LETTER

Core–shell composite of SiCN and multiwalled carbon nanotubes from toluene dispersion

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Introduction

Carbon nanotubes are known to have high thermal conductivity, and in bulk form, a topology that could constitute the matrix of an inhomogeneous solid [1]. Among the promised applications of carbon nanotubes is a composite material that is practical for thermal management and suitable for commercial products that behave as thermal emitters, absorbers, and interfaces. However, carbon nanotubes are known to oxidize in the temperature range of 400 to 600 °C, which limits the options for forming the composite and the applicability for high-temperature environments where such a composite is needed. A variety of polymer, metal, and ceramic composites bearing carbon nanotubes have been reviewed [2, 3]. More recently, Francis and Riedel [4] reported the use of polyureasilazane as a route to form a shell–core composite containing nanotubes. In their work, the SiCN shell is derived from polyureasilazane. However, the polyureasilazane is a viscous liquid in which nanotubes do not readily disperse. Francis and Riedel were able to report a multiple-step process that includes cross-linking (at 280 °C), pressing, mixing, ball milling, and baking again at higher temperature. We have found an alternate route of forming a similar

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composite that is facilitated by dispersing the nanotubes in toluene and then mixing with polyureasilazane. A single episode of baking forms a core–shell structure of amorphous SiCN surrounding MWCNTs (abbreviated hereafter as SiCN/MWCNT).

Our primary application is that of coating thermal detectors and other surfaces intended to absorb and thermalize laser radiation. The challenge is shared by other applications that demand heat dissipation without oxidation and melting. Before now, we have pursued nanotubes (single-walled and multi-walled) applied from a volatile suspension, grown vertically aligned, and bound in potassium silicate [5–7]. Here we report on the method of preparation and some aspects of surface chemistry that distinguish the shell–core composite from its constituents.

Coating preparation

The composite is formed in five stages: preparation of a nanotube dispersion, incorporation of the polyureasilazane resin, mixing, drying, and then baking. The sample dispersion was prepared from three constituents: 25 mL of toluene and 200 mg of MWCNTs produced by Bayer. The toluene and MWCNTs were sonicated with a horn sonicator for 10 min. 0.5 milliliters of polyureasilazane, commercially known as KDT Ceraset Polyureasilazane (manufactured by KiON Defense Technologies (KDT), Huntingdon Valley, Pennsylvania, USA.), was manually stirred into the dispersion and placed in a bath sonicator for 25 min and allowed to dry in a glass beaker for approximately 12 h. The residual solid was collected and placed in a zirconia crucible and baked in a nitrogen environment at ambient pressure. The temperature profile consisted of a 2-h ramp to 400 °C, soaking at 400 °C, followed by a 4-h

ramp to the high temperature (either 1100, 1200, or 1300 °C) and a 4-h soak at the high temperature.

X-ray diffraction (XRD) measurement results (not shown) are consistent with material containing carbon nanotubes, without features of crystalline SiCN. According to XRD studies by the manufacturer of Ceraset, the extent of crystallinity and proportions of Si, C, and N formed in the ceramic depend on the high-temperature soak. The manufacturer's specifications indicate that the ceramic is amorphous below 1500 °C.

Fourier transform infrared (FTIR) spectroscopy has been employed in the past to investigate the stoichiometry of Si, C, and N with respect to processing temperature. Bendeddouche et al., and separately Sandeep and Raj, indicate that features of interest for SiN and SiC are found in range of 898 and 790 cm^{-1}, respectively, with a broad feature near 480 cm^{-1} for SiCN [8, 9]. Our own FTIR results indicated spectral features weaker than those of Bendeddouche et al., but consistent with material containing SiCN [8, 9].

Measurements and results

A scanning electron microscopy (SEM) image that is representative of the composite is shown in Fig. 1. The image was obtained by use of a field emission SEM JSM 7401-F (JEOL Ltd., Tokyo, Japan). Figure 1 shows the mesh like morphology in which the nanotubes are coated and held together by the ceramic shell. The network of MWCNTs appears to be uniformly coated and retains a topology similar to that of the bulk nanotubes.

