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One-Step Fabrication of Ceramic and Carbon Nanotube (CNT) Composites by *In Situ* Growth of CNTs

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A ceramic (SiOC) and carbon nanotube (CNT) composite (SiOC/CNT) is fabricated by a one-step process via the in situ growth of CNTs in a ceramic body during its formation from a polymer precursor (polysiloxane) by pyrolysis. The in situ growth of CNTs is realized by premixing a metal catalyst in the precursor and adding a hydrocarbon (ethanol) at a certain pyrolysis temperature. The CNTs grow inside the pores that are developed in the ceramics at the intermediate stage of pvrolvsis through catalytic cracking of the hydrocarbon by the metal catalyst particles nestling in the pores during ceramic formation. The subsequent pyrolysis at a higher temperature leads to densification of the ceramic dispersed with the in situ-grown CNTs. Microstructural observation reveals a homogeneous growth of crystallized multiple-walled CNTs in nanosize pores formed in the ceramic. The in situ-grown CNTs combine well with the ceramic matrix that forms a strong interface bonding. The in situgrown CNTs increase the electrical conductivity of the ceramics by eight orders of magnitude compared with a CNT-free SiOC ceramic. This in situ growth strategy can be generalized as the fabrication of ceramic-CNT composites with promising mechanical and electrical properties.

I. Introduction

ARBON-FIBER-REINFORCED ceramic composites are lightweight, resistant to high temperature, oxidation, and thermal shock, and have been widely applied as structural materials in high-technology areas. The development of high-performance fiber-ceramic composites has led to the exploration of using carbon nanotubes (CNT), the novel one-dimensional nanomaterial, as reinforcing components because of their high specific areas, superior mechanical and electrical properties, and multifunctional properties.^{1–15} CNT/ceramic composites, such as $CNT/Al_2O_3^{1-8}$ and CNT/MgO_5^{5} have been fabricated along the powder sintering route involving mechanical mixing of CNTs and ceramic powders¹⁶ or compacting of ceramic powders with pregrown CNTs on the ceramic powder surface⁵ followed by high-temperature sintering,² hot press-ing,^{5,8} or sparking-plasma sintering.^{2,4} On the other hand, non-oxide ceramic CNT composites of CNT/SiCN are fabricated by a polymeric precursor pyrolysis process through mixing of the CNTs in a ceramic precursor and pyrolyzing at high temperatures.¹²⁻¹⁴ However, the composites fabricated from these processes have the common problems associated with CNT aggregation in the ceramic matrix,² which affects the reinforcement effect. Moreover, multistages of processing CNTs or

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ceramics are involved in these processes, such as acid purifications,¹⁵ ultrasonic agitations or mechanical stirring,¹⁶ and chemical functionalization,^{13,16} as required to disperse the CNTs in the ceramic powders or precursors.^{2,6,15} These physical, chemical, and mechanical processes, along with the hightemperature sintering, may lead to structural degradation of CNTs^{6,17,18} and/or the contamination of CNTs with impurities.¹⁵ In the physical mixing route, the CNTs form a bridge among the ceramic particles, which impedes the ability to sinter the ceramic to a high density.⁵ These problems become major obstacles that hinder the successful transfer of the mechanical and physical properties of CNTs into the ceramic matrix and have to be overcome for the development of high-performance CNT and ceramic composites.

In the present work, we report a novel, one-step process for the fabrication of a homogeneously dispersed CNT-ceramic composite through the in situ growth of CNTs in a ceramic body during its formation. The in situ growth of CNTs is based on the fact that CNTs can grow in a small pore at nanometer scales and such pores are commonly formed in a ceramic body at an intermediate stage of the ceramic formation during hightemperature sintering or pyrolysis. For the realization of the in situ growth of CNTs in these pores, the only need is a metal catalyst in the pores and the presence of a hydrocarbon source at a pyrolysis temperature in the range of that used for the growth of CNTs. It is known that CNTs can grow in a wide range of temperatures from 700° to 1300° C,^{19,20} and this temperature range falls well within that used for sintering or pyrolysis of a ceramic precursor.^{21,22} It is thus possible to grow CNTs in ceramics in a controlled manner through the choice of suitable growth and sintering (pyrolysis) conditions. This in situ and localized growth of CNTs could ensure the homogeneous dispersion of CNTs in the ceramic matrix with high purity and crystalline quality, as desired for the nanofiber/ceramic composite. Another important advantage of this process is that the ceramic composite, after the growth of CNTs at the intermediate stage of ceramic formation, can be densified in situ into a dense ceramic composite during subsequent sintering or pyrolysis at a higher temperature. This in situ fabrication process is promising for the development of novel CNT and ceramic composites with improved mechanical and functional properties.

