

Carbon Nanotube Reinforced Ceramic Composites and their Performance

Joseph A. Arsecularatne and Liangchi C. Zhang*

Centre for Advanced Materials Technology, The University of Sydney, Sydney NSW 2006, Australia

Received: April 5, 2007; Accepted: May 2, 2007; Revised: May 9, 2007

Abstract: Carbon nanotubes are considered as excellent reinforcements for improving the properties of ceramic composites. This paper reviews the reported techniques for the preparation of various ceramic coated CNTs, CNT-ceramic composites, CNT-ceramic composite coatings, etc. It is noted that a wide range of techniques have been used to fabricate these composites. Their characterisation has revealed that considerable improvements in electrical/thermal properties can be achieved, but only a few studies have demonstrated significant improvements in macro-scale mechanical properties of ceramics such as fracture toughness.

Keywords: Carbon nanotube, ceramic composite, ceramic reinforced CNT, nano-composite.

INTRODUCTION

Carbon nanotubes (CNTs) possess extremely high stiffness/strength, high electrical and thermal conductivities and favourable frictional properties. Their incorporation into ceramic/polymer/metal matrices, in analogy to composites with micron scale fibre additions, is expected to greatly enhance the mechanical, electrical, thermal and frictional properties of the composite. This has stimulated considerable research aimed at fabricating these composites during the past 15 years or so. Moreover, with continuously decreasing cost of CNTs as a result of the ability to synthesise in high yield by several techniques, the efforts to incorporate them in the above matrices is likely to accelerate. So far, the efforts to fabricate these composites have been met with challenges due to: uniformly dispersing the nanotubes (which have a tendency to agglomerate because of the strong van der Waals forces among CNTs); achieving the appropriate nanotube-matrix interfacial properties; composite consolidation without CNT degradation. Nevertheless continued attempts are being made to prepare CNT-based composites having matrices made of ceramic, polymer, metal and their combinations. The present paper will mainly review recent patents and relevant papers on ceramic matrix CNT composites and will not consider those on polymer/metal matrix composites. An up-to-date review of the polymer-based composites has been given by Mylvaganam and Zhang [1].

The structure of the present paper is as follows. It reviews the fabrication and characterization of reported ceramic coated/reinforced CNTs, CNT-ceramic composites, CNT-ceramic-metal composites, CNT-glass-ceramic composites, CNT-ceramic-polymer composites and CNT-ceramic composite coatings. Finally, applications of these composites and current and future directions will be discussed.

CERAMIC COATED/REINFORCED CNTS

These include CNTs with ceramic coating or ceramic particles with multiple CNTs bonded to particle's surface. Their fabrication followed by characterisation is now discussed.

Fabrication

Compared to pure CNTs (Fig. 1a), reinforced CNTs by formation of high hardness/strength boron carbide nanolumps (nano-particles of diameter 10-200 nm and irregular in shape) on the CNT walls (Fig. 1b) are considered to be superior reinforcing fillers for incorporation within a matrix material. This is due to modification of CNT morphology by the nanolumps which increase

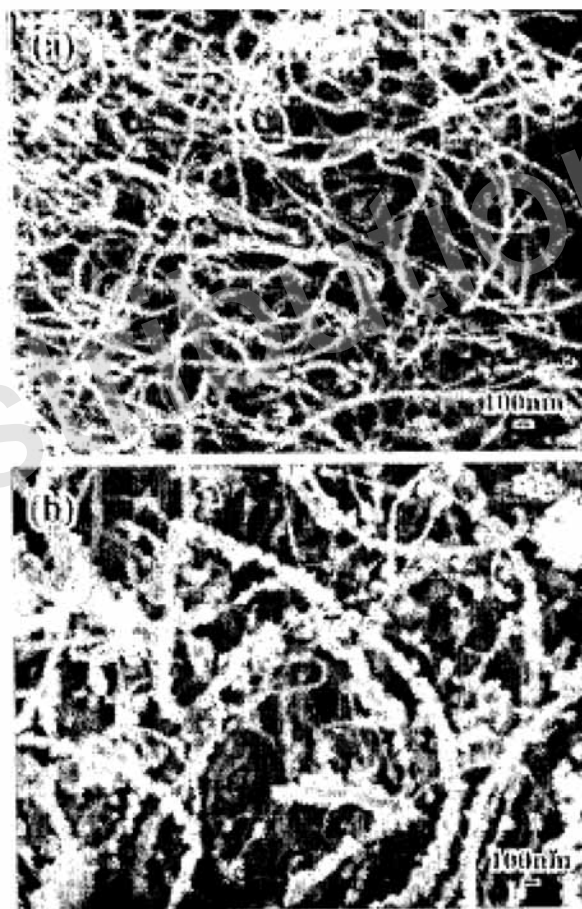


Fig. (1). (a) Purified CNTs; (b) Reinforced CNTs [2].

the load transfer efficiency between CNTs and matrix material. A method of reinforcing MWNTs by *in-situ* formation of these nanolumps was patented by Ren *et al.* [2]. They used the solid state reaction between a boron source material (e.g. magnesium diboride, MgB_2) and pre-formed CNTs. Their procedure for fabrication of reinforced CNTs was as follows: purified CNTs were first mixed with boron source powder (MgB_2). The mixture was wrapped with transition metal foil and heated in a ceramic tube furnace under vacuum to a temperature in the range 1000-1250°C. The enhanced chemical reactivity of thermally decomposed boron caused formation of boron carbide nanolumps on CNTs. A similar procedure was used to obtain reinforced CNTs with boron/magnesium oxide nano-lumps.

*Address correspondence to this author at the Centre for Advanced Materials Technology, The University of Sydney, Sydney NSW 2006, Australia; Tel: +61 2 9351 2835; Fax: +61 2 9351 7060; E-mail: zhang@aeomech.usyd.edu.au

A technique that achieved the opposite result of that obtained by Ren *et al.* [2] discussed above was patented by Chiang and Vander Sande [3]. In this technique, metal carbide, e.g., SiC, micro-particles were partially converted to CNTs by thermochemical treatment resulting in composite particles with SiC core onto which a surface layer of CNTs were grown. One end of CNTs was bonded to the SiC core. One of their methods for nucleation and growth of CNTs involved direct volatilization of Si as a vapour via the reaction $\text{SiC}_{(s)} \rightarrow \text{Si}_{(g)} + \text{C}_{(s)}$. The fraction of the composite particle that is SiC/CNT was controlled by the heat treatment atmosphere, time and temperature. With this method, it is also possible to fully convert SiC powder to obtain densely packed CNTs. Alternatively, the composite particles could be fabricated by an external source of carbon on SiC particles.

In order to disperse CNTs and bind them with nanosized α -alumina grains, Sun *et al.* [4] used the colloidal processing technique (also called heterogeneous coagulation reaction). In this method, the surface (electrostatic) properties of CNTs were adjusted by treating them in ammonia followed by dispersing in polyethyleneimine (PEI). The properties of alumina were adjusted by dispersing in poly acrylic acid (PAA). In order to separate possible agglomerates, both CNT/PEI and alumina/PAA suspensions were ultrasonicated separately before adding alumina/PAA dropwise into CNT/PEI. This process resulted in alumina coated CNTs due to presence of opposite electrostatic charges on CNTs and alumina. In subsequent work, similar procedures were used to coat CNTs with titania (TiO_2), zirconia (ZrO_2) and 3Y-TZP¹ nanoparticles [5-8]. Additionally, hydrolysis of TiCl_4 was used for coating SWNTs with TiO_2 nanoparticles [6].

A chemical route was used by Gomathi *et al.* [9] to bond TiO_2 onto the surface of MWNTs/SWNTs and obtain ceramic coated CNTs. In this method, acid treated CNTs (functionalised with surface hydroxyl and carboxyl groups) were made to react with TiCl_4 vapour which was followed by hydrolysis. This resulted in the formation of hydroxide layer on CNTs which reacted again with TiCl_4 . By repeating the process several times, followed by calcination, CNTs with chemically bonded TiO_2 coating were obtained.

Morisada *et al.* [10] prepared β -SiC coated MWNTs using SiO vapour at temperatures 1250-1550°C under vacuum. The coated layer was formed by deposition of SiC particles only when a carbon source existed by the reaction between SiO and CO gases. However, the surface of MWNTs was converted to SiC forming SiC nanorods when no carbon source existed.