The uniformity and thickness of the shell is revealed by transmission electron microscopy (TEM), shown in Fig. 2. The TEM sample was prepared for analysis by depositing
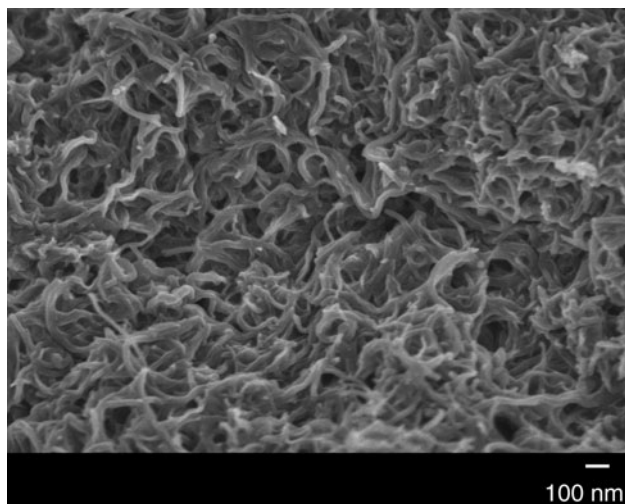

100 nm

Fig. 1 SEM image of SiCN/MWCNT material prepared at 1100 °C

SiCN/MWCNT material suspended in ethanol onto a grid of holey-carbon. After the ethanol evaporated, the grid was then mounted in a single-tilt sample holder for TEM observation. All images were acquired at 200 keV under low-dose operating conditions. (Low dose means that the electron flux onto the samples was restricted with a small condenser aperture, approximately 40 μm in diameter with sufficient illumination for a 2-s exposure.) All images were captured with a magnification of 300×103, with the objective lens at or near the so-called Scherzer defocus condition (which in our microscope is −76 nm). The diameter of the MWCNT is 5–10 nm wide and the shell is approximately 5 nm thick. The coating appears to be amorphous for four specimens processed at 1100, 1200, and 1300 °C. This is consistent with previous studies that show that polymer-derived SiCN resists crystallization up to 1500 °C. EDS, shown in the inset of Fig. 2, provides evidence that some amount of silicon (at 1.75 keV) and carbon (at 0.25 keV) and little oxygen (at 0.5 keV). The EDS is complimentary to our analysis, because we do not expect the EDS instrumentation to detect the presence of nitrogen.

Raman spectroscopy measurements were performed in the backscattering configuration by use of a 13 mW argon-ion laser with a wavelength of 488 nm. A 50 mm, f/1.40 lens focused the beam (circular area less than 0.25 mm^2) and collected the Raman-scattered light. The collected light passed through a 0.27 m grating spectrometer equipped with a holographic notch filter and a charge-coupled detector (operating at 77 K). Information derived from Raman scattering is important in terms of characterizing both the appearance of nanostructured carbon and the relative quantities of carbon impurities and the stoichiometry of silicon, carbon, and nitrogen in the ceramic [9]. Comparative spectra of three different samples consisting of MWCNTs, SiCN, and SiCN/MWCNTs is shown in Fig. 3. The results present a challenge because it appears that the dominant Raman modes of MWCNTs and SiCN appear at the same frequencies. The "G band" at 1500–1650 cm^{-1} is a compilation of bands originating from the in-plane vibrational modes of carbon in the curved graphite lattice, while the "D-band" at 1300–1400 cm^{-1} is generated by symmetry-lowering effects such as defects, tube ends, or the presence of nanoparticle or amorphous carbons. We expect the G band is shifted and broadened by the presence of the ceramic material as we would expect for "defective" nanotubes. Bendeddouche et al., show the splitting of a single peak for $SiC_{0.6}N_{0.35}$ near 1500 cm^{-1} for $SiC_{1.45}$ [9]. Our SiCN appears similar to Bendeddouche's $SiC_{1.45}$ from 1997 [9]. However, more recently, Jiang et al. [10] show "typical" peaks near 1360 cm^{-1} and 1580 cm^{-1} as representative of SiCN. Our Raman spectra show that the shell–core SiCN/MWCNT is different from SiCN or

