CNT-reinforced
ceramics and metals

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Recent research on the incorporation of carbon nanotubes (CNTs) into ceramic and metal matrices to form composite structures is briefly reviewed, with an emphasis on processing methods, mechanical performance, and prospects for successful applications.

CNTs have outstanding mechanical, thermal, and electrical properties. Thus, by placing nanotubes into appropriate matrices, it is postulated that the resulting composites will have enhanced properties. CNTs in polymer matrices are extensively reviewed elsewhere in this issue by Vaia and Wagner. In this article, we review literature on the topics of fabrication and properties of ceramic and metal matrix systems. In light of a previous review[1] on this topic in 2001, we focus on more recent results.

What are the specific motivations for the development of CNT-based composites? For ceramic matrix materials, the mechanical property of greatest importance is toughness or resistance to crack growth. Ceramics are already stiff and strong and so, in analogy to ceramic composites with micron-scale fiber additions, the incorporation of CNTs is aimed at enhancing toughness. For high-temperature applications, the high thermal conductance of CNTs suggests that their incorporation, even at low volume fractions, might provide the thermal transport needed to reduce material operating temperatures and improve thermal shock resistance. Electrical conductance can also be useful in ceramic-based materials, as heating elements and electrical igniters, for instance. Control of electrical resistance through the use of CNT additives is, therefore, an attractive alternative to other composite systems. For metal matrix materials, enhanced mechanical properties (stiffness, wear, and fatigue resistance) are also desirable, but a wider range of properties – electrical, magnetic, and vibrational – have been investigated in a few reported works.

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Fabrication of CNT composites

Unfortunately, materials fabrication difficulties have limited research on nanotube-reinforced composites. One of the key issues is obtaining a uniform dispersion of nanotubes in the matrix. Damage or destruction of the nanotubes is often a problem because of the high temperatures and highly reactive environments associated with many methods of forming ceramic and metal matrices. Limited availability of nanotubes has also restricted research efforts, although this seems to have become less of a problem in recent years as more groups produce their own nanotubes with catalyzed chemical vapor deposition (CVD) methods.

Powder processing methods have been used to fabricate both ceramic and metal matrices[2-10]. The small diameter and large aspect ratio of the nanotubes can make it difficult to obtain a good mixture of the two phases prior to sintering or hot pressing. Some success has been achieved with conventional milling techniques, primarily with the use of low to moderate nanotube volume fractions[3,6-10]. Peigney *et al.*[11] have successfully employed superplastic forming with mixtures of submicron powders and CNTs. Here the nanotubes appear to facilitate the high-temperature extrusion process. This method produces a ceramic matrix composite (CMC) in which the nanotubes are highly aligned. Another interesting approach is to use a mixture of ceramic powder and catalyst for nanotube growth (Fe, Ni, or Co), followed by a CVD process that grows nanotubes inside the particulate preform[2,4,5,12], as shown in Fig. 1. This can produce a uniform mixture of the two phases as long as mass transport of the carbon-containing gas (e.g. C_2H_2, CH_4, etc.) into the powder bed does not produce significant gradients.

In some cases, the nanotubes are damaged by high-temperature sintering. However, spark-plasma-sintering has been used to produce materials where the nanotube structure is retained[7,10]. The success of this method apparently results from the use of lower temperatures and shorter firing times. While the sintering of traditional whisker and fiber reinforced composites is typically plagued by differential densification rates, this may be less of a problem with nanotubes because of their small dimensions. Conventional hot-pressing and hot isostatic pressing methods have also been used to produce nanotube-reinforced composites[3-6]. The presence of CNTs should also inhibit grain growth during high-temperature processing[4]. This beneficial effect is also known to occur during high-temperature processing of a variety of other composite materials[13]. High-temperature fabrication of a ceramic matrix can create some difficulty in identifying nanotubes in the final composite, particularly when low volume fractions and relatively small nanotubes are used[7]. However, high-resolution scanning electron microscopy, as shown in Fig. 1, can often be used to image nanotubes directly. Raman spectroscopy is also a useful tool for characterizing the carbon bonding indicative of nanotubes[10].