Characterisation

Ren *et al.* [2] who disclosed the preparation of boron carbide reinforced CNTs characterized them by scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and fast-Fourier transformation (FFT). These analyses confirmed the formation of boron carbide nanolumps on CNTs and that the reaction between boron and CNTs was confined and the structure of CNTs preserved. The boron carbide had the general formula B_xC_y where x ranged from 4-50 and y ranged from 1-4. The spacing between B_xC_y nanolumps on CNTs was in the range 50-100 nm. The HRTEM images showed that these nanolumps were crystalline and the interface between CNT and nanolumps was sharp without amorphous layer. The CNT-SiC composite particles fabricated by Chiang and Vander Sande [3] by thermochemical treatment were characterized by X-ray diffraction (XRD), SEM and HRTEM. These confirmed the presence of CNTs on the surface of SiC particles.

Sun *et al.* [4], who used the colloidal processing technique, characterized the pristine, treated and coated CNTs and α -alumina (with/without PAA) by zeta potential measurements and by TEM. The surface charge characterization showed that, NH_3 treated CNTs had positive surface charge (hence positive zeta potential value) over a wide pH range. Addition of PEI further increased the zeta potential value. On the other hand, addition of PAA into alumina resulted in a negative surface charge over a wide pH range. Dropwise addition of alumina/PAA into CNT/PEI was found to change the zeta potential of the latter from positive to negative indicating the adsorption of alumina on to CNT surface. The TEM analyses confirmed this adsorption. Similar characterization was also carried out for CNTs coated with titania and zirconia nanoparticles [5,6,8]

The TEM analyses of TiO_2 coated MWNTs by Gomathi *et al.* [9] revealed that the coating thickness, obtained after 10 cycles, was 8-10 nm. The amorphous nature of the coating was revealed by XRD. Similar analyses of SiO vapour treated MWNTs by Morisada *et al.* [10] confirmed the β -SiC coating of CNTs in the presence of carbon source and CNTs conversion to SiC nanorods in the absence of carbon source. This was further supported by the SEM micrographs which showed different morphologies of treated CNTs with/without carbon source. The coated CNTs were found to have markedly improved oxidation resistance: ~90% survived after heating at 650°C for 60 minutes. As received MWNTs were, however, oxidized completely within 5 minutes.

CNT-CERAMIC COMPOSITES

Unlike the ceramic coated/reinforced CNTs discussed above, fabrication of CNT-ceramic composites involves the composite powder preparation followed by consolidation for improved electrical/mechanical/thermal properties. The reported composites have mainly been fabricated using pre-formed SWNTs or MWNTs. Considerable attempts have been made to disperse CNTs in the matrix. Some attempts for improving the CNT-ceramic interface adhesion are also reported. Ceramic powders used include alumina, silicon carbide/nitride ($\text{SiC}/\text{Si}_3\text{N}_4$), etc. Most of the investigators have used nano-crystalline ceramic powders (particle size 20-300 nm) since these are considered to be more compatible with CNTs. Composite consolidation has been achieved using high pressure and high temperature processing techniques. Some studies reported achieving near theoretical density of these composites. Their characterization is based on the microstructure and electrical/mechanical/thermal properties.

Fabrication

Fabrication of high quality CNT-ceramic composites requires uniform dispersion of CNTs in ceramic powders. Dry ball milling of as received CNTs and ceramic powders have been attempted and (0-5 wt%) MWNT boron carbide composites were fabricated by hot pressing² [11]. Their density, hardness, Young's modulus and flexural strength decreased with the increase in CNT content. SEM examination revealed the presence of CNTs in the composite as agglomerates as large as 100 μm , clearly indicating the insufficient degree of dispersion by this technique resulting in inferior mechanical properties. In order to avoid these issues, a commonly used CNT dispersed ceramic powder preparation method is as follows. CNTs are dispersed in a low viscosity, inert, liquid such as ethanol using ultrasonic shaker. Ceramic powder slurry that includes main ceramic component, sintering aids, etc, is also separately prepared by ultrasonication in ethanol. Dispersants (e.g., Seruna E503 [12]) may be used to improve the dispersion of CNTs and ceramic powders. The CNT and ceramic powder slurries are then combined and ball milled in a ceramic vessel using ceramic milling media to uniformly disperse CNTs with ceramic powders.

¹ 3Y-TZP: 3 mol% yttria-stabilized tetragonal polycrystalline zirconia

² Hot pressing (HP) involves simultaneous application of uni-axial pressure and heat.

The mixture is dried at temperature $\sim 100^\circ\text{C}$ and broken up, e.g., by mortar and pestle. The dry or wet (before ball milling) CNT-ceramic powder mixture is sometimes passed through 200-400 mesh sieve to separate possible agglomerates and further improve CNT dispersion. This type of procedure has been used by Ma *et al.* [13] for preparing MWNT-SiC powders and by Chang *et al.* [14] and Siegel *et al.* [15] for MWNT-alumina powders which were subsequently consolidated by HP. Zhan *et al.* [16-23] and Wang *et al.* [24] consolidated their SWNT-alumina/3Y-TZP powders by spark-plasma sintering (SPS)³ because of the considerably shorter processing times possible with this technique, for example, 5 minutes or less compared to one hour or more with HP. SPS was also used by Shi *et al.* [25] to fabricate a range of 3Y-TZP composites containing 0-10 wt% MWNTs. Balazsi *et al.* [26] used hot isostatic pressing (HIP)⁴ to fabricate MWNT-Si₃N₄ composites, while Tatami *et al.* [12] used HP and cold isostatic pressing (CIP)⁵ followed by gas pressure sintering (GPS)⁶. Some of their CIP/GPS samples were further densified by HIP. HIP normally requires preparation of a green body which can be compacted by adding a binder (e.g. wax) and lubricant to the CNT-powder mixture [12].

The alumina coated CNTs obtained by the colloidal processing method discussed in the previous section were used by Sun *et al.* [4] to fabricate a 0.1 wt.% CNT alumina composite. The alumina coated CNTs were added into an alumina/ethanol mixture which was subsequently milled, dried and ground to obtain the required CNT-alumina composite powder. It was then consolidated using SPS. Pure alumina compacts were also fabricated under same conditions for comparison. In later work [7], a similar procedure was used for preparing 3Y-TZP matrix composites containing 0.1-1.0 wt% MWNTs or SWNTs. Poyato *et al.* [27] also used the colloidal processing route to fabricate a 10 vol% (acid treated) SWNT-alumina composite by SPS. For comparison, a composite in which SWNTs and alumina were dispersed in a conventional way, i.e., by ultrasonic agitation and ball milling was also consolidated.

A novel approach to fabricate barium titanate (BaTiO₃) composites containing MWNTs was adopted by Huang and Gao [28,29] and Huang *et al.* [30,31]. They first immobilised nanosized (rutile) TiO₂ on acid treated MWNTs. It was then transformed to BaTiO₃-MWNT hybrid material by a hydrothermal process. This as synthesised BaTiO₃-MWNT was dispersed in nano-sized tetragonal phase BaTiO₃ powders by wet ball milling. The mixture was dried, ground and sieved to obtain the composite powders which were subsequently consolidated by HP and by SPS.

Compared to conventional ceramics prepared by sintering powders, polymer derived ceramics (PDCs) are synthesised by direct thermal decomposition of polymeric precursors. This chemical-to-ceramic route is suited to CNT-ceramic composites since CNT dispersion can be achieved with relative ease in liquid phase precursors just before pyrolysis. An *et al.* [32] adopted this route for preparing CNT reinforced ceramic (SiCN) composites containing 0, 1.3 and 6.4 vol% MWNTs using the following procedure. As received MWNTs were treated with HNO₃ (for removing catalyst particles and free carbon) and aniline (to assist their dispersion in polymer) before mixing with liquid phase precursor polyurea(methylvinyl)silazane by sonication and magnetic stirring to form a CNT containing suspension. It was then converted to dense CNT-ceramic composite by pressure assisted pyrolysis. Berger *et al.* [33] also adopted this PDC route and

fabricated a SiCO ceramic by pyrolysis of nickel acetate doped poly(methylphenylsilsesquioxane) in argon atmosphere between 800-1500°C. During the polymer-to-ceramic conversion, MWNTs were formed *in-situ* in the pores of the ceramic matrix. Nickel silicide nanoparticles acted as nuclei for the CNT growth and the number of CNTs formed increased with the increasing pyrolysis temperature.

The melt infiltration reaction bonding technique was adopted by Thostenson *et al.* [34] and Karandikar [35] to fabricate MWNT-SiC composites. The process involved fabrication of a preform made of dispersed MWNTs and a carbon source (e.g. pyrolyzed organic polymer). The preform was placed in contact with silicon (or its alloys) and heated above the melting point (1400°C). The molten silicon that infiltrates the preform and hence carbon reacts rapidly to form β -SiC *in situ*. The excessive exothermic reaction and volumetric change (due to formation of SiC) is controlled by using SiC as filler in the preform.

