



Research Signpost  
37/661 (2), Fort P.O.  
Trivandrum-695 023  
Kerala, India

## Review Article

Recent Res. Devel. Mat.Sci., 9 (2012): 45-116 ISBN: 978-81-308-0466-8

# 3. Carbon nanotubes (CNTs) and mechanical properties of $\text{Al}_2\text{O}_3$ and zirconia toughened alumina (ZTA) composites reinforced by them: A review

M.H. Bocanegra-Bernal<sup>1</sup>, A. Aguilar-Elguézabal<sup>1</sup> and J. Echeberria<sup>2</sup>

<sup>1</sup>*Centro de Investigación en Materiales Avanzados, CIMAV S.C., Miguel de Cervantes  
# 120 Complejo Industrial Chihuahua, 31109 Chihuahua, Chihuahua, Mexico*

<sup>2</sup>*CEIT and TECNUN (University of Navarra), 20018 San Sebastian, Spain*

**Abstract.** This review summarises the recent advances reported in the field of carbon nanotube reinforced alumina and zirconia toughened alumina (ZTA) based ceramics. Taking into account the excellent mechanical properties of carbon nanotubes (CNTs) and the current state of research, it is possible the creation of new strong and tough nanocomposite systems. The state of knowledge in processing, nanotube dispersion, characterization, and analysis of nanocomposites is reviewed as the basis for evaluating the toughening mechanisms and mechanical properties. In addition, we discuss the levels of reinforcement that have actually been achieved in order to obtain high functional properties for high end applications. Future work that needs attention is addressed.

Correspondence/Reprint request: MSci. M.H. Bocanegra-Bernal, Centro de Investigación en Materiales Avanzados CIMAV S.C., Miguel de Cervantes # 120 Complejo Industrial Chihuahua, 31109 Chihuahua Chihuahua, Mexico. E-mail: miguel.bocanegra@cimav.edu.mx

## 1. Introduction

The last few years have witnessed the discovery, development and, in some cases, large scale manufacturing and production of novel materials such as inorganic or organic matter within the nanometer scale [1]. Carbon nanotubes (commonly abridged as CNTs) are one of them. Although the discovery of hollow and nanometer tubes composed of graphitic carbon has been attributed to Sumio Iijima [2], Radushkevich and Lukyanovich [3] published clear images of approximately 50 nanometer diameter tubes made of carbon. Subsequently, Oberlin *et al.* [4] showed hollow carbon fibres with nanometer-scale diameters using a vapour-growth technique and Abrahamson *et al.* [5] reported evidence of carbon nanotubes at the 14<sup>th</sup> Biennial Conference of Carbon at Penn State University [1]. Carbon nanotubes are structures of nanometric dimension built up entirely by atoms of carbon and they have a ratio of length-to-diameter up to 10'000:1 and can be visualized as a graphene sheet that has been rolled into a tube with hemispherical caps at both ends [6, 7] where the walls of the tubes are hexagonal carbon. The carbon-carbon atomic bond is one of the strongest existing in nature and this leads to exceptional material properties that are a consequence of their symmetric structure. Many researchers have reported mechanical properties of carbon nanotubes that exceed those of any previously existing materials [8]. Their remarkable properties have attracted intense interest from the scientific community, as well as from industry, and nanotubes are currently the subject of around seven papers per day.

Nowadays, there is abundant experimental evidence of the outstanding properties of carbon nanotubes. Their stiffness and strength are phenomenal [9]. Novel mechanical tests on individual CNTs and atomistic calculations suggest that CNTs have high elastic moduli, approaching 1 TPa, and exceptional tensile strengths, in the range of 20-100 GPa [10]. On the other hand, for comparison, the stiffest conventional carbon fibres have Young's moduli of approximately 800 GPa, while glass fibres typically have moduli of about 70 GPa [9]. Two major structural forms of carbon nanotubes are commonly known to exist: single walled carbon nanotube (SWCNT) bundles and multi walled carbon nanotubes (MWCNT) [11]. Experimental measurements have indicated that single-walled nanotubes (SWCNTs) have Young's moduli ranging from 1 to 5 TPa meanwhile MWCNTs have an average value of 1.8 TPa. On the other hand, CNTs possess relatively low density, ranging from 1.2 g.cm<sup>-3</sup> for SWCNTs up to 1.8 g.cm<sup>-3</sup> for MWCNTs [12, 13]. Although single walled nanotubes possess better properties than multiwalled nanotubes, the relative simplicity in preparation of multiwalled

nanotubes and ease in its isolation and purification make it more economical for most applications including dispersing in ceramic matrix [6].

Carbon nanotube reinforced ceramic matrix composites have been developed in order to overcome the intrinsic brittleness. On the other hand, in addition to mechanical effects, the reinforced ceramic composite could gain other properties such as electrical conductivity, thermal expansion coefficient, hardness and thermal shock resistance [14, 15]. As was pointed out by Xia et al. [16] and Curtin [17], the transference of all these properties into correspondingly excellent mechanical properties in ceramic composites depends on the CNT/matrix interfacial adhesion, the CNT/matrix interfacial sliding behaviour after any decohesion, the interwall sliding within MWCNTs, and the fracture behaviour and fracture strength statistics of CNTs, among others. Likewise, the carbon nanotube reinforced ceramic matrix composites must be obtained in reasonable quantity at acceptable cost. Since the last decade, the vast majority of CNT composite work has focused on polymer matrices [18] while comparatively few investigations have explored ceramic or glass matrices as well as the potential toughening mechanisms associated with CNT reinforcements [15]. According to Bakshi et al. [19], this phenomenon can be attributed to the relative easiness of polymer processing which often does not require high temperatures for consolidation as needed for metals and ceramic matrixes. Indeed, the few studies on CNT reinforcement of ceramic matrix composites are focused on fibres including those based on SiC, carbon, alumina and mullite [15] although some investigation to date have been carried out mainly on alumina-based composites but with only limited work having done on other systems, e.g. those pertaining to zirconia toughened alumina (ZTA) [20, 21].

Although the role of CNTs in the sintering of ceramic composites is not completely clarified in literature, these can be processed using the regular processing route, where the carbon nanotubes are usually mechanically dry- or wet-mixed with the matrix or alternatively a matrix precursor and then densified by pressureless sintering (PLS), spark plasma sintering (SPS), hot-pressing (HP) and hot isostatic pressing (HIP) [22]. Some interesting work has been performed with the purpose to improve their mechanical properties. Zhan et al. [23] ball-milled SWCNT bundles and nanometric alumina powders and obtained by means of SPS at 1150 °C a composite with a fracture toughness of 9.7 MPa.m<sup>1/2</sup> (for 10 vol% CNTs), nearly three times that of pure nanocrystalline alumina (4.9 MPa.m<sup>1/2</sup>). However, these results were refuted by Wang et al. [24] who reported that CNT-alumina composites are highly contact damage-resistant and also showed that the fracture toughness of such composites could be strongly overestimated when is measured by the standard indentation method, which is the commonly used in

the characterization of the fracture toughness in ceramics. Other composites prepared by hot pressing mixture of MWCNTs and nano-SiC powders were reported by Ma *et al.* [25] but the dispersion of the MWCNTs was very poor. In spite of this, they claimed an increase in both the bending strength and fracture toughness when the carbon nanotubes content is around of 10 vol%. Siegel *et al.* [26] reported that the fracture toughness of 10 vol% MWCNTs alumina hot-pressed composites is increased by 24% (to  $4.2 \text{ MPa}\cdot\text{m}^{1/2}$ ) over that the pure alumina. Several detailed studies [20, 27, 28] have dealt with the manufacturing of nanotube-Fe- $\text{Al}_2\text{O}_3$ , nanotube-Co-MgO, and nanotube-Fe/Co-Mg $\text{Al}_2\text{O}_4$  composites using hot-pressing as consolidation tool. In these investigations, the nanotubes were grown in situ in the starting powders by a catalytic chemical vapour deposition (CCVD) method, resulting in a homogeneous dispersion of CNT between the metal oxide grains, in a way that may be impossible to achieve by mechanical mixing [28], obtaining nanotubes (mostly SWNTs and DWNTs) with branched bundles smaller than 50 nm in diameter, which appear to be very flexible. However, only modest improvements of properties have been reported in carbon nanotubes reinforced silicon carbide [25] and silic on nitride [29] matrix composites.

The above mentioned are only a few examples where both SWCNTs and MWCNTs have been used as reinforcement agent. For the case of carbon nanotube reinforced alumina based ceramic composites, it is noteworthy that different and contradictory results have been obtained and published when carbon nanotubes are used as toughening agent. Thus depending on different considerations, the best toughening agent can be different for each specific ceramic composition as was studied and reported by Bocanegra *et al.* [30]. A study of the efforts towards development of CNT-reinforced alumina and zirconia toughened alumina (ZTA) composites is of paramount importance in order to provide an important summary of the different works performed to date and what levels of reinforcements have actually been achieved. On the other hand, the authors consider that this review paper will serve as an important guideline for future researchers that are new in this field of carbon nanotubes reinforced ceramic matrix composites. Likewise, in this review paper we will explore briefly the properties of carbon nanotubes and the theory of fibre reinforcement as well as the techniques used in the literature to produce different ceramic–nanotube with improved mechanical properties.

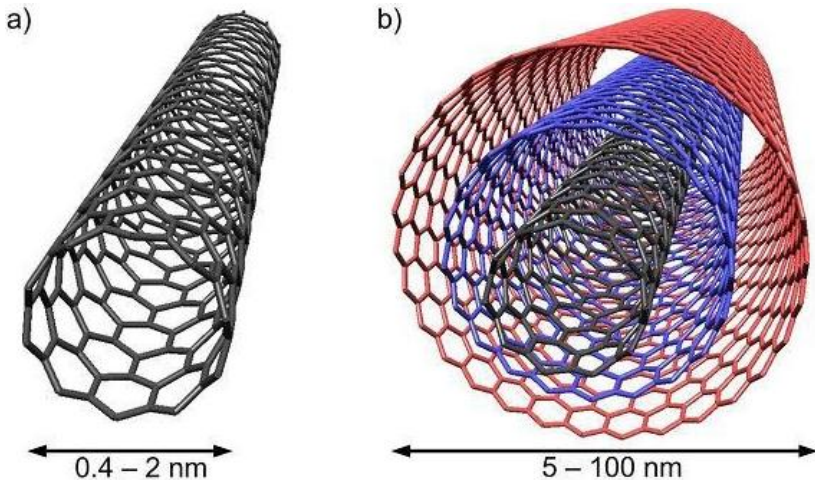
## 1.1. Structure and properties of carbon nanotubes

Carbon nanotubes can be visualized as a sheet of graphite that has been rolled into a tube in a hexagonal array where each carbon atom has three nearest neighbors [8]. CNTs represent one of the best examples of novel

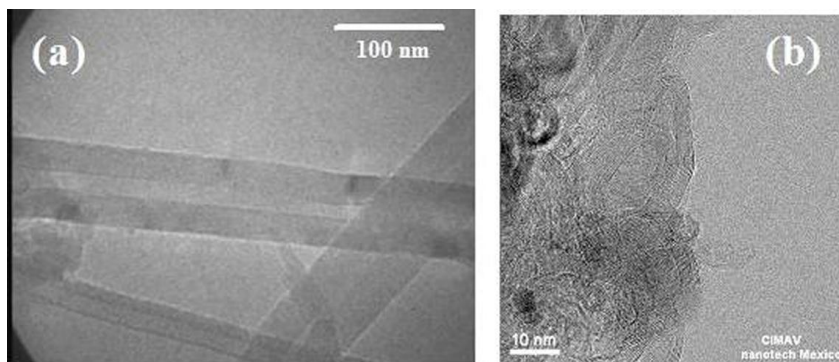
nanostructures derived by bottom-up chemical synthesis approaches, and can be formed with a single wall (SWCNT) which is closed at the two tips by half fullerenes or more complex structures including pentagons [20] or multiple walls (MWCNT) composed of concentrically rolled graphene sheets with an interlayer distance of approximately 0.34 nm which is very close to that measured between graphene sheets in graphite [20, 31-33].

Frequently SWCNT and MWCNT are found together in bundles where the intertube interaction may be strong. Fig. 1 shows a schematic of carbon nanotubes on the atomistic-scale. Experimentally, the tubes are generally less perfect than the idealized versions shown in Fig.1 and, as already noted, may be multiwalled or single-walled. SWCNT have diameters typically  $\sim 1$  nm with the smallest diameter reported to date of 0.4 nm and the lengths reach several micrometers and sometimes some tens of micrometers, giving therefore very high aspect ratios (1000-10,000). Meanwhile MWCNTs tend to have diameters in the range 2–100 nm and lengths from a few tens of nanometers to several micrometres [20].

Fig. 2a shows typical scanning electron microscopy (SEM) image showing the nano-structure of MWCNTs where the individual layers making up the concentric tubes are clearly evident. The average length of the MWCNTs



**Figure 1.** (a) Single-walled carbon nanotube (b) Multi-walled carbon nanotube [From Ben Cornwell-Mott, Effect of perfectly aligned CNTs under cohesive crack bridging in adhesive joints. A project submitted in conformity with the requirements for the degree of Master of Engineering Graduate Department of Mechanical and Industrial Engineering University of Toronto, 2010] [33].



**Figure 2.** Typical SEM image of longitudinal view of concentric MWCNTs (a); high magnification TEM image of longitudinal view of a SWCNT rope (b).

was approximately of tens of nanometers and an outer diameter ranging from about 30 to 50 nm. On the other hand, a high magnification transmission electron microscopy (TEM) image of a SWCNT rope is shown in Fig. 2b where it is clear the flexibility as a result of their very small diameters, which in turn lead to the SWCNTs to be curled and looped rather than straight. The SWCNTs tangle and interact with each other through van der Waals forces, which makes it difficult to obtain a homogeneous dispersion of CNTs in a ceramic powder [34]. However, both single and multi-walled nanotubes show unique properties that undoubtedly can be exploited for use in ceramic matrix composites [8].

There is a growing body of studies, theoretical and experimental, indicating that carbon nanotubes (both MWNT and SWNT) have indeed extraordinary mechanical properties [9, 35]. The CNTs are expected to have high stiffness and axial strength as a result of the carbon–carbon  $sp^2$  bonding according to reported by Robertson et al. [36]. On the other side, for an efficient application of the nanotubes it is required the study of the elastic response, the inelastic behavior and buckling, yield strength and fracture.

Nowadays, great efforts have been applied to the experimental [37, 38] and theoretical [39, 40], investigation of these properties. By measuring the amplitude of the intrinsic vibrations of the nanotubes in the TEM [37] and taking into account the inevitable experimental uncertainties such as the estimation of the nanotube length, the values of the Young's modulus have a considerable spread ranging from 410 GPa to 5.45 TPa [9], much higher than for typical carbon fibers of 680 GPa [41]. Therefore, the strength and toughness of nanotubes, properties that are of paramount importance for

structural applications cannot evaluate and therefore, it was not possible to state whether single-walled tubes are stiffer than multi-walled tubes. Later, this technique was also applied to measure Young's modulus of isolated SWNTs and the obtained value was  $1.25_{-0.35}^{+0.45}$  TPa [38]. Wong et al. [42] and Salvétat et al. [43] described a method of fixing nanotubes at one end, and then determining the bending force  $F$  of the CNTs as a function of displacement  $d$ . The results implied a value of  $\sim 1.28$  TPa for the Young's modulus. Determining the mechanical properties of SWCNTs presents an ever greater challenge than for MWCNTs. Notwithstanding, some measurements have been made using a nanostressing stage [44] yielding values for the Young's modulus ranging from 320-1470 GPa (mean 1002 GPa) as well as an average breaking strength of 30 GPa. [40]. The high bending strength of CNTs is associated with their high flexibility [21].

Although only bending experiments on CNTs have been performed so far [45], CNTs seem to behave as ideal carbon fibres that can be stiff yet flexible, associating very high modulus with very high strength. Tensile strength values as high as  $\approx 150$  GPa have actually been measured for perfect MWNTs from an electric arc [46], although the reason for such a high value compared to that measured for SWNTs is not clear. It probably reveals the difficulties involved in carrying out such measurements in a reliable manner. Even though the mechanical properties of CNTs have been extensively studied, the challenge remains of establishing a data base of mechanical properties of CNTs as a function of concentration and type of defects, temperature, chemical environment, presence of chemical functionality, cycling of load, lifetime, and so on [47]. However, considering the current measured values for the most important mechanical properties, both SWCNTs and MWCNTs have great potential for applications requiring high-modulus high-strength materials.

## 1.2. Methods of productions of CNTs

Since CNTs were discovered almost 30 years before, there have been a variety of techniques in order to synthesize them [8]. However, it is necessary to solve some problems that are more or less restrictive depending on the case. Examples include specifically controlling the configuration (chirality), the purity, or the structural quality of SWNTs, and adapting the production capacity to the application [28]. CNTs (single- or multi-walled) can be produced using different methods, which mainly involve gas phase processes. The industrial application of the carbon nanotubes requires the development of techniques for large-scale production of defect-free nanotubes, considering

that a cost effective method has yet to be discovered. The three most important production techniques are summarized as follows.

### 1.2.1. Arc discharge method

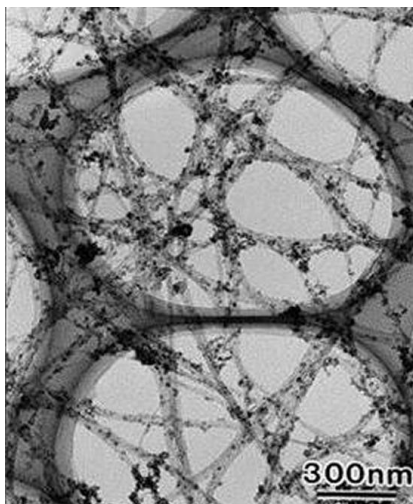
This technique was first brought to light by Krätschmer *et al.* [48] who utilized it to achieve the production of fullerenes in macroscopic quantities. Arc-discharge between carbon electrodes in inert gas atmospheres using Fe or Co as catalysts is a first way to produce CNTs and increase the quantity and length of the tubes and to favour the formation of SWCNTs [20, 49] at pressures ranging 50 to 700 mbar. Carbon rods are evaporated by a direct current of 50 to 100 amps driven by 20v which in turn will create high temperature discharge between two electrodes. With this method, the bulk production of CTNs depends mainly on uniformity of plasma arc and temperature of deposition [1]. SWCNTs with diameter of 1.2 to 1.4 nanometers are produced by arc-discharge. However, when argon inert gas with a lower diffusion coefficient and thermal conductivity is used, it is reached SWCNTs with diameter of 0.4 nm. By changing metal catalyst (Co and Mo), nanotubes with a diameter of 0.6 to 1.2 nm are produced. On the other hand, MWCNTs with a less number of defects [1] can be produced with the use of pure graphite arc with an inner diameter 1-3 nm and outer diameter 10 nm approximately. According to reported by Bhushan [28], it is worth noting that the products obtained do not consist solely of carbon nanotubes. Amorphous carbon, nanoparticles, fullerene-like structures including C<sub>60</sub>, poorly organized polyaromatic carbons, nearly amorphous nanofibers, multiwall shells and singlewall nanocapsules have all been obtained [20]. An example can be seen in Fig. 3.

For application of carbon nanotubes in ceramic composites, large quantities of nanotubes are required, and the scale-up limitations of the arc-discharge technique would make the cost of nanotube based composites prohibitive [8]. Up to now, an important lot of work has been carried out by many researcher groups using this technique with the purpose to understand the mechanisms of nanotube growth as well as the role played by the catalysts (if any) in the synthesis of MWNTs and/or SWNTs [28, 51, 52]. The Fig. 4 illustrates some examples of SWCNTs produced by arc-discharge technique using different metal catalyst.

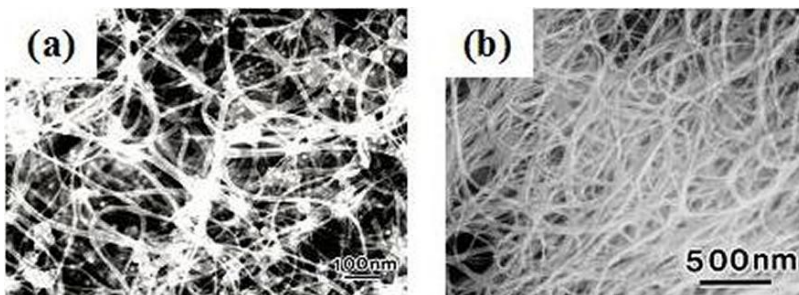
### 1.2.2. Laser-ablation (vaporization)

After the first laser was built in 1960, physicists immediately made use of it as a means of concentrating a large quantity of energy inside a very small





**Figure 3.** TEM image of entangled MWNTs produced by arc-discharge method exhibiting nanotubes, encapsulated particles as well as amorphous carbon. Diameter  $\sim 1\text{-}1.5\text{nm}$ , length  $> 10\text{ }\mu\text{m}$  [50].



**Figure 4.** SEM micrograph of arc-discharge-grown single-walled carbon nanotubes catalysed by Ni-Y mixture (25% Ni and 5% Y). Diameter  $\sim 1\text{-}1.5\text{nm}$  and length higher than  $10\text{ }\mu\text{m}$  (a); Bundle of SWNTs showing tangled, spaghetti-like carbon nanotubes catalysed by Fe ( $< 10\%$ ). Purity higher than 90%, diameter  $\sim 1\text{-}1.5\text{nm}$ , length  $> 10\text{ }\mu\text{m}$  (b) [50].

volume within a relatively short time [28]. Considering that this technique was successfully used to synthesize fullerene-related structures for the very first time [53], the synthesis of SWNTs by laser ablation took another ten years of research [54]. This method uses a series of laser pulses aimed at a

graphite sheet inside an enclosure that contains small amounts of Co and Ni powder and filled with Ar gas which are heated up to a temperature of 1200 °C [55]. In this technique, a YAG or CO<sub>2</sub> laser impinges on a carbon composite target situated in the center of a quartz tube sitting inside a tube furnace. The laser beam has sufficient energy density to convert the graphite into amorphous carbon, which in turn, within a flowing buffer inert gas such as Ar, leads to SWNT growth downstream of the target. On the other side, some experiments indicate that MWNTs can also be produced using a Nd-YAG laser targeted on graphite powder (in an Ar atmosphere) contained inside a quartz tube, which is inside a furnace at 1200 °C. This interesting method has proven successful at producing high quality SWNTs with a low density of defects and contaminants as well as with good diameter control, and is especially well-suited to produce CNTs with different dopant species [18]. Likewise, a combination of arc-discharge and laser vaporization accompanied of the high-temperature pulsed arc discharge method [56] also yields high-quality SWNTs with large diameters [57, 58].

