Integration of Carbon and Boron Nitride Nanotubes into Ceramic Materials

S. Lin[1], B. Simard*[1], K. Bosnick[2], M. O'Toole[2], A. Merati[3], M. Bielawski[3], J. Lo[4], R. Zhang[4], D. Walsh[4] and M. Bolduc[5]

[1]Security and Disruptive Technologies Portfolio, National Research Council Canada. Ottawa, ON, Canada, K1A 0R6.
[2]National Institute for Nanotechnology, National Research Council Canada, Edmonton AB, Canada, T6G 2M9
[3]Aerospace Portfolio, National Research Council Canada. Ottawa, ON, Canada, K1A 0R6
[4] CanmetMATERIALS, Natural Resources Canada, Hamilton, ON, Canada, L8P 0A1.
[5]DRDC-Valcartier, Quebec, QC, Canada, G3J 1X5

INTRODUCTION

Carbon nanotube (CNT) can be conceptualized as a rolled-up sheet of one (or more)-atom-thick layer of graphite, i.e. graphene. Owing to their extraordinary mechanical properties, e.g., tensile strength of up to ~100 GPa, CNTs find applications as additives to various structural materials, such as ceramics. The CNT-reinforced ceramics are capable of overcoming ceramic's intrinsic brittleness and relatively low fracture toughness by absorbing energy over a large area, and consequently increase the ballistic performance of the ceramic plate.

Over the past decade, varying degrees of improvements in the mechanical properties of the ceramic were reported, attributable to many factors such as the purity of the CNTs, the functionalization of the CNTs, the processing method of the CNT/ceramic composite, as well as the sintering method for the composite. Recent work by Weibel group (1) showed that when multi-walled carbon nanotubes (MWCNTs) were covalently functionalized with nitric acid, no mechanical reinforcement of Al_2O_3 was observed; whereas non-covalent functionalization of MWCNTs with gum arabic (GA), a water soluble polysaccharide, resulted in ~10% improvement in fracture toughness of Al_2O_3. Similar work done by Inam (2) showed that when MWCNTs were non-covalently functionalized with a mixture of two surfactants, GA and sodium dodecyl sulphate (SDS), a fracture toughness of 4.8 $MPa/m^{1/2}$ was obtained for the 1 wt% MWCNTs/Al_2O_3 compared to 3.1 $MPa/m^{1/2}$ for the pure alumina. Puchya, et al (3) reported the increase of indentation fracture toughness from 3.24 to 4.14 $MPa/m^{1/2}$ when 5% MWCNTs was ball milled with Al_2O_3 nanopowder and densified by Spark Plasma Sintering (SPS). High purity alumina–MWCNT composites were prepared (4) by an aqueous sol–gel processing route, consolidated by a combination of pressureless sintering (PS) and hot isostatic pressing (HIP). The MWCNTs/Al_2O_3 composite achieved a fracture toughness of 5.5 $MPa/m^{1/2}$.

Boron nitride nanotubes (BNNTs) are isoelectronic and structurally analogous to CNTs. BNNTs possess comparable mechanical properties to CNTs, which makes BNNTs a viable candidate for reinforcing various matrices such as ceramics. However, there have been far fewer publications on BNNTs/ceramic composites over the past decade when compared with the CNTs/ceramic counterparts, partly due to the shortage of substantial amount of BNNTs needed for composite studies. The National Research Council Canada has recently achieved a single day production of 200 g few-walled BNNTs (5). The as-produced BNNTs can be purified relatively easily as compared to SWCNTs, which is beneficial to the synthesis of high quality BNNTs/ceramic composites.

Notable improvements in mechanical properties on BNNTs-reinforced Al_2O_3 were reported by Wei-Li Wang, et al (6, 7). Compared to monolithic Al_2O_3, 2.0 wt% of hot pressed BNNTs/Al_2O_3 exhibited a bending strength increase of 67%, and the addition of 1.0 wt% of BNNTs led to a fracture toughness increase by 31%.

Another approach that can contribute to improved ceramic properties is by reinforcing ceramic matrix with ceramic fiber in the form of a 2-D mat. Typically, the 2-D mats are manually layered with ceramic powder between the layers and hot pressed. In this case, the fabric layers act as crack arresting barriers, resulting in increased fracture resistance of the composite ceramic. The next step would be to coat fiber mats with CNTs in order to create a 3-D reinforcement.