A low temperature microwave synthesis technique was used by Mitra and Iqbal [36] and Wang *et al.* [37] for the fabrication of a SWNT-SiC composite. The procedure involved preparation of a solution made of nitric acid treated SWNTs (free carbon and metal catalyst removed and CNTs functionalized by generating -COOH groups) and chloro-trimethylsilane which was subjected to microwave induced reaction for 10 min. This resulted in the decomposition of chloro-trimethylsilane and the simultaneous nucleation of nano-sized SiC particles on SWNT bundles. The bulk composite was a branched tree-like structure made of three-dimensionally arrayed SWNT-SiC.

Fabrication of electrically conducting nanocomposite materials comprising 10-25 vol% CNTs and 75-90 vol% biocompatible ceramic (alumina, titania or hydroxyapatite) for biomedical applications (e.g., to improve cytocompatibility) was patented by Supronowicz *et al.* [38]. However, the patent only gives details of the composites made of CNTs and biocompatible polymers.

Characterisation

With SiC-MWNT composites fabricated by HP, Ma *et al.* [13] achieved relative densities⁷ $\sim 95\%$ and $\sim 98\%$ for consolidating temperatures 2000°C and 2200°C, respectively. Their XRD analyses of hot-pressed pure MWNT specimens and composite showed that MWNT did not change to other types of materials. SiC-MWNT composite specimens were used for room temperature three point bending strength and fracture toughness tests made using specimens with precracks. These showed $\sim 10\%$ increase in bending strength and fracture toughness over monolithic SiC compacts. In spite of the higher density of the composite pressed at 2200°C, its mechanical properties were inferior due to the conversion of β -SiC to α -SiC at temperatures above 2100°C. Their SEM analyses showed partially embedded MWNTs in ceramic matrix indicating their survival of the high temperature/pressure processing (Fig. 2) and, crack deflection and debonding of CNTs near the crack tip revealing possible mechanisms for improved bending strength and fracture toughness.

Chang *et al.* [14] and Siegel *et al.* [15] who disclosed the preparation of alumina-MWNT also confirmed the stability of MWNTs during HP by XRD. No new phases due to the interaction between alumina and MWNTs were found. The relative densities of the composites were above 97%. The Vickers hardness results showed a decrease in hardness with the increase in MWNT content (Fig. 3): 18.3 GPa for ceramic with 0% MWNTs which decreased

³ In SPS a pulsed dc current directly passes through the graphite die and, if conductive, the powder compact. Since the heat is generated internally, very high heating/cooling rates and hence rapid sintering are achieved.

⁴ Hot isostatic pressing involves simultaneous application of isostatic pressure (that is, uniform pressure in all three directions) and heat.

⁵ Cold isostatic pressing (CIP) involves the application of isostatic pressure without heat.

⁶ Gas pressure sintering (GPS) is a high temperature process (typically above 1500°C) performed in an atmosphere of nitrogen gas (or other inactive gas or a gas mixture) at pressure in the range 2-100 atm.

⁷ Relative density is determined from the relation: relative density = $100 \times$ measured density/theoretical density. The density of the composite is measured by Archimedes method. The theoretical density of the composite, d_{th} is determined from the relation $d_{th} = fd_{CNT} + d_{SiC}(1-f)$, where f , d_{CNT} and d_{SiC} are volume fraction of CNTs and densities of CNTs and SiC, respectively.

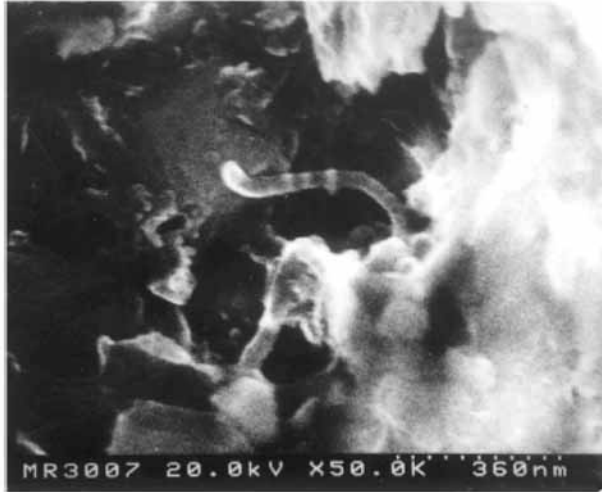


Fig. (2). SEM micrograph of CNTs in the composite after HP at 2000°C [13].

down to 13.6 GPa for the composite with 20 vol% MWNTs. The fracture toughness (estimated using non-standard indentation crack length method) for the 10 vol% MWNT composite showed a 24% increase compared to the alumina compact.

Zhan *et al.* [16-21] who disclosed the preparation of alumina-SWNT composites (with 0, 5.7, 10 and 15 vol% SWNTs) using SPS found that only the composites sintered at temperatures 1150 and 1200°C for 3 minutes reached relative density over 98%. The Vickers micro-hardness of these composites did not improve over pure alumina counterparts (Fig. 3). However, the fracture toughness of the composites (determined from indentation crack length method) with 5.7 and 10 vol% SWNTs showed 2-3 times higher values [16,17]. Their electrical conductivity, measured using a four point probe technique showed values in the range 1050-3345 S/m (for pure alumina and composite with 5.7% carbon black, conductivities were 10^{-12} and 15 S/m respectively). Moreover, electrical conductivity increased with SWNT content [18,19], as depicted in Fig. 4. Improvements in electrical properties were also reported by Shi *et al.* [25] with their MWNT/3Y-TZP composites which showed a dramatic increase in electrical conductivity for CNT contents between 1 and 2% (Fig. 4). The improvements in these electrical and mechanical properties were attributed to the percolation⁸ of CNTs and crack deflection along the interface between CNTs and alumina matrix grains, respectively. Zhan *et al.* [16-21] considered the above improvements to result from: extraordinary properties and near perfect structure of SWNTs; undamaged SWNTs strongly entangling the alumina matrix grains in dense composites; use of SPS that allowed lower sintering temperatures and short durations resulting in undamaged SWNTs in the composite.

Zhan *et al.* [20,21] measured the thermal conductivity/diffusivity of the SWNT-alumina composites (by Xenon flash thermal diffusivity system) in two directions: along the uniaxial compression axis and perpendicular to it. In the latter direction, the thermal characteristic showed no significant change whether the sample contained SWNTs or not. However, in the compression axis direction, it significantly decreased when CNTs were present, with a higher CNT content producing a greater drop in thermal conductivity/diffusivity. For the composite containing 15 vol% SWNTs, this drop was three fourth of that of pure alumina compact.

⁸ Formation of a large number of electrical pathways.

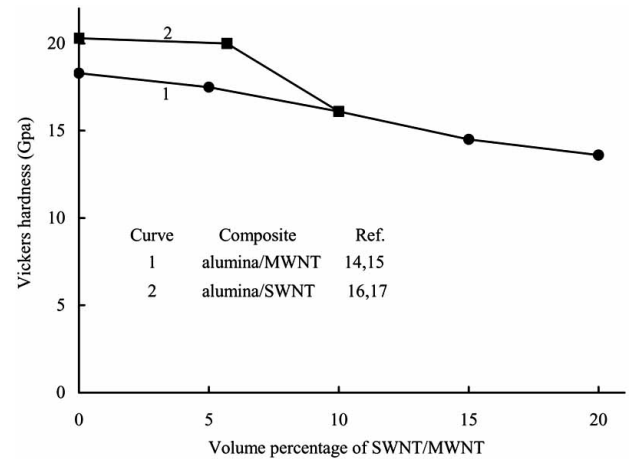


Fig. (3). Variation of Vickers hardness with vol% SWNT/MWNT for composites reported in [14-17].

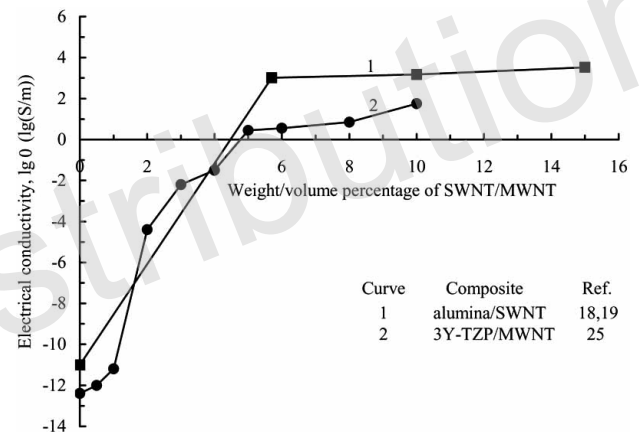


Fig. (4). Variation of electrical conductivity ($\log(\sigma)$) with vol/wt% SWNT/MWNT for composites reported in [18,19,25].

