An Optimized Process for *in situ* Formation of Multi-walled Carbon Nanotubes in Templated Pores of Polymer-derived Silicon Oxycarbide

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Abstract

A reliable and optimized process to grow carbon nanotubes (CNTs) in templated pores of polymer derived ceramic (PDC) matrix was developed. It is realized through the pyrolysis of a preceramic polymer, i.e., poly (methyl-phenyl-silsesquioxane) (denoted as PMPS), in argon atmosphere at 1000°C together with nickel-catalyst-coated poly-methyl-methacrylate (PMMA) microbeads (denoted as PMMA-Ni). PMPS served as both a precursor for the ceramic matrix and a carbon source for the CNT growth. PMMA microbeads were used as sacrificial pore formers and coated with nickel via an electroless plating method, which provides **much better an improved control of particle size of the catalyst and its distribution in the material**. The influence of PMMA-Ni loading on the *in situ* growth of CNTs and the properties of CNTs/SiOC nanocomposites were studied through thermogravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy, and density/porosity measurements. Under optimized conditions, uniform distribution of *in situ* grown CNTs was observed within the templated pores of the SiOC matrix. The optimized process leads to reproducible high yield of CNTs in the pores. The development of such novel CNT/cellular ceramic nanocomposite materials is of significant interest for a variety of sensor applications.

Keywords

Carbon nanotube; Polymer derived ceramics; Silicon oxycarbide; Electroless plating

1. Introduction

For nearly four decades, preceramic polymers have been used to fabricate advanced polymer-derived ceramics (PDCs) due to the tailorability of their molecular structures and ease of processing [1]. In particular, Si-based polymers have been shown to be promising. Polymers, such as polysiloxane, have been converted into various ceramic products and forms: ceramic foams [2], bulk composites [3], planar tapes [4] and engineering materials with high temperature and oxidative stability [5, 6]. Typical PDCs can be either insulating, like SiOC and SiOCN ($\sigma_{dc}(RT)=10^{-14}\sim 10^{-12}(\Omega\cdot cm)^{-1}$), or semiconducting, like SiC and SiCN ($\sigma_{dc}(RT)=10^{-4}\sim 10^2(\Omega\cdot cm)^{-1}$) [1]. Functionalizing and enhancing the electrical conductivity of SiOC ceramic foams, for example, could not only make use of their good mechanical, physical and chemical properties, but also potentially lead to several new applications, such as regenerable adsorber components or regenerable diesel particulate traps [7].

Different researchers [8, 9] have identified that the carbon content (graphite or graphene phase) and interconnectivity of the carbon network within PDCs could exert a major influence on their electrical properties. This is mainly determined by the carbon species (especially phenyl groups) in the starting polymer and processing methods, e.g., adding carbon-rich compounds, using special pyrolysis conditions. Alternatively, introducing carbon nanotubes (CNTs) into PDCs is expected to be an effective and promising method for further electrical property enhancement due to their high conductivity [10, 11]. However, there are two handicaps that hinder the use of CNTs in PDCs as either functional or structural reinforcement: high manufacturing cost and non-uniform dispersion in matrix materials. To overcome these handicaps, *in situ* formation of CNTs can be achieved by utilizing the hydrocarbon species released in a large amount during the thermal transformation of polymer precursor to ceramic.

With catalyst, these hydrocarbon species can be converted to CNTs in the intermediate temperature range and this process is a type of the so-called Catalyst Assisted Pyrolysis (CAP). In other words, CAP method could help turn waste gases into useful functional component: CNTs.

