



A REVIEW ON CARBON NANOTUBES REINFORCED CERAMIC COMPOSITE

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ABSTRACT

This review looks at carbon nanotubes (CNT) capabilities as toughening agent in ceramic composite. CNT have exceptional mechanical strength of up to 60 GPa and stiffness of 1 TPa. Ceramic however is hard, brittle and lack of toughness. CNT were found to be capable to provide up to 173% improvement in fracture toughness of ceramic with 19 vol.% CNT. The degree of toughness improvement on CNT ceramic composite is dependent on the following parameters; i) CNT homogenous dispersion in the composite, ii) inter-wall and interfacial strength between CNT and ceramic, iii) method of producing the CNT ceramic composite, and iv) the resultant toughening mechanisms.

Keywords: Carbon Nanotubes • Fracture Toughness • Ceramic Composite •

INTRODUCTION

Carbon nanotubes (CNT) have exceptional mechanical properties due to its defect free crystal arrangement. Its stiffness reaches as high as 1 TPa and tensile strength of up to 60 GPa [1-4]. It has excellent thermal conductivity of up to 3000 W/m.K and unique electrical conductivity characteristic. CNT can be as metallic or semiconductor material depending on its dimension and crystal structure arrangement [5-7]. Due to its outstanding properties, it has been widely research in application ranging from structural, electronics and energy management [8-11].

One of the particular interests is on exploiting CNT as reinforcement to ceramic materials to improve ceramic's toughness. Ceramic has been widely used in application where high strength, thermal and chemical stability are merited such as thermal protection coating [12]. In general, ceramic tends to have extreme hardness (of up to 100 GPa) [13] due to its strong atomic bond crystal structure which comes in the expense of brittleness and low fracture toughness (Fig. 1). This makes them susceptible to failure upon impact. This report will look into reinforcing ceramic with CNT in aiming to create a relatively hard but tough ceramic composite.

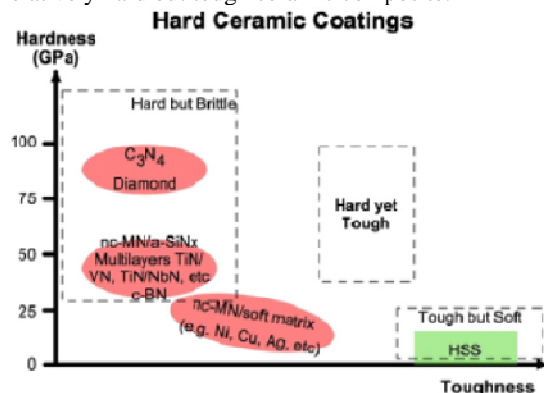


Fig. 1: Schematic status of hardness and toughness of current hard ceramic materials, after [13].

This report begins by providing information about the history of CNT. The properties of CNT in comparison with other materials are presented in the next section. The synthesis process of the CNT is presented in the following section. A case study on CNT reinforced ceramic composite is presented along with discussion on the CNT functionality as a mechanism in improving the toughness of ceramic. Critical criteria for successful CNT reinforced ceramic composite are also discussed. The report is concluded by highlighting the key main features of CNT as reinforcement in ceramic composite.

CARBON NANOTUBES (CNT)

Carbon nanotubes (CNT) characteristics

CNT are accidentally found by Ijima in 1991 [14]. It has been discovered during an attempt to produce carbon C60 and fullerene from arc evaporation of graphite. Upon observation of deposited carbon product on the graphite under HRTEM, Ijima discovers new form of carbon consists of multiple long slender graphene cylinder tube with diameter of about 10 nm with an end cape structurally-like fullerene. The schematic view of the arrangement is shown in Fig. 2. CNT are consisted of fullerene end cap and graphene cylindrical wall [15].

The 3 different arrangements between graphene and fullerene cap will determine the properties of the CNT. The armchair arrangement is recognised by having the fullerene-like cap to be attached to the graphene cylinder along the five-fold axis. The zigzag arrangement CNT is combines the fullerene cap and the graphene cylinder along the three-fold axis. The final arrangement of CNT is the combination of the fullerene cap with the helical arrangement of the graphene cylinder which is being called chiral structure [15].