Additionally, an investigation of the thermoelectric properties of 10 vol% (unpurified) SWNT/ Al_2O_3 , 10 vol% SWNT/3Y-TZP and 10 vol% SWNT/20 vol% 3y-TZP/ Al_2O_3 composites [22,23] showed that, their thermoelectric power (Seebeck coefficient) increased with increasing temperature having a *p*-type value of 50.4 $\mu\text{V/K}$ at 644 K which is comparable to that of pure SWNTs. The 10 vol% SWNT/3Y-TZP composite had a figure of merit, ZT ⁹ of ~ 0.02 ¹⁰ at 850 K, indicating potential for use as a thermoelectric material, e.g., in devices that convert thermal energy to electrical energy.

Wang *et al.* [24] also prepared an alumina-SWNT composite (with 10 vol% SWNTs), similar to that reported by Zhan *et al.* [16,21] and tested it for fracture toughness using the more reliable single edge V-notched beam (SEVNB) method. These test results showed no improvement in fracture toughness of alumina-SWNT composite over pure alumina compact or an alumina composite with 10 vol% graphite. Their Vickers indentation tests on alumina-SWNT and alumina-graphite composites showed little evidence of

⁹ Here $Z = S^2 / \alpha K$ where S is thermoelectric power or Seebeck coefficient, σ and K are electrical and thermal conductivities, respectively, and T is the absolute temperature. A high efficiency thermoelectric generator requires a conducting medium that has high Z value and large temperature differential [23].

¹⁰ This value is two orders of magnitude higher than that of pure SWNTs.

cracking which demonstrated that indentation method is not suitable for measuring fracture toughness of these composites. Based on these results, Wang *et al.* [24] argued that the SWNT-alumina composites are not tough but resistant to contact/indentation damage which appeared to be related to the presence of shear deformable SWNTs or graphite in the composite.

The MWNT-Si₃N₄ composite prepared by Balazsi *et al.* [26] by HIP using sintering aids Al₂O₃ and Y₂O₃ showed 15-37% improvement in the bending strength and elastic modulus (measured by three/four point bending tests) compared to other samples that contained graphite or carbon black/fibre, instead of CNTs. However, the composite without any carbon additions showed even better mechanical properties, attributed to its improved densification. Increasing the pressure and sintering time resulted in the disappearance of CNTs from composite structure which was confirmed by prompt-gamma-activation analysis (PGAA). The MWNT-Si₃N₄ composite consolidated by Tatami *et al.* [12] and contained sintering aids Al₂O₃, Y₂O₃, TiO₂ and AlN, had relative density >92% in the sample with 1.8 wt% CNTs. The density decreased slightly with increase in CNT content due to inhibition of densification by CNTs. The composites contained sintering aids only Al₂O₃ and Y₂O₃ had lower density and CNTs disappeared. A higher electrical conductivity, up to 30 S/m was noted for the composites consolidated with GPS and, GPS and HIP. This was attributed to the formation of (electrically conductive) SiC which was confirmed by XRD analysis. Greater densification was achieved with the composite consolidated by HP and contained sintering aids Al₂O₃, Y₂O₃, TiO₂ and AlN, though relative density slightly decreased with increasing CNT content. No SiC was detected in these samples by XRD. However, they showed even higher electrical conductivity, e.g., 79 S/m for the sample with 1.8 wt% CNTs, presumably due to percolation of CNTs. The composites' hardness, bending strength (measured by three-point bending tests), and fracture toughness (measured by the surface crack in failure technique) were found to be similar to those of the corresponding ceramic without CNTs.

The CNT-alumina composite prepared by colloidal processing and SPS by Sun *et al.* [4] showed only marginal improvement in hardness (~4%) compared to pure alumina compacts. The fracture toughness of the composite, also measured by Vickers indentations showed a 31% improvement. However, their subsequent CNT/3Y-TZP composites did not show any improvement in hardness or fracture toughness, though densities over 99% were reported [7]. In fact, hardness of the composite decreased with increase in the CNT content which was 27% for the composite with 1 wt% MWNTs. The fracture toughness did not show any significant change for composites with CNTs up to 0.5%. However, the fracture toughness decreased by 15% for the composite with 1 wt% MWNTs. These inferior mechanical properties were attributed to the lack of reinforcement due to poor CNT-ceramic bonding which was supported by their SEM micrographs. A striking revelation of their work was that, the mechanical properties (hardness and fracture toughness) of the two composites which were consolidated under identical conditions, one with 0.5 wt% SWNTs and the other with 0.5 wt% MWNTs, did not show any significant variation.

Interestingly, the Raman analyses on alumina composites prepared with AR-SWNTs¹¹ and colloidal AT-SWNTs¹² by Poyato *et al.* [27] indicated the selective destruction of small diameter metallic AR-SWNTs and any metallic¹³ AT-SWNTs during the SPS process. Thus only semiconducting SWNTs were found in the AT-SWNT/alumina composite. These analyses also revealed the formation of disordered graphite and defects in AR/AT-SWNTs

during SPS. Their SEM/TEM analyses revealed more uniform dispersion of SWNTs in the colloidal AT-SWNT/alumina composite (Fig. 5a) compared to the conventional AR-SWNT/alumina composite where clustered SWNT bundles were observed (Fig. 5b). The HRTEM images of the colloidal AT-SWNT/alumina composite confirmed the presence of SWNTs in the intergranular regions together with disordered graphite, carbon nano-onion like structures (3-7 nm diameter) and diamond nano-crystals (~5 nm diameter). It was argued that the SPS process was responsible for the formation of these non-SWNT carbon structures as well as the selective destruction of metallic SWNTs which may, however, allow control of the composite's microstructure for tailored mechanical, electrical and thermal properties.

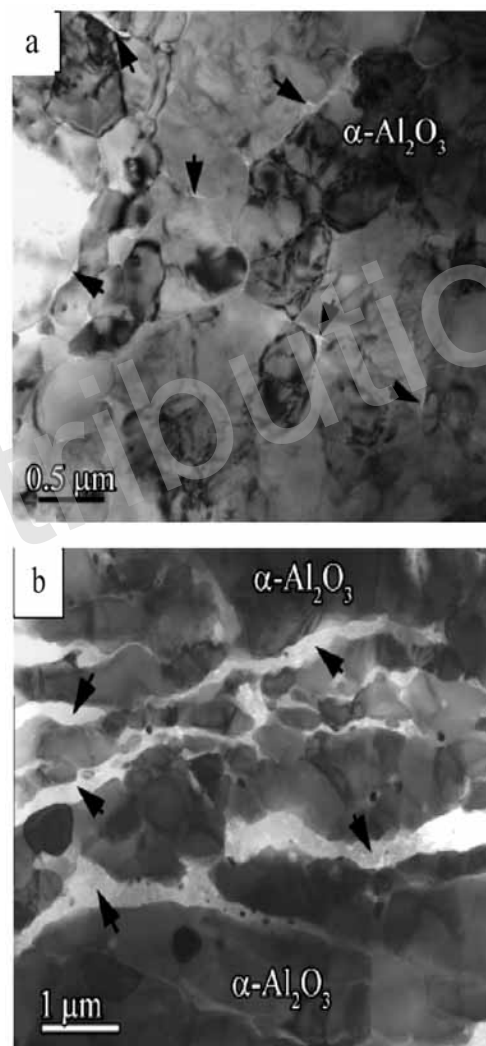


Fig. (5). Bright field TEM micrographs of (a) colloidal AT-SWNT/alumina composite; (b) conventional AR-SWNT/alumina composite. The light regions are SWNTs (arrows) and dark regions are alumina [27].

The BaTiO₃-MWNT composite fabricated by Huang and Gao [28] by HP had relative densities in the range 86-99%. It was influenced by the MWNT content and sintering temperature. Their SEM analyses revealed grain refinement due to incorporation of CNTs which were embedded in the BaTiO₃ grains instead of aggregating at the grain boundary. This and low aspect ratio of acid treated CNTs possibly inhibited CNT percolation which resulted in a decrease in the electrical conductivity of the composite with increase in CNT content. Moreover, BaTiO₃-MWNT composites

¹¹ AR-SWNTs: as received SWNTs

¹² AT-SWNTs: acid treated SWNTs

¹³ The acid treatment was found to selectively destroy all metallic SWNTs of small diameter.

were found to be *p*-type semiconductors while MWNT free BaTiO₃ was *n*-type.