Significant progress has been made in the production of nanostructures through the CAP method. Aside from turbostratic carbon, it has been shown that various nanostructures (whiskers [12], nanotubes [13-15], and nanowires [16]) can be produced directly from preceramic polymers. For example, Vakifahmetoglu *et al* [17] described the production of Si_3N_4 and SiC nanowires using poly(methyl-phenyl)silsesquioxane (PMPS) with a cobalt catalyst. Likewise, single-crystalline Si_3N_4 nanowires/nanobelts were produced from polysilazane, using FeCl_2 as catalyst [18]. Yang *et al* reported SiC nanorods that were synthesized using a similar methodology [19]. More specific ~~on~~regarding carbon species through CAP, Greil *et al* [20] showed that, in two types of polysiloxane derived Si-O-C ceramics, the precipitation of the amorphous carbon phase began with polymer decomposition, typically at 400°C, and was nearly completed at 1000°C. Above 1100°C, the crystalline carbon species were found, which resulted in percolation of the electrically conductive network of turbostratic carbon. Scheffler *et al* [21] observed for the first time the direct formation of multiwall carbon nanotubes (MWCNTs) only within the pores that formed during the polymer-to-ceramic conversion of PMPS ~~and~~which contained nickel acetate ~~at the same time~~. These active pores were described as “catalytic microreactors”. Later, they showed the *in situ* growth of CNTs when nickel acetate and silicon were incorporated together into the PMPS precursor/silicon mixture [22]. In a related study, using polymeric microbeads as sacrificial pore formers, Terry *et al* showed the formation of CNTs in these templated pores [23]. Furthermore, CNTs were synthesized from a borazine-based precursor including nickel catalyst

[24] and Ya-Li Li reported the fabrication of SiOC-CNTs composite by a one-step process via the *in situ* growth of CNTs during the pyrolysis of a preceramic polymer (polysiloxane) including FeCl₃ as catalyst [25]. Recently, Mantzel *et al* [26] took one step further to not only *in situ* form CNTs in pyrolyzed Si-O-C samples but also sinter/densify the ceramic body by field assisted sintering technology, and their results showed that CNTs could survive the harsh sintering conditions and significantly improve the mechanical properties, e.g., hardness, for the samples sintered at 1050°C when compared with CNT-free ones.

In most of these studies, the nanotubes and whiskers form on the exposed surface of the sample or on the wall of pores in the matrix. However, due to lack of control over the location/distribution of the catalyst and the quality of catalyst carriers, e.g., microbeads as pore formers, the full efficiency of the process has not been realized. For instance, simply mixing catalyst compound with preceramic polymer would lead to the random distribution of catalyst particles in the ceramic matrix, thus only a portion of them that happens to be on the pore/crack surfaces would contribute to the CNT growth. Even if the catalyst compound is coated on the shell of pore formers, CNTs could only grow on catalyst seeds/particles of a limited range of sizes, which imposes another technical challenge to the processing - control of the thickness of catalyst shell. Also, Finally, in many of the studies reported in the literature, some of the key details are lacking, making it hard to reproduce these results.

The present study focuses on a novel procedure for the *in situ* formation of CNTs inside templated pores of PMPS, aiming to significantly improve the quantity and uniformity of the grown nanostructures. In addition, the processing is described with sufficient details. Nickel, as the transition metal catalyst, was uniformly coated on the surface of PMMA microbeads, denoted as PMMA-Ni, via an optimized electroless plating method. And then PMMA-Ni microbeads

were added into PMPS polymer as the template porogen. By doing so, both catalyst particle distribution and porosity in the ceramic became well controllable, which in turn leads to a significantly higher yield of CNTs and more uniform distribution of the CNT network. These uniform composites are expected to have improved functional properties, including thermal and electrical conductivity.

2. Experimental Procedure

2.1 Material Processing

The ceramic matrix in this study was produced using the commercially available poly(methyl-phenyl-silsesquioxane) (PMPS, H44, WackerChemie AG, Burghausen, Germany). H44 is a solid polymer that has a good amount of carbon as methyl and phenyl groups, which serve as the major carbon source for MWCNT formation during H44 pyrolysis in an inert atmosphere. Poly-methyl-methacrylate (PMMA) microbeads (Microbeads AS, Skedsmokorset, Norway) with nominal size of 6 μm were coated with nickel ~~nano-particleless~~ shell in accordance with an electroless plating method described elsewhere [27]. These nickel coated PMMA microbeads, i.e., PMMA-Ni, were burned out during pyrolysis, leaving nickel nano-particles on the templated pore surfaces.