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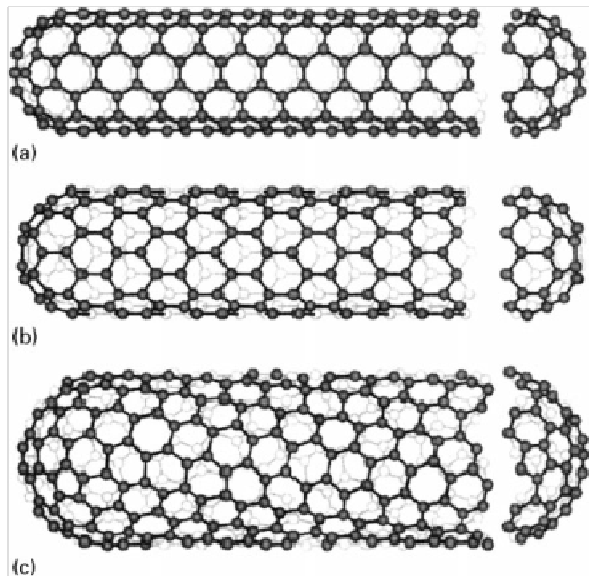


Fig. 2: Three classes of CNT structure; a) armchair, b) zigzag, and c) chiral arrangements, after [15].

CNT can be in either multiwalled carbon nanotubes (MWNT) or single-walled carbon nanotubes (SWNT) [16]. MWNT is assembled from multiple concentric graphene cylinders while SWNT consists of a single layer of graphene cylinder. **Fig. 3** shows the cross-sectional micrograph image of MWNT showing its construction made of the multiple graphene cylinders with attached fullerene end cap.

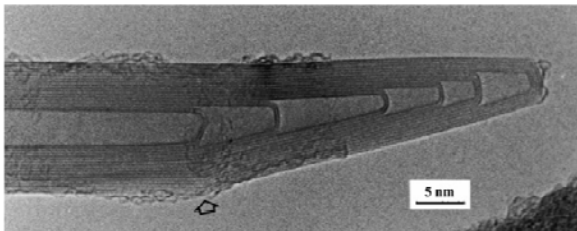


Fig. 3: High resolution transmission electron microscopy (HRTEM) image of typical construction of MWNT consists of fullerene end cap and multiple concentric graphene cylinders, after [15].

Micrograph image of SWNT is shown in Fig. 4. Due to the small diameter (few nm) of SWNT, it tends to be tangled and collected together to form rope-like structures (**Fig. 4a**). It also tends to get into loops and curled shape (**Fig. 4b**). Diameter of CNT can be found from 1 nm to 50 nm ranges and the length ranges from few nm to few μm [2, 7, 17 & 18]. The length to diameter ratio usually in few thousands factor [2, 7, 17 & 18].

Table 1 shows the comparison of CNT properties with other materials. It can be seen that CNT has tensile strength of more than 10 times greater than that of steel. At the same time it has the benefit of low density of about 1 to 2 g/cm^3 , which is similar to the density of carbon fibre

[2, 7 & 19]. The stiffness of CNT is about 5 times higher of steel and carbon fibre [2, 7 & 19].

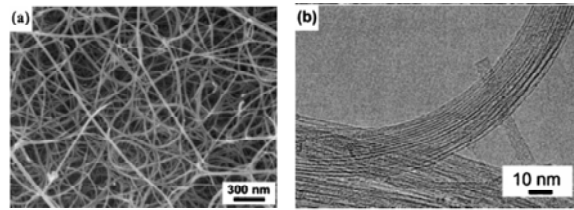


Fig. 4: a) Secondary electron microscopy (SEM) low magnification image, and b) HRTEM image of SWNT showing curled and tangled rope shaped, after [15].

Table 1: Comparison of mechanical properties of CNT with other materials, reproduced after [19].