In the present work, various synthesis parameters such as nanotube loadings, functionalization methods, and filler/matrix integration methods for SWCNTs/Al_2O_3 and BNNTs/Al_2O_3 composites have been explored. The synthesized composite materials were sintered either by PS or hot pressing (HP), followed by mechanical characterizations. Preliminary results were reported in Ref (8) and Ref (9). Herein we report the latest developments on these composites as well as 3-D CNT-coated alumina fiber reinforcements.

EXPERIMENTAL

The SWCNTs and BNNTs were produced in-house either by a double laser (10) or RF-plasma production system (11, 5). The as-received Al_2O_3 powder (99.7% pure, Accumet Materials) has a grain size of ~200 µm due to the built-in binder, but the grain size reduces to ~200 nm after the Al_2O_3 is suspended in water. $NaBH_4$, $AlCl_3$ and NH_4OH were purchased from Aldrich and used as received. Polyvinyl alcohol (PVA) was purchased from DuPont (Elvanol 50-42) and used as-received. Ball milling of the composite powders was done by using a US Stoneware ball mill (model 755 RMV) with stainless steel balls at medium rotating speed.

Synthesis of SWCNTs/Al_2O_3 Composites

Details on the syntheses of SWCNT/Al_2O_3 composites have been reported in Ref (9). Briefly, in order to achieve a uniform dispersion and effective interface between the filler and the ceramic matrix, SWCNT/Al_2O_3 composites were synthesized in a three-step process: 1) covalent functionalization of SWCNTs with OH groups via ozonolysis followed by sodium borohydride reduction, or non-covalent functionalization using PVA as a surfactant; 2) coating a layer of *in-*

situ Al_2O_3 onto these functionalized SWCNTs, and 3) integration of the Al_2O_3(*in-situ*)-coated SWCNTs with commercial Al_2O_3 matrix either by solution processing or by ball milling.

Synthesis of BNNTs/Al_2O_3 Composites

The BNNTs/Al_2O_3 composites were synthesized by solution processing. First, BNNTs were suspended in H_2O and tip-sonicated for 30 min, and added into an aqueous suspension of pre-sonicated Al_2O_3, and then the resulted mixture was mechanically stirred until a homogeneous composite was achieved. The results of the mixing process were assessed by SEM. The final product was centrifuged, decanted and washed with distilled water. The washing and centrifuging were repeated 3 times, and the collected product was dried in the oven at 110^{o}C and ground using a ceramic grinder.

Fabrication of Vertically Grown MWCNTs on Al_2O_3 Fiber Mats

As illustrated in Figure 1, MWCNTs were vertically grown on alumina fiber mats by a modified catalytic chemical vapour deposition (CCVD) method (12a, b). Firstly, the alumina mats were briefly treated with the catalyst precursor iron nitrate (Fe^{3+}), air dried, then vertically hung with high temperature nickel wire on a quartz fixture and loaded into the CVD reactor. Secondly, the $Fe(NO_3)_3$ was reduced to Fe^0 by passing 25% hydrogen in argon through the treated (stained) mats at 650^{o}C for 90 minutes. Finally, the carbon source for the MWCNTs (7% ethylene) was introduced into the gas flow for 20 minutes, and the growth of MWCNTs was catalyzed by the *in-situ* generated Fe^0.