H44 and 0.5wt% of aluminum acetylacetonate ($\text{Al}(\text{CH}_3\text{COCHCOCH}_3)_3$, the crosslinking agent) were completely dissolved in acetone (1 g H44 : 1 ml acetone) first, then the PMMA-Ni microbeads prepared as mentioned above were gradually added into the solution with vigorous stirring. Different volume ratios of PMMA-Ni to H44 were used in the experiments (30:70, 40:60, 50:50, and 60:40). The mixture was stirred on a hot plate until the solvent partially evaporated, and was then transferred to an aluminum mold for crosslinking (4 h at 200°C in air;

heating rate: 5°C/min). The crosslinked porous monolithic bodies were crushed into powder, then cold-pressed into pellets at room temperature. Samples of different compositions were pyrolyzed at 1000°C with heating rate of 2°C/min under ultrahigh purity argon (static, oxygen gettered) in a tube furnace, held for 1 h at peak temperature and finally cooled down at the rate of 3°C/min. Based on the volume percentage of PMMA-Ni used (with respect to the starting materials), samples were labeled as SiOC-Ni30, SiOC-Ni40, SiOC-Ni50, SiOC-Ni60. The processing route is schematically illustrated in Fig. 1.

2.2 Characterization Techniques

Thermogravimetric analysis was carried out in argon atmosphere up to 1200°C (STA 409, Netzsch GmbH, Selb, Germany) with heating rate 2°C/min. Three different types of samples were tested: pure H44, PMMA-Ni microbeads and cured PMMA-Ni/H44 (50:50 volume ratio).

The morphological analysis of fracture surfaces of the pyrolyzed samples was performed by scanning electron microscopy (SEM) (JSM-7000, JEOL, Tokyo, Japan) with an accelerating voltage of 10 keV.

X-ray diffraction (Bruker D8 FOCUS, Bruker AXS Inc., Madison, WI, USA) was used to study crystalline phases of different pyrolyzed samples. A Cu-K α radiation source was used and scans were carried out between the 2 θ value of 10-90° with a step size of 0.2 degree.

The bonding states of carbon species found in different samples were investigated with Raman spectroscopy (Renishaw inVia Raman Microscope, Renishaw Inc., Hoffman Estates, IL, USA). The argon laser source was attached to a confocal microscope and used the 514 nm line as the excitation wavelength. In order to minimize the measurement error as a result of a possible

nonhomogeneous distribution of MWCNTs, a minimum of 10 Raman spectra were collected for each sample from randomly selected sites.

The bulk density and open porosity of the ceramic were determined using the Archimedes method with deionized water as the buoyant medium. Volume shrinkage before and after pyrolysis was calculated by measuring the dimensional change of pellet samples (diameter and height).

3. Results and Discussion

3.1 Thermogravimetric (TG) and Differential Thermogravimetric (DTG) Analysis

In preliminary experiments, it was determined that careful selection of the crosslinking condition is critical for the success of the desired cellular microstructure. The PMMA-Ni microbeads must hold their positions and shape while H44 hardens due to crosslinking, and then burn out during the pyrolysis stage only, so that the pores left after burnout would maintain the spherical shape templated from the microbeads. However, the crosslinking temperature of H44 can be very close to the softening temperature of PMMA. If the former reaches or surpasses the latter, the PMMA and the resulting pores would not retain their shape in the pyrolyzed ceramic. Thus TGA was performed on H44, PMMA-Ni and their 50:50 volume ratio blend in argon (cured at 200°C for 4h). The results are shown in Fig. 2. **From these results, the amount of Ni in the PMMA-Ni microbeads is about 5 wt %.**