Several methods have been used to form nanotubes inside preexisting porous matrices. Rul *et al.*[14] formed a porous spinel structure with gel casting. This matrix also contained a small amount of Co catalyst, and subsequent CVD produced a relatively high nanotube volume fraction inside the porous oxide. Another method of producing nanotubes inside a porous ceramic is to use anodic alumina templates with controlled pore structures[15]. This approach is generally limited to coatings or membranes up to ~100 µm thick. The resulting materials consist of aligned nanotubes whose diameter is determined by the pre-existing cylindrical (or nearly cylindrical) pores in the alumina. This type of material is shown in Fig. 2. The dimensions of these materials make
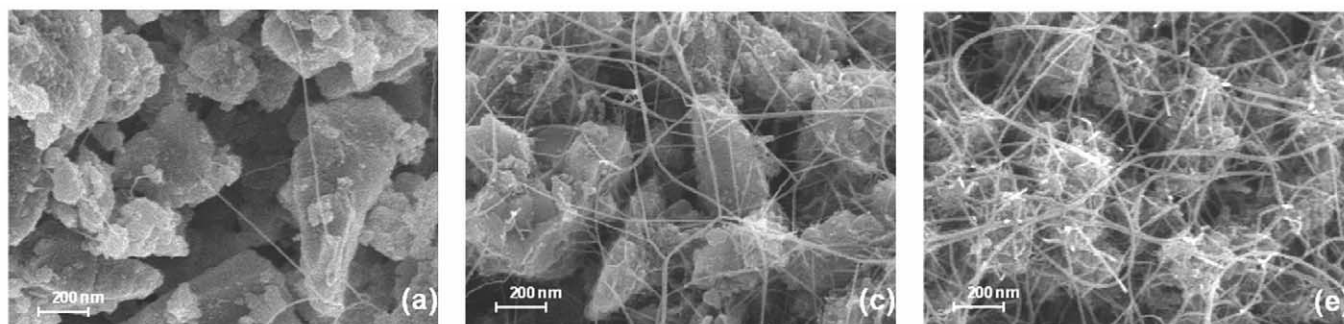

Fig. 1 High-resolution scanning electron micrograph of CNT-MgAl$_2$O$_4$ composite powders showing good distribution of CNTs in a continuous network between the oxide grains and increased agglomeration of CNTs into bundles with increasing CNT content. (Reprinted with permission from[12]. © 2004 Elsevier Ltd.)
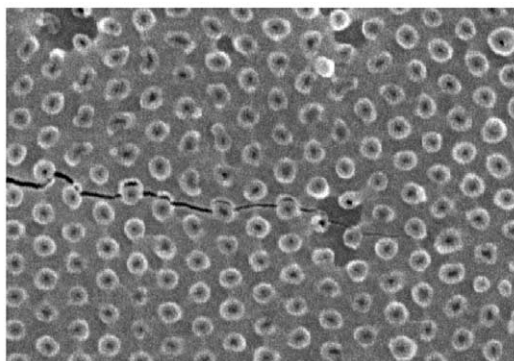
Fig. 2 Micrograph of deformation in a CNT-alumina composite fabricated using ordered porous alumina templates showing transverse crack deflection at the CNT/matrix interface for a thick multiwalled CNT material. (Reprinted with permission from[15]. © 2004 Elsevier Ltd.)

them potentially applicable as coatings. Also, the unidirectional microstructure is an advantage for fundamental investigations of mechanical properties.

Metal matrix materials have been produced by flowing a liquid into a porous array of nanotubes. Yang and Schaller[9] have accomplished this with gas-pressure infiltration of Mg. Other groups have used electroless plating to form either Co or Ni matrices that are not fully dense[16,17]. Liquid-based schemes for producing ceramic matrices can also be envisioned. Lupo et al.[18] have taken the first step in this direction by using a zirconium hydroxide solution to produce ZrO_2 crystals that appear to nucleate preferentially on CNTs.

Properties of CNT composites

We now turn to discuss the results to date on mechanical, thermal, and electrical properties.