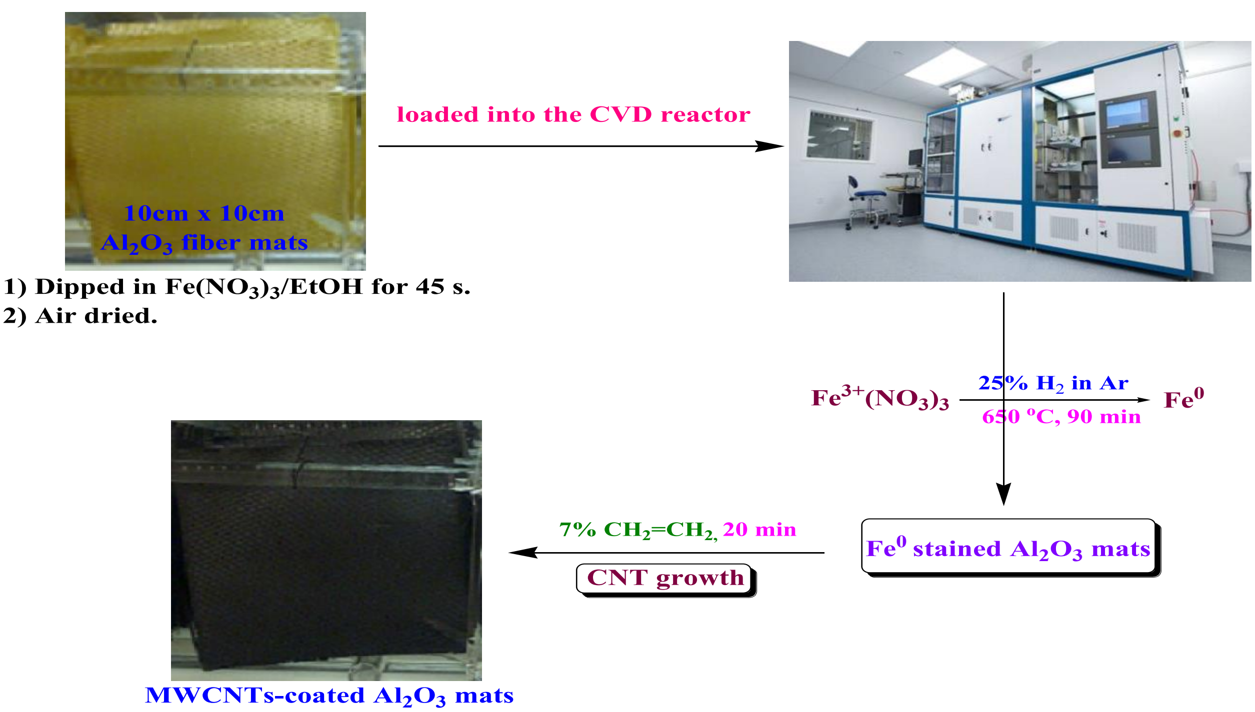

Figure 1 - Vertically grown MWCNTs on Al_2O_3 fiber mat

Hot Pressing and Pressureless Sintering

The synthesized $SWCNTs/Al_2O_3$ and $BNNTs/Al_2O_3$ composite powders were consolidated by HP, or PS, and in some cases followed by HIP. The experimental details were described in Ref (9). The MWCNT-coated Al_2O_3 fibers in Al_2O_3 matrix (3-D reinforcements) were sintered in a hot press at 1500 ^oC and 42 MPa.

RESULTS AND DISCUSSION

3-D Alumina Fiber Reinforcement

As shown in Figure 2(a, b), very pure MWCNTs were homogeneously grown on alumina fiber mats by CCVD. The MWCNT-coated mats were used as a reinforcement for the alumina matrix, and the hot pressed 3-D MWCNT-Al_2O_3(fiber)/Al_2O_3(matrix) coupons showed remarkable simultaneous increase of both the hardness (15%) and the fracture toughness (70%) as compared to pure alumina, which could bode well for the ballistic properties of the ceramic plates. However, these preliminary results need to be confirmed in more experiments and the toughening mechanism fully understood. This work is underway and more detailed results will be reported elsewhere.