Fig. 2 TEM images of a MWCNT coated with SiCN for specimen processed at a high-point temperature of 1100 °C. A thick ceramic coating (5–7 nm) covers the NT. Inset shows the TEM-X-ray energy dispersion spectrum (EDS) from the specimen
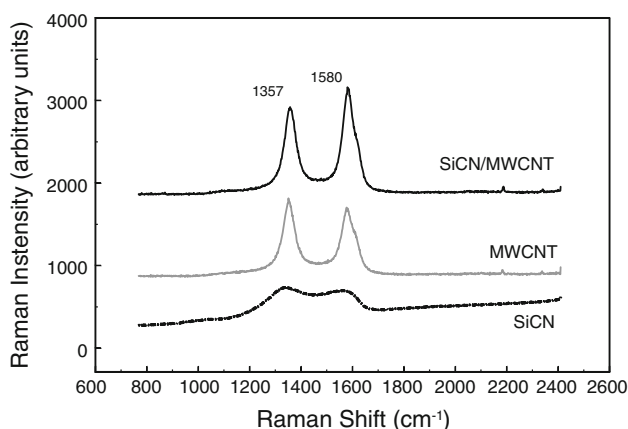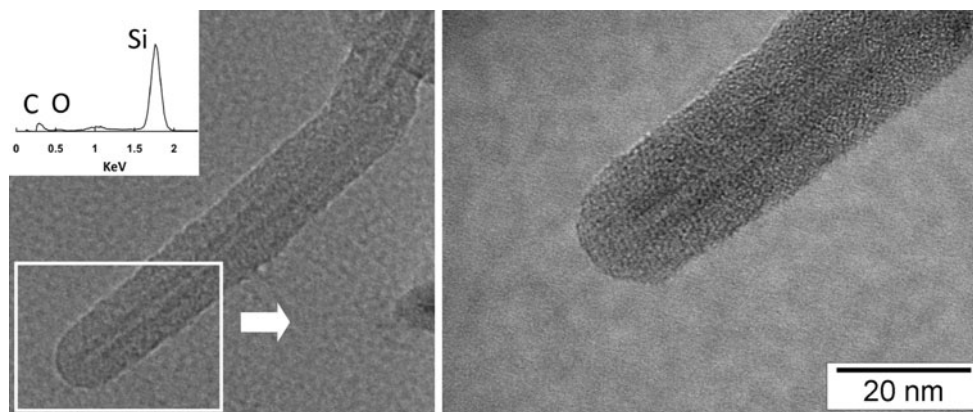

Fig. 3 Raman spectra generated by scattering 488 nm laser light on three different samples representing SiCN, MWCNT, and SiCN surrounding MWCNTs. The SiCN/MWCNT Raman scattering is qualitatively similar for all four production temperatures with different amounts of back ground scatter, probably due to the diffuse nature of the samples. The sample shown represents the measurement result having the least background scattering

Fig. 4 TGA of SiCN/MWCNT sample prepared at 1100 °C. The oxidation temperature at 717 °C is significantly higher than that of the MWCNTs alone (at 580 °C)

MWCNTs alone. The difference is manifested in the relative height of the peaks at 1357 cm^{-1} and 1580 cm^{-1}, the SiCN/MWCNT being dominated by a higher peak at 1580 cm^{-1}.