Their BaTiO₃-MWNT composites, prepared by SPS showed improved densification, with relative density 95-99.5% [29-31]. These composites, similar to their HP counterparts discussed above, also showed grain refinement and reduced electrical conductivity. Additionally, their thermal conductivity decreased with increase in CNT content, from 3.06 to 2.25 W/mK for the composites with 0 and 3 wt% MWNTs, respectively [31]. A 2 μm thick bi-layer ceramic, made with one layer BaTiO₃ and the other BaTiO₃-MWNT composite, showed excellent rectification characteristics (the ratio of currents, at forward and reverse voltage 1.5 V, was ~5.6 [29]). The fracture toughness of the composite, measured by Vickers indentations, showed improvements up to 240% compared to unreinforced ceramic [30].

The polymer derived (PDC) MWNT-SiCN composites fabricated by An *et al.* [32] had densities ~99%. The SEM observations of the fractured composite surfaces revealed uniform distribution of CNTs in ceramic matrix. HRTEM analyses revealed no indication of chemical reactions between CNTs and matrix at the interface. Young's moduli (determined from nano-indentation curves) and micro-hardness of the composite were found to increase with the increase in CNT content, both showing increases over 150% for the composite with 6.4 vol% CNTs. The HRTEM, EELS and ELNES analyses on the SiCO ceramic (also prepared by PDC route) confirmed that the carbon material in the pores of the ceramic was CNT and that nickel silicide nanoparticles initiated the CNT growth [33]. No mechanical, thermal, etc properties were investigated/reported.

The SEM/HRTEM analyses of the reaction bonded MWNT-SiC composite showed that CNTs were preserved during fabrication [34,35]. The elastic modulus (measured by standard ultrasonic technique) and flexural strength (measured by standard four point bending test) of the dense composites were not significantly influenced by the CNT content. However, the fracture toughness (measured by Chevron notch method) showed improvements up to 50% compared to the unreinforced compact. Moreover, composites' electrical conductivity showed marked increase with increase in CNT content, e.g., at 2.1 vol% CNT, it increased 16-fold, possibly due to percolation of CNTs.

The EDX and XRD analyses of the SWNT-SiC composite fabricated using the low temperature microwave synthesis technique indicated the presence of ~15 wt% SiO₂, in addition to SWNTs and SiC [36,37]. The Fourier transform infrared (FTIR) spectrum of treated SWNTs indicated the presence of carboxylic (-COOH) groups which were, however, absent on the composite suggesting that the reaction was initiated at these sites. According to the SEM and TEM analyses, once nucleation of SiC occurred on SWNT sidewalls, macroscopic composite structure seemed developed by randomly cross-linked SiC particles. The fine particles coated on SWNTs were confirmed to be SiC by EDX on TEM. No mechanical/electrical/thermal properties of the composite were investigated.

CNT-CERAMIC-METAL COMPOSITES

Compared to the composites that contained only CNTs and ceramic discussed above, these contain a substantial amount of metal e.g., iron, cobalt, nickel, niobium. A popular approach for composite powder preparation involves the utilisation of nanometric metal particles for nucleation and growth of CNTs *in-situ*.

Fabrication

Laurent *et al.* [39,40], Peigney *et al.* [41-44] and Flahaut *et al.* [45,46] prepared CNT - ceramic (Al₂O₃ or MgAl₂O₄) - metal (Fe/Ni/Co) nano-composite powders where CNTs (a mixture of SWNTs and MWNTs) were grown *in-situ* by catalytic decom-

position of hydrocarbons (H₂-CH₄) on nanometric metal particles. From their detailed study of CNT-Al₂O₃-Fe composite powders, it was found that a higher quantity of CNTs of high quality (determined by smaller CNT diameter and/or more carbon in tubular form) were obtained when Fe content was 5-10wt% and reduction temperature 900°C. The composite powders were consolidated by hot pressing [40-46]. In subsequent work, some of the CNT - ceramic (Al₂O₃ or MgO or MgAl₂O₄) - metal (Fe/Co) powders were consolidated by extrusion at temperatures 1500-1730°C [44].

An *et al.* [47] also prepared CNT-alumina-iron composite powders with *in-situ* grown CNTs using catalytic method. In the powder, the amount of iron catalyst (Fe(NO₃)₃·9H₂O) ranged from 0.1 to 5 mol%. They consolidated these powders by hot pressing. The estimated CNT content of the prepared specimens was in the range 0-12.5 wt%.

CNT-ceramic-metal composites discussed so far have been prepared by *in-situ* grown CNTs by catalytic decomposition followed by hot pressing/extrusion. However, Kuntz *et al.* [48] used pre-formed SWNTs for fabrication of SWNT-alumina-niobium composite by SPS with 5, 5 and 90 volume percentages of SWNTs, niobium and alumina respectively. The process for the composite preparation and the SPS conditions used were similar to those by Zhan *et al.* [16-23] discussed in the previous section. By adopting the same procedure, composites/compacts containing 90 vol% alumina and 10 vol% niobium (i.e., without SWNTs), 90 vol% alumina and 10 vol% SWNTs (i.e., without niobium) and 100% alumina were also prepared in [48] for comparison.

Characterisation

The SEM analyses of CNT-ceramic-metal nano-composite powders prepared with *in-situ* grown CNTs by Laurent *et al.* [39,40], Peigney *et al.* [41-44] and Flahaut *et al.* [45,46] showed bundles of CNTs of diameter <100 nm and length >10 μm well dispersed in the powders. Subsequent tests on the HP consolidated composites revealed that flexural strength (measured by three point bending test) was only marginally higher than that of alumina and much lower than that of carbon free iron-alumina nano-composites prepared in the same way [41-46]. In addition, compared to pure alumina compacts, no significant improvement in fracture toughness (measured by single edge notched beam method) of the CNT composites was observed. The SEM analyses confirmed the presence of CNTs in these consolidated composites but in smaller quantity than the starting powder (estimated to be 20 vol%) due to degradation of some of the CNTs leaving disordered graphitic layers that seem to gather at matrix grain junctions or pores. It appeared that some of the CNTs reacted with residual O₂ and formed gaseous species such as CO. Moreover, the composites did not reach the full density (the relative density was only 87-93% [44,45]) and the bonding between the CNT bundles and matrix seemed to be poor.

Some of their CNT - ceramic (Al₂O₃ or MgAl₂O₄) - metal (Fe/Co) composite powders prepared more or less the same way and consolidated by HP showed much higher electrical conductivity (40-400 S/m) compared to ceramics or ceramic-metal composites (conductivity < 10⁻¹¹ S/m) [45]. This higher electrical conductivity was attributed to the percolation of the CNTs [44]. Though some of the CNTs seemed destroyed during high temperature processing, the high aspect ratio of CNT bundles (>10²) made the electrical percolation possible. However, these CNT-ceramic-metal composites also did not show any significant improvement in strength/toughness possibly due to poor densification and degradation of some of the CNTs.

The SEM analyses of their CNT-ceramic-metal composites prepared by high temperature extrusion showed aligned CNTs. One composite showed an electrical conductivity as high as 2000 S/m measured in the extrusion direction. In the transverse direction, it

was only 95 S/m. This anisotropy in electrical conductivity also confirmed alignment of CNTs by superplastic forming and CNTs ability to withstand high shear stresses that occur during the process. Additionally, the electrical conductivity of the composite depended on the amount of CNTs. The preliminary tests have also indicated that these composites could retain their electrical conductivity at higher temperatures (400°C) in air.

The CNT-alumina-iron composites fabricated by An *et al.* [47] by HP showed that their hardness increased with increase in CNT content and reached a maximum value at 4.1% CNT (this maximum hardness was ~33% higher than that for specimen with 0% CNT). The hardness then decreased with further increase in CNT content. The increase in hardness (up to 4.1% CNT) was attributed to the reinforcement by CNTs and grain size effect (alumina grain size was found to decrease with increase in CNT content which in turn increased the composite's hardness). The decrease in hardness (above 4.1% CNT) was attributed to the poor cohesion between the CNTs and the matrix. The wear test results (from ball on reciprocating flat tester) reflected the relation between hardness and wear rate and showed minimum wear corresponded to the composite with 4.1% CNT. The coefficient of friction (μ) decreased with increase in CNT content with $\mu \approx 0.5$ for 0% CNT composite and $\mu \approx 0.3$ for 12.5% CNT composite. This decrease in μ with increase in CNT content was attributed to the lubricating properties of CNTs and possible rolling motion of CNTs at the interface.