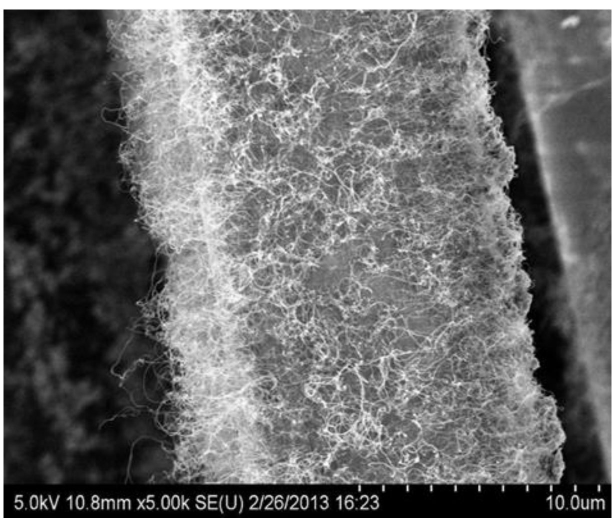

Figure 2a - MWCNTs grown on Al_2O_3 fiber mat

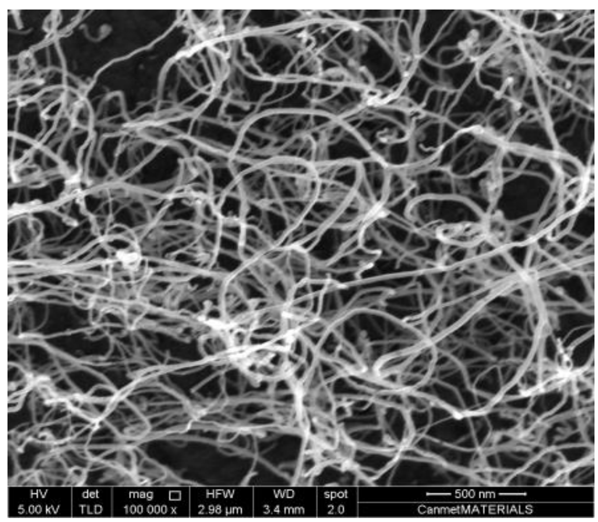

Figure 2b – Enlarge view of the MWCNTs

$SWCNTs/Al_2O_3$ Composites

Carbon nanotubes tend to stay in bundles due to Van der Waals attraction forces, which render them difficult to be dispersed in virtually any solvents. To facilitate the dispersion, the SWCNTs were either covalently functionalized with OH groups or wrapped non-covalently with PVA molecules. Figure 3a shows that covalent functionalization of SWCNTs with OH groups resulted in a stable dispersion in H_2O for 2+ months. Raman spectroscopy was used to study symmetrical covalent C=C bonds in CNTs. The D-band at ~1290 cm^{-1} reflects the disorder of the

CNTs structure, which can be caused by a number of factors, such as defects on the nanotubes, the presence of amorphous carbon, or chemical functionalization. It can be used to qualitatively calculate the degree of functionalization. Figure 3b depicts that both covalent functionalization with OH groups and non-covalent functionalization with PVA increase the D-band of the SWCNTs, which suggests that the surface of the nanotubes has been modified in both cases.