Material	Stiffness (GPa)	Tensile strength (GPa)	Density (g/cm^3)
Carbon nanotubes	1000	10-60	1.3-2
Steel	208	0.4	7.8
Carbon fibre	200-960	1.7-3.3	1.7-2.2
Epoxy	3.5	0.005	1.25
Wood	16	0.008	0.6

Carbon nanotubes (CNT) synthesis

There are 2 ways of producing CNT. The first method is by arc evaporation method as conducted by Iijima [14] and the second method is by catalytic method [20-22]. For the arc evaporation method, it is reported in [23] that current of about 50 amps is applied between graphite electrodes in helium environments to evaporate the graphite. CNT are produced as its condensing on the cathode electrode. SWNT is produced with addition of Co and Ni metal is added on the graphite anode electrode [19].

Catalytic method is conducted by decomposition of hydrocarbon [20-22] over catalyst made of nano-sized Fe, Co or Ni metal particles. The metal acts as decomposition agent for the hydrocarbon. The breakdown turns the gaseous molecules into carbon, and subsequently produces CNT. Catalytic method produced CNT with more defects compare to arc evaporation. The defects however can be reduced by heat treated the CNT [24].

The cost of CNT is about \$100 to \$500 per gram depending on the type of CNT, its fabrication route and purification [15]. The cost of producing SWNT is about twice more than the MWNT due to the stringent requirement for its purification [15]. The impurities in CNT are made up of metal particles and amorphous carbon. The CNT purity normally to be in the region of 5-10% purity [19]. The purification methods of CNT as presented in [25] and can be done by the following



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processes; air oxidation, acid refluxing and surfactant aided sonication, filtration and annealing.

HARD AND TOUGH CERAMIC

Ceramic has exceptional thermal stability with melting temperature between 1000°C to 2000°C [12]. Its application however is limited to low impact applications [13] due to its relatively small amount of energy absorption capability upon impact. One way of achieving a hard but tough ceramic material is through the implementation of reinforced ceramic composite. Engineering ceramic such as alumina (Al_2O_3) and zirconia (ZrO_2) have been used on advanced high performance structures for few different applications. It is of particular interest to increase the ceramics toughness through the introduction of CNT reinforcement as ceramic matrix composite.

Carbon nanotubes (CNT) ceramic composite

There are 2 common ways of producing CNT ceramic composite. They are either by spark plasma sintering (SPS) or hot pressing method. Hot pressing of ceramic powder mixed with CNT is the most common method to produce CNT ceramic composite. Hot-pressing is mostly applied in the pressure range of 20–40 MPa and at temperatures of 1300–2000 °C [26, 27].

The process of producing CNT ceramic composite starts with mixing the ceramic powder with CNT. Some of the mixing techniques used are ultrasonic in ethanol and milling process (Fig. 5) [26]. The aim is to produce a reasonably homogeneous dispersion of CNT amongst the ceramic powder without damaging the CNT. In some cases, CNT are grown on the ceramic by having metal catalyst to be part of the ceramic powder [20-22]. The subsequent step is forming the mixture by applying pressure of about 20-40 MPa. At the same time heat is supply to the mixture to sinter the ceramic at temperature in between 1000-1900°C [26]. In some cases, the heat does damage the CNT thus reducing its mechanical strength [26].

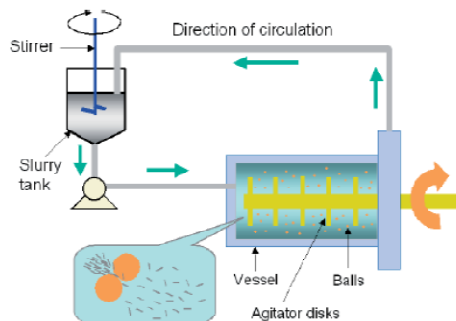


Fig. 5: Schematic view of dispersing MWNT in colloidal silica during attrition mill, after [26].

SPS is a process of using spark plasma as a source of heat to sinter the mixed CNT ceramic powder. The spark is generated between the gaps in the mixture by an instantaneous pulse of direct current (dc) applied through graphite die. The dc pulse parameters as reported

in [27] are pulse duration of 2 ms, interval between pulses 2 ms, maximum pulse current of 5,000 A, and voltage of 10V. The advantage of spark plasma sintering method is the temperature needed to sinter the ceramic powder is at lower temperature compare to the hot pressing method. The sintering temperature is about 1000-1800 °C with pressure of 40-60 MPa [27].