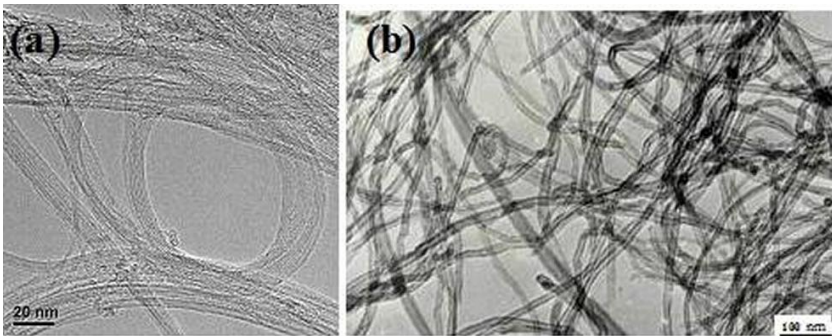
In the absence of catalysts in the target, the soot collected mainly contains multiwall nanotubes (c-MWNTs) with lengths of approximately 300 nm, and the quantity and structural quality are very dependent on the oven temperature. It is clearly demonstrated that the best quality is obtained for an oven temperature set at 1200 °C as mentioned above. When small quantities (a few percent or less) of transition metal such as Ni or Co, catalysts are incorporated into the graphite pellet, the products yielded undergo significant modifications, and SWNTs are formed instead of MWNTs [28]. These SWCNTs are supposedly “cleaner” than those produced using other techniques. Popov [40] pointed out that both arc-discharge and laser-ablation techniques have the advantage of high (>70%) yields of SWNTs and the drawback that i) they rely on evaporation of carbon atoms from solid targets at temperatures higher than 3000 °C, and ii) the nanotubes form ropes of about 100 to 500 parallel SWCNTs [55] which makes difficult the purification and application of the samples [28].

### 1.2.3. Chemical vapor deposition (CVD)

The third major technique for growing CNTs is chemical vapor deposition (CVD), a technique used since 1959 to produce carbon filaments and fibers [59]. During the CVD process, a substrate is loaded with metal catalyst particles (nickel, cobalt, iron, or their combination) at temperatures ~ 1100 °C while two gases are introduced into the reactor: a process gas (hydrogen, ammonia, or nitrogen) and a carbon-containing gas (methane, ethylene, acetylene, or ethanol) [60]. Different hydrocarbons, catalysts,

catalyst particle-sizes, and growth temperatures are used to vary the size, morphology, and quality of the CNTs [18]. The process has two main advantages: the nanotubes are obtained at much lower temperature, although this is at the cost of lower quality, and the catalyst can be deposited on a substrate, which allows for the formation of novel structures [61]. CVD technique has a variation which depends on the energy source and is denominated as plasma-enhanced CVD (PECVD) which has emerged as a key growth technique to produce vertically aligned CNTs and the growth temperature is necessarily maintained below the pyrolysis temperature of the particular hydrocarbon to prevent excessive production of amorphous [62].

The selectivity of the CVD method is generally better for the production of MWNTs although it is a general statement that MWNTs from CVD contain more structural defects (exhibit a lower nanotexture) than MWNTs from arc discharge, due to the lower temperature of the reaction, which does not allow any structural rearrangements. These defects can be removed by subsequently applying heat treatments in vacuum or inert atmosphere to the products [28]. One unique aspect of CVD techniques is its ability to synthesize aligned arrays of carbon nanotubes with controlled diameter and length [8], which is not possible using the other conventional methods [63]. Nanotube diameters range from  $\sim 0.4$  to greater than 3 nm for SWCNT and from 1.4 to at least 100 nm for MWCNT. Nanotube properties can thus be turned by changing the diameter [64]. As example, the Fig. 5 shows TEM images [50, 65] of carbon nanotubes prepared by CVD method.



**Figure 5.** TEM micrograph of carbon nanotubes produced by CVD method. (a) SWCNT with diameter  $\sim 1.5$  nm, length 1-5  $\mu\text{m}$ , purity  $> 95\%$ , and surface area of 1020  $\text{m}^2$  [50], and (b) MWCNT with an outer diameter of 10-20 nm, inside diameter 3-5 nm, length 10-30  $\mu\text{m}$ , purity  $> 95\%$  and surface area of 233  $\text{m}^2$ .g. Note the presence of soot. [65].

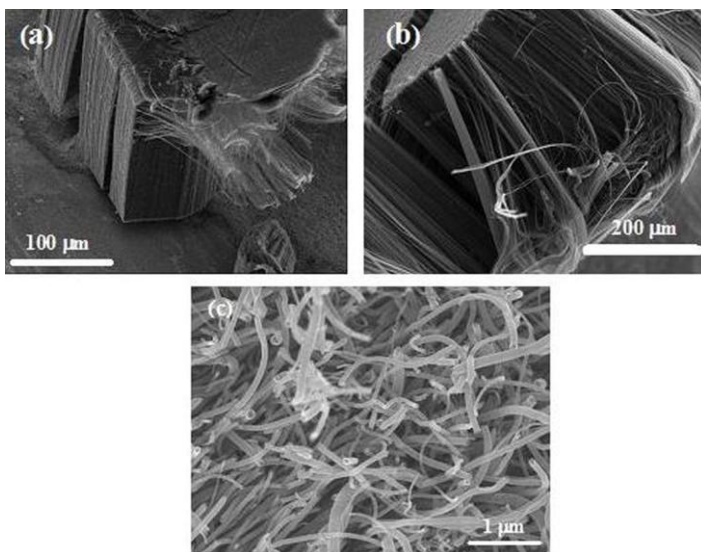
### 1.2.4. Spray pyrolysis method

There are several derivative methods related to thermal CVD such as floating catalyst, aerosol assisted, and spray pyrolysis. This technique is a type of CVD method, where the carbon source and the catalyst are introduced simultaneously into the reactor. Spray pyrolysis CVD is a well known technique for the preparation of thin films [66]. This method has also been used for the production of multi wall carbon nanotubes (MWCNTs) involving the spray of a metallocene/hydrocarbon solution in a furnace with gas flow inert or slightly reductive [67]. Similar to Aerosol assisted CVD (AACVD), the active solution is prepared by dissolving organometallic species in carbonaceous liquids. At high temperature, the solvent evaporates and acts as carbon source, while the organometallic species decomposes to provide the catalyst particles [68]. The metallic particles act as active nucleation centers for the nanotube growth [69]. In the beginning of CNTs formation, the metal clusters are surrounded by carbon being this incorporated to the end of the growing tube and the metal remains at this end, which is moving away of surface [66]. It is important to note that among the various techniques for carbon nanotubes production, spray pyrolysis CVD provides a controlled way of spraying complex carbonaceous liquids directly into the deposition chamber, spares the intermediate stage for catalyst preparation, and ensures semi-continuous growth of CNTs [68, 70].

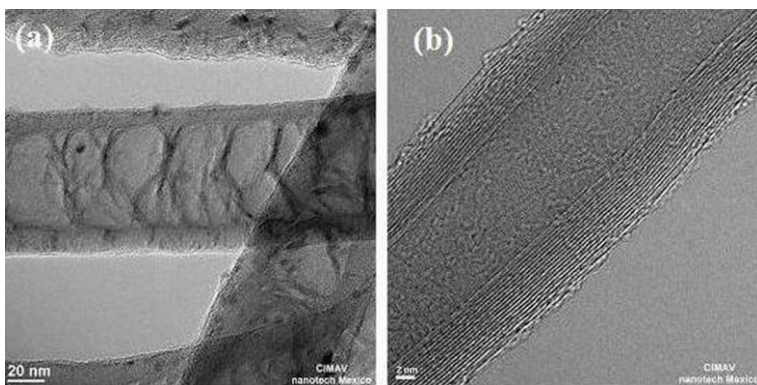
Spray-pyrolysis has the advantage of generating continuously catalytic particles throughout the entire growth cycle. The generation of the fresh catalytic particles prevents the formation of large amounts of amorphous carbon, which in turn would necessitate tedious purification steps [71]. On the other hand, with this method it is possible to produce well graphitized MWCNTs at low cost in large quantity and is promising for scaling up in industry [72]. In Figs. 6 and 7 we present SEM and TEM images, respectively, of some MWCNTs prepared by spray pyrolysis using ferrocene as catalyst precursor and different carbon sources.

### 1.3. Purification of carbon nanotubes

In all the above-mentioned preparation techniques, the nanotubes come with a number of impurities whose type and amount depend on the technique used for its production. The most common impurities are catalytic residues or fullerenes as well as some metals are the other types of impurities generally observed [73, 74]. These impurities will interfere with most of the desired properties of the CNTs. There are few methods available to remove unwanted nanostructures and amorphous carbon. However, the common industrial



**Figure 6.** SEM micrographs of MWCNTs prepared by spray pyrolysis on Quartz substrate at a temperature of 800 °C under argon flow and ferrocene as catalyst precursor. (a) Benzene, (b) toluene, and (c) acrylonitrile as carbon source.



**Figure 7.** TEM image of a bamboo-like MWCNTs prepared by spray pyrolysis on quartz substrate at a temperature of 800 °C using Ar as carrier gas, ferrocene as catalyst precursor and acrylonitrile flowing at  $1\text{mL}\cdot\text{min}^{-1}$  as carbon source. Note buckling and bending in the inner walls (a); TEM micrograph of a CNT showing no defects in the tube interior. The tube walls show a high degree of crystallinity (b). The curved walls of the bamboo compartment adhere perfectly to the nanotube walls in (a).

techniques use strong oxidation and acid refluxing techniques, which have an effect on the structure of the tubes and moreover. Economically feasible large-scale production and purification techniques still have to be developed [75]. Therefore, these two methods will be briefly explained below.

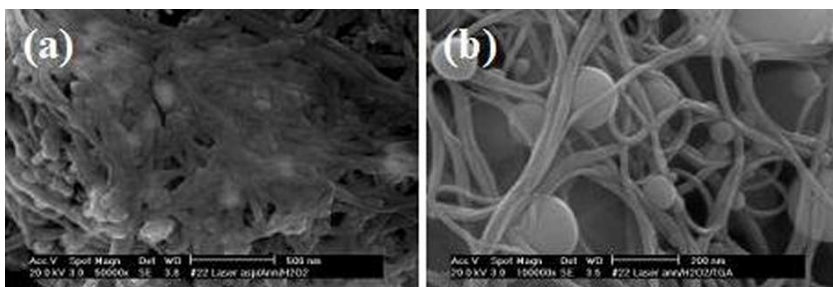
### 1.3.1. Thermal oxidation

When carbon nanotubes are produced by the arc-discharge method, the impurities can be purified by oxidation considering that the carbonaceous impurities have high oxidation rates. However, in this case, 95% of the starting materials are destroyed and the remaining samples require annealing at high temperature 2800 °C [76] and moreover, the tubes tend to be relatively short with random sizes [60]. To carry out purification by oxidation, two commonly approaches are followed: i) gas phase purification [76, 77] and ii) liquid phase purification [74, 78, 79]. Nevertheless, it is noteworthy that gas phase oxidation is commonly used as the purification method for MWNT [80, 81]. However, Dujardin *et al.* [80] have suggested that the same purification process would destroy single-wall carbon nanotubes and in a comprehensive article, Dillon *et al.* [82] have described an oxidation process that produces >98 wt % pure SWNTs. The reader is referred to consult this reference. The great disadvantages of the purification by oxidation are that not only the impurities are oxidised, but also the SWNTs. Luckily the damage to SWNTs is less than the damage to the impurities. It is important to note that these impurities have relatively more defects or a more open structure.

On the other side, another reason why impurity oxidation is preferred is that these impurities are most commonly attached to the metal catalyst, which also acts as oxidising catalyst [75]. Altogether, the efficiency and the yield of the procedure are highly dependable on factors such as metal content, oxidation time, environment, oxidising agent and temperature. Optimal oxidation condition is found to be at 673 K for 40 min [1]. Usually, in this oxidation process the hydrogen peroxide ( $H_2O_2$ ) or alternately sulfuric acid ( $H_2SO_4$ ) is directly applied in a hot air stream (thermal oxidation) [83]. The high temperature applied also causes the decomposition of the amorphous carbon and the fullerenes. As an example, the Fig. 8 illustrates SEM micrographs corresponding to a sample of SWCNTs prepared by laser ablation after vacuum annealing, oxidation by  $H_2O_2$ , and annealing in Ar flow.

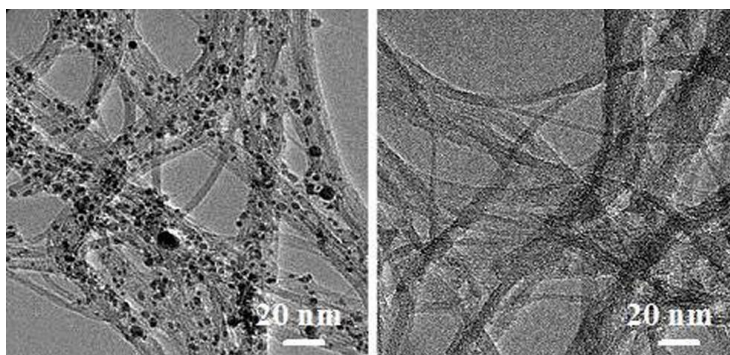
On the other hand, nowadays, the great challenge is to develop techniques to remove most, if not all, of these impurities which in turn is essential to their successful use in practical applications. A new method has been developed at the NASA Glenn Research Center [85] to purify gram- scale





**Figure 8.** Sample of MWCNTs purified by vacuum annealing +  $\text{H}_2\text{O}_2$  reflux before (a) and after (b) annealing in argon up to  $1100^\circ\text{C}$ . Note that the sample looks very clean after annealing [84].

quantities of SWCNTs. This method which is a modification of a gas-phase purification technique uses a combination of high-temperature oxidations and repeated extractions with nitric and hydrochloric acid. This improved procedure significantly reduces the amount of impurities (catalyst and non-nanotube forms of carbon) within the nanotubes, increasing their stability significantly. Careful analysis of the CNTs using inductively coupled plasma spectroscopy revealed that the iron content of the nanotubes was reduced from 22.7 wt% in the crude nanotubes to less than 0.02 wt%. Likewise, X-ray photoelectron spectroscopy revealed a decrease in iron content after purification as well as an increase in oxygen content due to the formation of carboxylic acid groups on the surface of the nanotubes. TEM micrographs showing the above mentioned are shown in Fig. 9.



**Figure 9.** TEM of SWCNTs. Left: Crude. Right: Purified. Note the absence of iron catalyst particles (black spots) in the purified nanotubes [85].

It is expected that high-temperature annealing in vacuum and in inert atmosphere helps to improve the quality of SWNTs by increasing crystallinity and reducing intercalation. A variation of the thermal oxidation is the purification of CNTs by chemical oxidation that is nothing but oxidation of amorphous carbon with the treatment of an oxidizing agent. Oxidizing agents commonly used are  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HNO}_3$ . In the interesting PhD Thesis by Bera [62] 30 wt%  $\text{H}_2\text{O}_2$  was used for oxidation of amorphous carbon where the oxidative treatment was carried out using 20 ml of  $\text{H}_2\text{O}_2$  taken in a 50 ml beaker. The unpurified CNTs and  $\text{H}_2\text{O}_2$  mixture was kept in a dark environment for 24 h at  $20 \pm 2$  °C. Then the liquid was dried at 100 °C in a furnace and the purified CNTs were collected from the beaker. Differences in weights, before and after treatment, were noted for a percent loss calculation.

TEM investigations carried out by Bera [62] on the treated sample revealed that the CNTs are highly pure after chemical oxidation. Amorphous carbon is removed from the sample by the treatment. It can also be noted that the  $\text{H}_2\text{O}_2$  can also oxidize defect-enriched CNTs. It was observed that similar amounts of weight loss can be reached from both oxidation results. The presence of the amorphous carbon is almost negligible after oxidations.

### 1.3.2. Acid treatment

In general the acid treatment purification technique will remove the metal catalyst [64] as well as fullerenes and hydrocarbons with organic solvents such as toluene, benzene, acetone, butanol, propanol, methanol, chloroform, decaline, ethyl ether, hexane, O-xylene, 1,2-dichlorobenzene, carbon disulfide, and some others. First of all, the surface of the metal must be exposed by oxidation or sonication. The metal catalyst is then exposed to acid and solvated [64, 84]. In this process, when is used  $\text{HNO}_3$ , the acid only has an effect on the metal catalyst. It has no effect on the SWNTs and other carbon particles. However, if a treatment is in  $\text{HCl}$ , the acid has also a little effect on the SWNTs and other carbon particles. The mild acid treatment (4 M  $\text{HCl}$  reflux) is basically the same as the  $\text{HNO}_3$  reflux, but in this the metal has to be totally exposed to the acid to solvate it. It is expected that in acid treatment technique, typically the extraction removes about 18 to 20% of the sample mass, out of which approximately half is soluble fullerenes and the rest are soluble hydrocarbons.

There still may be some insoluble fullerenes and hydrocarbons left [64]. Additional to hydrochloric acid ( $\text{HCl}$ ) and nitric acid ( $\text{HNO}_3$ ), sulphuric acid ( $\text{H}_2\text{SO}_4$ ) has also been experimented but the results have shown that  $\text{HCl}$  was to be the ideal refluxing acid according to reported by Hirlekar et al. [1].



Alternatively to the two purification methods mentioned previously, it is important to stress that an alternative method making use of nanoparticles and other graphitic contaminants was introduced in 1994 by a Japanese research group to purifying MWCNTs [65]. The research group was able to preferentially oxidize the nanoparticles away, using copper as an oxidation catalyst. Since 1994, this has become a popular method for purification of nanotubes. The product of this treatment, which contains intercalated nanoparticles and graphitic fragments, is then washed in ion exchanged water to remove excess copper chloride and potassium chloride. In order to reduce the intercalated copper chloride-potassium chloride metal, the washed product is slowly heated to 500 °C in a mixture of Helium and hydrogen and held at this temperature for 1 hour. Finally, the material is oxidized in flowing air at a rate of 10 °C.min<sup>-1</sup> to a temperature of 555 °C. Samples of cathodic soot which have been treated this way consist almost entirely of nanotubes. A disadvantage of this method is that some amount of nanotubes are inevitably lost in the oxidation stage, and the final material may be contaminated with residues of intercalates. A similar purification technique, which involves intercalation with bromine followed by oxidation, has also been described [86].

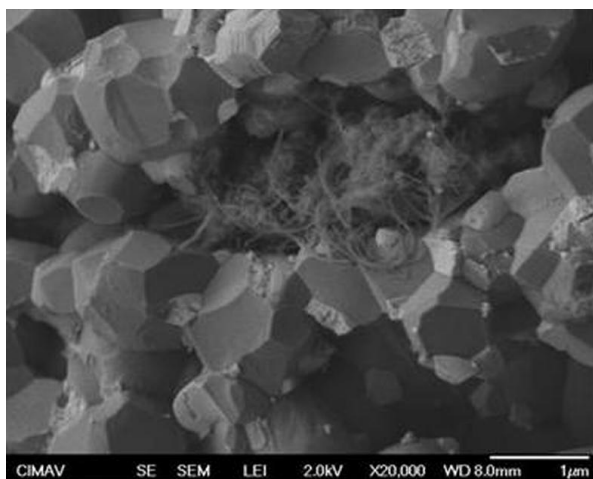
To obtain better CNT, further improvements have to be done in the growing or purification processes. As a concluding remark, the above-mentioned purification methods change the structural surfaces of CNTs. As a result, there may be change in the electrical and mechanical properties of purified nanotubes. Therefore, the main thrust of the research should be in the area of producing purified CNTs in a single-step process to conserve the fascinating features of CNTs.

#### 1.4. Dispersion of carbon nanotubes

Dispersion is the bane in the processing nanotube composites [15, 241]. This is due to the fact that CNTs have a great surface area exceeding in most of the cases 1000 m<sup>2</sup>.g<sup>-1</sup> (capped) or 2200 m<sup>2</sup>.g<sup>-1</sup> (uncapped) surpassing the value of 400–1,000 m<sup>2</sup>.g<sup>-1</sup> for HiPco samples. The agglomeration state is extremely undesirable, especially in ceramic matrices which lead to formation of clusters owing to Van der Waals forces [19] and concentration of reinforcement at certain point and this could lead to worsening of overall mechanical properties [15]. On the contrary, with a good dispersion, each nanotube is loaded individually over a maximum interfacial area and therefore, can contribute directly to the mechanical properties and to toughening mechanisms [19]. SWCNTs tend to cluster into ropes while MWCNTs produced by CVD are often tangled together like spaghettis [88].

It is well known that carbon nanotubes are molecules insoluble in water and organic solvents. However, if a surfactant is added to the dispersion, and with the use of sonication, a homogeneous and stable suspension can be obtained. With the purpose to prevent the bundelling effect, Sodium-Dodecyl-sulfate (SDS) can be used as surfactant according to the reported by Terrés [83]. In addition to the aforementioned problems, carbon nanotubes are not the simple, straight pipes they are being represented as. They can be curved, wrap around each other and are never evenly aligned, dispersed and distributed throughout a matrix, despite all efforts to make them that way [33, 89]. On the other hand, the sonication process is very necessary as a source of external mechanical energy which helps the particles to overcome the attractive Van der Waals forces. Sonication is a commonly used method for separating CNT aggregates in solution, because it quickly disperses CNT without the need for any chemical modification [90, 91]. Despite being the most commonly used method of dispersion in ceramic-matrix composites to date, many researchers still observed CNT aggregates after sonication in aqueous solution [92-94]. As example, the Fig. 10 shows typical microstructure of agglomerated SWCNTs/ceramic matrix composite.

To effectively disperse SWCNTs by sonication [65], it is required longer times to break apart the Van der Waals physical bonds which make the SWCNTs agglomerate into bundles (see Fig. 10). On the other side, since SWCNTs are



**Figure 10.** SEM image of fracture surface of a zirconia toughened alumina (ZTA) composite pressureless sintered at 1520 °C, 1 h showing SWCNT bundles after sonication in aqueous solution.

such a fine particle, the agglomerate bundles are harder to disperse and when remain in this state, a poor or absent interfacial bonding occurs and therefore, the CNTs may even act as a source of microcracks, leading to premature failure.

It is observed that high loading fractions favour agglomeration not only because the particles come into contact more often, but also because there can be a shortage of matrix material to ‘wet out’ the large surface area of the filler. It is very important to point out that a common result for nanocomposites is that properties are improved at low loading fractions but cannot be increased further due to CNT agglomeration above a few vol.% [30]. To obtain a good dispersion of the CNTs in the final composite, a suitable processing route needs to be obtained. Often the first step is to disperse the CNTs in a solvent, prior to mixing with a conventional ceramic powder (powder processing), a colloidal ceramic suspension (colloidal processing) or sol-gel precursor (sol-gel processing). In order to study in more depth this processes, the readers are referred to consult the excellent review by Cho et al. [15].

### **1.5. Requirements for mechanical reinforcement**

Four main system requirements for effective reinforcement have been identified. These are large aspect ratio (30-10.000), good and homogeneous dispersion of the reinforcing CNTs in the parent matrix, alignment and interfacial stress transfer [95]. Additional to this, it is important to avoid damage to the CNTs during processing [96]. As mentioned previously, the effects of a poor dispersion can be seen in a number of systems when the nanotube loading level is increased beyond the point where aggregation begins which in turn is accompanied by a decrease in strength and modulus [97]. On the other hand, alignment is a less crucial issue and although is necessary to maximise strength and stiffness, it is not always beneficial. Undoubtedly, the most important requirement for a nanotubes reinforced composite is that external stresses applied to the composite as a whole are efficiently transferred to the nanotubes, allowing them to take a disproportionate share of the load [95].