Here, we demonstrate the fabrication of CNT and silicon oxycarbide (SiOC) ceramic composites using this *in situ* growth process with polysiloxanes (PSO) as the ceramic precursor. An iron catalyst precursor is premixed with the polysiloxane, and ethanol is introduced as the carbon source at an appropriate temperature during pyrolysis of the polysiloxane for ceramic transformations. Microstructural observations reveal the growth of crystallized multiple-walled CNTs (MWNTs) during pyrolysis. These CNTs grow from the *in situ*-nucleated iron nanoparticles in the nanosize pores that developed in the SiOC ceramic. The *in situ*-grown CNTs are combined well with the ceramic matrix with strong interface bonding. The *in situ* growth of CNTs in the ceramic leads to a remarkable increase in the electrical conductivity, which was eight orders of magnitude higher than that observed without CNTs.

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II. Experimental Procedure

Poly(dimethylhydrosiloxane) (PHMS)(Me-[MeHSiO₂-]_n-Me, Zhejiang Shantai Factory for Organoslianes, Quzhou, China) (4 g, 44.4 wt%), 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcycletetrasiloxane (D₄Vi) ([MeViSiO]₄, Zhejiang Shanmen Co. Ltd. Ningbo, China) (2 g, 22.2 wt%), and polydimethylsiloxane (PDMS) (Me-[Me₂SiO₂-]_n-Me) (3 g, 33.3 wt%) were mixed by mechanical stirring. The platinum-divinyltetramethyldisiloxane complex (Pt[(ViMe₂Si)₂O][ViMe₂SiOSiMe₂OH], [Pt]: 3000 ppm, Shenzhen Platimiun Complexes Co. Ltd., Shenzhen, China) (0.06 g, 1.0 wt%) was added to the polysiloxane mixture as a catalyst (Pt-catalyst). Trichloride ions (FeCl₃) (Kewei, Tianjin, China) in an aqueous solution (1.2 g, 5 wt%) were then added to the mixture and magnetically stirred at 180 r/min for 36 h. The brown liquid precursor mixture obtained was transferred into a Teflon mold and placed in an oven for crosslinking at 60°C for 6 h and at 80°C for 4 h. A disk of crosslinked polysiloxane containing Fe with the dimensions of \emptyset 28 mm \times 2 mm was obtained after demolding from the mold.

The polysiloxane body was placed into an alumina crucible and pyrolyzed in a quartz tube reactor (\emptyset 69 mm × 1800 mm) located in a tube furnace with a heat zone of 400 mm. The quartz tube reactor was purged with an argon flow for 30 min, and, maintaining the argon flow at 300 sccm, the furnace was heated at a heating rate of 5°C/min. As the temperature was increased to 850°C, ethanol was injected via a syringe into the gas flow through a steel nozzle (\emptyset 120 mm × 0.2 mm) at an injection rate of 15 mL/h for 30 min. The temperature was then increased to 1000°C and held constant for 60 min to complete the pyrolysis. Ceramic bodies of CNT/SiOC were obtained after the pyrolysis. To optimize and understand the growth of CNTs, comparable experiments were conducted, including the growth of CNTs at 800° and 900°C, pyrolysis of polysiloxane without FeCl₃, and pyrolysis of Fe containing PSO at 850° and 1000° C without the injection of ethanol.