The decomposition process of PMMA-Ni (dash-dot line) starts slowly as it is heated from room temperature, accelerates after the transition in 230-250°C, and reaches the maximum rate of decomposition at a temperature ~335°C, as evident from the derivative of the thermogravimetric curve in Fig. 2.b. As expected, PMMA-Ni is close to complete burnout after ~400°C with only

~3% of the total weight left, which can be attributed to the plated nickel layer. In comparison, pure H44 exhibits two major peaks in its DTG curve (dash line), which correspond to the release of volatiles and oligomers during crosslinking at low temperature (maximum rate at ~277°C in Fig. 2.b) and the ceramization process at intermediate temperature (maximum rate at ~502°C). At 600°C, H44 still maintains ~76% of its original weight and then becomes fairly stable with increasing temperature, resulting in a ceramic yield of ~67% at 1000°C. In the final stage of H44 ceramization, the weight loss is mainly due to the molecular rearrangement of silicon sites, giving rise to the amorphous silicon oxycarbide. It has been shown that H44 can be thermally cured at temperatures of 100°C and above without the need of any curing agent[21, 28, 29]. The ceramization temperature range found here is also in good agreement with previously reported data, confirming that the ceramization of H44 predominantly occurs between 400°C and 600°C [21]. Therefore, the crosslinking temperature of 200°C chosen in this study minimizes the thermal decomposition of the space holder PMMA-Ni microbeads while H44 is cured (with long enough time).

The thermal behavior of the H44 + PMMA-Ni blend is a composite of the decomposition of the two components as shown in Fig. 2.a (solid line). The TG curve can be divided into three stages: 1. initial plateau (< 210°C); 2. final plateau (> 800°C); and 3. transition period in between (210~800°C), which consists of several processes. The significant weight loss that occurs at 353°C is attributed to the burnout of PMMA. This results in almost 50 % of the total weight loss. Moreover, the use of nickel could enhance the dehydrogenation activity in H44, leading to a decrease in ceramic yield and thermal stability, similar to what was reported for a nickel-containing polysiloxane [30]. After 800°C, weight of the blend stabilizes at roughly 36%.

There is another important observation during pyrolysis worth noting. Samples in this study were pyrolyzed in a tube furnace with argon atmosphere. If the argon gas continuously flew through the tube even at a slow rate, the CNT yield in the final product was very poor. However, if the gas was static, the growth of CNTs was excellent. It reveals that a high concentration of reactive hydrocarbon species surrounding the catalytic surfaces is necessary for the growth of CNTs.

3.2 Microstructure

The pyrolyzed SiOC samples were broken into pieces in order to reveal their interior fracture surfaces. Fig. 3 shows the micrographs of samples of three different compositions, namely, SiOC-Ni30 (Fig. 3.a), SiOC-Ni40 (Fig. 3.b) and SiOC-Ni50 (Fig. 3.c). All of these microcellular SiOC ceramic are decorated with a large amount of high-aspect-ratio nanostructures that are confirmed to be the *in situ* grown CNTs (Fig. 3.d). As shown in Fig. 3.d, the dark nanoparticles in the image are nickel [23] with size slightly less than 100 nm—a typical value for these particles to serve as seeds for the growth of CNT confirming the size of the grown CNTs as well. In addition, the “dense” wall and the hollow interior of the CNT structure can also be observed and confirmed in Fig. 3.d and it appears to be surrounded by the pyrolyzed SiOC matrix material, which corroborates the observation of nanostructure in the SEM images (Fig. 3.a to 3.c). The dense and intertwined CNTs “forest” have almost fully covered the entire micro-porous fracture surfaces of all the examined samples, which is unlike ~~what were found~~ the observations in many previous studies [17, 21, 23, 31]. From the close-up micrographs, it appears that the grown CNTs become longer and denser as PMMA-Ni content increases, however, no significant difference can be observed in terms of their general morphology. The CNT diameter