The nanotube reinforcements promise to increase the fracture toughness of the composites [6] by absorbing energy through their highly flexible elastic behaviour during deformation, which will be especially important for nanotube-based ceramic matrix composites. Therefore and to obtain an “ideal” ceramic composite, it is of paramount importance the connectivity with the matrix and uniform distribution within the matrix for stronger and tougher CNT/ceramic composites [98].

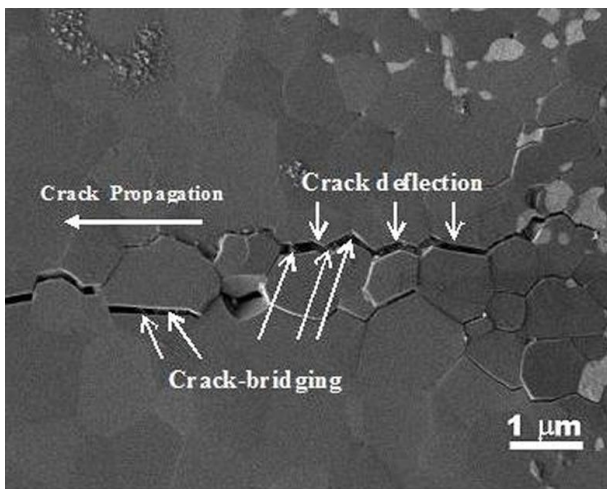
## 1.6. Toughening mechanisms in CNT ceramic composites

Nowadays, some technical applications require mechanical properties that can only be obtained with ceramic materials; for example, combinations of high temperature strength, creep resistance, high hardness and low density can be achieved with ceramics that are far superior to metallic materials [99]. It is well known that toughness of ceramic bulk materials can be improved by whisker and fiber reinforcement [100]. Toughening in ceramic matrix composites (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 [6]. This same concept is applied in toughening of ceramics where carbon nanotubes are used as fibers or whiskers in order to toughen ceramic nanocomposites [101].

Likewise, the toughening can also be obtained through phase transformation of particulate inclusions in a ceramic matrix (only associated with partially stabilized zirconias (PSZ) where under applied stress, this transformation occurs in the stress field around the tip of the crack, and the resultant strain involved in the transformation locally relieves the stress field and absorbs the fracture energy). There has been a need to continuously develop mechanistic models that relate the microstructure to the toughening mechanisms and mechanical behavior [99, 102]. Whereas the mechanisms of toughening discussed above are the ones of primary interest today, several others also contribute to toughening, for example: i) microcracking where stresses arising from the main crack nucleate microcracks in front of and to the side of the main crack. However, Claussen *et al.* [103] showed that micro cracking was effective in toughening polycrystalline aluminum oxide, but the process by itself does not increase the strength of ceramic materials, and ii) Crack bowing that occurs when sections of cracks are pinned by the microstructure, or by second-phase inclusions in the solid.

According to Lange [104], who suggested for first time this behavior for ceramics containing second-phase dispersion particles, the motion of pinned portions of the cracks is then retarded relative to the main portions of the cracks. The unpinned sections then bow around the pinning sites, much as dislocations bow around obstacles, and join up on the other side of the pinning sites to continue propagation [105]. Therefore, key factors that have contributed to improvements in mechanical properties include the homogeneous distribution of CNTs in the ceramic matrix and the degree of bonding between the reinforcement and the matrix [106]. A SEM micrograph

of a Vickers pattern using a deliberately load of 1 kg to produce a crack in a 0.01 wt% MWCNT-ZTA composite SPSeD at 1520 °C is shown in Fig. 11. Crack deflection is observed along the  $\text{Al}_2\text{O}_3$  grain boundaries. Likewise, crack-bridging by the MWCNTs is also observed. These two toughening mechanisms are indicated by arrow marks in the mentioned figure.



**Figure 11.** SEM micrograph of the indentation crack of a 0.01 wt% MWCNT-ZTA composite SPSeD at 1520 °C. Arrow marks explained in text.

## 2. Carbon nanotube $\text{Al}_2\text{O}_3$ based ceramic composites

Among different ceramics, alumina ( $\text{Al}_2\text{O}_3$ ) is one of the most widely used ceramic materials owing to its relatively high hardness (15-22 GPa), good oxidation resistance and chemical stability with iron or steel [107]. Moreover, this oxide ceramic has potential applications covering high speed cutting tools, dental implants, chemical and electrical insulators as well as wear resistance parts. An alternative and practical way to convert the  $\text{Al}_2\text{O}_3$  into a more useful material is to fabricate a composite [108, 109] by introducing microstructure refiners, enhancing crack length path, deflecting crack propagation, inducing secondary reinforcements for transformation toughening, crack bridging and adding impact dampening agents. Recently, CNTs have emerged as a strong reinforcing material because of its exceptional strength, modulus, tendency for crack deflection, and crack bridging ability [110]. Recent advances in nanomaterials, in particular carbon

nanotubes (CNTs), have offered exiting potentials for utilising these novel materials for the production of toughened polycrystalline  $\text{Al}_2\text{O}_3$  based ceramics [8, 111]. Indeed, nowadays most of the investigations on CNT-based composites have focused on improving the mechanical properties of a polymer matrix composite and most results for strengthening and toughening have been disappointing, and only little or no improvement of strengthening and toughening has been reported in CNT/ceramic materials [98] and successful cases are even fewer [112, 113].

On the other hand, in the open literature, few results have suggested that can be possible to toughen alumina based ceramics by cooperative addition of CNTs/ $\text{ZrO}_2$  with the nanometer zirconia particles loaded on surfaces of the CNTs [114]. Therefore, in spite of the different studies published by several investigators on zirconia toughened alumina (ZTA) composites, to the authors' knowledge, studies pertaining to the addition of carbon nanotubes to ZTA ceramic composites are very scarce.

## **2.1. Preparation and composite processing**

Ceramics in general, have high stiffnesses and thermal stabilities, but its strength is relatively low impeding their use as structural material. Therefore, the incorporation of carbon nanotubes into a ceramic matrix might be expected to produce a composite with high-temperature stability [9], exceptional creep resistance and high fracture toughness [8] by absorbing energy through their highly flexible behaviour during deformation [6]. However, the major concern is to obtain a uniform dispersion of CNTs in the ceramic. Moreover, one of the biggest challenges is to achieve a strong bonding between tubes and matrix. In this context, various approaches have been adopted for incorporating nanotubes into oxides such as alumina, alumina zirconia composites and so on [6, 8, 9]. Ceramic matrix composites can be processed using the regular processing route, where the nanotubes (SWCNTs or MWCNTs) are usually mechanically dry- or wet-mixed with the matrix (or a matrix precursor) and then densified using conventional sintering or alternatively hot-pressing sintering [28]. Some techniques are used nowadays in order to process CNT reinforced  $\text{Al}_2\text{O}_3$  ceramic composites, and the most important of them will be summarized briefly as follows.

### **2.1.1. Powder processing**

Nowadays, powder processing methods have been used to fabricate ceramic matrices. Almost all the ceramic composite reinforced by CNTs in previously studies were prepared by dry pressing [115] or under wet

conditions [15], followed by ultrasonication and/or ball milling and finally densified. 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. However, some success has been achieved with conventional milling techniques, primarily with the use of low to moderate nanotube volume fractions [6]. Peigney and co-workers have been among the pioneers in the synthesis of nanotube/oxide composites [116-118]. The authors developed an ingenious technique which involves the use of catalysts such as iron-containing  $\alpha$ -alumina. Passing a  $\text{CH}_4\text{-H}_2$  mixture over the catalysts resulted in the in situ growth of nanotubes on iron particles, producing the precursor for a nanotube/oxide composite. The resulting powders can then be hot pressed to form the final composite material [9]. Their SEM observations indicated that the CNT bundles, which are really flexible, could dissipate some fracture energy although the obtained fracture toughness values were lower than or similar to that of monolithic  $\text{Al}_2\text{O}_3$ .

A significant reinforcement effect was reported by An and Lim [119] who prepared CNT/ $\text{Al}_2\text{O}_3$  composites but using  $\text{C}_2\text{H}_2$  as the carbon source. Ma and co-workers [25] reported a 10% improvement in the strength and fracture toughness as compared to the monolithic ceramics with carbon-nanotube/ silicon-carbide (SiC) composites via mixing nano-particles of SiC with 10 wt.% carbon nanotubes and hot pressing. Nanotube/matrix debonding (pull-out) and crack deflection were the toughening mechanisms observed by the authors. Flahaut et al. [117] and Peigney et al. [20, 120-122] developed different techniques to synthesize carbon nanotubes in situ to form carbon-nanotube/metal-oxide composite powders which were subsequently hot pressed to form macroscopic composites. However, did not provide the expected improvement in mechanical properties owing to the bundles of long nanotubes. Concerning to carbon nanotube reinforced  $\text{Al}_2\text{O}_3$  composites [28], several studies have been carried out but the improvements in mechanical properties are not the best.

However and as mentioned earlier, one of the first studies of a SWNT/ceramic composite was described by Zhan et al. [23] whose results have not been reproduced up to now. Like Sun et al. [123], they used the SPS technique to prepare fully dense composites without damaging the SWNTs. The article by Sun et al. [123] illustrates the development of a colloidal route to coating the nanotubes with alumina particles prior to another mixing step with alumina particles and then densification by SPS. The result was a gain in fracture toughness (calculated from Vickers indentation) from  $3.7 \text{ MPa.m}^{1/2}$  for pure  $\text{Al}_2\text{O}_3$  to  $4.9 \text{ MPa.m}^{1/2}$  for an addition of 0.1wt% of SWNT nanotubes, but it is possible that the beneficial input of the nanotubes is due to the previous coating of the nanotubes before sintering, resulting in

improved bonding with the matrix [28]. Other studies that have contributed to increase the fracture toughness have been reported by Mo et al. [124] who reached an increase of 10% in fracture toughness with additions of 1.5 wt% MWCNTs to the alumina matrix meanwhile the fracture toughness of an Al<sub>2</sub>O<sub>3</sub> ceramic reinforced with 7 vol% of MWCNTs was increased 117% as reported by Ahmad and Pan [125] using the single edge notch bend (SENB) method.

It is very important to point out that many authors have questioned the validity of several previous studies in which  $K_{IC}$  had been determined by the conventional indentation fracture (IF) method. Nevertheless, they turned to macroscopic methods for  $K_{IC}$  determination, for example SENB test. However, this test showed virtually no improvement in fracture toughness of the CNT/alumina composites, in contrast to the earlier claims of Zhan et al. [23].

### 2.1.2. Colloidal processing

Nowadays there is a growing interest in using ceramic particles with similar diameters to the carbon nanotubes in order to create an intimate and homogeneous dispersion [15]. As was described by Lewis [126] in her elegant review, the term “colloid” is frequently used to describe particles that possess at least one dimension in the size range  $10^{-3}$ -1  $\mu\text{m}$ . An important characteristic of all colloidal systems is that the contact area between particles and the dispersing medium is large which in turn results in interparticle (or surface) forces strongly influence suspension behavior. This technique also known as colloid science, has led to technological advances in numerous areas, including ceramic processing, coatings, paints, inks, drug delivery, and so on. In this context, colloidal processing are becoming more and more important in the fabrication of advanced ceramics[127] because they provide the potential to reliably produce ceramic bulk materials through careful control of initial suspension behavior and its evolution during fabrication[128].

With the purpose to expand the great potential of CNTs for applications in ceramic composites, ZhiHui et al. [115] investigated tape casting, an important colloidal processing technique, to fabricate SiC films containing MWCNTs as reinforcements. The rheological behavior of the MWCNTs/SiC slurries was studied. However, they found that 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 alternatively hot pressing. Chemical treatments have been performed on CNTs to obtain better uniformity of dispersion during colloidal processing according to reported by Poorteman



et al. [129] and Sun et al. [130]. It is worth noting that these colloidal processing methods are still associated with the problem of poor interfacial bonding between the CNTs and alumina matrix after densification, as solid alumina particles are used as the precursor for the alumina matrix. Therefore, intimate interfacial bonding between the surfaces of CNTs and oxide particles would not be expected [131].

Nevertheless, some success has been achieved with conventional milling techniques, primarily with the use of low to moderate nanotube volume fractions and adjusting the surface chemistry of the colloidal suspensions and selecting proper processing conditions, it is very possible that the nanoparticles can be encouraged to coat the CNTs [15]. Generally, surfactants or dispersants can be used to tailor surface properties or both CNTs and ceramic particles. By using this colloidal processing, Yamamoto et al. [98] investigated  $\text{Al}_2\text{O}_3$  with additions of 0.9 vol% of MWCNTs and obtained a gain in fracture toughness of 25% applying the SENB method and ~ 56% by conventional indentation fracture. Likewise, Wei et al. [132] reported an increase in the fracture toughness of  $\text{Al}_2\text{O}_3$  reinforced with 3 vol% MWCNTs of 79 % by means of SENB technique. Similarly, applying the indentation fracture Estili and Kawasaki [133] reached an increase in the fracture toughness value of 99.5 % when the alumina was reinforced with 3.5 vol% MWCNTs. In order to study more in depth the colloidal processing, the readers are referred to consult references 15 and 126.

### 2.1.3. Sol-gel processing

As mentioned previously, various techniques have been used to prepare carbon nanotube/ceramic composites. Among them, sol-gel processing method provides an important alternative route to create an intimate dispersion of carbon nanotubes in inorganic matrices. In this method, the CNTs are carefully dispersed in a molecular precursor (solution) which then undergoes a condensation reaction with the purpose to generate a green body for subsequent consolidation by different methods [15]. The solution sol-gel technique, in particular, offers an opportunity to manufacture not only ultra-homogeneous materials but also heterogeneous or nanocomposite materials. Once they have been crystallized and densified, can be appropriate for structural applications [6]. It is important to mention that work to date has focused mainly on CNTs in silicate sol-gel systems such as investigations carried out by Seeger et al. [134], de Andrede et al. [135]. On the other hand, there have been a few investigations pertaining to preparing nanotube composites using aluminum oxide. According to Livage [136], Vorotilov et al. [137], Sen et al. [138], Sealy [139] and Ning et al. [140], sol-gel

technique presents advantages such as simple, low processing temperature, versatile, high chemical homogeneity, rigorous stoichiometry control, high purity products, formation of three dimensional polymers containing metal-oxygen bonds. Likewise, single or multiple matrices. Conversely, greater shrinkage, weak bonding, low wear-resistance, high permeability and difficult control of porosity compared to the mixing method are some of their limitations [141].

In spite of the sol-gel method has also been used to improve the poor interfacial bonding, the mechanical properties were not increased to the level expected such as was reported by Mo *et al.* [107] who only obtained a gain in fracture toughness (measured by indentation fracture method) of 10 % with 1.5 wt% of MWCNT added to  $\text{Al}_2\text{O}_3$  by means of sol-gel method. More detailed information concerning to nanocomposite systems, including ceramics reinforced with CNTs can be found in the interesting review by Cury Camargo *et al.* [141].

## **2.2. Mechanical properties of carbon nanotube $\text{Al}_2\text{O}_3$ and ZTA ceramic composites**

High performance ceramic matrix structural composites have been developed aiming to take advantage from nanostructures [142]. During the last decade, there has been a steady increasing interest in development of advanced ceramic composites with improved mechanical and physical properties by incorporating second phase particles/whiskers or alternatively carbon nanotubes (CNTs). [143]. Aluminum oxide or alumina ( $\text{Al}_2\text{O}_3$ ), as one of the most common groups of advanced ceramics [144], has a great potential due to its hardness as well as good chemical and thermal stabilities. However [131], it has low fracture toughness, which is an intrinsic characteristic of ceramic materials. In this context, if these properties of alumina can be improved, this important ceramic would be expected to have applications such as cutting tools, dies, dental implants and chemical and electrical insulators, among others. On the other hand, Zirconia ( $\text{ZrO}_2$ ) [114] and Zirconia-toughened alumina (ZTA) [145] ceramics have received significant scientific and technological attention due to their high melting point, excellent room temperature strength, toughness and wear resistance [146].

Nevertheless, the investigations to date have focused mainly on alumina ceramics with only limited work having been done on alumina-based composites, ZTA or  $\text{ZrO}_2$ , for example [21]. In some field application, the tendency nowadays is the elimination of the metallic parts, including implant restorations and orthopaedic replacements. Therefore, taking into account this, the use of alumina and zirconia with high density like biomaterial have

been proposed. Moreover, alumina has shown excellent biocompatibility and wear resistance however exhibits low flexural strength and toughness, as mentioned earlier. On the other side, the pure zirconia cannot be used in the manufacture of different parts without the addition of stabilizers (the more commonly used  $\text{Y}_2\text{O}_3$ ) [147]. Owing to the stabilizing effect of yttria ( $\text{Y}_2\text{O}_3$ ), tetragonal zirconia polycrystalline (TZP) ceramics can be processed. The  $t \rightarrow m$  phase transformation in the yttria stabilized zirconia can be induced in its surface leading to the aging phenomena with degradation by surface roughening, microcracking at the surface limits the use of yttria stabilized zirconia as a biomaterial. Considering the aforementioned, it is necessary to manufacture ceramic materials with mechanical properties compared to alumina and improved *in vivo* stability compared to Y-SZP such as reported Benzaid et al. [148].

In order to avoid or to limit aging phenomena and to obtain excellent mechanical properties, some zirconia-alumina composites have been developed [149]. In spite of the improvements to the fracture toughness have not been sufficient with the addition of second phases such as a metal into the alumina matrix [131], it is believed that among different nanomaterials, CNTs have undoubtedly attracted much attention as reinforcement agents in ceramic matrices due to their outstanding mechanical properties, high Young's modulus as well as very good electrical characteristics and good thermal and chemical stabilities [108]. Therefore, up to now, investigations pertaining to  $\text{Al}_2\text{O}_3$  ceramics reinforced with CNTs (SWCNTs or MWCNTs) have been reported and the resulting composites have shown variations in density, flexural strength, fracture toughness, hardness [98, 113] but also better room temperature mechanical properties over pure alumina [144]. Nevertheless, the homogeneous dispersion of CNTs in ceramic matrix and the interfacial bonding between the two materials are the two great challenges in the processing of carbon nanotubes as reinforcement. Since the application of engineering ceramic is limited by their brittleness, evaluating the fracture toughness becomes highly critical in terms of designing a structural ceramic component [110].

It is important to keep in mind that hot pressing (HP) and Spark Plasma Sintering (SPS), two commonly techniques used to densify CNT/ $\text{Al}_2\text{O}_3$  and CNT/ZTA composites, are practically inappropriate for the manufacturing composites of varied geometry due to high cost, limited continuous production as well as difficulty to manufacture complex geometries of different sizes at affordable price. Therefore, it is of vital importance to attempt the manufacture of ceramic composites by means of simple and cost-effective process, such as pressureless sintering, with commercial raw materials guaranteeing excellent mechanical properties [150]. Taking this

into account, here we review the hardness and fracture toughness of  $\text{Al}_2\text{O}_3$  and ZTA composites consolidated by pressureless sintering mainly, with different SWCNTs or MWCNTs contents and using the indentation Vickers and other commonly methods to obtain hardness and fracture toughness values.

### **2.2.1. Effect of CNTs on the hardness of $\text{Al}_2\text{O}_3$ and ZTA composites**

The poor fracture toughness or brittleness of the aluminium oxide ( $\text{Al}_2\text{O}_3$ ) is nowadays the main issue. Therefore, an alternative to overcome such weakness could be making it as composite materials [151]. There have been several attempts in order to manufacture reinforced alumina with particulates, whiskers, both short and large fibers with enhanced hardness and fracture toughness. It is well known that when alumina is reinforced with particles such as zirconia ( $\text{ZrO}_2$ ), the resulting composite is commonly denominated Zirconia Toughened Alumina (ZTA) which has received significant scientific and technological attention for use in cutting tools or prosthesis components due to their excellent room temperature strength, toughness and wear resistance combined with a moderate hardness [145]. Up to now, there are several reports concerning to alumina reinforced with carbon nanotubes [106] but the obtained results have shown inferior mechanical properties than expected and, in some extreme cases, these mechanical properties are even worse than those monolithic ceramics [23, 26]. On the other hand, a small number of investigations that correlate the effects of the CNTs with the hardness as well as fracture toughness when they are added to ZTA composites have been published. However, Bocanegra et al. [30] and Echeberria et al. [152] have recently published important results in mechanical properties in ZTA composites reinforced with carbon nanotubes in the form of SWCNTs or MWCNTs and consolidated by pressureless sintering or alternatively, by Spark Plasma Sintering (SPS).

According to the open literature, it is believed that the carbon nanotubes (CNTs) can upgrade both  $\text{Al}_2\text{O}_3$  and ZTA and therefore, make them suitable for numerous and specific applications. However, different amounts of CNTs and sintering processes have been used but regrettably wide differences in the mechanical properties were found with the different CNTs content investigated [23, 27, 98, 113, 153, 154] due probably to the weak bonding between CNTs and ceramic matrix and/or alternatively to inhomogeneous distribution of CNTs within the ceramic matrix. A degradation of carbon nanotubes during sintering has also been reported as the responsible for decreased mechanical properties [155]. Nevertheless, some of the variations may purely arise from different testing techniques used [111]. Indeed, owing

to the controversial results reported in the literature on CNT/ $\text{Al}_2\text{O}_3$  and CNT/ZTA composites, the question is: ***Which is the optimum CNTs addition to a ceramic matrix in order to obtain the highest values of hardness and fracture toughness?***. We consider that the performance of MWCNTs and SWCNTs as reinforcement of this kind of ceramic oxide composites will depend in a great measure on variables like dispersion method, nature of matrix, surface charges of particles and particle size distribution as well as dimensions of CNTs [30]. Thus depending on the above mentioned considerations, it is very venturous to determine which will be the optimum vol% or wt% CNTs content to obtain high mechanical properties values considering that each specific ceramic composite can have different composition. Our appreciations are agreed with investigations by Sarkar and Das [150] who investigated nanocomposites with additions of 0.3 vol% MWCNTs pressureless sintered at 1700 °C in inert atmosphere (Argon) during 2 h and obtained an improvement in hardness around of 23 % (~ 21 GPa) than  $\text{Al}_2\text{O}_3$  (~ 18 GPa) free of carbon nanotubes due to sufficient densification which in turn formed a better interface ensuring therefore, an effective load sharing. Conversely, composites with MWCNTs content higher than 0.3 vol% offered lower improvements in hardness as a consequence of presence of nanotubes agglomeration and probably due to poor dispersion of CNTs in matrix.