The CNT/SiOC ceramic body was broken with a hammer and the fractural surfaces of the ceramic pieces were observed by scanning electronic microscopy (SEM) (Hitachi S-4800, Tokyo, Japan) and transmission electron microscopy (TEM) (Tecnai G2 F20, Philip, Eindhoven, the Netherlands). For observation of the inner structure of the ceramic, the fractural surfaces of the ceramic pieces were etched with bases by immersing them into an aqueous solution of NaOH (1 mol/L). Phase analysis was performed by X-ray diffraction (XRD) analysis (D/max 2500v pc, Rigaku, Tokyo, Japan). Thermal gravimetry (TG) coupled with differential scanning calorimetry (DSC) was performed (TGA, Netzsch STA 449C, Waldkraiburg, Germany) using flowing air and a heating rate of 10°C/min. Shrinkage was determined by measuring sample dimensions before and after pyrolysis. The densities of SiOC/CNT were measured using the Archimedes method with water as a medium. Electrical conductivities were measured for a SiOC–CNT specimen (\emptyset 8 × 1.5 mm disk) by the three-pole method using a multimeter (Keithley Instruments Inc., Cleveland, OH) with an Ag paste for the electrodes.

III. Results and Discussion

The CNT/SiOC ceramic body obtained was broken by compression, and the freshly formed fractural surface was observed under SEM. The SEM image reveals the formation of nanofibers in the ceramic body, as shown in Fig. 1(a). The fibers are isolated and perpendicular to the fractural surface, with their ends still buried in the ceramics. The diameter of the nanofibers is around 30 nm and the length exposed from the fracture surface is 50–100 nm. To confirm the growth of CNTs inside the ceramic body, the fractural surfaces of the ceramic pieces were



Fig. 1. Microstructures of the *in situ*-fabricated silicon oxycarbide–carbon nanotube composite observed by scanning electron microscopy (a) a fractural surface, (b) a fractural surface after etching in NaOH for 5 days, (c) a fractural surface after etching for 50 days, and (d) an enlarged field of (c).

etched by immersing them in an aqueous solution of NaOH. After etching for 5 days, more and longer fibers were exposed from the etched surface, as shown in Fig. 1(b), compared with those on the as-fractured surfaces (Fig. 1(a)). The nanofibers were homogeneously distributed on the fractural surface with an interfiber distance of ~120 nm. The number density of the nanofibers was estimated to be ~36/ μ m² and their volume fraction was estimated to be ~2.5 vol% based on the areal density and the fiber diameters. The length of the nanofibers exposed on the etched surface increased with prolonged etching. Longer nanofibers over several micrometers long were observed after etching for 50 days (Figs. 1(c) and (d)). Such micrometer-long fibers should be sufficient for the reinforcement of ceramics as the typical flaw size in ceramics is on the micrometer scale.

TEM reveals that the nanofibers grown in the ceramic are wellcrystallized multiwall CNTs (MWNTs). Figure 2 shows the morphology of the CNTs observed in the SiOC/CNT composite after powdering the ceramic. Although most of the CNTs were covered by the SiOC phase with their inner structure invisible (as shown in Fig. 2(e)), a few clean CNTs could be found in the sample. Figure 2(a) shows a CNT having a clean surface with its end still connected to the SiOC matrix. The enlarged image shows the wellcrystallized side walls of the MWNT (Fig. 2(b)). Figure 2(d) shows another MWNT observed in the sample corresponding to the CNT in Fig. 2(c), showing the clear hollow structure of the MWNT. The interlayer distance of the graphite walls of the MWNTs was measured to be 0.34 nm, equal to the lattice distance of (002) for graphite. The observation of other MWNTs in the ceramic revealed that they have uniform diameters of around 30 nm and lengths of over 200 nm. The number of graphite layers in the side walls of the MWNTs is between 13 and 16.

The in situ-grown CNT/SiOC composite was analyzed by TG coupled with DSC performed in flowing air. The TG-DSC curve is shown in Fig. 3, along with that for a CNT-free SiOC ceramic for comparison. The CNT/SiOC composite shows a major weight loss between 700° and 900°C, similar to that of the SiOC ceramic, but with a larger weight loss above 730°C owing to the oxidation of CNTs in the composite. The oxidation of CNTs in the composite is evident from the emergence of an exothermal peak at 793°C in the DSC curve. This exothermal peak is not observed for the SiOC ceramic in accordance with the absence of CNTs in this sample. The weight loss curve indicates that the CNTs in the composite start to be oxidized at 730°C. This onset of the oxidation temperature is somewhat higher than that between 650° and 710° C for MWNTs grown under free conditions by CVD synthesis.²³ This phenomenon may indicate that the CNTs in the composite resist higher temperatures under oxidation conditions, probably due to being enclosed in the SiOC ceramic. The TGA curves indicate a total weight loss for the composite of 11.9 wt% by 1000°C, and the