ranges from ~50 to ~100 nm. In comparison, Fig. 4 shows the fracture surface for samples without nickel catalyst (thus, without the growth of CNTs). Thus it can be concluded that the closely packed pores are completely hidden behind the ‘dense forest’ of CNTs in Fig. 3. And it is because the CNTs touch and interconnect with each other on a large scale both in and out of the pores, this type of ‘dense forest’ microstructure with numerous highly-conductive branches stretching out is expected to substantially improve the electrical conductivity and other functional properties of SiOC ceramic [32].

Due to the uniform PMMA microbeads (averaging 6 μm) used in this study, the pores after 1000°C pyrolysis shrink to ~4 μm but maintain their uniform size and spherical shape (Fig. 4). As PMMA content increases (from 30 to 50 vol.%), the microbeads get closer packing in the cold-pressed sample, which consequently leads to higher pore density and thinner matrix walls between pores. It should be noted that all three compositions, including the highest volume fraction PMMA, have pores uniformly distributed within the SiOC matrices as seen in Fig. 4. In Fig. 4.c, there are holes that can be seen on pore surfaces, which is beneficial for improving SiOC’s electrical conductivity, because the electricity-conducting network in the sample is expected to be overlapping CNTs not only within one pore but also between adjacent pores. For the case in which nickel plated PMMA microbeads are used, in each pore, a nickel layer uniformly covers the entire pore surface. This uniform nickel layer is made possible by using the electroless plating method [24]. All of the processing factors and parameters discussed above lead to the high density of the CNTs in the templated pores observed in Fig. 3.

The microstructures in Figures 3 and 4 were obtained by crosslinking at 200°C for 4 hours as discussed in section 3.1. However, it is noteworthy to demonstrate the consequence of crosslinking at a higher temperature. The crosslinking temperature of 270°C was also

investigated. When this higher temperature is used, the PMMA microbeads soften and dissolve in the viscous matrix material, so that almost no pore are formed from the microbeads as shown in Fig. 5.a. The small white particles seen in this micrograph are coarsened nickel catalyst (Fig. 5.b), which are embedded in the solid matrix due to the premature softening of PMMA. The lack of fine nickel catalyst and absence of pores leads to conditions, under which CNTs are not formed. This experiment demonstrates the importance of careful control of processing parameters at all stages.

3.3 X-Ray Diffraction (XRD) Analysis

Fig. 6 presents the XRD patterns of 1000°Cpyrolyzed SiOC samples of different PMMA (thus, different Ni) contents. Sharp peaks at $44.36^\circ(2\theta)$ and $52.0^\circ(2\theta)$ are characteristic for metallic nickel [30], implying that the electroless plating method succeeded in depositing nickel layer onto the surface of PMMA microbeads. Carbon (graphite, 2H) at $26^\circ(2\theta)$ is observed in all samples, which is most likely due to the formation of MWCNTs of sp^2 hybridized carbon. Two weak peaks at $39^\circ(2\theta)$ and $49^\circ(2\theta)$ are attributed to the Ni_2Si phase [30], a product of the reaction between nickel particles and SiOC matrix at high temperatures (850—1000°C) [21]. Comparing the Ni_2Si peaks with nickel it can be concluded that nickel is the dominant phase due to much higher intensity of nickel peaks. According to the Debye-Scherrer equation, the size of nickel particles (crystallites) from SiOC-Ni 30, 40, 50, and 60 samples is 29.78 nm, 28.56 nm, 27.67 nm and 22.70 nm, respectively. Although overall nickel content is different among the four samples, their particle sizes are reasonably close, averaging 27.18 nm. Based on the approximately 5 wt % Ni in the PMMA-Ni microbeads, it is estimated that the amount of Ni in this samples ranges from 1.7 wt % (for samples with 30 vol % PMMA-Ni microbeads) to 2.7 wt %