It is well known that clusters of CNTs act as defects with no load carrying ability. From Sakar and Das work [150], it is noteworthy to stand out that the composites were produced by conventional wet mixing of “as received” MWCNTs and  $\text{Al}_2\text{O}_3$  without previous treatment followed by conventional sintering at different temperatures. On the other hand, the extent of hardness improvement reached in this investigation was undoubtedly higher than reported by Mo et al. [107], Ahmad et al. [108], Zhang et al. [112], and Sun et al. [123]. This improvement in hardness suggests good dispersion at low additions of CNTs. On the other side, a 12% increase in hardness with 2 wt% CNTs addition to nanometer  $\text{Al}_2\text{O}_3$  matrix ( $\theta < 40$  nm) consolidated by HP at 1600 °C for 1 h was reported by Ahamad et al. [154]. Unsatisfactory results were reported by them after the addition of CNTs up to 5 wt% where the hardness was suppressed approximately 7 %. This behaviour can be attributed to the densification difficulties arising with higher concentrations of CNTs in the nanocomposites that can also affect the elimination of pores and mass transportation through bulk diffusion, parameters of paramount importance to reach full density according to pointed out by Jinpeng et al. [153]. This phenomenon can occurs even if the CNTs are well-dispersed and more for high volume of CNTs inasmuch as the existence of carbon nanotubes at grain boundaries prevents the grains closing

during densification resulting in nanocomposites with fine grain size by grain pinning [111]. Therefore, composites with lower densities could be obtained. Now, with a novel process to manufacture CNT/ $\text{Al}_2\text{O}_3$  nanocomposites, consisting of a molecular level mixing process and subsequently in situ SPS consolidation, it is expected that the chemical bonding between carbon nanotubes and the matrix mixing CNTs and Al ions enhance the load transfer from ceramic matrix to CNTs according to investigation carried out by Cha et al. [106]. Similar to different studies, they found that hardness was increased up to 1 wt% MWCNTs, but due to the severe agglomeration produced with CNTs content higher than 2 wt%, the hardness decreases. A good dispersion of carbon nanotubes undoubtedly produces, in some cases, marginal improvements in hardness values such according to reported by Ahmad et al. [111] in their investigations with nanometer  $\delta\text{-Al}_2\text{O}_3$  (mean size 40 nm) and additions of 2 and 5 wt% pre-treated MWCNTs and consolidated by means of hot pressing at 1600 °C for 1 h. Slight improvement in hardness at 2 wt% CNT additions was associated to that good dispersion. Nonetheless, when the CNTs content is 5 wt%, significant reduction in hardness was observed and the authors justified this behaviour with serious difficulties in achieving good dispersion of carbon nanotubes for high levels of these.

Deterioration in the mechanical properties of CNTs/ $\text{Al}_2\text{O}_3$  composites can also be due to the destruction of carbon nanotubes during hot pressing process [117]. However, this technique offers nanocomposites with relatively good hardness and fracture toughness. Maensiri et al. [144] reported that the hardness in  $\text{Al}_2\text{O}_3$  (mean particle size  $\sim 400$  nm) hot pressed at 1450 °C was reduced for CNTs content higher than 1 wt%. These results differ slightly of those obtained by Ahmad et al. [111]. It seems to be that the adequate dispersion of CNTs in the alumina matrix is the common problem to achieve high mechanical properties values.

Fractographic studies carried out by Ahmad et al. [108] on fracture surface of  $\text{Al}_2\text{O}_3$  ceramics reinforced with 10 vol% MWCNTs revealed blocks of CNT leading to significant drop in hardness suggesting, again, a poor dispersion of CNTs, which in turn is reflected in a lower densification with elongated pores existing in the composite. Kim et al. [156] undertook an investigation on  $\text{Al}_2\text{O}_3$  matrix composites (pressureless sintered at 1550 °C under argon gas atmosphere) varying the addition of pre-treated MWCNTs up to 3 vol% and they found that the CNT addition to the monolithic alumina unfavourably affects the densification of the composite deteriorating the hardness. With the increasing of CNTs content, systematically the hardness was decreasing up to obtain a value of 9.30 GPa for 3 vol% of MWCNTs, representing a drop in hardness of approximately 57 % compared to monolithic  $\text{Al}_2\text{O}_3$  ceramic. This result differs of the obtained by Ahmad et al.

[108, 111], who reached hardness values around of 17 GPa for CNTs content of 4 vol%. The notable difference in these values can be attributed to sintering process, starting  $\text{Al}_2\text{O}_3$  powder as well as the processing of the MWCNTs.

As mentioned earlier, in spite of the different studies published concerning to zirconia toughened alumina (ZTA) composites, there is an absolute lack of information about the behaviour of these ZTA composites when are reinforced with carbon nanotubes. It is very important to stress that in applications like load bearing orthopaedic joints, where the hardness is of paramount importance, ZTA could have some drawbacks, as the introduction of zirconia into the hard alumina matrix results in a decrease in hardness of the ceramic. Therefore, it is very attractive to explore the behaviour of these ceramic composites reinforced with carbon nanotubes in order to obtain a ceramic composite as hard as alumina, toughened by phase transformation, toughened and reinforced by the presence of CNTs [157]. Therefore, the behaviour of ZTA/CNTs could be a breakthrough in the application of ceramics in the field of arthroplasty.

Following this, Echeberria et al. [158] reported that the hardness can be increased up to  $\sim 17\%$  after hot isostatic pressing (HIP) treatment ( $1475\text{ }^\circ\text{C}$  1h at 150 MPa) in ZTA ( $\text{Al}_2\text{O}_3 + 0.025\% \text{ MgO} + 13\% \text{ TZ-3Y} + 2\% \text{ ZrO}_{2(\text{m})}$ ) composites with additions of 0.01 wt% MWCNTs compared to the “as sintered” (pressureless sintered in an anti-oxidant sagger with graphite powder bed at  $1520\text{ }^\circ\text{C}$  during 1 h in air) composites free of carbon nanotubes and  $\sim 9\%$  compared to monolithic  $\text{Al}_2\text{O}_3$  free of HIP. Doubtless, a lower amount of CNTs favors the dispersion and therefore, the increasing in mechanical properties. More recently [30], studies on ZTA composites reinforced with both SWCNTs and MWCNTs have shown some increase of hardness ( $\sim 6\%$ ) with additions as low as 0.01 wt% SWCNTs for composites pressureless sintered at  $1520\text{ }^\circ\text{C}$  during 1 h in air using a graphite bed powder. Considering the experimental error, it is observed that the measured Vickers hardness remains approximately constant for pure ZTA and CNTs reinforced ZTA composites. On the other hand, when 0.01 wt% of SWCNTs or MWCNTs are added to pure  $\text{Al}_2\text{O}_3$ , a drop in hardness is observed ( $\sim 15\%$  referenced to monolithic alumina). Although the decreasing of hardness with very low CNTs content is clear in this investigation, it is noteworthy that even, with a good dispersion of carbon nanotubes within the alumina matrix, the mechanical properties can be diminished due to factors such as: (a) the interaction between the ceramic phases (in this case alumina and zirconia), (b) CNTs surface charges of particles and particle size distribution, and (c) diameter and length of CNTs, as was registered by Bocanegra et al. [30]. Nevertheless, it is clear that for a same ceramic matrix and CNTs content, the

mechanical properties can be different considering the processing route followed in the consolidation of the composite.

As we mentioned earlier, both HP and SPS are two commonly techniques used to densify CNT/ $\text{Al}_2\text{O}_3$  and CNT/ZTA composites with outstanding mechanical properties. However, nowadays these techniques are practically inappropriate for the consolidation of composites owing to high cost, difficulty to manufacture complex geometries of different sizes at affordable price. In this context, it is important to attempt to obtain the excellent mechanical properties reached with HP and SPS with the conventional sintering processes in order to produce ceramic composites at low cost, complex geometries and sizes. It is well known that with SPS it is possible to prepare fully densified ceramic composites at comparatively lower temperature with substantial short holding [159].

In the manufacture of CNT- $\text{Al}_2\text{O}_3$  composites, several studies have been carried out applying HP and SPS with the purpose to improve their mechanical properties. A study on a SWCNT/ceramic composite has been described by Zhan *et al.* [23]. This group uses the technique of SPS to prepare  $\text{Al}_2\text{O}_3$  composites containing 5.7 and 10 vol% SWCNTs. The measured hardness was maintained constant for CNTs content of 5.7 vol% ( $\sim 20.0$  GPa) compared to  $\text{Al}_2\text{O}_3$  free of carbon nanotubes (both SPSed at  $1150^\circ\text{C}$  during 3 min). However, when the CNTs content was increased at 10 vol%, the hardness decreases dramatically at sintering temperatures of  $1100^\circ\text{C}$  3 min (4.40 GPa). The authors attributed this behaviour to loose network with a lack of interfacial contact. On the other hand, for the same CNTs content (10 vol%) but for sintering temperature of  $1150^\circ\text{C}$  3 min, the hardness was surprisingly increased to 16.1 GPa being slightly more low than pure  $\text{Al}_2\text{O}_3$  (20.3 GPa). The authors suggested that stronger bonding of ropes with the matrix was the reason for the abrupt increasing in hardness. These results contrast with the obtained by Wang *et al.* [24] in  $\text{Al}_2\text{O}_3$  reinforced with 10 vol% SWCNTs and SPSed at temperatures as high as  $1550^\circ\text{C}$  in vacuum. For the same relative density ( $\sim 95\%$ ), Zhan *et al.* [23] reached a hardness of 9.30 GPa at  $1150^\circ\text{C}$  2 min with 10 vol% SWCNTs content meanwhile Wang *et al.* [24] reported a hardness of 9.0 GPa at  $1550^\circ\text{C}$  with hold time at peak temperature 3 to 10 min for the same CNTs content. Undoubtedly, the surprisingly here are the 16.1 GPa reached by Zhan *et al.* [23] at  $1150^\circ\text{C}$  3 min compared to the 9.0 GPa reported by Wang *et al.* [24] under the above conditions. Although both work teams [23, 24] used in their experiments the same starting  $\text{Al}_2\text{O}_3$  powders, the variations reported in hardness could depend on the SPS conditions.

The results obtained by Zhan *et al.* [23] and Wang *et al.* [24] have elucidated nowadays important points of reference. On the addition of



MWCNTs up to 2.48 wt%, the hardness was decreased by 13% compared to  $\text{Al}_2\text{O}_3$  free of carbon nanotubes according to reported by Lee et al. [131] with  $\text{Al}_2\text{O}_3$  ceramics by incorporating MWCNTs ranging from 0 to 2.5 wt% and sintered by SPS at 1375 °C under vacuum for 5 min. Although no consensus on the hardness has been reached by several authors [15, 23, 107, 130], we speculate that the variations occurred during the processing of the composites could be responsible of the different mechanical properties that can be obtained. This appreciation can be supported with the results from Zhan et al. [23] who obtained a hardness of 16.1 GPa at 1150 °C 3 min with additions of 10 vol% (approximately 5 wt%) of SWCNTs compared to 16 GPa obtained at 1375 °C 5 min with additions of 2.48 wt% of MWCNTs registered by Lee et al. [131], and Zhang et al. [34] who showed that the hardness is highly dependent on both the CNT content and the sintering temperature in  $\text{Al}_2\text{O}_3$  nanocomposites with variable CNT content and directly synthesized by chemical vapour deposition (CVD) and subsequently densified by SPS at 1150 and 1450 °C during 10 min. The investigators revealed in their work that at sintering temperature of 1150 °C the hardness of the composites with different CNT content is much lower than that of the pure alumina (8.60 GPa), while at 1450 °C, the hardness of some samples is slightly higher as compared to the  $\text{Al}_2\text{O}_3$  free of CNTs (9.21 GPa). The highest hardness value was 9.98 GPa obtained for 7.39 wt% CNT- $\text{Al}_2\text{O}_3$  nanocomposite at 1450 °C. Therefore, it is very possible to get high hardness values by using both SPS or alternatively pressureless sintering at different temperatures and times.

A novel structure for CNT reinforced  $\text{Al}_2\text{O}_3$  composites with improved mechanical properties has been developed by Yamamoto et al. [98] based on the modification of the MWCNTs with acid treatment combined with a mechanical interlock induced by the chemically modified MWCNT leading to improved mechanical properties. Their composites were prepared by SPS at 1500 °C in vacuum for 10 min. In order to develop a rigorous study, the author's also prepared similar processes using pristine MWCNTs as starting material for comparison. The higher hardness for the acid-treated MWCNT/ $\text{Al}_2\text{O}_3$  composites may be attributed to more homogeneous dispersion of MWCNTs compared with the pristine MWCNT/alumina composites such as was revealed by means of SEM studies carried out by Yamamoto et al. [98]. However, the hardness decreasing compared with pure alumina when the MWCNTs content is increased up to 3.7 vol% for both acid-treated MWCNT/ $\text{Al}_2\text{O}_3$  (~ 24%) and pristine MWCNT/ $\text{Al}_2\text{O}_3$  (~ 36%) composites was reported. With the purpose to reach an intimate dispersion of carbon nanotubes in ceramic matrices, Mo et al. [107] investigated on MWCNT reinforced alumina matrix nanocomposites (aluminium tri-sec-butoxide ( $\text{Al}(\text{OBu}^s)_3$ ) used as precursor of alumina) carefully prepared by

sol-gel technique (These processes are used for the preparation of homogeneous ceramic products at low temperatures) with additions of 1.5 and 3.3 vol% MWCNT and followed by SPS at 1650 °C for 5 min. Then, the obtained samples were annealed at 1000 °C for 6 h in order to remove carbon diffused from the graphite mold used. Regardless of the volume fraction of carbon nanotubes, the sintered density varied from 99.5 to 100%.

Contrary to results from Yamamoto *et al.* [98] and Zhan *et al.* [23], the hardness of MWCNT/Al<sub>2</sub>O<sub>3</sub> nanocomposite increases with increasing the volume fraction of carbon nanotubes. It is mainly due to a difference in distribution of carbon nanotubes within alumina matrix and interfacial strength between CNTs and Al<sub>2</sub>O<sub>3</sub> matrix. In reason of this, the effective load transfer from the matrix to CNTs is possible, and therefore a significant load sharing of carbon nanotubes mainly enhances the hardness of CNT/alumina nanocomposites [107]. This behaviour has also been observed in carbon nanotube reinforced polymer nanocomposites [160].

An interesting study related with the effect of sintering temperature on single-wall carbon nanotube-reinforced Al<sub>2</sub>O<sub>3</sub>-based nanocomposite consolidated by SPS was reported by Jiang *et al.* [155]. The starting materials used in this investigation were the same employed by Zhan *et al.* [23] in their work. The hardness decreases drastically when the sintering temperature is increased above 1150 °C being reached at this temperature the maximum hardness value (~ 15.8 GPa). This behaviour can be attributed to by the conversion of CNT to graphite, as was confirmed by the authors by means of Raman Spectroscopy studies. Likewise, the existence of pores residing in the grains, grain boundaries as well as the presence of bundles of CNTs in the Al<sub>2</sub>O<sub>3</sub>-10 vol% SWCNT composite sintered at 1350 °C, contribute to a low hardness (~ 10.5 GPa). This result in particular differs from the reported by Wang *et al.* [24] for the same SPS temperature and starting alumina powder. Jiang *et al.* [55] suggested that the difference in hardness could be due to the lower mechanical load used during SPS process by Wang *et al.* [24]. It is well known that high applied pressure leads to a composite more dense and, hence, a ceramic one with high hardness. Recently, a novel method to obtain advanced fine-grained Al<sub>2</sub>O<sub>3</sub> by addition of 1 vol% of carbon nanotubes has been developed by Inam *et al.* [161]. With this investigation, the authors reported that the CNTs can be used as reinforcement agent and/or as grain growth suppressant in alumina matrix. For it, after sintering by SPS at 1450 °C during 5 min, the ceramic composite was heat treated at temperatures between 1300 and 1500 °C with the aim of oxidize CNTs and density the remaining 1 vol% porosity in the composites. Therefore, a good dispersion of nanotubes is of paramount importance to retard grain growth by reducing their mobility during sintering [162]. A 25% improvement in hardness was

registered for monolithic alumina produced after the heat treatment of  $\text{Al}_2\text{O}_3$  + 1 vol% CNT composite, as compared to alumina free of carbon nanotubes. The improved hardness in heat treated composites is solely due to the refinement in grain size and improved density contradicting to Jiang et al. [155] who suggest the presence of residual compressive stresses.

Based on the fact that some of the CNT/ceramic composites have not presented outstanding mechanical properties expected as consequence of the weak bonding between carbon nanotubes and matrix or also due to poor dispersion of CNTs within the matrix, He et al. [163] undertook an investigation on the synthesis of CNT with a low Ni content (0.3 wt%)-reinforced  $\text{Al}_2\text{O}_3$  matrix composites producing a network structure of CNT(Ni)- $\text{Al}_2\text{O}_3$  composite powder to obtain homogeneous implantation of the CNTs within the alumina powder ensuring a bond strong between alumina matrix and CNTs. SPS processing at 1300 °C during 6 min produced a composite with remarkable mechanical properties. The introduction of 1.5 wt% CNTs into alumina matrix improved the hardness from 17.1 GPa (monolithic alumina) to 21.1 GPa representing an increase of ~ 17.5%. On the other hand, when 2.4 wt% CNTs is added into alumina matrix, the hardness is only 19.0 GPa (decreasing of ~ 5.8% compared with alumina free of CNTs). These results present a more effective and obvious improvement in hardness compared with the reported by Xia et al. [16], Mo et al. [107] and Sun et al. [130].

Taking into account that the hardness is crucial for applications such as cutting tools, wear and abrasion-resistant parts, prosthetic hip-joint balls and sockets, ballistic armor, molds and dies, valves, and seals [164, 165] and considering also the absence of open literature pertaining to the behaviour of ZTA-CNT ceramics under SPS conditions, Echeberria et al. [152] have explored this theme investigating the mechanical properties of ZTA composites reinforced with MWCNTs or SWCNTs fabricating very dense composites and demonstrating that 0.1 wt% of CNTs added to ZTA is enough to obtain high hardness and fracture toughness at indentation loads of 1, 5, and 10 kg. It is well known that the introduction of zirconia into the hard alumina matrix results in a decrease in hardness of the ceramic. However, the work of Echeberria et al. [152] reported a maximum hardness value of 21.65 GPa measured at 1 kg of applied load for the ZTA composite with additions of 0.1 wt% MWCNTs and sintered by SPS at 1520 °C approximately 5-6 min. Compared to monolithic  $\text{Al}_2\text{O}_3$  sintered consolidated by SPS, it is clear that this value is higher than 19.0 GPa registered by Wang et al. at 1550 °C [24], 20.3 GPa reported by Zhan et al. [23] at 1150 °C, 19.7 GPa reported by Trombini et al. [166] at 1300 °C, 17 GPa registered by Rattanachan et al. [167] at 1300 °C, 20.3 GPa measured by Zhan et al. [168] at 1150 °C, 19.7

GPa reported by Akin *et al.* [169] at 1350 °C using the same starting alumina powder than Echeberria *et al.* [152].

On the other side, for all indentation loads, the composites reinforced with 0.1 wt% MWCNTs reached the maximum hardness, meanwhile ZTA composites with additions of 0.1 wt% SWCNTs exhibited and even lower hardness compared to ZTA composite without additions of CNTs suggesting an agglomerate state of the SWCNTs [152]. With this investigation it is demonstrated that it is possible to maintain practically the excellent hardness of the alumina matrix when zirconia was added it. Interested readers are remitted to consult [152] for more details.

In closing this section, regardless of the processing methods, ceramic matrix and carbon nanotubes used in different investigations, there are works that have reported no effect, for example An and Lim [119] and Ahmad and Pan [125], or improved hardness by the incorporation of carbon nanotubes according to reported by Chan *et al.* [106], Peigney *et al.* [170] and Burghard *et al.* [171]. However, the improvements obtained by some authors have been marginal but unfortunately; no comments were presented explaining in detail the interfacial interactions between hard ceramic particles and the carbon nanotubes.

### **2.2.2. Effect of CNTs on the fracture toughness of Al<sub>2</sub>O<sub>3</sub> and ZTA composites**

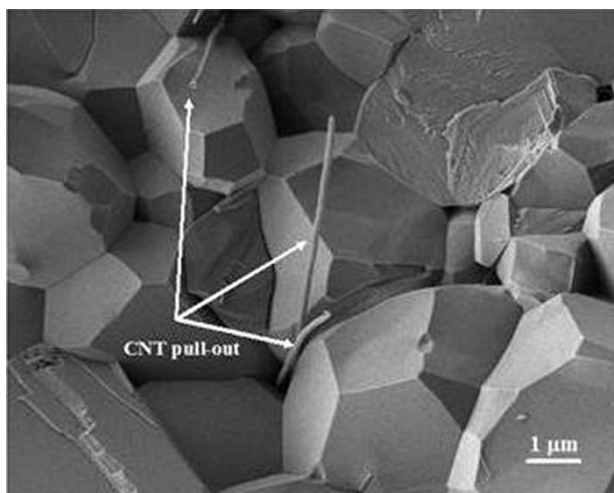
Aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) and Zirconia toughened alumina (ZTA) ceramics have received significant scientific and technological attention for different applications such as impact resistant coatings, line inserts, heat exchangers, cutting tools or prosthesis components due to their excellent room temperature strength, toughness and wear resistance combined with a moderate hardness [145]. However, the brittleness of these ceramics has limited, no doubt, their potential use in structural and functional applications [172]. The basic cause of this brittleness is the marked degree of covalent bonding in the ceramic, which in turn leads to low dislocation mobilities and to crystal structures of low symmetry with insufficient slip systems to blunt existing cracks [173]. Likewise, it is important to stress that the most of fabrication processes involve high-temperature powder technology and so give rise to defects as pores of varying sizes and positions, to inclusions as well as grain-boundary phases, to poorly bonded grains, and to grains of different size and shape.

Despite these great difficulties [172], attempts have been made in order to devise ways of controlling the microstructure of ceramics so as to enhance their fracture toughness. Due to their excellent mechanical properties, carbon

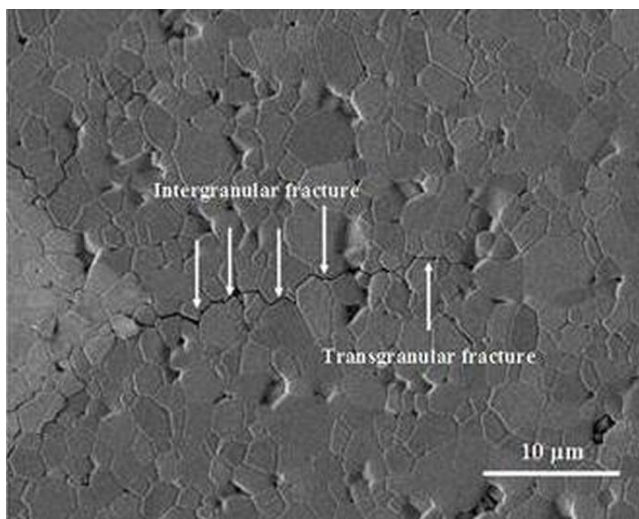
nanotubes (CNTs) have been used as reinforcing agent, mainly in polymeric matrices [174]. However, nowadays, ceramic–CNT systems are studied to obtain novel nanocomposites with improved fracture toughness [23, 175, 176]. A very few researchers have added CNTs to ceramic matrices such as SiC,  $\text{TiO}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{Al}_2\text{O}_3$ , and ZTA for improvement of fracture toughness [23, 24, 30, 118, 152, 158, 177, 178]. Nevertheless, the toughening behaviour observed in the most of the CNT-reinforced matrix is mainly linked to CNT crack bridging, CNT dispersion and crack deflection [16, 179].