Fig. 2. Transmission electron microscopy (TEM) images of carbon nanotubes (CNTs) grown in silicon oxycarbide (SiOC) (a) a typical CNT; (b) enlarged side wall of the CNT in (a); (c) another CNT observed in SiOC/CNTs; (d) enlarged portion of (c) clearly showing the structure of multiple wall CNTs; and (e) CNTs coated with SiOC. The samples for TEM observations are prepared by crushing the SiOC/CNT body and loading it on a Cu grid. Most of the CNTs observed in the samples are similar to those shown in (e), indicating the strong adhesion of SiOC to the multiple walled CNTs surface.



Fig. 3. Thermal gravimetric (TG) analysis and differential scanning calorimetry curves of the *in situ*- fabricated silicon oxycarbide (SiOC)– carbon nanotubes (CNT) composite and a CNT-free SiOC ceramic between 25° and 1000° C in flowing air (30 sccm) using a heating rate of 10° C/min.

weight loss is 2.9 wt% larger than that of the CNT-free SiOC, which is 9.0 wt%. The difference indicates that the fraction of CNTs in the composite is 2.9 wt%, close to that of 2.6 wt% obtained by weighing the bulk ceramics with and without the growth of CNTs. The weight percentage of the CNTs allows an estimation of the volume fraction of CNTs, which is 2.8 vol% using the CNT density (1.3 g/cm³). The volume fraction is close to that of the 2.5 vol% estimated from the areal density of the CNTs in the composite based on TEM observation.

Comparable experiments were conducted, coupled with microstructural observations, to reveal the key control to the

growth of the CNTs in the ceramic. The results indicate that the CNTs grew in the pores of the ceramic through catalytic cracking of the input ethanol by the iron particles nestled in the pores. A SiOC ceramic was pyrolyzed under the same conditions but without the injection of ethanol. SEM observation of the ceramic did not find CNTs in the ceramic but did reveal the formation of pores with sizes between 10 and 30 nm. The pore sizes are slightly smaller than the CNT diameters (25-30 nm) owing to the shrinking of the ceramic free of CNTs. A second comparable experiment was conducted by pyrolysis of the polysiloxane precursor without the addition of FeCl₃ and with the injection of ethanol. In this case, again, no fibrous products were observed in the ceramic. This confirms that the iron catalyst is responsible for the growth of CNTs in the ceramic. The formation of iron particles in the pores and the rooting CNTs are actually observed in the composite by TEM. The iron particles are likely formed in the pores during the organic-to-inorganic transformation of the polysiloxane network before the growth of CNTs. They are formed in the pores during the buildup of the SiOC network as it does not tolerate the interstitial iron particle, driving the iron phase toward the free pore space. This indicates the validity of the design of a catalyst for the growth of CNTs in a ceramic body through the precursor mixing route.

The growth of CNTs in the ceramics was also conducted at other pyrolysis temperatures between 800° and 900° C. The 800° C grown CNTs are less uniform and aggregate locally in the ceramic (Fig. 4(a)) as compared with those grown at 850° C. The nonuniform growth of CNTs at 800° C is probably due to the formation of nonuniform pores that were less developed because of the lower pyrolysis temperature. In contrast, the CNTs grown at 900° C are sparse (Fig. 4(b)), likely due to the closing of most pores resulting from the higher pyrolysis temperature (900° C). It appears that there exists an optimal temperature, 850° C, under the present fabrication condition for the growth of



Fig. 4. Scanning electronic microscopic images of the fractural surfaces of ceramics formed under different conditions. (a) Silicon oxycarbide (SiOC)– carbon nanotubes (CNT) with CNTs grown at $T_G = 800^{\circ}$ C and pyrolyzed at $T_P = 1000^{\circ}$ C, (b) SiOC–CNT $T_G = 900^{\circ}$ C $T_P = 1000^{\circ}$ C, (c) SiOC–CNT $T_G = 850^{\circ}$ C and (d) SiOC $T_P = 850^{\circ}$ C.