Kuntz *et al.* [48] who used SPS to fabricate SWNT-alumina-niobium, SWNT-alumina, alumina-niobium and pure alumina compacts achieved relative densities over 98%. The fracture toughness (measured by the indentation crack length method) of the SWNT-alumina-niobium composite was much higher than those of the SWNT-alumina and alumina-niobium composites and was over four times that of the pure alumina compact. The observed high fracture toughness was attributed to a 'synergetic effect' of SWNT-niobium combination in alumina.

CNT-GLASS-CERAMIC COMPOSITES

Fabrication

A CNT-glass-ceramic composite containing 0-15 vol% MWNTs and barium aluminosilicate (BAS, containing BaO, SiO₂ and over 20 wt% alumina) was fabricated by Ye *et al.* [49]. The composite powder was prepared in a conventional way, i.e., by ultrasonic agitation and ball milling. It was then consolidated by HP.

Characterisation

Ye *et al.* [49] achieved the near theoretical density for MWNT-glass-ceramic composites containing up to 10 vol% MWNTs. However, the one with 15 vol% CNTs reached only 97% of theoretical density. The TEM analyses of the composites revealed CNTs bonded with BAS grains and SEM of fractured surfaces revealed CNT pull out and residual holes left by CNTs (Fig. 6a). The SEM micrographs of crack propagation paths produced by Vickers indentations showed crack bridging effect (Fig. 6b). The flexural strength and fracture toughness of these composites were measured by three point bending tests and single edge notched beam (SENB) tests, respectively. Compared to unreinforced composites, with increase in CNT content up to 10 vol%, both flexural strength and fracture toughness increased which were 192% and 143% respectively. This strengthening and toughening was attributed to crack bridging by CNTs and their pullout. However, the strengthening/toughening observed with composite having 15 vol% CNTs was lower. This was attributed to composite's lower relative density due to agglomeration of CNTs.

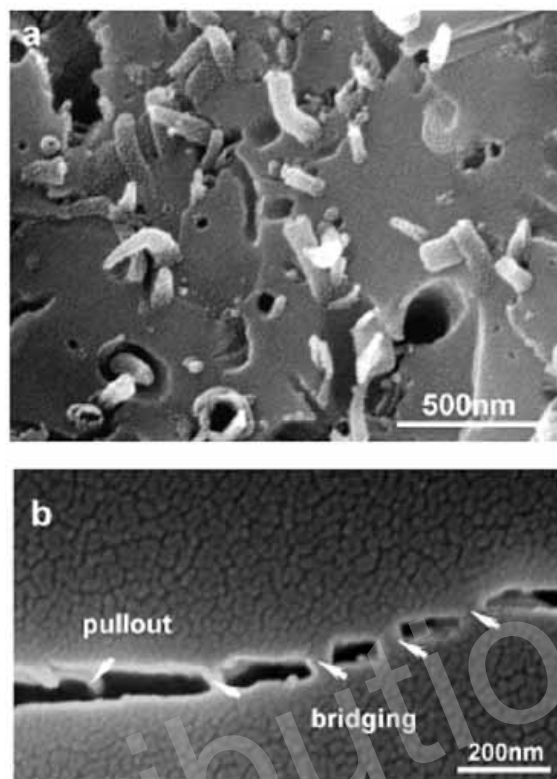


Fig. (6). SEM micrographs (a) fractured surface showing CNT pullout; (b) indentation crack showing bridging effect by CNTs [49].

CNT-CERAMIC-POLYMER COMPOSITES

Fabrication

Miyake *et al.* [50] disclosed the fabrication of CNT-ceramic-polymer composites with low weight and high thermal conductivity. In these composites, the CNTs were bonded to the ceramic matrix via a polymer compound and moulded to form a sheet/film to be used as a heat radiation sheet/film for suppressing the temperature rise due to LSI heating for improved performance of electronic devices such as, computers, digital cameras and mobile phones. For the composite's matrix, alumina or boron nitride was preferred due to its low thermal expansion coefficient which would reduce separation at the interface. Epoxy/silicon resin was selected as the polymer due to its high thermal conductivity and ability to be formed into thin coating film. The composite preparation process started with mixing of CNTs and alumina. The mixture was incorporated in the polymer and kneaded. It was then treated in a centrifugal defoaming apparatus followed by curing in a mould under controlled conditions.

Characterisation

In the patent by Miyake *et al.* [50], all the details given on characterisation were for vapour grown carbon fibre (VGCF) reinforced ceramic-polymer composites. No information on the characterisation of a CNT reinforced composite was available.

CNT-CERAMIC COMPOSITE COATINGS

Fabrication

So far, one of the issues in assessing the toughening mechanisms in CNT-ceramic composites has been the difficulty in fabricating composites with well controlled micro/nano-structures.

Xia *et al.* [51] attempted to overcome this problem by fabricating a highly ordered MWNT reinforced alumina composite. They first prepared nano porous alumina matrix on aluminium substrate. The low temperature CVD process was then used to grow MWNTs up the pore walls creating a unidirectional CNT-ceramic matrix composite in the form of a coating with thickness up to 90 μm .

Now turning to the application side, composite coatings consisting of CNTs and HA¹⁴/TiO₂ ceramic particles are considered to be suitable for the attachment and proliferation of cells, thus potential bioactive materials. Singh *et al.* [52] used the electrophoretic deposition¹⁵ (EPD) technique to co-deposit MWNT and the above ceramic nanoparticles to produce these CNT-ceramic composite coatings on metallic (stainless steel and Ti alloy) substrates of different shapes (wires or planer surfaces). For CNT-HA coatings, sol-gel derived, nanosized HA powder dispersed in CNT-ethanol suspension at pH \approx 3.5 was used. For CNT-TiO₂ coatings, titania nanopowders and acid treated CNTs in aqueous suspensions at pH \approx 5 was used. Prior to EPD, both solutions were ultrasonicated to improve dispersion and separate possible agglomerates. The EPD deposition voltage and time determined the thickness and homogeneity of the composite coatings.

Characterisation

The highly ordered MWNT-alumina composite coating fabricated by Xia *et al.* [51] was examined by SEM after controlled cracks were introduced by nanoindentation. The images clearly showed that, the three key characteristics associated with toughening mechanisms operating in micron-scale fibre reinforced composites (crack deflection at the fibre-matrix interface, crack bridging by fibres and fibre pull out on the fracture surface) do indeed occur in a CNT ceramic composite at the nano-scale. Additionally, the CNT-ceramic composite and the porous ceramic showed a new crack resisting mechanism of CNT/pore collapse in 'shear bands' not observed in large scale composites. For both composite and unreinforced ceramic coatings, hardness and (effective) Young's modulus measured by nanoindentation were in the range 6-12 GPa and 70-140 GPa respectively. Both decreased with the increasing distance from the aluminium-alumina interface possibly due to the effect of the pore size variation. The TEM analyses of CNTs (obtained by dissolving the alumina matrix) showed prevalence of various defects. Considering that the corresponding composite exhibited toughening behaviour indicates that perfect CNTs are not essential for activating toughening mechanisms in the CNT-ceramic composites.

The bioactive HA/TiO₂-MWNT composite coatings deposited on metallic substrates by Singh *et al.* [52] were characterized by EDX/SEM/XRD analyses. These confirmed the presence of HA/TiO₂ and CNTs in the coatings. SEM also revealed that these composite coatings were homogeneous and uniform. Presence of only crystalline HA phase was confirmed by XRD. Further characterization of these composite coatings based on mechanical/biological properties were considered necessary for assessing their possible biomedical applications.

APPLICATIONS OF CNT-CERAMIC COMPOSITES

A wide range of applications in aerospace, biomedical, defence, electrical, electronic, manufacturing, etc. have been envisioned due to the remarkable improvements in material properties. The ceramic coated/reinforced CNTs [2] and the ceramic particles with multiple CNTs bonded on the particle surface [3] will be useful

reinforcements for fabricating a range of CNT reinforced ceramic composites.

Ceramic composites effectively reinforced with CNTs are expected to possess greatly improved fracture toughness¹⁶ to complement their high hardness/strength at room and elevated temperatures, resistance to corrosion, etc. They will be ideal cutting tools and be able to increase ceramics' market share substantially in the multi-billion dollar cutting tool industry. Additionally, these novel composites with excellent room/high temperature mechanical properties combined with the lubricating properties of CNTs will be ideal for the manufacture of parts for high temperature applications such as heat engines, gas turbines, etc.