The most interesting and challenging applications for CNT-ceramic matrix composites (CNT-CMCs) are as tough materials. Toughening in CMCs is typically achieved by a weak fiber/matrix interface coupling that permits debonding and sliding of the fibers within the matrix. The closing forces exerted by fibers on matrix cracks that propagate around the fibers constrains the crack growth, and the work required to pull broken fibers out against residual sliding friction at the fiber/matrix interface imparts significant fracture toughness to CMCs. Weak interfaces between a CNT and many ceramic matrices is expected, and pyrolytic carbon is the most common interface material deposited onto fibers to induce such debonding. Thus the mechanisms of interface debonding and sliding, and associated toughening, should be operative in CNT-CMCs unless the sliding resistance is too low (see below). Most work on CNT-CMCs has focused on the

measurement of toughness using the indentation/crack-length technique, which is nominally suitable for small volumes of material, with little emphasis on uncovering actual mechanisms of any toughening. Unfortunately, most results for toughening have been disappointing. Data has shown very little or no increase in toughening upon introduction of CNTs – either single- or multi-walled – into various ceramic matrices[2,3,11].

Zhan et al.[7], however, have reported significant fracture toughness improvements, three times higher than an unreinforced matrix, based on indentation measurements. On the other hand, new results from Wang et al.[10] demonstrate that the indentation/crack-length technique is not valid in these materials. Wang et al. fabricated CNT-alumina materials using the method of Zhan et al., but performed the far more reliable single edge V-notched beam test, which showed no enhanced toughening and thus refutes the claims of high toughness by Zhan et al. To reinforce their conclusion, Wang et al. performed indentation tests on the CNT-CMCs and on composites containing only graphite particles and showed that the indentation behavior is similar in the two materials: cracking is suppressed so that the 'apparent' toughness is high (Fig. 3). These works show that careful measurements are required and also strongly suggest that indications of enhanced toughening should be supported by direct evidence of potential toughening mechanisms. Although not tough in a traditional sense, the CNT-CMCs and graphite-CMCs are 'damage tolerant' under contact loading, i.e. they do not crack easily, which is explained by noting that the carbon additions may accommodate deformations by shear under the indenter.

New work by Xia et al.[15] has emphasized the identification of toughening mechanisms, rather than the determination of numerical values for toughness. They used a novel CNT-CMC material consisting of an aligned, ordered array of (imperfect) multiwalled CNTs embedded in an alumina matrix. The interaction of cracks, induced by nanoindentation, with the nanotubes could be directly observed for several orientations. The key phenomena of crack deflection at the matrix/nanotube interface (Fig. 2), crack bridging by nanotubes (Fig. 4a), and nanotube pull-out on the fracture surface all indicate that appropriate toughening mechanisms can operate in a CNT-CMC. They also show direct evidence of a novel shear deformation mode that is consistent with the arguments of Wang et al.[10] regarding 'damage tolerance'
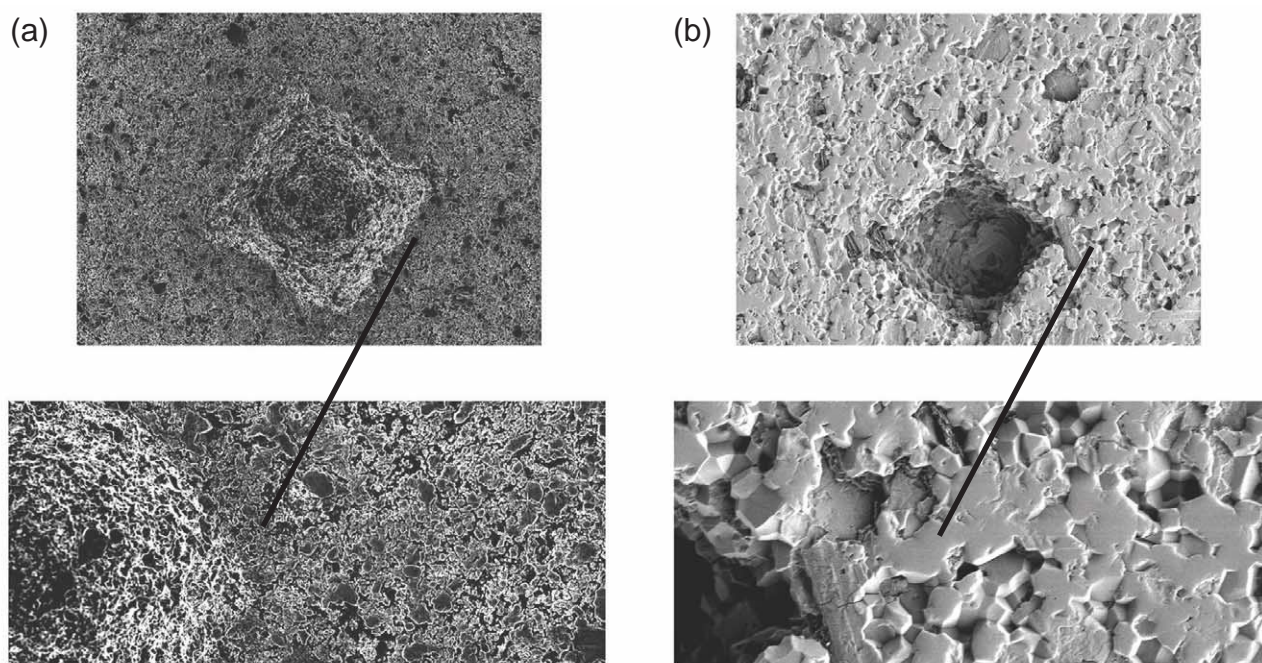
Fig. 3 Indentation deformation in (a) CNT-alumina and (b) graphite-alumina, showing the prevention of cracking at the indent corners in both systems; the materials are not tough but are damage tolerant under contact loading. (Reprinted with permission from[10]. © 2004 Nature Publishing Group.)