(for samples with 50 vol % PMMA-Ni microbeads). Interestingly, when nickel particles are large, in the range of ~100 nm to ~1 μ m, no CNTs can be observed (Fig. 5.b). Thus, nickel particle size needs to be small in order to serve as catalysts for the growth of CNTs [33]. Similarly, FazleKibria *et al* [34] reported the synthesis of CNTs over an iron-nickel catalyst and concluded that smaller catalyst particle size and homogeneous dispersion of the catalyst were favored for the high density growth of CNTs. The typical diameter of CNTs in their article is 20-50 nm, which is comparable to this study. In our case, nickel particle size can be tuned by varying nickel layer thickness on PMMA microbeads during electroless plating, which is achieved by adjusting the plating time.

3.4 Raman Spectroscopy

Essentially, both sp^2 and sp^3 hybridized carbon could possibly exist in the pyrolytic product of H44 due to the methyl and phenyl groups in the polymer. However, with nickel catalyst, the released carbon-containing gaseous species were captured to grow CNTs so the form of carbon in the final product is dependent of the grown CNTs. Raman spectroscopy is a well-established technique to obtain information about the nature the carbon form [21, 30, 31, 33, 34].

The samples for Raman spectroscopy (Fig. 7) were processed in exactly the same way with only one difference: without (a) or with (b) nickel-catalyst layer coated outside the PMMA microbeads. Therefore, the (a) method yields ‘clean’ porosities due to the PMMA porogen of 30-50 vol.% (with respect to the starting material), whereas the (b) method leads to *in situ* grown CNTs in significant quantity. As can be seen from Figure 7.a and 7.b, the amount of PMMA has almost no effect on the resulting Raman spectra indicating that the nature of the carbon species is

unaffected by the volume fraction of PMMA. However, the spectra of samples with and without nickel are very different.

In Fig. 7.a, the G-bands found near 1582 cm^{-1} are due to the C-C bond stretching in all types of sp^2 carbon forms, which don't necessitate the existence of six-fold rings. However, substantial disorder can be observed in the sp^2 network of the possible carbon structures in catalyst-free samples as the D-bands that appear around 1336 cm^{-1} are almost as strong as the G-bands. It indicates that the carbon left in the pyrolyzed matrix is highly defective and unable to form typical sp^2 structures on large scale. In addition, both the broad linewidth (notice the 'high valley' between D- and G-bands) and the high intensity of D-bands often suggest the presence of amorphous carbon (sp^3 -hybridized) in the material [33]. In addition, the broad bands around $2500\sim 3250\text{ cm}^{-1}$ are the Raman signature of amorphous carbon.

With CNTs grown in the SiOC matrix, the intensity of the disorder-induced D-bands decreases significantly compared with the G-bands. Both peaks (D and G) become sharper and their width decreases. One reasonable explanation is that the massive growth of CNTs utilizes a large portion of the carbon sources that should have originally deposited back into the matrix as defective carbon. Thus, it is believed that SiOC with CNTs has lower disordered carbon content in the matrix. The other evidence of the growth of CNTs in the material lies in the appearance of dispersive G'-bands near $\sim 2690\text{ cm}^{-1}$ instead of the broad band of amorphous carbon in the CNT free samples. Although G'-bands are common to graphitic sp^2 materials, they are not observed in the CNT-free samples (Fig. 7.a), implying that the second-order Raman scattering in them is weak. The highly ordered CNT structure is thought to be the main contributor of the formation of G'-bands in the materials with CNTs.