The SWNT-ceramic composites or their coatings with anisotropic thermal properties have potential for applications: in a miniature scale, in microprocessors and integrated circuit packages for effective heat dissipation/spreading; on a larger scale, on high temperature components in turbine engines, reactors and space vehicles [20,21]. Moreover, some of these SWNT-ceramic composites show promise as thermoelectric materials with high degree of thermoelectric efficiency due to high electrical and low thermal conductivities. Thus these composites with further improved electrical conductivity should be effective for thermoelectric power generation under the Seebeck effect and/or for transport of thermal energy by absorption/evolution under the Peltier/Thomson effects [22,23]. The electrically conductive MWNT-Si₃N₄ ceramic composites are likely to be used in manufacturing components for extremely severe mechanical and environmental conditions such as ceramic bearings for high speed, high temperature, and corrosive environments and as novel functional materials with high durability and electrical conductivity [12].

The CNT-ceramic-polymer composites with low weight and high thermal conductivity have potential applications for suppressing the temperature rise due to LSI heating for improved performance of electronic devices such as, computers, digital/video cameras and mobile phones [50]. The composite coatings consisting of CNTs and HA/TiO₂ ceramic particles fabricated by EDP on metallic substrates (e.g. stainless steel, titanium alloy) are suited for biomedical applications, in particular, for the attachment and proliferation of cells [52].

CURRENT & FUTURE DEVELOPMENTS

In the CNT-ceramic composite powder preparation (with/without metal), both *in-situ* grown CNTs and pre-formed CNTs have been used. An advantage of *in-situ* grown CNTs is their uniform dispersion. A major disadvantage, however, is that the composite powders also contain other forms of carbon species such as thick graphene layers, etc which can be detrimental to the mechanical properties of the consolidated composite. On the other hand, use of pre-formed CNTs allows precise control of the CNT content without introducing impurities. A widely used method for dispersion of these CNTs involves ultrasonic agitation followed by ball milling. However, the recent analyses of Poyato *et al.* [27] showed superior dispersion of CNTs in ceramic powders by aqueous colloidal processing compared to ultrasonication and ball milling.

The most widely used powder consolidation methods are HP and SPS. SPS allows relatively low temperatures and short durations compared to HP. Those who used SPS generally reported higher densities (>98%) compared to HP, where densities achieved were 89-95%. The lower HP densities (89-93%) were achieved with composite powders having *in-situ* grown CNTs. Due to relatively low temperatures and short durations possible, SPS has been considered to preserve CNTs during consolidation [16,17].

¹⁴ Hydroxyapatite: a crystalline ceramic (chemical formula Ca₅OH(PO₄)₃) with high tissue compatibility and bone conduction potential and hence used as a bone substitute.

¹⁵ With electrophoretic deposition, the article to be coated is made either the anode or cathode, and a dc voltage is then applied across a liquid medium containing charged particles. Due to the migration of particles towards the electrode bearing the opposite charge, an electrodeposited coating is produced.

¹⁶ Unreinforced ceramics' lack of toughness and the resulting tendency to chipping has been cited by Trent and Wright [53] as the major reason for their inability to occupy a significant market share in the huge cutting tool industry.

However, recent results have indicated selective destruction of CNTs (e.g. metallic SWNTs) during SPS resulting in the formation of disordered graphite, nano-onion like structures and diamond in the intergranular regions [27].

The microwave consolidation technique in [36,37] has advantages: (a) it uses relatively low temperature microwave induced reaction, leading to fast reaction kinetics (hence high yield), (b) minimal requirement of energy and chemicals and hence being environmentally friendly. A major disadvantage, however, is that the technique has not yet been developed to fabricate dense composites. On the other hand, PDC [32,33] and melt infiltration reaction bonding [34,35] techniques have been successfully used to prepare dense composites. These also have advantages of relatively short processing times and scalability of the processes.

In terms of composite properties, greatly improved electrical conductivities have been reported with SWNT-alumina composites fabricated by SPS (up to 3345 S/m [18,19]) or by extrusion (up to 2000 S/m [44]), compared to those fabricated by HP or by GPS/HIP (up to 400 S/m) [12,45]. It was also noted that some SWNT ceramic composites could function as thermoelectric materials with high degree of thermoelectric efficiency due to high electrical and low thermal conductivities. One particular SWNT-ceramic composite had a figure of merit value of ~ 0.02 at 850K which is two orders of magnitude higher than that of pure SWNTs [22,23]. However, compared to other thermoelectric materials, the electrical conductivity of these SWNT-ceramic composites is low. This may be further improved by using pure metallic SWNTs (due to their much higher electrical conductivity) which, however, poses challenge of effective SWNT separation.

The property mainly aimed at improving by CNT reinforcement of ceramics is fracture toughness [54]. In order to achieve this, it is necessary that the CNT-matrix interface is neither too strong nor too weak [45]. This will allow absorption of some energy under stress by debonding at the interface which is followed by CNT pull out. In the reported CNT-ceramic composites, a number of researchers have microscopically observed the characteristics associated with toughening mechanisms such as CNT pull out [35,49,51], crack bridging by CNTs [35,49,51] and crack deflection at CNT-ceramic interface [13,16,17,51]. These have been observed in spite of the defects present in the CNTs, indicating that perfect CNTs are not essential for activating the above toughening mechanisms [51]. However, this toughening behaviour has not been clearly demonstrated at macroscopic scale. Although some researchers have reported significant improvements in fracture toughness (measured by the non-standard indentation crack length method), these improvements have not been confirmed by standard testing techniques. In fact, those who have used standard techniques have reported insignificant improvements in fracture toughness. Disappointingly, well after Wang *et al.* [24] demonstrated the invalidity of the indentation crack length technique for measuring the fracture toughness of the CNT-ceramic composites, it still remains a popular technique for these materials!

In summing up, the powder preparation techniques for CNT-ceramic composites require further developments for improved CNT dispersion. The colloidal processing technique appears to be promising. It also seems that the present high temperature consolidation methods destroy some of the CNTs resulting in the formation of disordered graphite, etc, which may be detrimental to the composite's property enhancement. Thus more research is required for developing the appropriate consolidation techniques and/or conditions. For effective reinforcement, it is necessary to achieve the optimal CNT-ceramic interface bonding so that the microscopic toughening mechanisms are activated and the resulting toughening behaviour is demonstrated at macroscopic scale. Finally, when testing the fabricated composites, in particular, for fracture toughness, standard testing procedures should be adopted.

ACKNOWLEDGMENTS

The authors wish to thank the Australian Research Council for financial assistance.