Fig. 6 shows stiffness comparison between 2 CNT ceramic composite produced by hot pressing and SPS method [28]. It can be seen that stiffness of CNT ceramic composite produced by SPS is 3 times higher than the hot pressed composite and with higher composite density. The reduction of the modulus of elasticity is coming from the damaged CNT sintered at higher temperature during the hot pressing method. Higher densification of the composite is also achieved by SPS method with undamaged CNT is distributed around the grain boundaries (Fig. 7).

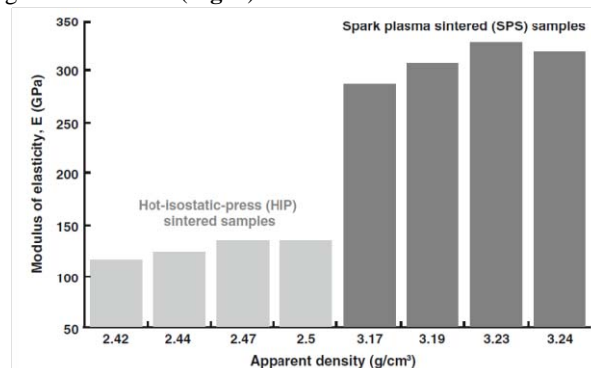


Fig. 6: Modulus of elasticity as a function of apparent density for Si_3N_4 composite containing 6 wt% MWNT produced by hot pressing and spark plasma sintering method, after [28].

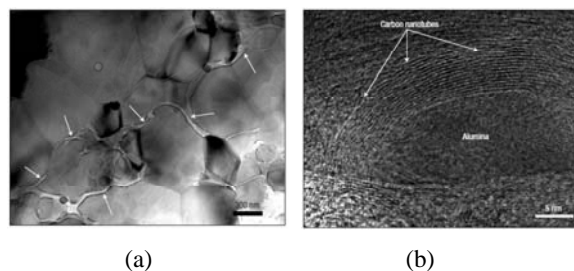


Fig. 7: SWNT morphology in 5.7 vol.% SWNT Al_2O_3 composite produced from SPS method, transmission electron microscopy (TEM) images; a) bright-field TEM image, and b) HRTEM; the arrows indicate the SWNT phase, after [29].

Toughness improvement

Sun et al. [30] studied yttria stabilized tetragonal polycrystalline zirconia (3Y-TZP) ceramic composite with 0.1–1 wt.% of MWNT and SWNT using SPS synthesis method. It was found that the hardness value of the composite is decreasing with the amount of CNT in the composite. The fracture toughness found is similar to non-CNT reinforced 3Y-TZP for the case of 0.5 wt.% MWNT



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3Y-TZP composite. The fracture toughness of the composite however decreased to $4.47 \text{ MPa}\cdot\text{m}^{1/2}$ as the MWNT content raised to 1.0 wt.%. Similar behaviour is also observed for SWNT 3Y-TZP composite. No improvement on the mechanical properties of 3Y-TZP is observed for 0.5 wt.% SWNT 3Y-TZP composite. The observation is confirmed by Ukai et al. [31] and Duszová et al. [32] on CNT reinforced zirconia composite (**Fig. 8**).

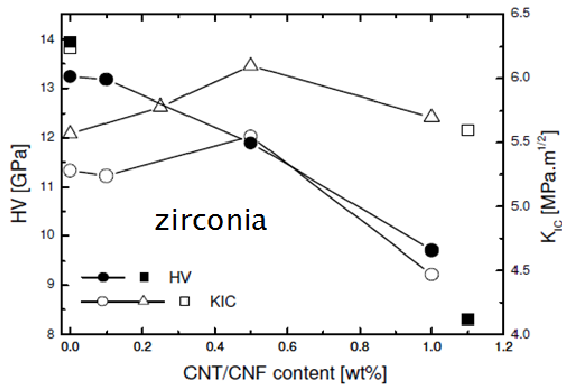


Fig. 8: Influence of the CNT addition on the Vickers hardness and fracture toughness of zirconia based composite, after Sun et al. [30] (circles), Ukai et al. [31] (triangles), and Duszová et al. [32] (squares).