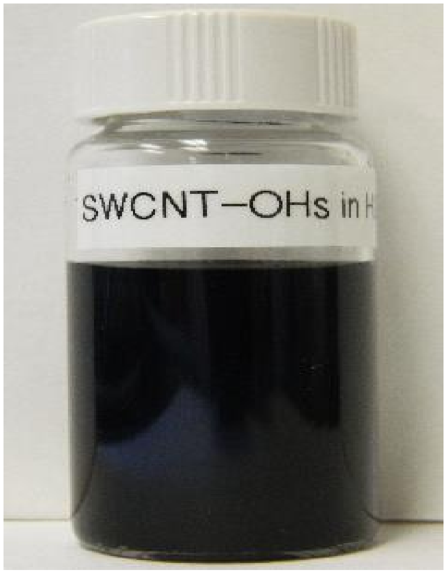

Figure 3a – OH-functionalized SWCNTs in H_2O after 2+ months

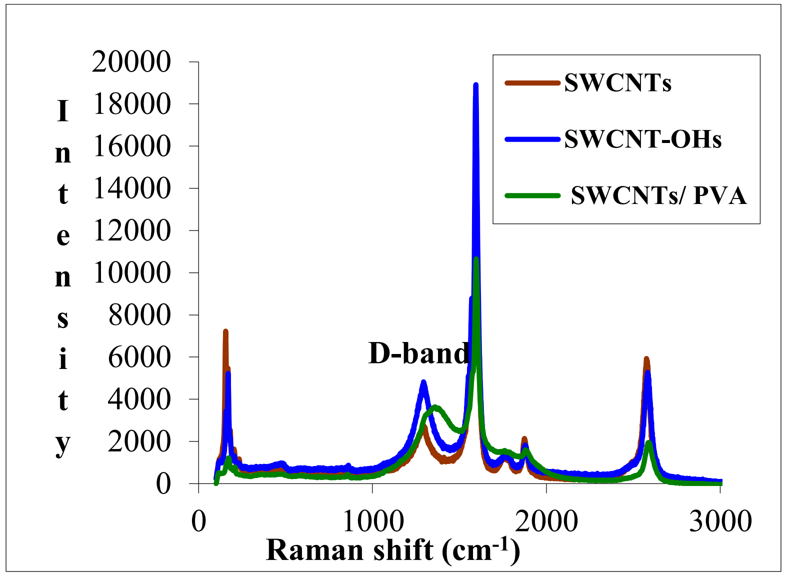

Figure 3b – Raman spectra of SWCNTs, SWCNT-OHs, and SWCNTs/PVA

The SWCNTs/Al_2O_3 composites with SWCNT loads 1-10 wt% were synthesized and mechanically evaluated. Previous results (9) from both PS and HP indicated that 5 wt% and 10 wt% SWCNT loadings resulted in softer coupons and lower fracture toughness, owing to the elasticity of the nanotubes and the increasing difficulty in dispersion with higher nanotube concentrations. Therefore, the 1 wt% loading samples have been the focus of recent studies. Table I shows that for the 1 wt% covalently functionalized samples, ball milling integration produced higher Vickers hardness as well as fracture toughness compared to those of pure Al_2O_3, whereas solution processing resulted in lower values for both the hardness and the fracture toughness. This suggests that the method for the integration of the filler with the matrix plays an important role in the mechanical properties of the composites. Figure 4a demonstrates that solution processing resulted in a more homogeneous dispersion of SWCNTs along the Al_2O_3 grain boundaries. However, when the cracks in the matrix are sufficiently large, the well-dispersed nanotubes from solution processing become inadequate in terms of gap bridging, and the nanotube clusters from ball milling (Figure 4b) seem to work more efficiently, therefore better fracture toughness was observed.

Table I – Vickers Hardness and Chevron Notch Toughness of the hot-pressed SWCNTs/Al_2O_3 Composites

Sample	Vickers hardness—HV1/15 (GPa)	Chevron notch toughness ($MPa.m^{1/2}$)

Al_2O_3	15.57	3.83
1 wt% SWCNT-O-Al_2O_3(BM)	17.49	4.00
1 wt% SWCNT-O-Al_2O_3(SP)	14.40	3.12

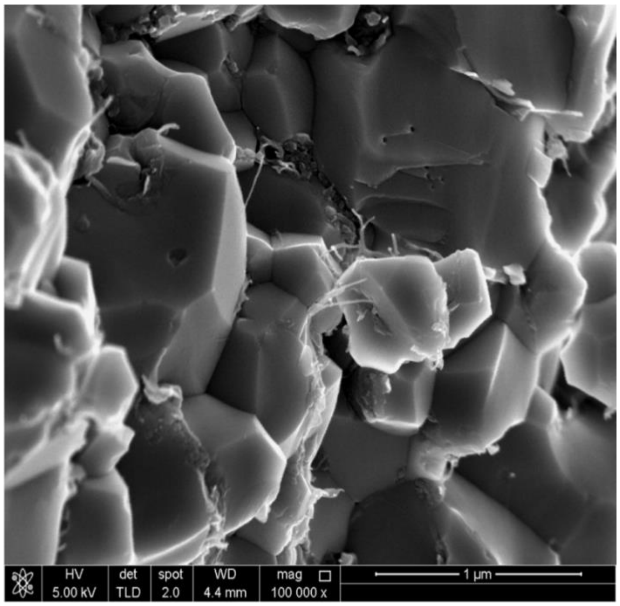

Figure 4a – Hot-pressed 1wt% SWCNT-O-Al_2O_3(SP)

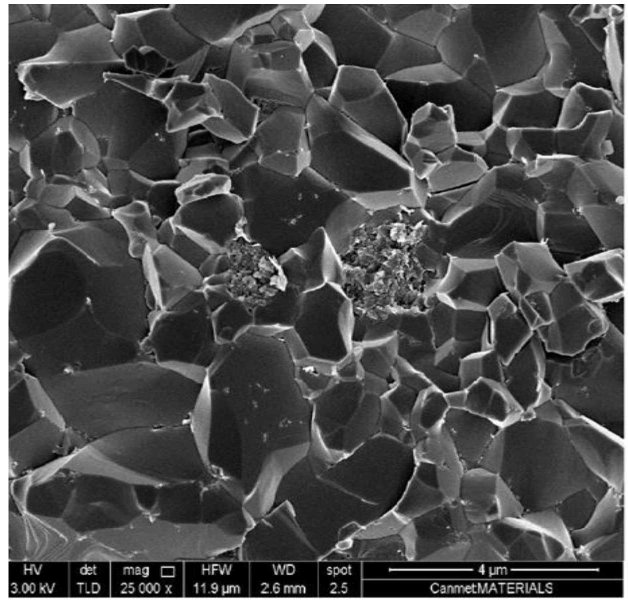

Figure 4b – Hot-pressed 1wt% SWCNT-O-Al_2O_3(BM)

BNNTs/Al_2O_3 Composites

As depicted in Figure 5a, the in-house produced BNNTs have a high degree of purity, and they reside along the alumina grain boundaries in the composite (Figure 5b).