REFERENCES

- [1] Mylvaganam K, Zhang LC. Fabrication and application of polymer composites comprising carbon nanotubes. *Rec Patents Nanotechnol* 2007; 1; 59-65.
- [2] Ren, Z., Wen, J. G., Lao, J. Y. and Li, W.: US20056911260 (2005) and WO03060209 (2003).
- [3] Chiang, Y. M., Vander Sande, J. B.; WO04037714 (2004).
- [4] Sun J, Gao L, Li W. Colloidal processing of carbon nanotube/alumina composites. *Chem Mater* 2002; 14; 5169-5172.
- [5] Sun J, Gao L. Development of a dispersion process for carbon nanotubes in ceramic matrix by heterocoagulation. *Carbon* 2003; 41 (5); 1063-1068.
- [6] Sun J, Iwasa M, Gao L, Zhang Q. Single-walled carbon nanotubes coated with titania nanoparticles. *Letters to the Editor/ Carbon* 2004; 42; 895-899.
- [7] Sun J, Gao Lin, Iwasa M, Nakayama T, Niihara K. Failure investigation of carbon nanotube/ 3Y-TZP nanocomposites. *Ceramics Int* 2005; 31; 1131-1134.
- [8] Sun J, Gao L. Attachment of inorganic nanoparticles onto carbon nanotubes. *J Electroceram* 2006; 17; 91-94.
- [9] Gomathi A, Vivekchand SRC, Govindaraj A, Rao CNR. Chemically bonded ceramic oxide coatings on carbon nanotubes and inorganic nanowires. *Adv Mater* 2005; 17; 2757-2761.
- [10] Morisada Y, Maeda M, Shibayanagi T, Miyamoto Y. *J Am Ceramic Soc* 2004; 87(5); 804-808.
- [11] Woodman RH, Klotz BR, Dowding R. Evaluation of a dry ball-milling technique as a method for mixing boron carbide and carbon nanotube powders. *Ceramics International* 2005; 31; 765-768.
- [12] Tatami J, Katashima T, Komeya K, Meguro T, Wakihara T. Electrically conductive CNT-dispersed silicon nitride ceramics. *J Am Ceram Soc* 2005; 88(10); 2889-2893.
- [13] Ma RZ, Wu J, Wei BQ, Liang J, Wu DH. Processing and properties of carbon nanotubes-nano-SiC ceramic. *J Mater Sci* 1998; 33; 5243-5246.
- [14] Chang, S., Doremus, R. H., Siegel, R. W., Ajayan, P. M.: US20026420293 (2002) and WO0218296 (2002).
- [15] Siegel RW, Chang SK, Ash BJ, *et al.* Mechanical behaviour of polymer and ceramic matrix nanocomposites. *Scripta Mater* 2001; 44: 2061-2064.
- [16] Zhan, G. D., Mukherjee, A. K., Kuntz J. D., Wan, J.: US20056858173 (2005) and WO04110950 (2004).
- [17] Zhan GD, Kuntz JD, Wan J, Mukherjee AK. Single wall carbon nanotubes as attractive toughening agents in alumina based nanocomposites. *Nat Mater* 2003; 2: 38-42.
- [18] Zhan, G. D., Kuntz J. D., Mukherjee, A. K.: US20056875374 (2005) and WO04077521 (2004).
- [19] Zhan GD, Kuntz JD, Garay JE, Mukherjee AK. Electrical properties of nanoceramics reinforced with ropes of single-walled carbon nanotubes. *Appl Phys Lett* 2003; 83(6); 1228-1230.
- [20] Zhan, G. D., Kuntz J. D., Mukherjee, A. K.: US20056976532 (2005) and WO05033036 (2005).
- [21] Zhan GD, Kuntz JD, Wang H, Wang CM, Mukherjee AK. Anisotropic thermal properties of SWNT reinforced nanoceramics. *Philosoph Mag Lett* 2004; 84; 7; 419-423.
- [22] Zhan, G. D., Kuntz J. D., Mukherjee, A. K.: WO05098981 (2005).
- [23] Zhan GD, Kuntz JD, Mukherjee AK, Zhu P, Koumoto K. Thermoelectric properties of carbon nanotube/ceramic nanocomposites, *Scripta Mater* 54; 2006; 77-82.
- [24] Wang XT, Pature NP, Tanaka H. Contact damage resistant ceramic/single wall carbon nanotubes and ceramic/graphite composites. *Nat Mater* 2004; 3; 539-544.
- [25] Shi SL, Liang J. Effect of multiwall carbon nanotubes on electrical and dielectric properties of Ytria-stabilized zirconia ceramic. *J Am Ceram Soc* 2006; 89(11); 3533 -3535.
- [26] Balazsi Cs, Konya Z, Weber F, Biro LP, Arato P. Preparation and characterization of carbon nanotube reinforced silicon nitride composites. *Mater Sci Eng* 2003; C 23; 1133-1137.
- [27] Poyato R, Vasiliev AL, Pature NP, Tanaka H, Nishimura T. Aqueous colloidal processing of single-wall carbon nanotubes and their composites with ceramics, *Nanotechnology* 2006; 17; 1770-1777.
- [28] Huang Q, Gao L. Manufacture and electrical properties of multiwalled carbon nanotube/BaTiO₃ nanocomposite ceramics. *J Mater Chem* 2004; 14; 2536-2541.
- [29] Huang Q, Gao L. Multiwalled carbon nanotube/ BaTiO₃ nanocomposites: Electrical and rectification properties. *Appl Phys Lett* 2005; 86; 123104.

- [30] Huang Q, Gao L, Sun, J. Effect of adding carbon nanotubes on microstructure, phase transformation, and mechanical property of BaTiO₃ ceramics. *J Am Ceram Soc* 2005; 88(12); 3515-3518.
- [31] Huang Q, Gao L, Liu Y, Sun J. Sintering and thermal properties of multiwalled carbon nanotube - BaTiO₃ composites. *J Mater Chem* 2005; 15; 1995 - 2001.
- [32] An L, Xu W, Rajagopalan S, *et al.* Carbon-nanotube-reinforced polymer-derived ceramic composites. *Adv Mater* 2004; 16 (22); 2036-2040.
- [33] Berger A, Pippel E, Woltersdorf J, Scheffler M, Cromme P, Greil P. Nanoprocesses in polymer-derived Si-O-C ceramics: Electron microscopic observations and reaction kinetics. *Phys Stat Sol* 2005; (a) 202 (12); 2277-2286.
- [34] Thostenson ET, Karandikar P.G., Chou, T.W., Fabrication and characterization of reaction bonded silicon carbide/carbon nanotube composites, *Journal of Physics D: Appl Phys* 2005; 38(21): 3962-3965.
- [35] Karandikar, P.G.: WO06080936 (2006).
- [36] Mitra, S., Iqbal, Z.: WO06099392 (2006).
- [37] Wang Y, Iqbal Z, Mitra S. Rapid, low temperature microwave synthesis of novel carbon nanotube - silicon carbide composite. *Carbon* 2006; 44; 2804-2808.
- [38] Supronowicz, P., Ajayan, P., Bizios, R., Siegel, R.: WO0187193 (2001).
- [39] Laurent Ch, Peigney A, Quenard O, Rousset A. Novel ceramic matrix nanocomposite powders containing carbon nanotubes. *Key Eng Mater* 1997; 132-136; 157-160.
- [40] Laurent Ch, Peigney A, Dumortier O, Rousset A. Carbon nanotubes-Fe-Alumina nanocomposites. Part II: Microstructure and mechanical properties of the hot pressed composites. *J Eur Ceramic Soc* 1998; 18: 2005-2013.
- [41] Peigney A, Laurent Ch, Rousset A. Synthesis and characterization of alumina matrix nanocomposites containing carbon nanotubes. *Key Eng Mater* 1997; 132-136; 743-746.
- [42] Peigney A, Laurent Ch, Dumortier O, Rousset A. Carbon nanotubes-Fe-Alumina nanocomposites. Part I: Influence of the Fe content on the synthesis of powders. *J Eur Ceramic Soc* 1998; 18: 1995-2004.
- [43] Peigney A, Laurent Ch, Flahaut E, Rousset A. Carbon nanotubes in novel ceramic matrix nanocomposites. *Ceramics Int* 2000; 26: 677-683.
- [44] Peigney A, Flahaut E, Laurent Ch, Chastel F, Rousset A. Aligned carbon nanotubes in ceramic-matrix nanocomposites prepared by high-temperature extrusion. *Chem Phys Lett* 2002; 352; 20-25.
- [45] Flahaut E, Peigney A, Laurent Ch, Marliere Ch, Chastel F, Rousset A. Carbon nanotube-metal-oxide nanocomposites: Microstructure, electrical conductivity and mechanical properties. *Acta Mater* 2000; 48; 3803-3812.
- [46] Flahaut E, Rul S, Lefevre-Schlick F, Laurent Ch, Peigney A. Carbon nanotubes-ceramic composites. *Ceramic Nanomater Nanotechnol II*; 2004; 71-82.
- [47] An J-W, You D-H, Lim D-S. Tribological properties of hot pressed alumina-CNT composites, *wear*, 2003; 255: 677-681.
- [48] Kuntz, J. D., Zhan, G. D., Mukherjee, A. K.: WO05028394 (2005).
- [49] Ye F, Liu L, Wang Y, Zhou Y, Peng B, Meng Q. Preparation and mechanical properties of carbon nanotube reinforced barium aluminosilicate glass-ceramic composites. *Scripta Mater* 2006; 55; 911-914.
- [50] Miyake, S., Takahashi, Y., Masuko, T.: WO06057458 (2006).
- [51] Xia Z, Riestler L, Curtin WA. Direct observation of toughening mechanisms in carbon nanotube ceramic matrix composites. *Acta Mater* 2004; 52: 931-944.
- [52] Singh I, Kaya C, Shaffer MSP, Thomas BC, Boccaccini AR. Bioactive ceramic coatings containing carbon nanotubes on metallic substrates by electrophoretic deposition. *J Mater Sci* 2006; 41: 8144-8151.
- [53] Trent EM, Wright PK. *Metal Cutting*, Butterworth-Heinemann, 2000.
- [54] Curtin WA, Sheldon BW. CNT reinforced ceramics and metals. *Mater Today* 2004; 7(11); 44-49.

Not For Distribution