CNTs in the ceramic to match the pore development in the ceramic. Under the optimal growth conditions, the growth of CNTs in the ceramic pore is quite efficient, as the area density $(36/\mu m^2)$ of the CNTs is close to that of the pore area density, which is $\sim 48/\mu m^2$, estimated from a ceramic pyrolyzed at 850°C without the injection of ethanol (Fig. 4(d)). These data indicate that nearly 80% of the pores were grown with CNTs.

The present one-step fabrication of bulk ceramic/CNT composites during ceramic formation is different from the previously reported *in situ* growth of CNTs in the fabrication of CNT/ceramic composites involving the growth of CNTs over a ceramic powder and sintering.^{7,8,18} It is also different from the process of growing CNTs in a porous ceramic^{3,24,25} that involves the creation of a porous ceramic, preloading catalysts in the pores, and growing CNTs inside the pores with the derived "ceramic composite," usually a porous and/or a thin sample.

The present process not only allows the direct growth of CNTs in the ceramic but also allows the formation of ceramic and CNT composites in a dense bulk body through the simple *in situ* pyrolysis at higher temperatures that leads to the further densification of the ceramic with the grown-in CNTs. The direct growth of CNTs in ceramics is important considering that residual pores are often left in ceramics after powder sintering or pyrolysis process, and these are the major flaws affecting ceramic properties. The *in situ*-grown CNTs fill these pores and eliminate these flaws by replacing them with a reinforcing phase of CNTs.

Density measurements show that the SiOC/CNT composites have a bulk density of 1.98 g/cm³, which is higher than that of SiOC monolithic (1.88 g/cm³) formed at 1000°C under the same fabrication conditions. A similar density increase was observed for the ceramics obtained at 800°C, from 1.59 g/cm³ for SiOC to 1.67 g/cm³ for the SiOC/CNT composite. The density contribution from the *in situ*-grown CNTs is estimated to be 0.06 g/cm^3 based on the volume fraction of CNTs in the composite (2.8%).

The ceramics were pyrolyzed at a higher temperature after the growth of CNTs at 850°C, and the subsequent pyrolysis stage led to further shrinking of the ceramics with the embedded CNTs in the ceramic body. This shrinkage could produce an axial compression force in the in situ-grown CNTs, favoring the interface bonding between the CNT and the ceramic matrix. Dimensional measurements show that the ceramic shrank linearly from 24.16% at 850°C to 26.83% at 1000°C, an increase of 2.67%. When the ceramics were cooled down immediately to room temperature after the growth of CNTs, without the final stage of pyrolysis, thicker CNTs with diameters between 30 and 100 nm were observed in the ceramic (Fig. 4(c)). The CNTs appeared to have a thin wall with a larger hollow center, and some appear to be compressed during cooling, thus becoming flattened. In contrast, the CNTs are dense and combined well with the SiOC matrix after pyrolysis at 1000°C.

The *in situ*-fabricated SiOC–CNT composite shows characteristics of strong interface bonding between the CNTs and SiOC. Figure 5(a) shows a crack generated on a piece of CNT/ SiOC ceramic created by breaking the ceramic using a sharp metal. Many CNTs bridge the cracks, with some CNTs breaking in the middle (Figs. 5(b) and (c)). Large irregular cavities (30–80 nm) can be observed on the fractural surface, resulting from the pulling out of the CNTs from the SiOC matrix (arrowed in Fig. 5(b)). Figure 5(d) shows a broken CNT observed at another location in the crack. Clear hollows of the CNT are exposed from the two breaking ends of the CNT, further confirming the hollow CNT structure. Despite the breakage, the two separated parts of the CNT are still firmly buried in the ceramic matrix without furling at the interface.



Fig.5. Scanning electronic microscopic images of cracks (a–c) formed on a piece of ceramic during mechanical processing (polishing) and a fracture surface resulting from compression-induced damage (d, e). The samples came from the same piece of a silicon oxycarbide (SiOC)–carbon nanotubes (CNT) ceramic formed under the typical growth and pyrolysis conditions. (a) The crack is caused during mechanical polishing of a piece of ceramic (b) and (c) are local enlargements of (a), and (d) shows the pulled out CNTs on a fractural surface.

(a)





Fig. 6. Scanning electronic microscopic images of fractural surfaces of heavily broken carbon nanotubes/silicon oxycarbide pieces created by pressing a ceramic with a metal corner. (a) Counterparts of two broken pieces. (b) An enlarged region in (a). (c) Another enlarged region in (a).