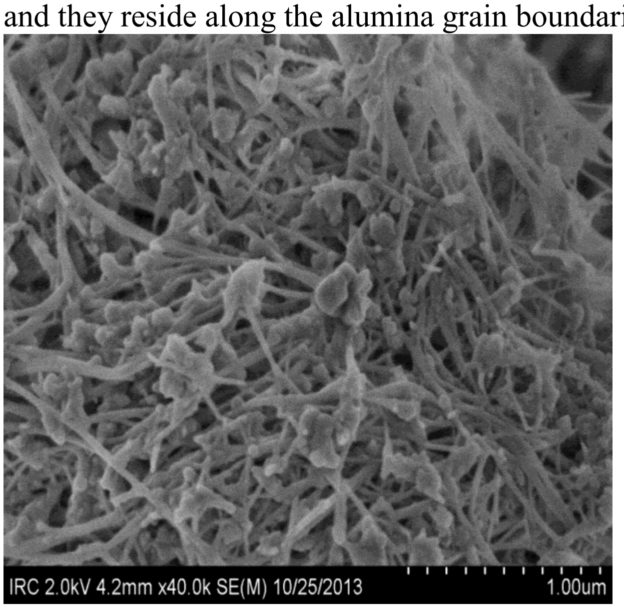

Figure 5a – Purified BNNTs

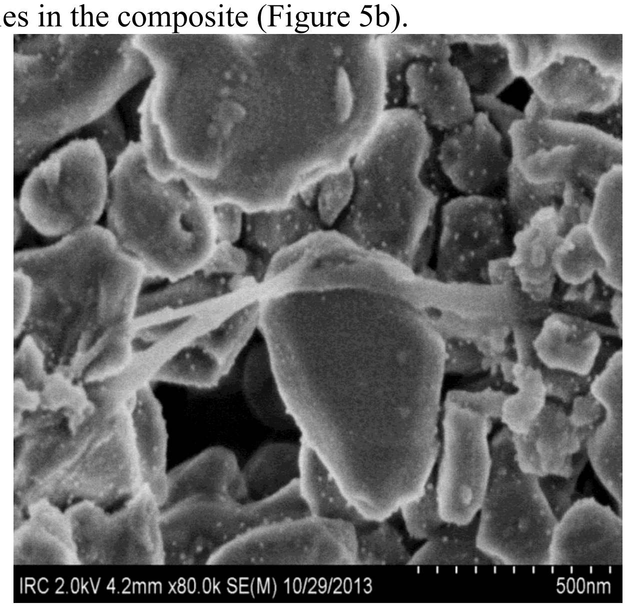

Figure 5b – 1wt% BNNT/Al_2O_3(SP)

Table II shows that 1wt% BNNTs(purified)/Al_2O_3 composite by solution processing has an 8% increase in Vickers hardness and moderate improvement in fracture toughness, compared to pure Al_2O_3. For comparison purposes, a sample with the same composition is currently being made by shear mixing, on the consideration that residual chemicals and solvents trapped in the open-ended BNNTs during the solution processing might have affected the mechanical properties of the composite.

Table II – Vickers Hardness and Chevron Notch Toughness of the hot-pressed BNNTs/Al_2O_3 Composite

Sample	Vickers hardness—HV1/15 (GPa)	Chevron notch toughness ($MPa.m^{1/2}$)
Al_2O_3	15.57	3.83
1 wt% BNNTs/Al_2O_3(SP)	16.83	3.96

CONCLUSIONS

Close to 30 batches of SWCNTs/Al_2O_3 composites with 1~10wt% SWCNT loadings and various sample sizes have been synthesized and sintered by PS and HP, followed by mechanical evaluations. It was found that 1 wt% composites gave better hardness and fracture toughness than 5 wt% and 10 wt% composites. Integration of the surface modified SWCNTs with the Al_2O_3 matrix by ball milling led to better mechanical results than by solution processing. A batch of 1 wt%, 3.5 kg SWCNT-O-Al_2O_3(*in-situ*+commercial) will be subject to HP and ballistic testing shortly.