driven by shear (Fig. 4b). Further work on such model systems, as well as more practical systems, is needed to establish quantitative toughening levels, however.

Other mechanical properties, such as hardness and elastic modulus, have been investigated as well, with inconclusive results. CNT additions to silicon nitride show some variation in strength and modulus[6], but the CNTs change the density of the material and the strongest correlation in mechanical properties is with density. An et al.[4,5] investigated CNT-alumina materials and found an increase in hardness and decrease in wear resistance for moderate (2-4%) CNT additions. However, the CNTs change the grain size of the resultant matrix and the hardness correlates with the grain size changes as well. These results demonstrate that processing-induced changes in the matrix may have greater effects on mechanical properties than the actual presence of CNTs. Thus, correlations of properties solely with CNT content can be highly misleading.

CNT-CMC materials have demonstrated significant enhancements in electrical conductivity. Physically long, thin, and electrically conducting nanotubes create an interconnected percolating network of conducting paths through an otherwise insulating matrix to yield high conductivity at relatively low CNT volume fractions. Work by
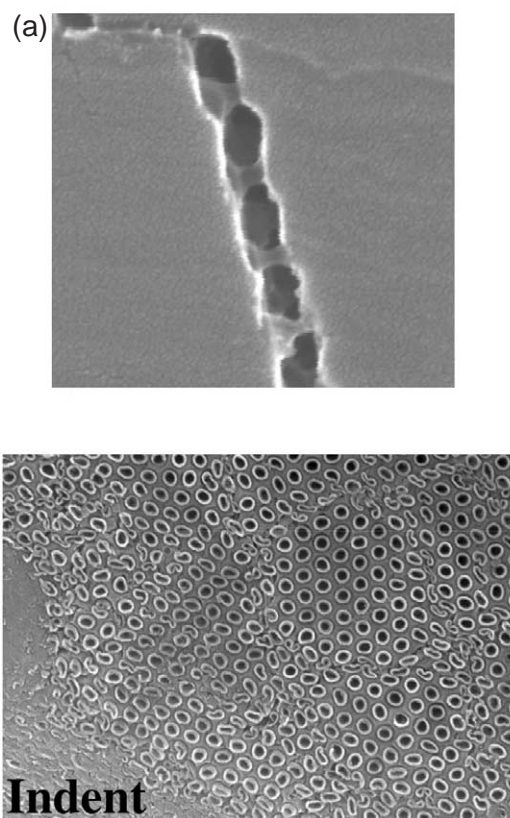

Fig. 4 Micrographs of deformation in CNT-alumina composites fabricated using ordered porous alumina templates: (a) CNTs bridging longitudinal matrix cracks; (b) shear collapse of nanotubes around an indent for a thin multiwalled CNT material. (Part (b) reprinted with permission from[15]. © 2004 Elsevier Ltd.)