Thermogravimetric analysis (TGA) was performed by use of a commercially available analyzer (TA Instruments Q5000) with rapid infrared heating. Results obtained from TGA include the residual mass after heating and the oxidation temperature. Measurement samples were prepared in 100 µL ceramic pans containing 40 mg of material. From a starting temperature of 40 °C, each sample was heated at a rate of 10 °C/min to 1100 °C while air was introduced at a rate of 25 mL/min. TGA was completed on MWCNT as well as SiCN/MWCNT material prepared at 1100, 1200, and 1300 °C. The oxidation temperature of the MWCNTs and SiCN/MWCNT materials prepared at 1100 °C is shown in Fig. 4. The MWCNTs had an average
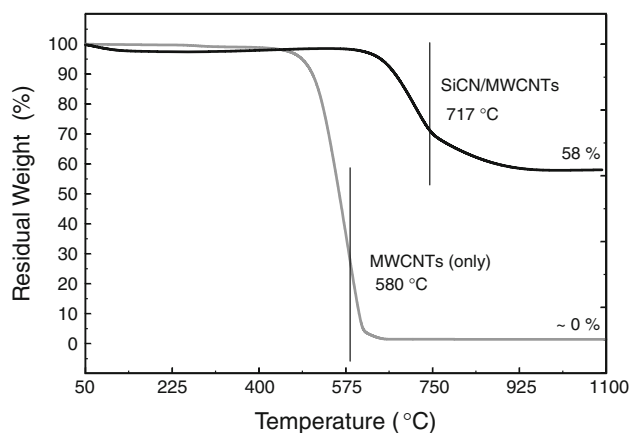
oxidation temperature of 579.5 °C and the nanotube content was greater than 97% (residual mass of 1.45% at 800 °C), which is consistent with the manufacturer's specification. The oxidation temperatures of SiCN/MWCNT samples prepared at 1100, 1200, and 1300 °C were 718.9, 710.7, and 715.8 °C, respectively. The residual masses of the SiCN/MWCNT material were 57.7%, 58.8%, and 61.0% for material prepared at 1100, 1200, and 1300 °C, respectively. The higher oxidation temperature of the SiCN/MWCNT material is attributable to the ceramic shell [11].

Discussion

Polyureasilazane is a viscous resin at room temperature that does not readily disperse nanotubes. Therefore, we sought a liquid in which the nanotubes would disperse uniformly and that would also be compatible with the polyureasilazane resin. Based on knowledge of the resin's precursors, we considered both acetone and toluene. We

found good dispersal of the nanotubes in acetone, however after the formation of the SiCN upon heating, voids or pores in the material were created. These were likely caused by the evolution of gaseous oxygen-containing species. The final heat-cured material prepared with acetone appeared grayish in color in some areas and black in others. The gray areas may indicate the appearance of SiO_2. Rather than the mat of tubes obtained with toluene dispersions shown in Fig. 1, acetone dispersions create something with the appearance of nanotubes buried in clumps of ceramic (like sticks in mud). Alternatively, we found that toluene provided a superior dispersion of nanotubes. It is well known that aromatic hydrocarbons are good dispersants for nanotubes. By the use of toluene, the addition of oxygen to the mixture was avoided, and the resulting baked material was dense and black. Without the evolution of oxygen, voids were not created and ultimately created a more uniform coating of ceramic around the nanotubes.

Conclusion

We have documented a route to prepare a high-temperature composite that requires shorter and fewer processing steps than that reported previously. The emphasis of the present work has been to establish that the nanotubes are uniformly coated and well dispersed and that the ceramic distinguishes itself from either MWCNTs or SiCN alone. Imaging indicates that the MWCNT material is uniformly coated with an amorphous shell. Raman spectroscopy reveals that the composite is similar to previously reported material that shows evidence of SiCN and that is different from either SiCN or MWCNTs alone. For the sake of evaluating the potential of the composite having a high oxidation temperature compared to MWCNTs, we undertook TGA experiments. The SiCN/MWCNT has an oxidation temperature that is approximately 50% higher than that which we measured for MWCNTs. XRD, FTIR, and EDS measurements were also undertaken, and the results

demonstrate qualitatively that the SiCN and composite are comparable to similar material prepared by different routes such as other polymer precursors or chemical vapor deposition. There are other properties that we have yet to investigate. The composite is electrically conducting, and this property may bear further investigation for other applications. The material appears black in the visible spectrum, so additional spectroscopy at wavelengths where we desire an optical absorber having a high laser damage threshold bears investigation. Forming a composite with SWCNTs is also of interest, and research may show that we can achieve some desirable optical and electronic properties of SWCNTs while mitigating some of the undesirable properties such as low-temperature oxidation and degradation from environmental exposure.

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