1 wt% BNNTs/Al_2O_3 composite by solution processing gave an 8% increase in Vickers hardness and moderate improvement in fracture toughness, compared to pure Al_2O_3. The making of a 1 wt% BNNTs/Al_2O_3 composite by shear mixing is currently underway.

Remarkable improvements in the hardness and the fracture toughness have been observed for the 3-D MWCNT-Al_2O_3(fiber)/Al_2O_3(matrix) composite ceramics. Detailed examination is underway and the results will be reported elsewhere.

REFERENCES

1. A. Kasperski, A. Weibel, C. Estourne`s, C. Laurent, and A. Peigney. "Multi-walled carbon nanotube–Al_2O_3 composites: Covalent or non-covalent functionalization for mechanical reinforcement", Scripta Materialia, 75, 2014, 46–49.

2. F. Inam, A. Heaton, P. Brown, T. Peijc, M. J. Reece, "Effects of dispersion surfactants on the properties of ceramic–carbon nanotube (CNT) nanocomposites". Ceramics International, 40, 2014, 511–516.
3. V. Puchya, P. Hvizdosa, J. Duszaa, F. Kovaca, F. Inam, M. J. Reece, "Wear resistance of Al_2O_3–CNT ceramic nanocomposites at room and high temperatures". Ceramics International, 39, 2013, 5821–5826.
4. S. Rani, I. Reeta, M. Francis, N. V. Jaya, A. Kumar, "Processing and properties of sol gel derived alumina–carbon nanotube composites". Ceramics International, 38, 2012, 4065–4074.
5. K. S. Kim, C. T. Kingston, A. Hrdina, M. B. Jakubinek, J. Guan, M. Plunkett, and B. Simard, "Hydrogen-Catalyzed, Pilot-Scale Production of Small-Diameter Boron Nitride Nanotubes and Their Macroscopic Assemblies". ACS Nano, 2014, 8, 6211–6220.
6. W. Wang, J. Bi, S. Wang, K. Sun, M. Du, N. Long, Y. Bai, "Microstructure and mechanical properties of alumina ceramics reinforced by boron nitride nanotubes". J. Eur. Ceram. Soc. 31, 2011, 2277–2284.
7. W. Wang, J. Bi, K. Sun, M. Du, N. Long, and Y. Bai, "Fabrication of Alumina Ceramic Reinforced with Boron Nitride Nanotubes with Improved Mechanical Properties" J. Am. Ceram. Soc., 94, 2011, 3636–3640 .
8. M. Bolduc, S. Lin, J. W. Guan, B. Simard, M. Bielawski, J. Lo, P. Au, "Exploration of Nano-Composite Ceramic Materials Concept for Ballistic Application", Proceedings (CD) of Personal Armour Systems Symposium PASS 2012, 31 May - 1 June, 2012, Furth, Germany.
9. S. Lin, J. Guan, B. Simard, D. Morphy, M. Bielawski, P. Au, J. Lo, M. Bolduc, "Development of SWCNTs/Al_2O_3 Composites for Ballistic Applications". Proceedings of the 19th International Conference on Composite Materials. July 28 – August 2, 2013. Montreal, Canada.
10. C. T. Kingston, Z. J. Jakubek, S. Denommee, B. Simard, "Efficient laser synthesis of single-walled carbon nanotubes through laser heating of the condensing vaporization plume". Carbon, 42, 2004, 1657–1664.
11. K. S. Kim, G. Cota-Sanchez, C. T. Kingston, M. Imris, B. Simard, and G. Soucy, "Large-scale production of single-walled carbon nanotubes by induction thermal plasma". J. Phys. D: Appl. Phys., 40, 2007, 2375–2387.
12. a) K. Bosnick, L. Dai, "Growth Kinetics in a Large-Bore Vertically Aligned Carbon Nanotube Film Deposition Process", J Phys Chem C 114, 2010, 7226. b) L. Dai, P. Wang, K. Bosnick, "Large-scale production and metrology of vertically aligned carbon nanotube films", JVSTA, 27, 2009, 1071.