3.5 Shrinkage, Open Porosity and Density

High porosity is favored for the growth of CNTs in the SiOC matrix, but the amount of porosity is limited by the packing limit of PMMA microbeads. In fact, samples with PMMA loadings higher than 60 vol. % could not be made using the method presented here. Porosity in the final product comes from two sources: pores created by the porogen, and cracks or voids in the matrix due to incomplete densification during pyrolysis of SiOC. As shown in Fig. 8, starting from 30 vol. % of PMMA-Ni, open porosity increases from ~19% to ~32%, while volume shrinkage of the pyrolyzed body increases from ~30% to ~35%. The measured open porosity is considerably lower than the original PMMA-Ni loading, which is from 30% to 60%. This is mainly attributed to the significant matrix shrinkage (>30%) and uncounted closed porosity. In contrast, bulk density decreases from ~1.15 g/cm³ to ~0.975 g/cm³ as the volume fraction of PMMA increases.

4. Concluding Remarks

A novel and reproducible processing route for synthesizing *in situ* grown CNTs within SiOC, a PDC matrix, is presented in this paper. The use of nickel coated PMMA microbeads serves two important functions: first, a uniform size porogen (on micron level) that provides controllable uniformly distributed porosity in the matrix; second, templated pore surfaces have uniform layer of nano-scale nickel catalyst particles. These two factors lead to reproducible and high density formation of carbon nanotubes. The synthesized CNT/SiOC nanocomposites for a series of PMMA loadings show dense CNT growth. An appropriate deposition time for the nickel layer during electroless plating (resulting in nano-sized nickel particles with high catalytic activity) and a suitable crosslinking temperature (200°C) are critical for the success of this

process. With a PMMA loading ranging from 30 % to 60 % in the starting mixture, the final products exhibit open porosities between ~19% to ~32%. The reason the open porosity in the product is considerably lower than the starting material is attributed to the large volume shrinkage in the SiOC matrix due to pyrolysis and the residual closed porosity. The optimized microstructure of CNT/SiOC nanocomposites is promising for further investigation of the properties of these materials. In addition, the process developed here can be extended to other ceramic systems, especially those made from polymeric precursors.

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Figure Captions

Fig. 1. Schematic for the *in situ* growth of carbon nanotubes in the templated porous SiOC ceramic (not to scale).

Fig. 2. TGA (a) and DTG (b) curves for the pure H44, PMMA-Ni microbeads and their 1 : 1 volume ratio blend (H44/ PMMA-Ni).

Fig. 3. SEM micrographs from the fracture surfaces of samples made from different volume ratios of “PMMA-Ni: H44” pyrolyzed at 1000°C in Ar: (a: SiOC-Ni30; b: SiOC-Ni40; c: SiOC-Ni50). The intertwined nanostructures of high density found in the templated pores of SiOC matrices are high-aspect-ratio CNTs as shown in the TEM micrograph from SiOC-Ni40 (d) of one CNT grown on nickel nanoparticle.

Fig. 4. SEM micrographs from the fracture surfaces of samples with (a) 30 vol.% PMMA, (b) 40 vol.% PMMA and (c) 50 vol.% PMMA, all of which have no deposited nickel layer on the PMMA.

Fig. 5. SEM micrographs from the SiOC-Ni30 samples crosslinked at 270°C, then pyrolyzed at 1000°C in Ar. (a) overview; (b) close-up showing coarsened nickel particles. No CNTs can be observed in this case.

Fig. 6. XRD patterns of samples (SiOC-Ni30, 40, 50, 60) pyrolyzed at 1000°C in Ar.

Fig. 7. Raman spectra of SiOC (a) without and (b) with *in situ* grown CNTs at different porosities, i.e., different PMMA loadings.

Fig. 8. Volume shrinkage, open porosity and bulk density of the SiOC/CNT ceramic composite as a function of the PMMA-Ni porogen loading. (The volume ratio here refers to the composition in the starting materials.)

Figure 1

Figure 2 a

Figure 2 b

Figure 3 a

Figure 3 b

Figure 3 c

Figure 3 d

Figure 4 a

Figure 4 b

Figure 4 c

Figure 5 a

Figure 5 b

Figure 6

Figure 7 a

Figure 7 b

Figure 8