It is found from the micrograph images of the composite (**Fig. 9**) that cluster of accumulation of SWNT at the 3Y-TZP grain boundary contribute to the reduction of mechanical properties. Rather than acting as reinforcement to the ceramic, the agglomerated CNT weaken the composite. The weak bonding between SWNT with the 3Y-TZP along with presence of pores from poor densification of the composite also contributes to the reduction in mechanical properties.

CNT Al_2O_3 composite synthesised using SPS method is studied by [29] containing up to 10 vol.% SWNT. The work reports that SWNT Al_2O_3 composite has achieved fracture toughness of $9.7 \text{ MPa}\cdot\text{m}^{1/2}$, i.e. three times higher than that of pure alumina ($3.3 \text{ MPa}\cdot\text{m}^{1/2}$) (**Fig. 10**). They have concluded that better sintering process at low temperature using SPS method coupled together with superior SWNT has produces better composite.

Peigney et al. [20] have shown mechanical properties improvement for up to 6.7 vol.% CNT Al_2O_3 ceramic composite produced by using hot pressed technique (**Fig. 10**). $\text{Fe-Al}_2\text{O}_3$ particles are used as a catalyst to grow the CNT on the Al_2O_3 as $\text{CH}_4\text{-H}_2$ mixture decomposed. The CNT produced are a mixture of SWNT and MWNT. The resultant CNT-Fe-Al powder then is hot pressed to from the composite.

The overall improvement on the mechanical properties of the reinforced Al_2O_3 however is disappointing. The fracture strength is slightly higher than Al_2O_3 monolithic ceramic but lower than Fe- Al_2O_3 composite. Similar observation has been found from Flahaut et al. [11] on hot pressed CNT Fe-Al Fe- Al_2O_3 composite. They have concluded that hot pressing

technique at high temperature usually damages the CNT in the composite.

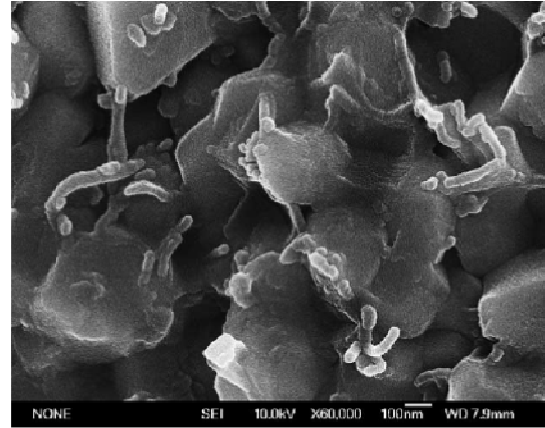


Fig. 9: SEM image of the fractured surface of 0.5 wt.% SWNT 3Y-TZP composite reveals agglomerated bundle of CNT along the ceramic boundaries, after [30].

Siegel et al. [23] however have found increases in fracture toughness of 24% (from 3.4 up to $4.2 \text{ MPa}\cdot\text{m}^{1/2}$) on hot pressed 10 vol.% MWNT Al_2O_3 composite (**Fig. 10**). The reason for different observation as compared to Peigney et al. [20] is that the CNT used in Siegel et al. [23] are produced by arc evaporation method which contain less defect compared to CNT produced by catalytic method.

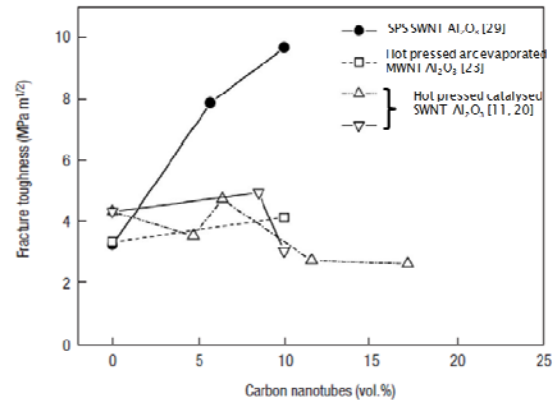


Fig. 10: Fracture toughness variation as a function of nanotubes content, after [29].