The effective use of CNTs in nanocomposites requires a homogeneous dispersion of CNTs, strong interfacial adhesion between CNTs and ceramic matrix, and a certain volume content of CNTs in order to achieve an improvement in properties such as hardness and fracture toughness. In spite of the difficulty to achieve these requirements with the traditional ceramic processing, this technique continues being widely used inasmuch as it is possible to obtain complex geometries with different sizes at low cost. In the open literature, several reports pertaining to the fracture toughness of ceramic nanocomposites with different volume content of both SWCNTs and MWCNTs and consolidated by means of different sintering techniques have been published. As mentioned earlier, few lots of reports are found in the literature about pressureless sintered  $\text{Al}_2\text{O}_3$  ceramics reinforced with CNTs. However, Sun et al. [180] pressureless sintered in air atmosphere (1350 to 1500 °C for 2 h) alumina matrix composites containing 0.1 to 2 wt% of MWCNTs. They calculated the fracture toughness from measurements of the lengths of cracks generated by Vickers indentation method and these waved around  $2.5 \text{ MPa}\cdot\text{m}^{1/2}$  and were lower than those of the monolithic  $\text{Al}_2\text{O}_3$  ceramics.

We can speculate that poor dispersion of CNTs within the alumina matrix could create weak regions where cracks can originate leading therefore, to decreasing of fracture toughness. These results contrast [181] for monolithic alumina ( $3.34 \text{ MPa}\cdot\text{m}^{1/2}$ ),  $\text{Al}_2\text{O}_3 + 0.01 \text{ wt\% MWCNTs}$  ( $3.05 \text{ MPa}\cdot\text{m}^{1/2}$ ), and  $\text{Al}_2\text{O}_3 + 0.1 \text{ wt\% MWCNTs}$  ( $2.78 \text{ MPa}\cdot\text{m}^{1/2}$ ), all sintered at 1520 °C during 1 h in air atmosphere using graphite as powder bed (very similar to the experimental sagger structure used by Sun et al. [180]). We attribute this increase in fracture toughness to good dispersion of CNTs in the alumina matrix due to the lower CNTs content producing a tight bonding between CNTs and  $\text{Al}_2\text{O}_3$  matrix, pullouts of the MWCNTs from matrix (Fig. 12), most of them broken during fracturing, as well as crack deflection (zigzagged cracks) where the fracture pattern is almost exclusively intergranular with cracks occasionally propagating through the smaller grains (Fig. 13). Considering that under hot pressing [27] or SPS [182, 183] the formation of simple geometries and moderate sizes is very limited as



**Figure 12.** SEM micrograph of the fracture surface of  $\text{Al}_2\text{O}_3$  with additions of 0.05 wt% MWCNTs pressureless sintered at 1520 °C 1 h in air atmosphere. Arrow marks indicate pull-out of CNTs from the matrix [181]



**Figure 13.** SEM micrograph of the indentation crack of a 0.05 wt% MWCNT- $\text{Al}_2\text{O}_3$  composite pressureless sintered at 1520 °C 1 h in air atmosphere. Arrow marks shown the fracture mode. [181]

mentioned above, the development of pressureless sintering technique is needed in order to enable the commercially viable fabrication of complex geometries to near-net shape using conventional ceramic powder processing method according to works carried out by Zhang et al. [112].

These authors densified by pressureless sintering without damage to the CNTs (purified by acid treatment and then dispersed in water at pH 12), alumina ceramics reinforced with 1, 3, and 5 vol% MWCNTs at 1500 °C for 2 h. The composite containing 1 vol% CNTs had the highest fracture toughness,  $4.1 \text{ MPa}\cdot\text{m}^{1/2}$  compared to monolithic alumina and alumina containing 3, and 5 vol% CNTs supporting the appreciation of Echeberria et al. [158] who reported improvement in mechanical properties (hardness and fracture toughness) with lower carbon nanotubes content. Zhang et al. [112] suggested the increase in fracture toughness to crack deflection and crack bridging as well as a combination of them.

A decreasing of fracture toughness was observed with increasing CNTs addition above 1 vol%, even though the toughness values were still higher than monolithic  $\text{Al}_2\text{O}_3$ . Kim et al. [156] prepared four CNT/ $\text{Al}_2\text{O}_3$  composites varying the addition of carbon nanotubes up to 3 vol% and consolidated by using conventional sintering at 1550 °C in argon atmosphere during 2 h. The fracture toughness measurements were obtained by the indentation fracture testing method [184] with applied loads from 2 to 10 kg. As the CNT content increases, the fracture toughness is enhanced up to  $4.68 \text{ MPa}\cdot\text{m}^{1/2}$  for 3 vol% carbon nanotubes addition showing an increase around 40% referred to monolithic  $\text{Al}_2\text{O}_3$  which in turn is reflected in the resistance to crack initiation and propagation. This result is in disagreement with the results described by Zhang et al. [112] who reached the maximum fracture toughness with 1 vol% of CNTs content. Kim et al. [156] attributed the notable increases in fracture toughness to a homogeneous CNTs distribution within the alumina matrix, although fractographic studies by SEM revealed the existence of some pores and little CNT aggregates that affected other mechanical properties such as hardness and wear resistance. By means of pressureless sintering at temperatures higher than 1500 °C in argon, Sarkar and Das [150] registered investigations on  $\text{Al}_2\text{O}_3$  ceramics with additions of MWCNTs varying from 0.15 to 2.4 vol% to assess their effect on fracture toughness which was measured from the cracks produced by the conventional indentation fracture technique at an applied load of 9.8 N (1 kg) and alternatively, by single edge notched beam (SENB) method. For sintering temperature of 1500 °C practically all tested samples (except  $\text{Al}_2\text{O}_3$  with 1.20 wt% CNTs) improved the fracture toughness than pure alumina. Meanwhile, at temperatures of 1600 and 1700 °C an additional enhancement in  $K_{IC}$  was observed with minor scatter of individual  $K_{IC}$  values indicating a better reproducibility reflected in

uniform toughening effect in composites. From all samples, that with 0.3 vol% of CNT content was the specimen with the highest fracture toughness (approximately an increase of 34% over monolithic alumina) evaluated both indentation fracture and SENB technique. Mechanisms such as crack bridging and crack deflection contributed to enhance the fracture toughness suggesting, no doubt, the presence of useful CNT/Al<sub>2</sub>O<sub>3</sub> interface for an efficient sharing load.

Sarkar and Das [150] found also an extensive “bamboo” structure formed during exposure of CNTs at high temperatures contributing therefore to enhance the fracture toughness and to create structural anchors that improve the connectivity between the alumina matrix and MWCNTs, mitigating “telescopic effect” in MWCNTs, which was observed in investigations of Echeberria *et al.* [152] in ZTA composites reinforced with 0.01 wt% MWCNTs. Bamboo structures offer better mechanical properties than hollow MWCNTs due to better connectivity with the matrix and higher pull-out resistance according to reported by Olek *et al.* [185]. The improvement in  $K_{IC}$  of the specimens from Sarkar and Das [150] was among 6 and 64% which is in accordance with other reported results [98, 112, 123, 124, 130]. On the other hand, lower increase in fracture toughness than the achieved in hot pressing or SPS has also been reported [108, 113, 132, 186]. Some evidence for inadvertent MWNT telescopic extension can be found in severe mechanical stress failure mode studies, including studies of MWNTs embedded in a stressed polymer composite [187].

In the scientific literature there is reports pertaining to alumina ceramics reinforced with CNTs and consolidated by uniaxial hot pressing technique. In spite of considerable progress reached by HP or SPS, some critical issues need to be further addressed such as severe CNTs oxidation at high temperatures, low sintered densities and weak interfacial bonding promoting the CNTs pull-out from the surface. However it is important to highlight some investigations developed by means of this method. The fracture toughness of 1 wt% MWCNTs-Al<sub>2</sub>O<sub>3</sub> hot pressed at temperatures between 1350 and 1500 °C for 1 was explored by Sun *et al.* [130]. They observed that the fracture toughness varied with the HP temperature. Considering the experimental error range, the maximum  $K_{IC}$  (indentation fracture measurements) of 4.0 MPa.m<sup>1/2</sup> obtained at temperature of 1350 °C is almost the same compared to pure alumina (3.9 MPa.m<sup>1/2</sup>). In general, the fracture toughness decreased sharply at temperature of 1500 °C probably due to destruction of some CNTs during exposure at high temperature judging for the SEM fracture surfaces studies where is prominent that fewer MWCNTs existed after sintering at this high HP temperature. The damage or destruction of CNTs during hot pressing has already been reported [117]. A fracture



toughness of 5.5 MPa.m<sup>1/2</sup> (1.8 times that the monolithic alumina and determined by SENB method) with high MWCNTs additions (12 vol%) to the Al<sub>2</sub>O<sub>3</sub> matrix and then hot pressed at 1500 °C during 1 h (same temperature and time than Sun et al. [130]) was reported by Fan et al. [113]. The interface strength between CNTs and Al<sub>2</sub>O<sub>3</sub> matrix was enhanced due to their improved chemical compatibility leading to effective load transference from the matrix to carbon nanotubes through the interface between them.

From SEM studies on the fracture surfaces, bridge the cracks was identified as the mechanism that contributed to high  $K_{IC}$  in the composite [113]. Nevertheless, agglomeration of CNTs and residual part of aggregate when the other part was pulled out, were the other prominent features observed in the microstructure. On the other hand, the pretreatment of MWCNTs seems also to be significant in the improvement of mechanical properties. It is noteworthy that the result by Fan et al. [113] are significantly higher than the registered by Sun et al. [130] under the same hot pressing conditions and 2.02 times that the determined by Maensiri et al. [144] who only obtained a maximum  $K_{IC}$  of 2.74 MPa.m<sup>1/2</sup> (determined by indentation fracture technique) in an Al<sub>2</sub>O<sub>3</sub> composite with additions of 2.5 vol% CNTs compared to 2.41 MPa.m<sup>1/2</sup> determined in pristine Al<sub>2</sub>O<sub>3</sub> hot pressed at 1450 °C for 1 h in argon atmosphere. The toughening mechanism found by Maensiri et al. [144] was identified as crack bridging as suggested for the case of alumina reinforced with carbon nanotubes [123, 124]. An interesting investigation carried out by Zhu et al. [188] revealed that the fracture toughness of hot pressed 2 wt% CNTs-Al<sub>2</sub>O<sub>3</sub> composites at 1500 °C under vacuum can be increased when an ac electric field is applied during the preparation of composites with MWCNTs. The fracture toughness was improved by about 23% (4.66 MPa.m<sup>1/2</sup>) compared to pure Al<sub>2</sub>O<sub>3</sub> (3.78 MPa.m<sup>1/2</sup>) and ~ 14% (4.09 MPa.m<sup>1/2</sup>) referred to the specimen prepared without the effect of an electric field. It is well known that MWCNTs can improve the mechanical properties while locating at the Al<sub>2</sub>O<sub>3</sub> grain boundaries. From microstructural studies on the fracture surfaces, it is clear that the representative toughening mechanisms were the outcrops of CNTs which can absorb a fraction of fracture energy during the fracture processes so that the  $K_{IC}$  could be improved.

On the other side, bridging of the carbon nanotubes between alumina grains can also dissipate some fracture energy during rupture processes. However, it is very important to stress that only the MWCNTs lying perpendicular to the fracture surface contribute significantly to the improvement of mechanical properties. On the other hand, a fracture toughness value of 6.4 MPa.m<sup>1/2</sup> (measured by SENB method), which is twice as high as that unreinforced alumina, was obtained by Wei et al. [190]

in alumina with additions of 1 wt% SWCNTs consolidated by hot pressing at 1600 °C for 1 h in argon atmosphere. A good dispersion of CNTs within the alumina matrix was observed in fracture surfaces where some SWCNTs are embedded into the alumina grains to pin neighboring alumina grains. However, CNT bundles of approximately 100 nm were also observed in the grain boundaries of the matrix. The location of SWCNTs in the composite leading to strong interface between CNTs and matrix. Likewise, pullout from grain boundaries of the alumina matrix and alumina grains, were identified as other mechanisms that contributed to reinforcing effect along with crack deflection around the CNTs along relative poor bonding interface of CTN/matrix according to reported by Zhan *et al.* [191]. The toughness registered by Wei *et al.* [190] contrast with the obtained by Ahmad *et al.* [154] (indentation fracture method) under same hot pressing conditions but with CNT content higher than 2 wt%. A 32% increase in fracture toughness was observed with 2 wt% CNTs additions. However, a further addition of carbon nanotubes up to 5 wt% increased fracture toughness approximately 35% compared with pristine  $\text{Al}_2\text{O}_3$ . No doubt, the increase of mechanical properties at low CNTs content can be due to the well-dispersed carbon nanotubes within the matrix as well as load sharing between the matrix and CNTs. Fractography of the destroyed samples shows also that crack bridging could have contributed to the enhancement of fracture toughness due to the excellent elastic properties of CNTs.

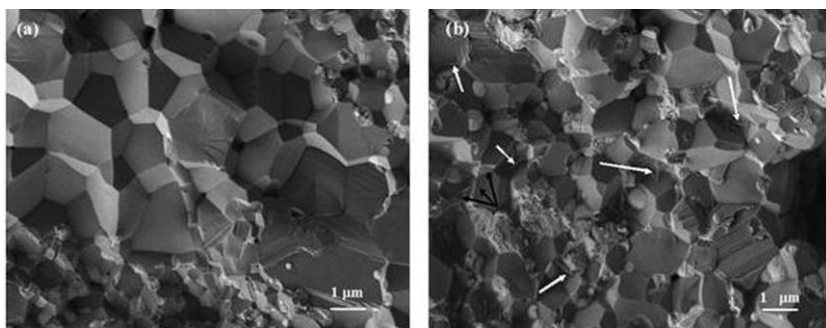
When compared with pure  $\text{Al}_2\text{O}_3$ , Ahmad *et al.* [108] in interesting research work (experimental hot pressing conditions similar to [154]), reported that the fracture toughness obtained by means of SENB technique was 94% and 66% improvement for 4 and 10 vol% CNTs additions, respectively. Similarly, their results by using the conventional indentation fracture and indentation strength bending method (ISB) were an increase by 42% and 47% for IF method, and by 32% and 35% for the ISB technique, for the same 4 and 10 vol% of carbon nanotubes additions, respectively. A homogeneous dispersion of carbon nanotubes seems to be responsible to improvement in fracture toughness. Studies by TEM revealed a strong bond between three grains at the junctions leading possibly to strengthen the grain boundaries of nanocomposites. This behaviour is reflected by the change of fracture mode evidenced in the fracture surface of composites inasmuch as the transgranular fracture is only possible when the strength of the grain boundary is close to that of the matrix grain. This observation has also been registered by Kim *et al.* [192]. Bridging features of CNTs evidenced by SEM investigations and CNT energy dissipation mechanism via elastic deformation (having both end firmly attached with the matrix), played their part in the investigated composites [111]. Therefore, in order to exploit the

elastic property of CNTs, it is of paramount importance a strong interfacial connection at  $\text{Al}_2\text{O}_3$ /CNTs interface.

Taking into account that zirconia ( $\text{ZrO}_2$ ) is one of the more important materials used in the industry because their excellent properties such as high melting point, high mechanical properties, low thermal conductivity, between others, their high temperature phases (*t*- and *c*-phases) could be used as an important tool as reinforcement for toughening alumina through three mechanisms: i) phase transformation, ii) second phase conversion, and iii) microcracking. In this context, Zhu et al. [114] investigated on  $\text{ZrO}_2$  nanoparticles in-situ synthesized on the surface of CNTs and subsequently applied to alumina ceramics. They obtained for the composites containing 1.5 wt% of CNTs and 25 wt% of  $\text{ZrO}_2$ , a fracture toughness of 119% higher ( $7.8 \text{ MPa}\cdot\text{m}^{1/2}$ ) that of the monolithic alumina ceramics ( $\sim 3.56 \text{ MPa}\cdot\text{m}^{1/2}$ ). On the other side, the peak value of the fracture toughness was around 76% higher ( $\sim 6.3 \text{ MPa}\cdot\text{m}^{1/2}$ ) than that of alumina ceramics with only use 2 wt% of CNTs but without  $\text{ZrO}_2$  particles.

The toughening effect of CNTs in ZTA ceramics was mainly attributed to two kinds of mechanisms: crack bridging and pullout on the fracture surfaces. From a crack growth resistance viewpoint, the fracture toughness of the ZTA materials can be assumed as the sum of the intrinsic toughness of the  $\text{Al}_2\text{O}_3$  matrix and the toughness increment owing to toughening mechanisms probably introduced by the zirconia particles [193-195].

A well dispersed and small amount of MWCNTs (up to 0.01 wt%) was enough to produce an increase of fracture toughness in ZTA composites according to investigations carried out by Bocanegra et al. [30]. Fracture toughness in MWCNT-reinforced ZTA increased 41% over ZTA free of the toughening agent ( $3.32 \text{ MPa}\cdot\text{m}^{1/2}$ ) and 44% over ZTA reinforced with SWCNTs ( $3.25 \text{ MPa}\cdot\text{m}^{1/2}$ ). These composites were pressureless sintered to densities higher than 95% of the theoretical density at temperature of  $1520^\circ\text{C}$  in air atmosphere using graphite as bed powder. As was mentioned earlier, although some reliability problems pertaining to the fracture toughness measured by Vickers indentation in ceramics, the absolute toughness values resulting could be overestimated, no doubt, this technique has proved to be able to provide consistent evidence of the toughening role of MWCNTs and SWCNTs in the ZTA composites [156]. Compared to the fracture surface of pure ZTA composite (Fig. 14a), crack deflection was the mainly toughening mechanism that contributed to the improvement of fracture toughness. The observed cracks in ZTA with additions of 0.01 wt% MWCNTs, are characterized by a great number of deviations at large angles (Fig. 14b) and therefore, a tortuous path of the propagating cracks occurs explaining the high efficiency of this mechanism and therefore, an increase in fracture



**Figure 14.** SEM micrograph of fracture surface of the pure ZTA (a), and ZTA with additions of 0.01 MWCNTs.

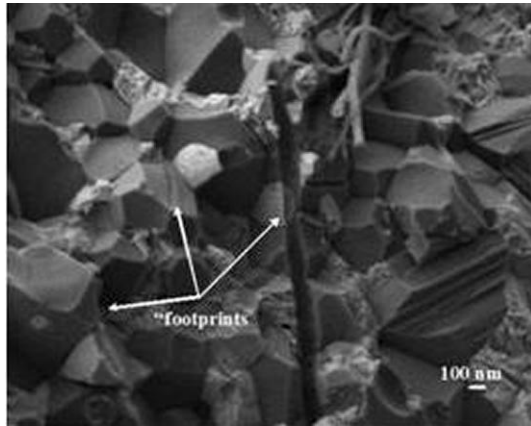
toughness. White arrow marks in Fig. 14b indicate CNTs implanted inside the  $\text{Al}_2\text{O}_3$  ceramic grains, and contribute to the ceramic grain locking as can be shown by black arrows in the same Fig. 14b. However, it is important to stress that some of the CNTs shown in Fig. 14b (white arrows) could not have contributed to the matrix crack bridging inasmuch as no frictional pullout occurred [186].

In order to be effective this reinforcement, the CNTs must be good dispersed in a variety of orientations rather than aligned in specific directions which cannot effectively suppress cracks propagating in different orientations but only those perpendicular to the aligned direction of the fibers according to studies by Estili and Kawasaki [133].

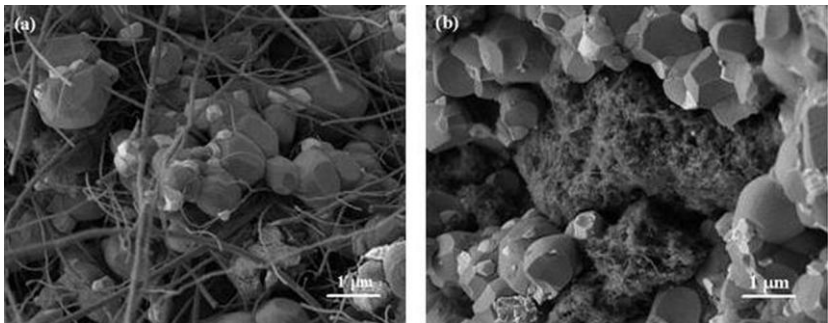
Likewise, MWCNT pull-outs and its debonding from the alumina matrix leaving traces (“footprints”, arrow marks in Fig. 15) on the fracture surface suggesting therefore, a strong bonding between CNT and  $\text{Al}_2\text{O}_3$  matrix with significant load transfer from the matrix to carbon nanotubes during loading were also evidenced. From this same figure 15, it is clear the presence of elastic deformation without fracture of MWCNTs during consolidation indicating an outstanding flexibility of the nanotubes. Similar behavior has been observed by Yamamoto *et al.* [98] in acid-treated MWCNT/alumina composite and Mo *et al.* [124].

However, a good interfacial bonding would make the ceramic too brittle [196] due to the higher concentration of CNT where the grain growth as well as the congregation of alumina grains during sintering could be greatly inhibited leading to detrimental grain boundary cohesion [170]. This observation is supported with the fracture surfaces of our sintered ZTA reinforced with 10 vol % MWCNT and 10 vol % SWCNT composites

illustrated in the Fig 16a and b, respectively. From these images it is clear that composites reinforced with large CNTs content affect enormously the sintering ability leading to a very poor densification (40% and 60% of theoretical density for  $\text{Al}_2\text{O}_3$  reinforced with 10 vol % MWCNTs (Fig. 16a) and 10 vol % SWCNTs (Fig. 16b), respectively). In spite of a major dispersion of MWCNTs (Fig. 16a) are observed few grain boundaries meanwhile for composites with SWCNTs (Fig. 16b), bundles of CNTs are formed and the sintering has progressed sufficiently to form grain boundaries,



**Figure 15.** SEM micrograph of fracture surface of ZTA composite with additions of 0.01% MWCNTs. Arrow marks explained in text.



**Figure 16.** SEM of fracture surfaces of ZTA reinforced with (a) 10 vol % MWCNT (40% of theoretical density) and (b) 10 vol % SWCNT (60 % of theoretical density) sintered at 1520 °C during 1 h. Bundles of SWCNTs is shown in (b).

therefore, a major sintered density has been reached. We speculate that probably by means of conventional sintering full density is not reached although by using SPS as consolidation tool, the full density can be reached as can be reported Zhan et al. [23] for the same CNTs content in alumina matrix.

Different strategies have been proposed to improve the mechanical properties of nanocrystalline oxide ceramics by using reinforcement by a second phase to develop nanometre-scale composite materials [23, 197]. A considerable amount of research works have been directed toward the development of ceramic nanocomposites using SPS as sintering technique [198] because it avoids the excessive grain growth that would prevent obtainment of a truly nanocrystalline material. There are different investigations on alumina based ceramics reinforced with both MWCNTs and SWCNTs and consolidated by SPS with a variety of results related to the fracture toughness depending on the starting materials.

A fracture toughness value determined by indentation fracture of  $9.7 \text{ MPa.m}^{1/2}$  was obtained by Zhan et al. [23]. This investigation has been considered a one of the first studies related to alumina composites reinforced with 5.7 and 10 vol% of SWCNT contents and fully densified (100 % TD) by SPS technique at temperatures higher than  $1100^\circ\text{C}$ . However, up to now this toughness has not been reproduced. Nevertheless, previous to the work of Zhan et al. [23], Siegel et al. [26] reported only a 24% increase in toughness in 10 vol% MWCNT- $\text{Al}_2\text{O}_3$  nanocomposites indicating that SWCNTs seems to have an optimum performance compared to MWCNTs as reinforcement agent. It is speculated that there are some differences related to the transfer load from the matrix to the nanotubes and therefore, the fracture toughness values have notably varied. Now, from SEM and TEM studies, crack deflection is possibly one of the toughening mechanisms, although Zhan et al [23] have also considered that the fast sintering at low temperatures with short durations retain the CNTs integrity in the sintered specimens, which is of paramount importance to reach an effective reinforcement.