Rul et al.[12] has carefully determined the electrical conductivity, σ, versus CNT volume fraction, p, and demonstrates a power-law relation of the form $\sigma = k(p-p_c)^t$ with a percolation threshold $p_c = 0.0064$ and an exponent $t = 1.73$. The absolute magnitude of the conductivity reached 10 S/cm. Zhan et al.[8] measured the conductivity of their alumina-based materials and obtained values two orders of magnitude larger than found with carbon black additions at the same volume fraction, and as high as 15 S/cm at about 15% CNTs. These results are indeed excellent and, with a high degree of controllability and low CNT content, hold promise for creating a host of conducting ceramic systems.

The recent literature on metal matrix materials is far more sparse. Chen et al.[17] fabricated CNT-Ni/P materials and tested them under lubricated wear conditions. Decreased friction coefficient and wear rate were measured, relative to similar materials with SiC or graphite additions and to virgin Ni/P itself. The potential for CNT-enhanced lubricity and/or the potential enhancement of hardness or damage tolerance make these types of systems attractive for further investigation. CNT-Mg materials have been fabricated and their damping characteristics have been investigated but with little notable effects over other metal matrix materials[9].

CNTs have been combined with metals for several electromagnetic applications. In these systems, metal particles are deposited around or on networks of CNTs. Deposition of Sb or Sn/Sb particles has shown that CNT-Sb/Sn materials used as anodes in Li$^+$ batteries can show enhanced cyclability and reversible capacity[19], attributable to the nanoscale of the metal phase and the mechanical robustness of the CNTs. Work on coating CNTs with Co, continuously or discontinuously (Fig. 5), has shown such 'composite' nanowires have high magnetic coercivities with values of ~1100 Oe reported[16]. This is approximately twice as large as values obtained for Co nanowires fabricated by other means. The use of such systems in real applications is unexplored, and the mechanisms by which enhancements are realized are largely unknown at present. It can only be stated that these systems show promising results that must be corroborated and expanded upon.

Future prospects

The work reviewed here demonstrates that a variety of methods for producing ceramic and metal matrix nanotube composites have been investigated in recent years, but with mixed results on mechanical performance. Further research on these approaches will almost certainly lead to better materials. Better mechanical properties are likely to result from higher nanotube volume fractions and, in some cases, the use of longer nanotubes. Both of these variations create additional processing challenges because it is more difficult to obtain a uniform dispersion of nanotubes and, in some cases, more difficult to obtain a dense matrix.

A key issue that has not yet been explored in any detail is the control of the interface between the nanotubes and the matrix. Experience with other composites indicates that these interfaces will be critical for mechanical performance. In particular, it is well established that debonding and interfacial sliding are critical in conventional CMCs. In a CNT-reinforced material, interface behavior is expected to be significantly different from conventional carbon fibers because of the unique chemical bonding inherent in CNTs. Experiments have shown that high-quality, multiwalled CNTs exhibit very easy interwall sliding, with inner graphitic walls able to be extracted from outer walls in a 'sword and sheath' mechanism at low applied forces[20]. Moreover, this behavior is not frictional in nature – the pull-out forces do not scale with embedded length. Molecular dynamics simulations have shown that the pull-out forces are increased when the inner walls have a fractured end[21]. The fractured end of the inner wall(s) would naturally deform outward but is constrained by the outer wall(s), generating high local stress (Fig. 6), requiring pull-out forces four times larger than capped-end
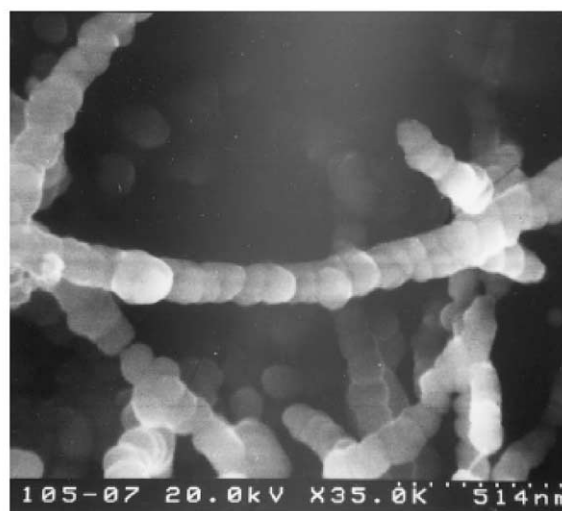