DISCUSSION

The introduction of CNT in ceramic matrix is expected to improve the toughness of the hard ceramic through the transfer of energy to the CNT during the fracture process. This section will discuss the mechanisms which contribute to improvement on the fracture toughness in CNT ceramic composite. The main characteristics of the toughening mechanism which will be discussed here are; i) CNT homogenous dispersion, ii) crack bridging and crack deflection, iii) interfacial CNT/ceramic binding and CNT inter wall strength.



CNT homogenous dispersion

The lack of improvement on the fracture toughness of the reinforced composite has been seen coming from the agglomerated CNT in certain location [8]. The issue arises due to difficulties on dispersing the CNT in ceramic. The van der Waals force of CNT and poor solubilisation of CNT causes its clustering in the composite. Uniform dispersion of the CNT can be achieved by ultrasonic dispersion and in-situ growth of CNT on the ceramic [20, 29].

Zhan et al. [29] has reported that by using ethanol ultrasonic bath homogenous mixture of SWNT with alumina ceramic can be achieved. SWNT were initially dispersed in ethanol ultrasonic mixture before alumina was added. The mixture then were sieved using 200 mesh and milled for 24 hours in ethanol using zirconia ball which has shown to preserve the SWNT for any damage. Improvement of fracture toughness is observed as reported earlier. Fig. 11 shows smaller crystal size arrangement in the composite suggests that CNT hinder the grain growth during the sintering. The CNT in the Al₂O₃ CNT were well attached to the alumina grains and were located mainly in the intergranular places [33].

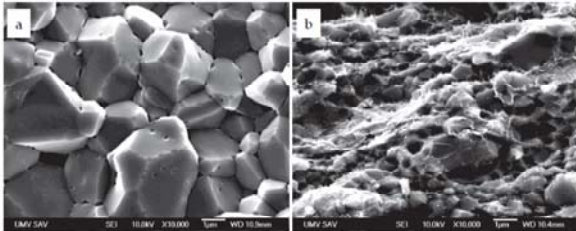


Fig. 11: Fracture surfaces of; a) monolithic Al₂O₃, and b) 3.5 wt.% CNT alumina composite, after [33].

Crack bridging and crack deflection

CNT act as crack deflection site and also holding the crack off during the crack propagation. This increases the toughness of the ceramic through fracture energy dissipation of CNT. A highly oriented MWNT in Al₂O₃ has been successfully produced by Xia et al. [34] using in situ CNT growth method. It is found that the crack is deflected as it travels near the CNT (Fig. 12). CNT also hold the crack off providing toughness improvement. Similar mechanisms of toughening are also observed by Guo et al. [26] comparing monolithic ceramic crack pattern and CNT reinforced ceramic crack pattern of SiO₂ (Fig. 13).

Interfacial CNT/ceramic binding and CNT inter wall strength

The interfacial binding between CNT and ceramic in the composite also contributes to the toughening of the ceramic. The interface binding should provide adequate stress transfer capability during the fracture process. Highly strong interfacial binding will hinder the toughness improvement, while poor binding will weaken its strength. In situ grown CNT on ceramic is

in favour on increasing ceramic toughness due to the anchoring nature of the CNT on the ceramic. The beneficial effect however is hindered by the lower quality CNT produced by catalytic process [20].

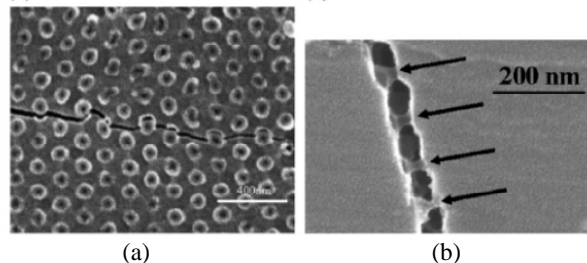


Fig. 12: CNT Al₂O₃ composite; a) top view of as fabricated highly oriented showing deflected crack round CNT, and b) longitudinal view of CNT crack bridging, after [34].