Zhan et al. [23, 199] and Jiang et al. [155] have revealed a positive dependence of fracture toughness on the density in the 10 vol% SWCNT/ $\text{Al}_2\text{O}_3$  composite in addition to increase of hardness with the density. However, the dependence of hardness on density has always been reasonable mean while the positive dependence of toughness is contrary to conventional expectation. There are inconsistencies considering that the reported fracture toughness values for 5.7 vol% and 10 vol% SWCNTs- $\text{Al}_2\text{O}_3$  composites were  $7.9 \text{ MPa.m}^{1/2}$  and  $9.7 \text{ MPa.m}^{1/2}$ , respectively, under same experimental conditions. It is noteworthy that both composites had 100% TD and 200 nm grain size. In this context, will be expected for the same density

the same fracture toughness value. Nevertheless, the authors have argued that this behaviour could be related to the extent of bonding of CNTs in the alumina matrix as a function of density. So far, the best reported fracture toughness has been this [23] but regrettably, has not been reproduced. Conversely, Wang et al. [24] using the same  $\text{Al}_2\text{O}_3$  starting powder and similar purified SWCNT ropes as Zhan et al. [23] found that by means of indentation fracture their composites were highly contact-damage resistant due to the lack of crack formation. On the other hand, the  $K_{IC}$  they determined by single-edge V-notched beam (SEVNB) method was  $3.32 \text{ MPa.m}^{1/2}$  for  $\text{Al}_2\text{O}_3/10 \text{ vol\% SWCNT}$  using SPS, which within the experimental scatter is practically the same than pristine  $\text{Al}_2\text{O}_3$  ( $3.22 \text{ MPa.m}^{1/2}$ ).

Considering that under indentation fracture method the composite showed resistance to contact or indentation damage, undoubtedly the results clearly show that this composite are no tough, suggesting that the highly shear-deformable SWCNTs heterogeneities in the ceramic composite could help to redistribute the stress field under indentation imparting therefore, the composites with contact-damage resistant which present great opportunities in specific applications such as wear parts, armour, prostheses, among others. The fracture toughness of MWCNTs/alumina composites fabricated by sol-gel process and with relative densities after SPS at  $1650^\circ\text{C}$  for 5 min varying from 99.5 % to 100% regardless of the volume fraction of carbon nanotubes (between 0 and 3.3 vol%) was only 10% higher than pure  $\text{Al}_2\text{O}_3$  according to reported by Mo et al. [107]. The strengthening mechanism based on the load transfer between the alumina matrix and CNTs contributed to the slight improvement of fracture toughness. When the carbon nanotube alumina nanocomposite (volume fraction of CNTs varied from 0 to 1.8 vol%) was fabricated by molecular level mixing process followed by SPS at  $1500^\circ\text{C}$  during 5 min, the fracture toughness reported by Cha et al. [107] increases with increase volume fraction of CNTs, which is comparable to the results of Mo et al. [107]. Fracture surfaces revealed homogeneous dispersion of carbon nanotubes within the alumina matrix or alternatively at grain boundaries. The main characteristics in these fracture surfaces were pulled-out of CNTs during fracture process indicating therefore, that the CNTs bear significant stress by sharing a portion of the load toughen the matrix by the bridging effect. Jiang et al. [155] reported fracture toughness values (determined by indentation fracture) of  $8.6 \text{ MPa.m}^{1/2}$  and  $6.9 \text{ MPa.m}^{1/2}$  for  $\text{Al}_2\text{O}_3\text{-}10\text{vol\% SWCNTs}$  SPSed at temperatures of  $1350^\circ\text{C}$  and  $1550^\circ\text{C}$ , respectively. In all cases, the  $K_{IC}$  yet remains at least twice as high as that the monolithic alumina. The decrease in toughness was attributed by the authors to the conversion of carbon nanotube to graphite as confirmed by Raman

spectra. On the other hand, the high fracture toughness can be attributed to crack bridging by CNT consequence of the high strength of carbon nanotube. From SEM studies was concluded that crack deflection and CNT pull-out contribute also to the improvement in toughness.

Nowadays, the discrepancies related to the characterization of crack resistance by the conventional indentation fracture in ceramic reinforced with CNTs remains in doubt and the difference in indentation response could be attributed to the immediate microstructural difference [155]. The differences in results reported by Zhan *et al.* [23, 155] and Wang *et al.* [24] for the same starting materials can be due to the difference in the applied mechanical pressure during SPS process. It is obviously believed that high pressure leads to obtainment of densely sintered body.

As we mentioned earlier, the preservation of CNTs during sintering is very important to improve mechanical properties. Thomson *et al.* [200] studied in detail by means of Raman spectroscopy the preservation of the carbon nanotube structure in CNT-reinforced  $\text{Al}_2\text{O}_3$  nanocomposite consolidated by SPS, considering that few experimental reports have confirmed the integrity of CNTs after sintering at high temperatures. This could be the reason to explain why some reports in the open literature reveal that carbon nanotube additions benefit mechanical properties [23, 26, 30, 106, 123, 113, 158] and why other do not [24, 117].  $\text{Al}_2\text{O}_3$  ceramics with additions of 5-10 vol% SWCNTs and SPSed at temperatures of 1150, 1350, and 1550 °C during 3 min and 1550 °C for 5 min. Regardless of the obtained fracture toughness, Thomson *et al.* [200] found that CNTs were preserved in alumina composites at SPS sintering temperatures up to approximately 1250 °C. At higher temperatures than this, carbon nanotubes break down. Although the authors have mentioned that the serious inconsistencies found in the literature pertaining the effects of addition of CNTs to alumina matrix may be attributed to high sintering temperatures where retaining of these CNTs is questionable.

Two recent investigations have demonstrated that even with high sintering temperatures both SWCNTs and MWCNTs can be preserved in ZTA composites with additions of 0.01 wt% MWCNTs and SWCNTs and pressureless sintered at 1520 °C in air using graphite as powder bed [30] and ZTA composites with 0.1 wt% of SWCNTs and MWCNTs consolidated at 1520 °C by SPS during 5 min [152]. These assertions were confirmed by Raman spectroscopy studies. Likewise, employing the SPS approach (1500 °C for 10 min), Estili *et al.* [186] prepared surfactantless, hydrophilic, slightly disordered, crystalline, MWCNTs which were homogeneously dispersed in an alumina matrix following similar procedures [201-203]. A 67% increase in the fracture toughness ( $5.2 \text{ MPa}\cdot\text{m}^{1/2}$ ) compared to pure alumina ( $3.12$



$\text{MPa.m}^{1/2}$ ) determined by Vickers indentation method at 10 kg load, was reached in the  $\text{Al}_2\text{O}_3$  composite with 3.5 vol% MWCNTs whose sintered density was approximately 99% TD in relation to 95% TD measured for monolithic alumina. Important interactions between CNTs and alumina matrix were carefully observed: i) crack deflection along the continuous CNT-matrix interface rather than propagating through the CNT supported by the “footprints” in the crack plane which is required to cause a bridging mechanism, consistent with the reported by Xia et al. [16], ii) the length of the embedded MWCNTs and their orientation and position respect to the crack planes, may strongly influence the bridging and pullout mechanisms. CNTs having approximately the same embedded lengths in the upper and lower crack planes, are considered as the most effective for the bridging process inasmuch as contribute efficiently to frictional sliding when are located perpendicular to the crack plane, iii) pullout of the CNTs which are implanted inside the ceramic grains owing to the novel powder processing carried out by Estili et al. [133]. It is observed that the substantial improvement of toughness in these composites is due to effective load transfer at the interface carbon nanotubes-alumina matrix creating a good interfacial compatibility and wetting. Yamamoto et al. [98] using colloidal processing as was mentioned previously, obtained a marginal improvement of toughening (25% applying the SENB method and 56% by conventional indentation fracture) with their 0.9 vol% MWCNTs- $\text{Al}_2\text{O}_3$  composites sintered by SPS at 1500 °C for 10 min in vacuum. Under TEM studies, interesting geometric structure was observed revealing that a nanodefekt on the acid-treated MWCNT is filled up with alumina crystal. This novel structure resembles a nanoscale anchor with an alumina crystal spiking the surface of the MWCNTs. With these results, it was found that the surface modification of the carbon nanotubes can be effective in improvement the toughness of the CNTs reinforced  $\text{Al}_2\text{O}_3$  ceramics. The maximum  $K_{IC}$  was 5.9  $\text{MPa.m}^{1/2}$  obtained with the 0.9 vol% acid-treated MWCNT/ $\text{Al}_2\text{O}_3$  composite (~ 38% increase respect to pure alumina (4.25  $\text{MPa.m}^{1/2}$ )).

Now, applying the Vickers indentation technique in the same MWCNTs-alumina composite, the toughness reached was approximately 6.64  $\text{MPa.m}^{1/2}$ . It is important to note that for all cases, the toughness of the acid-treated MWCNTs was higher than those of the  $\text{Al}_2\text{O}_3$  without CNTs addition. The relative increase in fracture toughness may be due to the crack bridging effect accompanied by frictional resistance between MWCNTs and the alumina matrix. Likewise, numerous individual CNTs pullout on the fracture surface were directly observed as well as some of them broken in the outer layers showing evidence of “telescopic effect” which can be found in several mechanical stresses failure mode studies [204]. Taking advantage of these

results, An *et al.* [205] and Yamamoto *et al.* [206] have reported potential applications for these composites to tribomaterials such as joint prostheses due to good lubrication properties.

To attempt the obtainment of CNTs-alumina ceramics with improved fracture toughness, Ahmad and Pan [125] investigated a new class of alumina composites reinforced with different MWCNTs content and with concurrent reinforcement of 1 vol% of SiC nanoparticles followed by SPS at 1550 °C in vacuum. They decided to use SiC nanoparticles inasmuch as these promote the removal of residual stresses at the grain boundaries [207-209], as residual stresses are undesirable to optimize the cracking behaviour in alumina ceramics reinforced with carbon nanotubes [10, 16]. Other reason to use SiC was that radial cracks were clearly observed by Vickers indentation. However, Ahmad and Pan [125] revealed that cracks in specimens not containing SiC could not be observed due to accommodation of shear deformation of CNTs under the indenter according to reported by Wang *et al.* [24], Xia *et al.* [16] and Curtin and Sheldon [176]. Nonetheless, this assertion contrast with results by Bocanegra *et al.* [30] and Echeberria *et al.* [158] who registered visible radial cracks by indentation fracture in ZTA composites reinforced with lower MWCNTs content without additions of SiC nanoparticles. Similar results have been reported by Cha *et al.* [106.] and Mo *et al.* [107]. The addition of 5 vol% of MWCNT has a significantly increased the fracture toughness in the 1 vol% SiC/alumina composite (~ 95% compared to pure  $\text{Al}_2\text{O}_3$ ). On the other hand, when the CNTs content was increased from 5 to 7 vol% the fracture toughness was newly enhanced in approximately 11% and 118% respect to 1 vol% SiC/alumina reinforced with 5 vol% MWCNTs and monolithic alumina, respectively. For MWCNTs content higher than 7 vol%, the toughness was diminished but always was higher than pure alumina. A good dispersion of 5 and 7 vol% MWCNTs results in high fracture toughness values. Likewise, SEM observations of crack bridging, crack deflection and CNT pull outs provide undoubtedly, a direct and clear evidence of fiber toughening by the presence of MWCNTs. A low vol% of SiC can be used successfully in order to obtain an additional improvement in fracture toughness in alumina composite reinforced with MWCNTs.

Within the novel fabrication processes of CNT/Alumina composites including concurrent reinforcement agents, He *et al.* [163] investigated the behaviour of CNT(Ni)- $\text{Al}_2\text{O}_3$  composites consolidated by SPS at temperature of 1300 °C for 6 min in inert atmosphere. First of all, the authors reported that the inclusion of 1.5 wt% CNTs and 0.3 wt% Ni to the alumina matrix has no effect on the sintering process. Now, when the CNTs content is increased to 2.4 wt% in the alumina matrix the density is sharply down due probably to

the inhibition of some diffusion process according to reported by Flahaut et al. [117]. However, the fracture toughness was increased 67% (6.3 MPa.m<sup>1/2</sup>) with respect to pure alumina (3.8 MPa.m<sup>1/2</sup>) in the composite containing 1.5 wt% CNTs and 0.3 wt% Ni. This value was obtained applying the indentation fracture method at a load of 10 kg for 10 s following the Evans and Charles equation [210]. SEM and TEN studies revealed a good bonding between CNTs and alumina matrix with the presence of a network structure of carbon nanotubes at the intergranular positions which could induce strengthening and toughening of the nanocomposites. Likewise, fracture surfaces showed evidence of additional toughening mechanisms such as crack bridging, crack deflection as well as some CNTs pull outs. From these results and the obtained by Ahmad and Pan [125] it is concluded that the use of concurrent reinforcement agents in CNT/alumina composites can be a promising route to improve the mechanical properties of alumina based ceramics. Zhang et al. [34] reported that the fracture toughness of the CNT-Al<sub>2</sub>O<sub>3</sub> nanocomposites sintered by SPS at 1150 °C were much lower than that pure Al<sub>2</sub>O<sub>3</sub>, due to the poor densification or high porosity at this low SPS temperature. For example, the maximum fracture toughness reached by these investigators was 1.74 MPa.m<sup>1/2</sup> for CNT content of 8.25 wt%, which is about half of the fracture toughness of 3.50 MPa.m<sup>1/2</sup> for pristine Al<sub>2</sub>O<sub>3</sub> sintered at the same temperature. The amount of porosity is of primary importance in determining the fracture toughness since the minimum solid area will be sought by the propagating crack. This result contrasts with the one obtained by Zhan et al. [23] who at the same temperature obtained a fracture toughness between 8.1 and 9.7 MPa.m<sup>1/2</sup> in Al<sub>2</sub>O<sub>3</sub> ceramics with additions of 10 vol% SWCNTs.

The addition of CNTs above the optimal value does not account for the toughness enhancement of the Al<sub>2</sub>O<sub>3</sub>. On the other side, seems to be that the mechanical properties depend of the raw materials used as start materials. Now, contrary to much observations, Lee et al. [131] found an enhance in fracture toughness on the addition of MWCNTs in nanocomposites fabricated by a sequential two-step processing of ultrasonic spray pyrolysis and SPS. They reported an increase in the fracture toughness of 152% for MWCNTs content of 2.48 wt% compared to pure alumina. A transition of transgranular crack path in alumina free of carbon nanotubes to an intergranular crack path on increasing the amount of MWCNT seems to be responsible to fracture toughness improvement accompanied with decreasing of grain size of the alumina which in turn favours the occurrence of more crack deflections, which also can retard the propagation of crack. Although there are a number of conflicting reports on the experimental relationship between grain size and fracture toughness, the difficulties arise at least in part because the

micromechanisms operating have not been determine in all cases [173]. SEM studies revealed that the MWCNTs formed bridges across the crack and then were pulled out on the fractures surface. According to Cho et al. [15] it is possible to estimate the energy absorbed by the fibers per unit area of composite using the following equation:

$$G_{\text{pull-out}} = V_f L^2 \tau_i / r,$$

where,  $V_f$  is the volume fraction of a fiber,  $r$  is the radius of a fiber,  $L$  is the length of a fiber, and  $\tau_i$  is the sliding shear stress. Therefore, assuming that the volume fraction and sliding shear stress are fixed, the thinner and longer CNTs are advantageous as toughening fillers [131]. From the observed toughening mechanism, it is clear that MWCNTs are considered to play a very important role of load transfer from the alumina matrix.

It is well known that alumina based composites are nowadays a new generation of ceramic materials as an alternative to biomedical-grade alumina and zirconia and therefore, the most promising candidates for replacing metallic bearing parts in the orthopedic field [211]. In this context, the use of ZTA composites with different percents of CNTs can be a promise biomedical material for medical and dental applications given its large increase in fracture toughness over pure alumina and the observed relief from aging issues of zirconia. Moreover, ZTA composites have many applications in which wear resistance and mechanical strength are required. As mentioned earlier, regrettably the investigation on ZTA composites reinforced with different amounts of CNTs is practically new and an absolute lack of investigation reports on these important ceramic composites is evident.

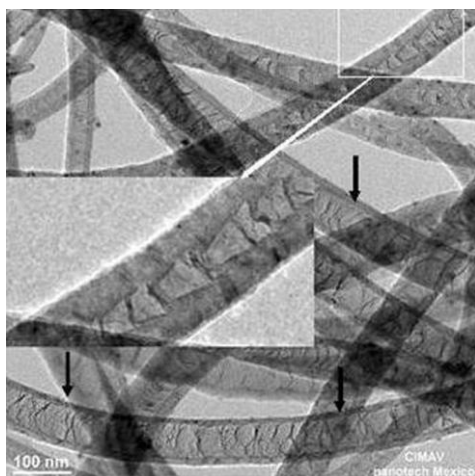
However, Echeberria et al. [152] undertook an interesting investigation by using SPS at 1520 °C to study more in depth the effect that on the fracture toughness (measured by the indentation fracture at applied loads of 1, 5, and 10 kg) has a low addition of both SWCNTs and MWCNTs to ZTA composites. For example, they found that 0.1 wt% of multiwall carbon nanotubes (MWCNTs) or alternatively 0.1 wt% of single-walled carbon nanotubes (SWCNTs) added to ZTA ceramic composites is enough to obtain high hardness and fracture toughness, even at indentation loads higher than 1 kg commonly used in the characterization of fracture toughness by means of indentation fracture method. However, at lower MWCNTs content than 0.01 wt%, the fracture toughness of ZTA composites was increased around 41% compared to pure ZTA and 44% compared to the ZTA composite but with additions of the same content of SWCNTs [30].

On the other side, when hot isostatic pressing is applied to ZTA composites after conventional sintering, it is possible to obtain an increase in

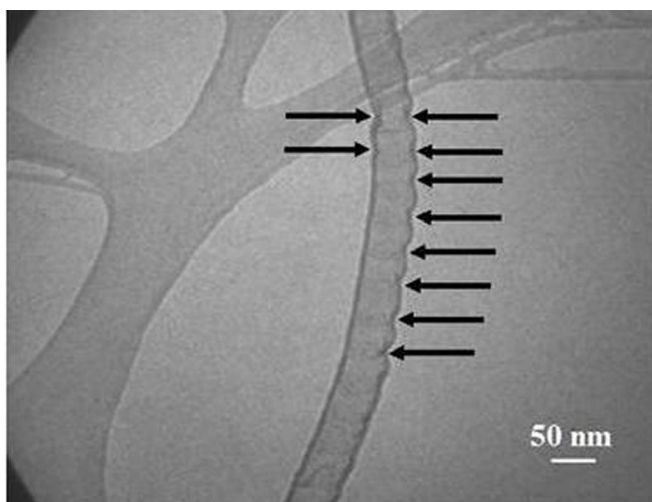
fracture toughness of  $\sim 7\%$  and  $\sim 36\%$  compared to the “as sintered” composites with 0.01 wt.% MWCNTs and free of carbon nanotubes, respectively, according to results by Echeberria et al. [158]. Pullout of CNTs as well as bridged cracks were the main responsible mechanisms to improve the fracture toughness in ZTA composites studied by Echeberria et al. [152, 158] and Bocanegra et al. [30]. An additional increase in fracture toughness in these investigations can be due to sword-in-sheath mechanism taking into account evidences obtained by SEM studies. Considering the open literature and having studied in depth different reports regarding to alumina based ceramics with high and low CNTs content, we have speculated that the high fracture toughness values obtained with very low carbon nanotubes content [30, 152, 158] in comparison to other investigations [23, 34, 98, 101, 125, 186] where have been used high concentration of CNTs, could be explained considering the observations by Sarkar and Das [150], Harris [9], and Bhushan [28] who found the so-called herringbone texture (h-MWNTs), in which the graphenes make an angle with respect to the nanotube axis. The angle value varies upon the processing conditions (such as the catalyst morphology or the composition of the atmosphere). Likewise, an extensive “bamboo” structure formed during exposure of CNTs at high sintering temperatures contributing therefore, increasing the fracture toughness of the composite. With the herringbone texture and bamboo structure can create important connectivity between the alumina matrix and MWCNTs. Echeberria et al. [152] observed similar behaviour in their investigations in ZTA composites reinforced with very low amount of carbon nanotubes (0.01 wt.% MWCNTs). The Fig. 17 shows transmission electron microscopy image of a herringbone and “bamboo” multiwall nanotube (bh-MWNT, longitudinal view) prepared by prepared by spray pyrolysis.

These structures also called “nanodefects” on the surface of the MWCNTs (arrow marks in Fig. 18), are commonly filled up with alumina matrix resembling a nanoscale anchor with an alumina crystal spiking the surface of the MWCNTs as was mentioned earlier. On the other hand, the “bamboo” nanotube core segments are truly independent sections (see Fig. 19) with weak end-to-end binding. Short independent “bamboo” sections might serve as ultralow-friction linear or rotational bearings that are firmly embedded in a common long, stiff cylindrical housing [204] suggesting that this behaviour is beneficial to nanomechanical or nanoelectromechanical systems (NEMS) applications.

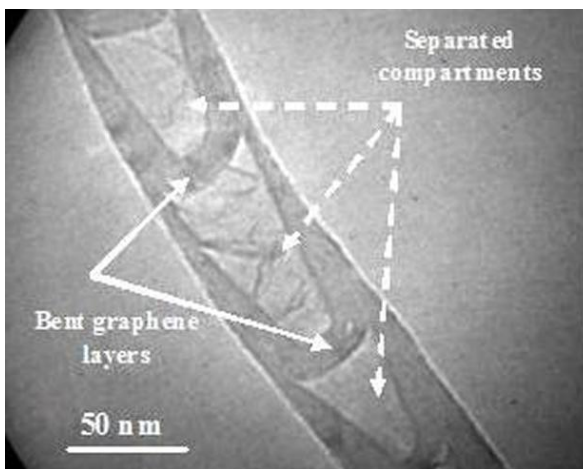
As mentioned earlier, bamboo structures can offer better mechanical properties than hollow MWCNTs taking advantage of that the “knots” on the bamboo-like MWCNT stem afford tighter matrix connectivity with the ceramic following a similar behavior to that of the steel rebars in the



**Figure 17.** TEM image showing a herringbone multiwall nanotube (bh-MWNT, longitudinal view) prepared by prepared by spray pyrolysis on quartz substrate at a temperature of 800 °C using Ar as carrier gas, ferrocene as catalyst precursor and acrylonitrile flowing at  $1\text{ mL}\cdot\text{min}^{-1}$  as carbon source. The black arrow marks show the “bamboo” MWCNT structure, similar to shown in Fig. 7 (a).