Figure 6 shows two counterpart fractural surfaces created by heavily pressing a CNT/SiOC ceramic with a corner of a metal. The ceramic partly fragmented predominantly on the surface regions. In the bulk fractural region, a few CNTs were exposed on the fractural surface. The CNTs exposed are heavily covered with a layer of SiOC and bonded with SiOC particles. The SiOC cover can be confirmed by the TEM image, as shown in Fig. 2(e), which should represent the morphology of the CNT after debonding from SiOC, as the sample was prepared for TEM observation by powdering. The root region of the fiber shows a strong combination of the fiber and the SiOC matrix. A broken end of the CNT on the left-hand side in Fig. 6(b) shows that the CNT breaks evenly in the middle without interwall furling. Cavities created by the pulling out of fibers can be observed on the upper fractural surface (hollow arrows). The right cavity appears to be caused by pulling out from the fiber bonded to the fractural surface of the lower part (dense arrow). The enlarged image of the cavity in Fig. 6(c) shows that collapsed particles filled in the cavity. This may indicate damage to the SiOC matrix surrounding the fiber while it was being pulled out.

The strong interface bonding in our in situ fabricated CNT and ceramic composite differs from the pulling out phenomena observed in other MWNTs and ceramic composites, such as MWNT/SiCN fabricated from the precursor mixing route.¹⁴ Kothari et al.²⁶ have recently observed interwall sliding of MWNTs from pulling out in MWNT and amorphous silicon nitride films fabricated by vapor-phase infiltration of MWNT arrays. The breaking end and the pulling out characteristic of CNTs in our composite does not show this breaking characteristic, owing to the strong interface bonding between the two phases. Moreover, the compressive force produced on the CNT due to SiOC matrix shrinkage during the final stage of pyrolysis may resist interwall sliding in the MWNT because the graphite interwall bonding increases remarkably for MWNTs under compression.²⁷ Padture²⁸ has recently observed CNTs anchored in Al₂O₃ grains at the grain boundaries, forming a strong bond against furling among the two phases, and revealed a promising

reinforcement mechanism for CNT/ceramic composites. The strong interface bonding and the resistance against interwall sliding of our in situ fabricated ceramic composites, in combination with the high strength of CNTs with nanoscale diameters,^{29,30} have distinct advantages in phase combinations with potential reinforcement effects in ceramics.

SiOC ceramics resist high temperatures and oxidation, and they are also electrically conductive, making them promising for use as electrical thermal sensors.³¹ Our *in situ*-grown CNTs in SiOC composites with a good interface bonding increase the electrical conductivity of the ceramic remarkably. The electrical conductivity of the SiOC-CNT composite obtained by pyrolysis at 1000°C is 18.5 S/m, which is eight orders of magnitude higher than that for the CNT-free SiOC ceramic, for which the conductivity is below 10^{-7} S/m. Moreover, the electrical conductivity of the 850°C pyrolyzed SiOC-CNT composite was also measured and was 4.3×10^{-2} S/m. The electrical conductivity is also much higher than that of the SiOC monolithic, although it is two orders of magnitude lower than that of the 1000°C pyrolyzed composite. The higher electrical conductivity for the 1000°C produced SiOC/CNT composite can be attributed to a tighter contact of the CNTs and the SiOC ceramic matrix, as is known from the larger shrinkage of the ceramics after pyrolysis at the higher pyrolysis temperature. Therefore, the in situ growth of CNTs could effectively transform an electrically less conductive ceramic into a highly conductive ceramic with a tailored electrical conductivity controllable by pyrolysis.

In summary, the present work demonstrates the possibility for one-step fabrication of bulk CNT and ceramic composites via the in situ growth of CNTs in the ceramic body during ceramic formation. These in situ fabricated CNT and ceramic composites show excellent interface bonding, which may help improve the mechanical properties of the ceramics. Moreover, the in situ- grown CNTs significantly increase the electrical conductivity of the ceramics. Although this process is demonstrated for the fabrication of the SiOC-CNT composite via polymer pyrolysis, it can be extended to other ceramic systems. Moreover, the process can be extended to the fabrication of ceramic composites in the powder sintering process and to the infiltration process for making carbon fiber ceramic composites.

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