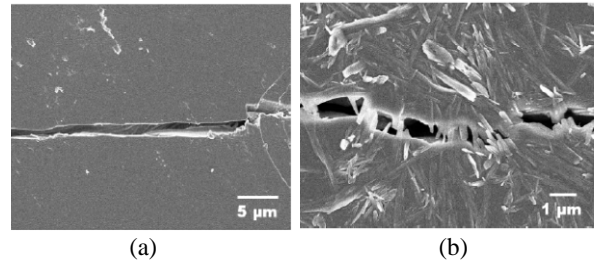


Fig. 13: SEM images of crack propagation; a) the pure SiO₂ compact, and b) 5 vol.% SiO₂ MWCN composite consolidated by SPS, after [26].

Yamamoto et al. [8] has studied the acid treated MWNT Al₂O₃ composite. Defect induced CNT act as an anchor site for the alumina to grow thus increasing bonding between alumina and CNT (Fig. 14). Improvement on fracture toughness of the composite between acid-treated and pristine composite can be seen on Fig. 15. The improvement however is limited to the vol.% of MWNT due to severe segregation of CNT.

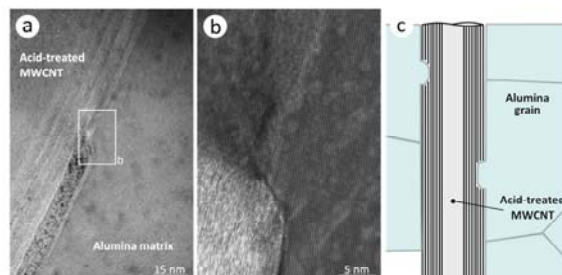


Fig. 14: MWNT morphology in the composite; a) a nano-defect on the acid-treated MWNT is filled up with alumina crystal, b) enlarged TEM image, taken from the square area, and c) schematic description of MWNT morphology in the composite, after [8].

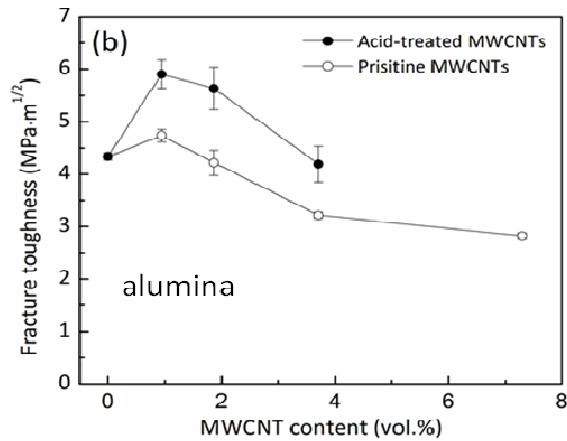


Fig. 15. a) Bending strength, and b) fracture toughness as a function of MWNT content, after [8].

Upon inspection of the fracture surface; it is found that the sword-in-sheath CNT pull out failure on CNT has been observed (**Fig. 16**). The CNT is pulled out from the ceramic but rather than debonding between CNT and ceramic, the debonding occurs in the interlayer between the walls of MWNT in nature like sword-on-sheath. **Fig. 17** shows schematic mechanism of the toughening mechanism of the MWNT. It has suggested that there should be a balance on the interfacial strength of the CNT and ceramic to provide the toughening effect. Yu et al. [4] has described the failure as telescopic mechanism as the CNT are slide past each other during the process. Ideally SWNT is more effective in providing the toughening capability [29].

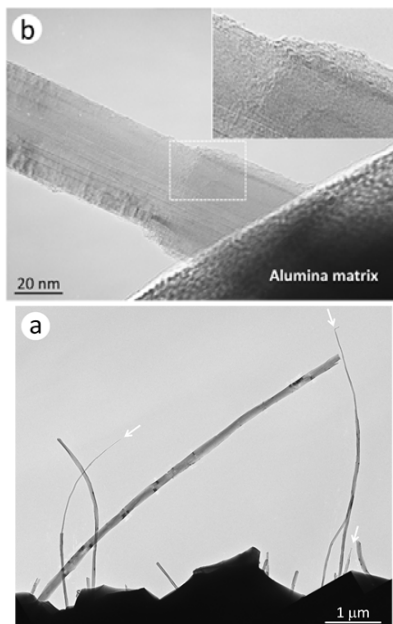


Fig. 16: TEM images of the fracture surface of the composite, a) low, and b) high magnification images, after [8].

