computer systems, France).

TEM specimens were produced by *in situ* FIB lift-out and transferred to a copper grid. To measure the elastic properties and strength, FIB milling was used to produce micro-cantilever beams of triangular cross-section in the bulk composite and on unreinforced glass. The length of the cantilever was in the alignment direction of the MWCNTs in the composite specimens. Microcantilever bend tests were performed on an MTS XP nanoindenter fitted with a piezoelectric stage that allows constant force scanning mode images to be obtained in order to position the load point accurately on the specimen. The loading of the microcantilever beam was done by positioning the indenter tip at a location along the centre line of the top face of the beam, near the free end and applying displacement at a rate of 20 nm/s. More details of the basic technique are given in [16]. Five microcantilever beams were tested for the ABS glass and five for the CNT/ABS composite. Fractography was carried out using the SEM.

3. Results and analysis

3.1. Microstructural characterisation

Inspection of the polished sections of the specimens showed that although the CNT preforms had been broken up by the hot