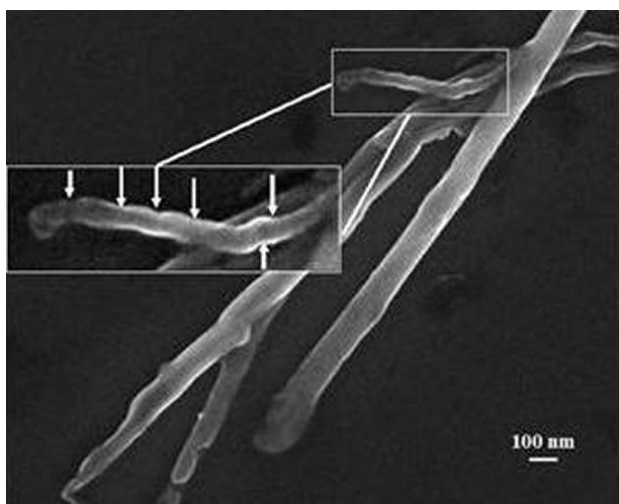
**Figure 18.** TEM image of MWCNT obtained by spray pyrolysis. Arrow marks indicate the position of the nanodefects.



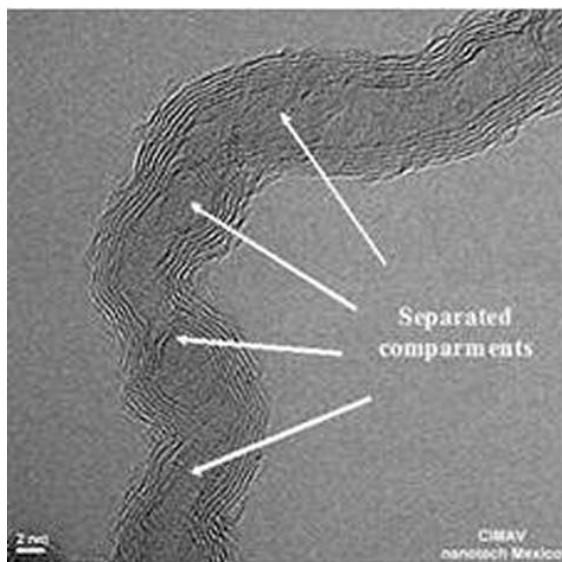
**Figure 19.** TEM image showing a “bamboo” MWCNT (prepared by spray pyrolysis) indicating the independent sections.

concrete. Moreover, they decrease the effect of telescopic extension of MWCNT diminishing therefore, the Young modulus and ultimate strength [185]. With the purpose to corroborate the formation of bamboo structures at high temperatures, our multiwall carbon nanotubes were subjected to heat treatment at  $1520\text{ }^{\circ}\text{C}$  during 1 h in air using graphite powder as bed powder. A little quantity of MWCNTs was sandwiched between two pure sintered alumina discs and these were protected by the bed powder during all heat treatment. SEM and TEM studies revealed that some of the CNTs presented bamboo structure after heat treatment. The Fig. 20 is a SEM micrograph showing periodic buckling patterns in MWCNTs thermally treated at  $1520\text{ }^{\circ}\text{C}$  suggesting probably that a major factor that contributes to this buckling mode is the radial deformability of the tubes according to reported by Ruoff et al. [47]. On the other side, Salvétat et al. [45] exposed that one possible reason for this, could be the inhomogeneous stress that results from the rippling of the graphite layer on the compressed side.

The Fig. 21 shows a TEM image of a MWCNT heated at  $1520\text{ }^{\circ}\text{C}$  where is clearly seen a bamboo-like MWCNTs structure where some disorder of graphite layers in outer walls and inner compartment can be found, indicating therefore, that these bamboo-like MWCNTs possess more defects, curves, and dislocations on graphitic sheets. These observations are in agreement with experimental results reported by Xue et al. [212] who obtained in their investigation MWCNTs with dominant bamboo-like morphology.



**Figure 20.** SEM image showing a MWCNT (prepared by spray pyrolysis) after heat treatment at 1520 °C during 1 h. Arrow marks indicate periodic buckling patterns.

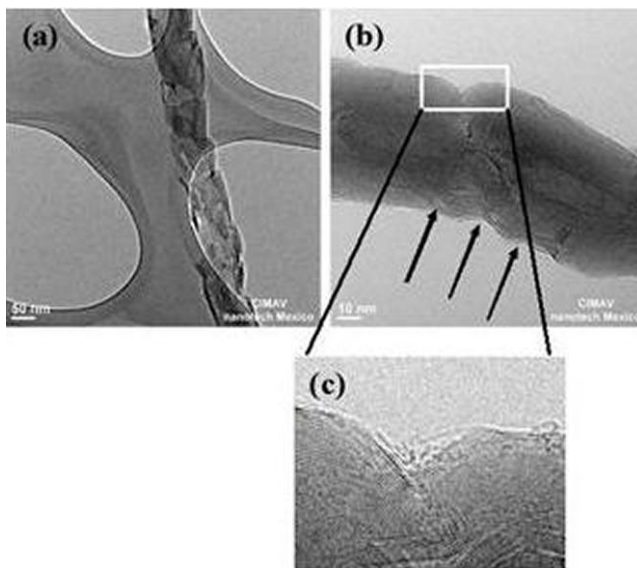


**Figure 21.** TEM image of a MWCNT thermally treated at 1520 °C for 1 h showing a bamboo-like structure. The independent sections are indicated by arrow marks.



Likewise, after heat treatment carried out at 1520 °C during 1 h in air using graphite as powder bed in order to protect the carbon nanotubes, the so-called herringbone texture in which the graphenes make an angle with respect to the nanotube axis was obtained and is illustrated in the Fig. 22 (a). Similarly, a high-magnification TEM image showing a nanod defect on the MWCNT surface is shown in Fig. 22 (b), which could be filled up with the ceramic matrix during grain growth in the sintering process creating a strong bond between the CNT and ceramic matrix, suggesting therefore, a decreasing in the telescopic extension phenomenon as well as higher pull-out resistance. An enlargement of the nanod defect indicated by the square in Fig. 22 (b) is shown in Fig. 22 (c).

In closing, as was mentioned earlier, these structures obtained in the carbon nanotubes in the preparation technique of them as well as during exposure at high temperatures in the different sintering processes and although commonly are called as nanod defects, they can be effective in improvement of mechanical properties such as fracture toughness bending strength of the MWCNT/alumina and MWCNT/ZTA ceramic composites. It is for all the above mentioned that the carbon nanotubes may give a



**Figure 22.** TEM image of heat treated MWCNTs showing a herringbone structure (a); nanod defect on the surface of the CNT (b). (c) is the enlargement of the square indicated in (b). Arrow marks in (b) indicate the position of the nanod defects.

promising future in reinforcing structural ceramic components (mainly alumina based ceramic nanocomposites) and other materials systems as well.

### 3. Conclusions

Taking into account the exceptional mechanical and physical properties demonstrated for carbon nanotubes that, combined with their low density, make this new form of carbon an excellent candidate for the application in composite reinforcement and in purely nanotube-based materials. It is noteworthy that the processing routes, microstructural characteristics as well as mechanical and functional properties of carbon nanotubes have been a subject of intensive study during last 10 years. Given the costs of the materials and processes involved, there is a need for development of nanotube production techniques at the scale needed for producing macroscopic composites that are cost-effective.

Full understanding about of thermo-mechanical behavior of ceramic nanocomposites reinforced with both single wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs), requires a wide knowledge of the elastic and fracture properties of carbon nanotubes as well as of interactions at the nanotube/matrix interface. In this review has been shown that alumina ( $\text{Al}_2\text{O}_3$ ) and zirconia toughened alumina (ZTA) with additions of CNTs exhibit all of the features associated with toughening behavior in the field of fiber reinforced composites as follows: crack deflection, crack bridging, and fiber pullout. Very scarce investigations have been reported on this subject. On the other hand, in the field of nanotubes, it is clear that the progress has been extremely rapid, as evidenced not only by the large number and quality of scientific studies dealing with nanotubes, but also by the great numbers of applications which have been proposed for these materials. However, only a relatively small number of these new and attractive materials have been used commercially and there are still many problems to overcome before the full potential of nanotube containing composites can be realised.

However, before one can think of any commercialization of nanotubes, undoubtedly several milestones in their production and processing need to be achieved. In reason of this, associated with the production of carbon nanotubes are the issues of their manipulation, purification and characterization, so that these nanotubes with specified properties and characteristics can be 'made to order'. Now, it is of paramount importance to explore in detail the control of the interface between the nanotubes and the matrix in order to understand the mechanical performance considering that in a CNT reinforced ceramic material, interface behavior is expected to be

significantly different from conventional carbon fibers because of the unique chemical bonding inherent in CNTs.

Although has been reported by several authors that the better mechanical properties are product of use higher nanotube volume fractions and, in some cases, the use of longer nanotubes, in this review has been highlighted up that to now the results related with the fracture toughness are ambiguous. In most cases the fracture toughness decreases, particularly for higher fractions of carbon phases. Yet, the potential for improving in this area by toughening mechanisms such as fiber pull-out, crack bridging and deflection has been recognized. However, nowadays it is very difficult to speculate which is the optimal carbon nanotubes addition to ceramics based alumina with the purpose to reach higher fracture toughness. In spite of that SWCNTs are more commonly used in order to improve the mechanical properties in alumina ceramics, 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 improving in some cases, the mechanical properties compared to SWCNTs.

Also, the interactions of nanotubes with biological systems (in possible biological applications) and with 'conventional' nanostructure technologies are important topics that very much demand active research. Finally, we can look forward to hearing more about this new and important class of materials in the near future while rigorous investigations in processing, characterization, and analysis/modeling will carry out before the structural and functional properties of this new class of ceramic nanocomposites can be optimized. The work reviewed here demonstrated that mixed results on mechanical properties can be obtained by means of a variety of methods for producing ceramic nanotube composites in recent years. Further research on these approaches will almost certainly lead to better materials such as those based alumina.

## Acknowledgements

The authors wish to express their appreciation to Manuel Román and Wilber Antúnez for the preparation of MWCNTs and SEM work, respectively. Special acknowledgement must be extended to Carlos Ornellas for the assistance with the TEM studies.

## References

1. Hirlekar R, Yamagar M, Garse H, Vij M, Kadam V. Carbon nanotubes and its applications: A review. *Asian J Pharm Clin Res* 2009;2(4):17-27.
2. Iijima S. Helical microtubules of graphitic carbon. *Nature* 1991;354(6348):56-8.

3. Radushkevich LV, Lukyanovich VM. Carbon structure formed under thermal decomposition of carbon monoxide on iron. *Sov J Phys Chem* 1952;26:88-95.
4. Oberlin A, Endo M, Koyana T. Filamentous growth of carbon through benzene decomposition. *J Cryst Growth* 1976;32(3):335-49.
5. Abrahamson J, Wiles PG, Rhodes B. Structure of carbon fibers found on carbon arcs anodes. *Carbon* 1999;37(11):1873-75.
6. Sekhar Samal S, Bal S. Carbon nanotube reinforced ceramic matrix composites- A review. *J Miner Mater Charact Eng* 2008;7(4):355-370.
7. Mazzucco D, Squizzatoa D, Mantovania S, Canonico P. Nano-toughened carbon fibers composite materials. SAATI Group (SEAL S.p.A.), a partner of Nanoledge. 2009.
8. Thostenson ET, Ren Z, Chou T-W. Advances in the science and technology of carbon nanotubes and their composites: a review. *Compos Sci Technol* 2001;61(13):1899-1912.
9. Harris PJF. Carbon nanotube composites. *Int Mater Rev* 2004;49(1):31-43.
10. Xia Z, Curtin WA, Sheldon BW. Fracture toughness of highly ordered carbon nanotube/alumina nanocomposites. *J Eng Mater-T ASME* 2004;126(3):238-244.
11. Qian D, Liu WK, Ruoff RS. Load transfer mechanism in carbon nanotube ropes. *Compos Sci Technol* 2003;63(11):1561-1569.
12. George R, Kashyap KT, Rahul R, Yamdagni S. Strengthening in carbon nanotube/aluminium (CNT(Al) composites. *Scr Mater* 2005;53(10):1159-1163.
13. Liao J-Z, Tan M-J, Sridhar I. Spark plasma sintered multi-wall carbon nanotube reinforced aluminum matrix composites. *Mater Design* 2010;31(1):S96-S100.
14. Sternitzke M. Structural ceramic nanocomposites. *J Eur Ceram Soc* 1997;17(9):1061-1082.
15. Cho J, Boccaccini AR, Shaffer MSP. Ceramic matrix composites containing carbon nanotubes. *J Mater Sci* 2009;44(8):1934-1951.
16. Xia Z, Riester L, Curtin WA, Li H, Sheldon BW, Liang J, Chang B, Xu JM. Direct observation of toughening mechanisms in carbon nanotube ceramic matrix composites. *Acta Mater* 2004;52(4):931-944.
17. Curtin WA. Stress-strain response of brittle matrix composites. In: Kelly A, Zweben C, editors. *Encyclopedia of composites*. Holland: Elsevier; 2000.
18. Ramírez AP. Carbon nanotubes for science and technology. *Bell Labs Tech J* 2005;10(3):171-185.
19. Bakshi SR, Lahiri D, Agarwal A. Carbon nanotube reinforced metal matrix composites- a review. *Int Mater Rev* 2010;55(1):41-64.
20. Peigney A, Laurent Ch, Flahaut E, Rousset A. Carbon nanotubes in novel ceramic matrix nanocomposites. *Ceram Int* 2000;26(6):677-683.
21. Duszová A, Dusza J, Tomásek K, Morgiel J, Blugan G, Kuebler J. Zirconia/carbon nanofiber composite. *Scr Mater* 2008;58(6):520-523.
22. Takano Y, Ozawa T, Yoshinaka M, Hirota K, Yamaguchi O. Microstructure and mechanical properties of ZrO<sub>2</sub> (2Y)-toughened Al<sub>2</sub>O<sub>3</sub> ceramics fabricated by spark plasma sintering. *J Mater Synth Proces* 1999;7(2):107-11.

23. Zhan GD, Kuntz JD, Wan J, Mukherjee AK. Single-wall carbon nanotubes as attractive toughening agents in alumina-based composites. *Nature Mater* 2003;2(1):38-42.
24. Wang X, Padture NP, Tanaka H. Contact-damage-resistant ceramic/single-wall carbon nanotubes and ceramic/graphite composites. *Nature Mater* 2004;3(8): 539-544.
25. Ma RZ, Wu J, Wei BQ, Liang J, Wu DH. Processing and properties of carbon nanotube/nano-SiC ceramic. *J Mater Sci* 1998;33(21):5243-5246.
26. Siegel RW, Chang SK, Ash BJ, Stone J, Ajayan PM, Doremus RW, Schadler LS. Mechanical behaviour of polymer and ceramic matrix nanocomposites. *Scr Mater* 2001;44(8-9):2061-2064.
27. Laurent C, Peigney A, Dumortier O, Rousset A. Carbon nanotubes-Fe-alumina nanocomposites. Part II: Microstructure and mechanical properties of the hot-pressed composites. *J Eur Ceram Soc* 1998;18(14):2005-2013.
28. Bhushan B. Introduction to carbon nanotubes, Chapter 3. In: Bhushan B, editor. *Springer Handbook of Nanotechnology*. Springer; 2007, pp. 43-112.
29. Balázsi C, Kónya Z, Wéber F, Biró LP, Arató P. Preparation and characterization of carbon nanotube reinforced silicon nitride composites. *Mater Sci Eng C* 2003;23(6-8):1133-1137.
30. Bocanegra-Bernal MH, Echeberria J, Ollo J, Garcia-Reyes A, Domínguez-Rios C, Reyes-Rojas A, Aguilar-Elgueazabal A. A comparison of the effects of multi-wall and single-wall carbon nanotube additions on the properties of zirconia toughened alumina composites. *Carbon* 2011;49(5): 1599-1607.
31. Zhou G, Duan W, Gu Binglin. First principles study on morphology and mechanical properties of single-walled carbon nanotubes. *Chem Phys Lett* 2001;333(5):344-349.
32. Xie S, Li W, Pan Z, Chang B, Sun L. Mechanical and physical properties on carbon nanotube. *J Phys Chem Solids*. 2000;61(7):1153-1158.
33. Cornwell-Mott B. Effect of perfectly aligned CNTs under cohesive crack bridging in adhesive joints. Master Thesis, Department of Mechanical and Industrial Engineering University of Toronto, 2010.
34. Zhang T, Kumari L, Du GH, Li WZ, Wang QW, Balani K, Agarwal A. Mechanical properties of carbon nanotube-alumina nanocomposites synthesized by chemical vapor deposition and spark plasma sintering. *Compos Part A* 2009;40(1):86-93.
35. Yakobson BI, Avouris P. Mechanical properties of carbon nanotubes. In: M. S. Dresselhaus, G. Dresselhaus, Ph. Avouris (Eds.): *Carbon Nanotubes, Topics Appl Phys* 80, 287-327, Springer-Verlag Berlin Heidelberg; 2001.
36. Robertson DH, Brenner DW, Mintmire JW. Energetics of nanoscale graphitic tubules. *Phys Rev B* 1992;45(21): 12592-12595.
37. Treacy MMJ, Ebbesen TW, Gilson JM. Exceptionally high Young's modulus observed for individual carbon nanotubes. *Nature (London)* 1996;381(6584):678-680.
38. Krishnan A, Dujardin E, Ebbesen TW, Yianilos PN, Treacy MMJ. Young's modulus of single-walled nanotubes. *Phys Rev B* 1998;58(20):14013-14019.

39. Sánchez-Portal D, Artacho E, Soler JM, Rubio A, Ordejón P. Ab initio structural, elastic, and vibrational properties of carbon nanotubes. *Phys Rev B* 1999;59(19):12678-12688.
40. Popov VN. Carbon nanotubes: properties and application. *Mater Sci Eng R* 2004;43(3):61-102.
41. Jacobsen RL, Tritt TM, Guth JR, Ehrlich AC, Gillespie DJ. Mechanical properties of vapor-grown carbon fiber. *Carbon* 1995;33(9):1217-1221.
42. Wong EW, Sheehan PE, Lieber CM. *Science* 1997;277(5334):1971-1975.
43. Salvétat JP, Briggs GAD, Bonard JM, Bacsá RR, Kulik AJ, Stöckli T, Burnham NA, Forró L. Elastic and shear moduli of single-walled carbon nanotube ropes. *Phys Rev Lett* 1999;82(5):944-947.
44. Yu MF, Files BF, Arepalli S, Ruoff RS. Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties. *Phys Rev Lett* 2000;84(24):5552-5555.
45. Salvétat JP, Bonard JM, Thomson NH, Kulik AJ, Forró L, Benoit W, Zuppiroli L. Mechanical properties of carbon nanotubes. *Appl Phys A* 1999;69(3):255-260.
46. Demczyk BG, Wang YM, Cumings J, Hetamn M, Han W, Zettl A, Ritchie RO. Direct mechanical measurement of the tensile strength and elastic modulus of multiwalled carbon nanotubes. *Mater Sci Eng A* 2002;334(1-2):173-178.
47. Ruoff RS, Qian D, Liu WK. Mechanical properties of carbon nanotubes: theoretical predictions and experimental measurements. *C R Physique* 2003;4(9):993-1008.
48. Krätschmer LD, Lamb LD, Fostiropoulos K, Huffman DR. Solid C60: a new form of carbon. *Nature* 1990;347(6291):354-58.
49. Iijima S, Ichihashi T. Single-wall carbon nanotubes of 1-nm diameter. *Nature* 1993;363(6430):603-5.
50. <http://www.nano-lab.com/nanotubes-research-grade.html>, accessed on 17-08-2011.
51. Ebbesen TW, Ajayan PM. Large-scale synthesis of carbon nanotubes. *Nature* 1992;358(6383):220-221.
52. Lange H, Huczko A, Sioda M, Pacheco M, Razafinimanana M, Gleizes A. Influence of gadolinium on carbon arc plasma and formation of fullerenes and nanotubes. *Plasma Chem Plasma Process* 2002;22(4):523-536.
53. Kroto HW, Heath JR, O'Brien SC, Curl RF, Smalley RE. C<sub>60</sub> Buckminsterfullerene. *Nature* 1985;318(6042):162-163.
54. Guo T, Nikolaev P, Rinzler AG, Tomanek D, Colbert DT, Smalley RE. Self-assembly of tubular fullerenes. *J Phys Chem* 1995;99(27):10694-10697.
55. Mohseni PK, Paribello D, Poupore R. Carbon nanotubes and the carbon nanotube field effect transistor. Engineering Physics 4F03, Department of Engineering Physics, McMaster University, Hamilton, Ontario, Canada, April 2005.
56. Sugai T, Yoshida H, Shimada T, Okazaki T, Shinohara H. New Synthesis of High- Quality Double-Walled Carbon Nanotubes by High-Temperature Pulsed Arc Discharge. *Nano Lett* 2003;3(6):769-773.
57. Bandow S, Asaka S, Saito Y, Rao AM, Grigorian L, Richter E, Eklund PC. Effect of the Growth Temperature on the Diameter Distribution and Chirality of Single-Wall Carbon Nanotubes. *Phys Rev Lett* 1998;80(17):3779-3782.

58. Terrones M. Science and technology of the twenty-first century: Synthesis, Properties, and Applications of Carbon Nanotubes. *Annu Rev Mater Res*. 2003;33:419-501.
59. Walker PL, Rakszawski JF, Imperial GR. Carbon Formation from Carbon Monoxide-Hydrogen Mixtures over Iron Catalysts, I. Properties of Carbon Formed. *J Phys Chem* 1959;63(2):133-140.
60. Druzhinina T. Carbon Nanotubes: Their Synthesis and Integration into Nanofabricated Structures, Technische Universiteit Eindhoven, PhD Thesis, 2011
61. Khare R, Bose S. Carbon Nanotube Based Composites- A Review. *J Min Mater Character Eng* 2005;4(1):31-46.
62. Bera D. Arc-discharge in solution: a novel synthesis method for carbon nanotubes and in situ decoration of carbon nanotubes with nanoparticles, Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, Florida, PhD Thesis, 2005.
63. Coville NJ, Mhlanga SD, Nxumalo EN, Shaikjee A. A review of shaped carbon nanomaterials. *S Afr J Sci* 2011;107(3/4), Art # 418, 15 pages. DOI:10.4102/sajs.v107i3/4.418.
64. Sachin BJ. Synthesis of Carbon Nanotubes and Development of Remote Actuators, Department of Mechanical, Industrial and Nuclear Engineering, University of Cincinnati, Mster Thesis, 205
65. <http://www.cheaptubesinc.com/MWNTs.htm>, accessed on 23-08-2011.
67. Aguilar- Elguézabal A, Antúnez W, Alonso G, Paraguay F, Espinosa F, Miki-Yoshida M. Study of carbon nanotubes sintesis by spray pryrolysis and modelo f growth. *Diam Relat Mater* 2006;15(9):1329-1335.
68. Charanjeet S, Shaffer MSP, Kozoil KK, Klinloch IA, Windle AH. *Chem Phys Lett* 2003;372(5-6):860-865.
69. Ionescu MI, Synthesis of one-dimensional and two-dimensional carbon based nanomaterials, The School of Graduate and Postdoctoral Studies, The University of Western Ontario, PhD Thesis, 2011.
70. Deck CP, Vecchio K. Growth mechanism of vapor phase CVD-grown multi-walled carbon nanotubes. *Carbon* 2005;43(12):2608-2617.
71. Kamalakaran R, Terrones M, Seeger T, Kohler-Redlich P, Ruhle M, Kim YA, Hayashi T, et al. Synthesis of thick and crystalline nanotube arrays by spray pyrolysis. *Appl Phys Lett* 2000;77(21):3385-3387.
72. Biró LP, Horváth ZE, Koós AA, Osváth Z, Vértesy Z, Darabonta AI, Kertésza K, et al. Direct synthesis of multi-walled and single-walled carbon nanotubes by spray-pyrolysis. *J Optoelectron Adv M* 2003;5(3):661-666.
73. Darabont AI, Nemes-Incze P, Kertésza K, Tapasztó L, Koós AA, Osváth Z, Sárközi Zs, et al. Synthesis of carbon nanotubes by spray pyrolysis and their investigation by electron microscopy. *J Optoelectron Adv Mater* 2005;7(2): 631-636.
74. Ebbesen TW. Production and purification of carbon nanotubes. In Ebbesen TW, Ed. *Carbon Nanotubes: Preparation and Properties*, Boca Raton, FL: CRC, 1997, pp. 139-162.