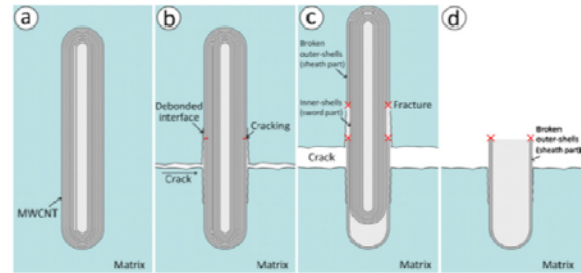


Fig. 17: Schematic description of possible fracture mechanisms of the MWNT; a) initial state of a MWNT, b) tensile stresses lead to matrix crack and partial debonding formation, c & d) failure in the outer shells and the inner core is pulled away, leaving the fragment of the outer shells in the matrix, after [8].

Table 2 shows the comparison between few CNT reinforced Al_2O_3 composite. The general trend is the fracture toughness will be reducing as the CNT content increases. Reduction of fracture toughness up to 36% compared to monolithic ceramic was observed as the CNT content reaches 7 vol.%. This situation has confirmed the difficulty in dispersing the CNT within the ceramic grain. The most improvement made in fracture toughness is 173% on SWNT contents of 19 vol.% with SPS synthesised composite. Superior mechanical properties of SWNT which contains less defect along with less damaging SPS technique has contributed to the improvement. MWNT synthesised by arc evaporation is found to be more effective in providing increase of fracture toughness (24% increases for 10 wt.% CNT content). Acid treatment of CNT also contributes to increase the fracture toughness as the toughness on MWNT acid treated has 28% higher fracture toughness compare to untreated MWNT with the same 10 vol.% CNT content. This suggesting improvement on CNT ceramic bond.

CONCLUSIONS

CNT have been studied to increase the fracture toughness of ceramic materials. The CNT reinforced ceramic composite however show disappointing improvement on the fracture toughness of the ceramic. The following key points are highlighted in ensuring CNT capability in toughening ceramic materials:

- SPS method is a better technique in producing CNT ceramic composite. Almost double improvement of stiffness is observed between hot pressed and SPS technique (from 100 to 300 MPa).
- Homogenous dispersion of CNT is fundamental in having positive effect of the CNT in improving mechanical properties of the ceramic composite by 173% to $9.7 \text{ MPa m}^{1/2}$.
- CNT must be sufficiently bonded to the matrix to act as a load transfer medium during the fracture process.



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Table 2: Comparison on fracture toughness improvement on CNT reinforced Al₂O₃ composite and its associated improvement mechanism.

CNT type	CNT synthesis	CNT content	Composite synthesis	Fracture toughness improvement over monolithic	Comments on improvement mechanism	Ref.
MWNT	catalytic, acid treated	1 vol.%	SPS	37%	acid treated increase CNT/ceramic bonding, agglomerated of CNT as content increases SPS doesn't damaged CNT.	[8]
		2 vol.%		30%		
		4 vol.%		-5%		
MWNT	catalytic, non-acid treated	1 vol.%	SPS	9%	agglomerated of CNT as content increases, SPS doesn't damaged CNT.	[8]
		2 vol.%		-5%		
		4 vol.%		-26%		
		7 vol.%		-35%		
SWNT	catalytic	5 vol.%	SPS	142%	SPS doesn't damaged CNT, superior SWNT compare to MWNT.	[29]
		19 vol.%		173%		
SWNT	catalytic	1.64 wt.%	Hot pressing	-18%	superior SWNT compare to MWNT, hot pressing damaged CNT, agglomerated of CNT as content increases.	[20]
		3.65 wt.%		9%		
		5.79 wt.%		-39%		
		6.71 wt.%		-36%		
MWNT	arc evaporation	10 vol.%	Hot pressing	24%	Arc evaporation provides better CNT.	[23]

- SWNT are preferred than the MWNT in providing the increase in toughness for the ceramic composite. Inter wall MWNT provides little interfacial strength thus provide the point of failure during fracture.
- Toughening mechanisms of CNT on ceramic composite are acted by crack deflection, crack bridging and CNT ceramic interfacial strength and fibre pull out.

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