Fig. 5 Scanning electron micrograph of a Co-coated CNT network, which exhibits enhanced magnetic behavior over Co nanoparticles. (Reprinted with permission from[16]. © 2000 Elsevier Ltd.)
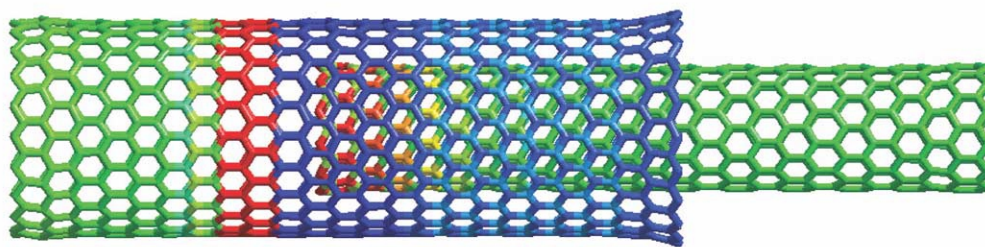
Fig. 6 Forces in a double-walled nanotube during pull-out of the inner tube (red = high; blue = low). Note that forces are highly concentrated in the region where the inner, fractured nanotube interacts with the outer nanotube. (Courtesy of Z. Xia, Brown University.)

nanotubes, consistent with experiments[20]. The behavior is still not frictional, however, and incorporation of nearly perfect CNTs may not be the appropriate direction for design of high-performance materials. The behavior demonstrated in Fig. 4a was obtained on imperfect nanotubes, for instance, and it may be that nanocarbon fibers rather than nanotubes hold most promise for providing the balance of properties (strength and interfacial sliding behavior) needed for good mechanical performance.

The smaller length scales associated with nanotubes will also create differences in comparison with traditional composites. For ceramic composites with micron-sized carbon or ceramic fibers, the interface properties are typically controlled with a layer of pyrolytic carbon or boron nitride that is at least several hundred nanometers thick. An analogous, proportionally sized layer for CNTs would potentially involve control of nanotube-matrix bonding at or near the atomic length scale. It is also important to note that work done to date has utilized both single- and multi-walled nanotubes with a variety of different structures, with the choice of CNT material often dictated by availability or processing considerations. For example, in situ methods based on CVD at moderate temperatures typically produce

multiwalled nanotubes with a relatively disordered structure. It is not yet clear how these different nanotube structures will affect mechanical behavior, and processing issues associated with both nanotube degradation and interfacial bonding are likely to depend, at least in part, on the structure of the nanotubes. Properties that do not rely on high synergy between the matrix and CNTs, such as electrical conductivity, have already shown notable enhancements. The synergy attending other electromagnetic behaviors in CNT-metal systems is encouraging, but not yet fully studied.

Conclusion

In summary, CNT-based composite systems continue to hold promise but with significant challenges to real success. Given the costs of the materials and processes involved, it is not sufficient to obtain marginal improvements in properties over traditional micron-scale composites or virgin matrices. Yet, with few exceptions, notable enhancements have not been observed. The traditional interplay of careful processing and evaluation, coupled with mechanistic assessment of properties, remains a valid paradigm at the nanoscale and should be assiduously applied to future research in CNT-composite systems. MT

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