75. Sinha N, Yeow JT. Carbon Nanotubes for Biomedical Applications, *IEEE Trans Nanobioscience* 2005;4(2):180-195.
76. Daenen M, de Fouw RD, Hamers B, Janssen PGA, Schouteden K, Veld MAJ. The Wondrous World of Carbon Nanotubes: a review of current carbon nanotube technologies. Report Eindhoven University of Technology, February 2003.
77. Ebbesen TW, Ajayan PM, Hiura H, Tanigaki K. Purification of nanotubes. *Nature* 1994;367(6463):519.
78. Gajewski S, Maneck HE, Knoll U, Neubert D, Dorfel I, Mach R, et al. Purification of single walled carbon nanotubes by thermal gas phase oxidation. *Diamond Relat Mater* 2003;12(3-7):816-820.
79. Hiura H, Ebbesen TW, Tanigaki K. Opening and purification of carbon nanotubes in high yields. *Adv Mater* 1995;7(3):275-276.
80. Vaccarini L, Goze C, Aznar R, Micholet V, Journet C, Bernier P. Purification procedure of carbon nanotubes. *Synth Met* 1999;103(1-3):2492-2493.
81. Dujardin E, Ebbesen T, Krishnan A, Treacy M. Purification of Single-Shell Carbon Nanotubes. *Adv Mater* 1998;10(8):611-613.
82. Chiang IW, Brinson BE, Smalley RE, Margrave JL, Hauge RH. Purification and Characterization of Single-Wall Carbon Nanotubes. *J Phys Chem B* 2001;105():1157-1161.
83. Dillon AC, Jones KM, Bekkedahl TA, Kiang CH, Bethune DS, Heben MJ. *Nature* 1997;386(6623):377-379.
84. Terrés i Güerri B, Transparent conductive coatings based on carbon nanotubes. Synthetic Nanostructures Group, Max Planck Institute Stuttgart, September 2008.
85. Gorelik OP, Nikolaev P, Arepalli S. Purification Procedures for Single-Wall Carbon Nanotubes. NASA/CR-2000-208926.
86. Lebron M, Meador MA. New Method Developed To Purify Single Wall Carbon Nanotubes for Aerospace Applications. Research and Technology, Glenn Research Center at Lewis Field, Cleveland, Ohio, NASA/TM-2003-21990, pp. 29-30.
87. Harris PF. Carbon Nanotubes and Related Structures: New Materials for the Twenty-first Century. Cambridge University Press, 1999, p. 49.
88. Dai HJ. Carbon nanotubes: Opportunities and challenges. *Surf Sci* 2002;500(1-3):218-241.
89. Thostenson ET, Li Ch, Chou T-W. Nanocomposites in context. *Compos Sci Technol* 2005;65(3-4):491-516.
90. Meguid SA, Wernik JM, Cheng ZQ. Atomistic-based continuum representation of the effective properties of nano-reinforced epoxies. *Int J Solids Struct* 2010;47(13):1723-1736.
91. Smart SK, Cassady AL, Lu GQ, Martin DJ. The biocompatibility of carbon nanotubes. *Carbon* 2006;44(6):1034-1047.
92. Hilding J, Grulke EA, Zhang ZG, Lockwood F. Dispersion of carbon nanotubes in liquids. *J Dispers Sci Technol* 2003;24(1):1-41.
93. Lam C, James JT, McCluskey R, Hunter R. Pulmonary toxicity of single-wall carbon nanotubes in mice 7 and 90 days after intratracheal instillation. *Toxicol Sci* 2004;77(1):126-34.



94. Muller J, Huaux F, Moreau N, Misson P, Heiler JF, Delos M, et al. Respiratory toxicity of multi-wall carbon nanotubes. *Toxicol App Pharmacol* 2005;207(3):221-31.
95. Jia G, Wang H, Yan L, Wang X, Pei R, Yan T, et al. Cytotoxicity of carbon nanomaterials: single-wall nanotube, multi-wall nanotube and fullerene. *Environ Sci Technol* 2005;39(5):1378-83.
96. Coleman JN, Khan U, Blau WJ, Gun'ko YK. Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites. *Carbon* 2006;44(9):1624-1652.
97. Mukhopadhyay A, Chu BTT, Green MLH, Todd RI. Understanding the mechanical reinforcement of uniformly dispersed multiwalled carbon nanotubes in alumino-borosilicate glass ceramic. *Acta Materialia* 2010;58(7):2685-2697.
98. Machado MAL, Valentini L, Biagiotti J, Kenny JM. Thermal and mechanical properties of single-walled carbon nanotubes-polypropylene composites prepared by melt processing. *Carbon* 2005;43(7):1499-505.
99. Yamamoto G, Omori M, Hashida T, Kimura H. A novel structure for carbon nanotube reinforced alumina composites with improved mechanical properties. *Nanotechnology* 2008;19(31):315708.
100. Fünfschilling S, Fett T, Hoffmann MJ, Oberacker R, Schwind T, Wippler J, et al. Mechanisms of toughening in silicon nitrides: The roles of crack bridging and microstructure. *Acta Mater* 2011;59(10):3978-3989.
101. Fu YQ, Gu YW, Du HJ. SiC whisker toughened  $\text{Al}_2\text{O}_3$ -(Ti, W)C ceramic matrix composites. *Scripta Mater* 2001;44(1):111-116.
102. Halitim F, Ikhlef N, Boudoukha L, Fantozzi G. Microhardness, Young's modulus and fracture toughness of alumina implanted with  $\text{Zr}^+$ ,  $\text{Cr}^+$ ,  $\text{Ti}^+$  and  $\text{Ni}^+$ . The effect of the residual stresses *J Phys D: Appl Phys* 1997;30(3):330-337.
103. Zhang S, Sun D, Fu Y, Du H. Toughening of hard nanostructural thin films: a critical review. *Surface Coatings Technol* 2005;198(1-3):2-8.
104. Claussen N, Steeb J, Pabst RF. Effect of induced microcracking on the fracture toughness of ceramics. *Bull Am Ceram Soc* 1977;56(69): 559-562.
105. Lange FF. Interaction of Crack Growth with Second Phase Dispersion. *Philos Mag* 1970;22(179):983-992.
106. Wiederhorn SM. Brittle fracture and toughening mechanisms in ceramics. *Ann Rev Mater Sci* 1984;14:373-403.
107. Cha SI, Kim KT, Lee KH, Mo ChB, Hong SH. Strengthening and toughening of carbon nanotube reinforced alumina nanocomposite fabricated by molecular level mixing process. *Scripta Mater* 2005;53(7):793-797.
108. Mo ChB, Cha SI, Kim KT, Lee KH, Hong SH. Fabrication of carbon nanotube reinforced alumina matrix nanocomposite by sol-gel process. *Mater Sci Eng A* 2005;385(1-2):124-128.
109. Ahmad I, Cao H, Chen H, Zhao H, Kennedy A, Zhu YQ. Carbon nanotube toughened aluminium oxide nanocomposite. *J Eur Ceram Soc* 2010;30(4):865-873.
110. Osayande L, Okoli OI. Fracture toughness enhancement for alumina system: a review. *Int J App Ceram Technol* 2008;5(3): 313-323.

111. Rishabh A, Joshi MR, Balani K. Fractal model for estimating fracture toughness of carbon nanotube reinforced aluminium oxide. *J App Phys* 2010;107(12):123532-1-123532-7.
112. Ahmad I, Unwin M, Cao H, Chen H, Zhao H, Kennedy A, Zhu YQ. Multi-walled carbon nanotubes reinforced  $\text{Al}_2\text{O}_3$  nanocomposites: Mechanical properties and interfacial investigations. *Compos Sci Technol* 2010;70(8):1199-1206.
113. Zhang ShC, Fahrenholtz WG, Hilmas GE, Yadlowsky EJ. Pressureless sintering of carbon nanotube- $\text{Al}_2\text{O}_3$  composites. *J Eur Ceram Soc* 2010;30(6):1373-1380.
114. Fan J, Zhao D, Wu M, Xu Z, Song J. Preparation and microstructure of multi-wall carbon nanotubes-toughened  $\text{Al}_2\text{O}_3$  composite. *J Am Ceram Soc* 2006;89(2):750-753.
115. Zhu Y-F, Shi L, Liang J, Hui D, Lau K-t. Synthesis of zirconia nanoparticles on carbon nanotubes and their potential for enhancing the fracture toughness of alumina ceramics. *Compos B* 2008;39(7-8):1136-1141.
116. ZhiHui L, DongLiang J, JingXian Zh, QingLing L. Preparation and properties of multi-wall carbon nanotube/SiC composites by aqueous tape casting. *Sci China Ser E-Tech Sci* 2009;52(1):132-136.
117. Peigney A, Laurent C, Dobigeon F, Rousset A. Carbon nanotubes grown in situ by a novel catalytic method. *J Mater Res* 1997;12(3):613-615.
118. Flahaut E, Peigney A, Laurent C, Marliere C, Chastel F, Rousset A. Carbon nanotube-metal-oxide nanocomposites: microstructure, electrical conductivity and mechanical properties. *Acta Mater* 2000;48(14):3803-3812.
119. Peigney A, Flahaut E, Laurent C, Chastel F, Rousset A. Aligned carbon nanotubes in ceramic-matrix nanocomposites prepared by high-temperature extrusion. *Chem Phys Lett* 2002;352(1-2):20-25.
120. An JW, Lim DS. Effect of carbon nanotube additions on the microstructure of hot-pressed alumina. *J Ceram Process Res* 2002;3(3):201-204.
121. 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 Ceram Soc* 1998;18(14):1995-2004.
122. Peigney A, Laurent Ch, Dumortier O, Rousset A. Carbon nanotubes-Fe-alumina nanocomposites. Part II: microstructure and mechanical properties of the hot-pressed composites. *J Eur Ceram Soc* 1998;18(14):2005-2013.
123. Peigney A, Laurent Ch, Rousset A. Synthesis and characterization of alumina matrix nanocomposites containing carbon nanotubes. *Key Eng Mater* 1997; 132-136:743-746.
124. Sun J, Gao L, Li W. Colloidal processing of carbon nanotube/alumina composites. *Cem Mater* 2002;14(12):5169-5172.
125. Mo CB, Cha SI, Kim KT, Lee KH, Hong SH. Fabrication of carbon nanotube reinforced alumina matrix nanocomposite by sol-gel process. *Mater Sci Eng A Strcut Mater* 2005;395(1-2):124-128.
126. Ahmad K, Pan W. Hybrid composites: a new route towards tougher alumina ceramics. *Compos Sci Technol* 2008;68(6):1321-1327.
127. Lewis JA. Colloidal Processing of Ceramics. *J Am Ceram Soc* 2000;83(10): 2341-2359.

128. Omatete OO, Janney MA, Strehlow RA. Gel casting-A new ceramic forming process. *Am Ceram Soc Bull* 1991;70(10):1641-1649.
129. Lange FF. Powder processing science and technology for increased reliability. *J Am Ceram Soc* 1989;72(1):3-15.
130. Poorteman M, Traianidis M, Bister G, Cambier F. Colloidal processing, hot pressing and characterisation of electroconductive MWCNT-alumina composites with compositions near the percolation threshold. *J Eur Ceram Soc* 2010;29(4) 669-675.
131. Sun J, Gao L, Jin XH. Reinforcement of alumina matrix with multi-walled carbon nanotubes. *Ceram Int* 2005;31(6):893-896.
132. Lee K, Mo CB, Park SB, Hong SH. Mechanical and electrical properties of multiwalled CNT-alumina nanocomposites prepared by a sequential two-step processing of ultrasonic spray pyrolysis and spark plasma sintering. *J Am Ceram Soc* 2011;1(6). doi: 10.1111/j.1551-2916.2011.04689.x.
133. Wei T, Fan ZJ, Luo GH, Wei F. A new structure for multi-walled carbon nanotube reinforced alumina nanocomposite with high strength and toughness. *Mater Lett* 2008;62(4-5) 641-644.
134. Estili M, Kawasaki A. An approach to mass-producing individually alumina-decorated multi-walled carbon nanotubes with optimized and controlled compositions. *Scripta Mater* 2008;58(10) 906-909.
135. Seeger T, Redlich P, Grobert N, Terrones M, Walton DRM, Kroto HW, Ruhle M. SiO<sub>x</sub>-coating of carbon nanotubes at room temperature. *Chem Phys Lett* 2001;339(1-2):41-46.
136. de Andrede MJ, Lima MD, Bergman CP, Ramminger GD, Balzaretti NM, Costa TMH, Gallas MR. Carbon nanotube/silica composites obtained by sol-gel and high-pressure techniques. *Nanotechnology* 2008;19:265607.
137. Livage J. Sol-gel processes. *Curr Opin Solid ST M*. 1997; 2(2):132-136.
138. Vorotilov KA, Yanovskaya MI, Turevskaya EP, Sigov AS. Sol-gel derived ferroelectric thin films: avenues for control of microstructural and electric properties. *J Sol-Gel Sci Techn* 1999;16(2):109-118.
139. Sen S, Choudharya RNP, Pramanik P. 62. Synthesis and characterization of nanostructured ferroelectric compounds. *Mater Lett*. 2004;58(27-28):3486-3490.
140. Sealy C. Stronger by a hair - composites: glassy route to ultrahard ceramics: composites: uncommon behavior in ceramic composites: composites. *Mater Today* 2004; 7(10):15-15.
141. Ning J, Zhang J, Pan Y, Guo J. 74. Fabrication and mechanical properties of SiO<sub>2</sub> matrix composites reinforced by carbon nanotube. *Mater Sci Eng A* 2003; 357(1-2):392-396.
142. Cury Camargo PH, Satyanarayana KG, Wypych F. Nanocomposites: Synthesis, Structure, Properties and New Application Opportunities. *Mater Res* 2009;12(1)1-39.
143. Guimaraes FAT, Silva KL, Trombini V, Pierri JJ, Rodrigues JA, Tomasi R, Pallone EMJA. Correlation between microstructure and mechanical properties of Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> nanocomposites. *Ceram Int* 2009;35(2):741-745.

144. Duszová A, Dusza J, Tomásek K, Blugan G, Kuebler J. Microstructure and properties of carbon nanotube/zirconia composite. *J Eur Ceram Soc* 2008;28(5):1023-1027.
145. Maensiri S, Laokul P, Klinkaewnarong J, Amornkitbamrung V. Carbon nanofiber-reinforced alumina nanocomposites: Fabrication and mechanical properties. *Mat Sci Eng A* 2007;447(2):44-50.
146. Sarkar D, Adak S, Mitra NK. Preparation and characterization of an  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  nanocomposite, Part I: Powder synthesis and transformation behaviour during fracture. *Compos Part A Appl S* 2007;38(1):124-131.
147. Kerkwijk B, Winnbst L, Mulder EJ, Verweij H. Processing of homogeneous zirconia-toughened alumina ceramics with high dry-sliding wear resistance. *J Am Ceram Soc* 1999;82(8):2087-2093.
148. Corrêa de Sá e Benevides de Moraes MC, Elias CN, Filho JD, Guimaraes de Oliveira L. Mechanical properties of alumina-zirconia composites for ceramic abutments. *Mater Res* 2004;7(4):643-649.
149. Benzaid R, Chevalier J, Saâdaoui M, Fantozzi G, Nawa M, Diaz LA, Torrecillas R. Fracture toughness, strength and slow crack growth in a ceria stabilized zirconia-alumina nanocomposite for medical applications. *Biomaterials* 2008;29(27):3636-3641.
150. De Aza AH, Chevalier J, Fantozzi G, Schehl M, Torrecillas R. Crack growth resistance of alumina, zirconia and zirconia toughened alumina ceramics for joint prostheses. *Biomaterials* 2002;23(3):937-945.
151. Sarkar S, Das PK. Microstructure and physicochemical properties of pressureless sintered multiwalled carbon nanotube/alumina nanocomposite. *Ceram Int* (2011), doi:10.1016/j.ceramint.2011.07.023.
152. Oungkulsolmongkol Th, Salee-Art P, Buggakupta W. Hardness and fracture toughness of alumina-based particulate composites with zirconia and strontia additives. *JOM-J Min Met Mats* 2010;20(2):7178.
153. Echeberria J, Rodríguez N, Vleugels J, Vanmeensel K, Reyes-Rojas A, Garcia-Reyes A, Domínguez-Ríos C, Aguilar-Elguézabal A, Bocanegra-Bernal MH. Hard and tough carbon nanotube-reinforced zirconia-toughened alumina composites prepared by spark plasma sintering. *Carbon* 2012;50(2):706-717.
154. Jinpeng F, Zhao D, Song J. Preparation and microstructure of multi-walled carbon nanotubes toughened  $\text{Al}_2\text{O}_3$  composites. *J Am Ceram Soc* 2006;89(2):750-753.
155. Ahmad I, Fay M, Kennedy A, Zhu YQ. Interfacial investigations and mechanical properties of carbon nanotubes reinforcing  $\text{Al}_2\text{O}_3$  nanocomposites. *Proceedings of 17<sup>th</sup> International Conference on Composite Materials, ICCM 17 2009, Edinburgh, UK.*
156. Jiang D, Thomson K, Kuntz JD, Agerb JW, Mukherjee AK. Effect of sintering temperature on a single-wall carbon nanotube-toughened alumina-based nanocomposite. *Scr Mater* 2007;56(7):959-962.
157. Kim SW, Chung WS, Sohn K-S, Son Ch-Y, Lee S. Improvement of wear resistance in alumina matrix composites reinforced with carbon nanotubes. *Metal Mater Trans* 2010;41A(2):380-388.

158. Piconi C, Maccauro G, Muratori F, Brach Del Prever E. Alumina and zirconia ceramics in joint replacements. *J Appl Biomater Biomech* 2003;1(1):19-32.
159. Echeberria J, Ollo J, Bocanegra-Bernal MH, Garcia-Reyes A, Domínguez-Rios C, Aguilar-Elguezabal A, Reyes-Rojas A. Sinter and hot isostatic pressing (HIP) of multi-wall carbon nanotubes (MWCNTs) reinforced ZTA nanocomposite: Microstructure and fracture toughness. *Int J Refract Met H* 2009;28(3):399-406.
160. Balázs Cs, Shen Z, Kónya Z, Kasztovszky Zs, Wéber F, Vértesy Z, Biró LP, Kiricsi I, Arató P. Processing of carbon nanotube reinforced silicon nitride composites by spark plasma sintering. *Compos Sci Technol* 2005;65(5):727-733
161. Mamedov AA, Kotov NA, Prato M, Guldi DM, Wicksted JP, Hirsch A. *Nature Mater* 2002;1(3):190-194.
162. Inam F, Peijs T, Reece MJ. The production of advanced fine-grained alumina by carbon nanotube addition. *J Eur Ceram Soc* 2011;31(15):2853-2859.
163. Inam F, Yan HX, Peijs T, Reece MJ. The sintering and grain growth behaviour of ceramic-carbon nanotube nanocomposites. *Compos Sci Technol* 2010;70(6):947-952.
164. He CN, Tian F, Liu SJ. A carbon nanotube/alumina network structure for fabricating alumina matrix composites. *J All Compd* 2009;478(1-2):816-819.
165. Quinn GD. Fracture toughness of ceramics by the Vickers indentation crack length method. A critical review. *Mechanical Properties and Performance of Engineering Eeramics II: Ceramic Engineering and Science Proceeding* 2006;27(2):1-16.
166. Swab JJ. Recommendations for determining the hardness of armor ceramics. *Intl J App Ceram Tech* 2004;1(3):941-944
167. Trombini V, Pallone EMJA, Munir ZA, Tomasi R.  $\text{Al}_2\text{O}_3$ -SiC nanocomposites sintered by spark plasma sintering (SPS). *Cerâmica* 2008;54(331):361-365.
168. Rattanachan S, Miyashita Y, Mutoh Y. Microstructure and fracture toughness of a spark plasma sintered  $\text{Al}_2\text{O}_3$ -based composite with  $\text{BaTiO}_3$  particulates. *J Eur Ceram Soc* 2003;23(8):1269-1276.
169. Zhan G-D, Kuntz J, Wan J, Garay J, Mukherjee AK. Alumina-based nanocomposites consolidated by spark plasma sintering. *Scripta Mater* 2002;47(11):737-741.
170. Akin I, Yilmaz E, Ormanci O, Sahin F, Yucel O, Goller G. Effect of  $\text{TiO}_2$  Addition on the Properties of  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  Composites Prepared by Spark Plasma Sintering. *Bioceramics Development and Applications 2011 Vol 1*, Article ID D110147, 3 pages, doi:10.4303/bda/D110147.
171. Peigney A, Garcia FL, Estournes C, Weibel A, Laurent C. Toughening and hardening in double-walled carbon nanotube/nanostructured magnesia composites. *Carbon* 2010;48(7):1952-1960.
172. Burghard Z, Schon D, Garstel P, Bill J, Aldinger F. Polymer-derived Si-C-N ceramics reinforced by single-wall carbon nanotubes. *Int J Mater Res* 2006;97(12):1667-1672.
173. Zhan G-D, Mukherjee AK. Processing and characterizations of nanoceramic composites with interesting structural and functional properties. *Rev Adv Mater Sci* 2005;10(3):185-196.

174. Pratt PL. Micromechanisms of crack extension in ceramics. *Metal Sci* 1980;14(8-9):363-373.
175. Balani K, Agarwa A. Wetting of carbon nanotubes by aluminium oxide. *Nanotechnology* 2008;19(16):165701.
176. Balani K, Bakshi SR, Chen Y, Laha T, Agarwal. A Role of powder treatment and carbon nanotube dispersion in the fracture toughening of plasma-sprayed aluminium oxide-carbon nanotube nanocomposite. *J Nanosci Nanotechnol* 2007;7(10): 3553.
177. Curtin WA, Sheldon BW. CNT-reinforced ceramics and metals. *Mater Today* 2004;7(11): 44-49.
178. Balazsi C, Weber F, Kover Z, Shen Z, Konya Z, Kasztovszky Z, Vertesy Z, Biro LP, Kiricsi I, Arato P. *Current Appl Phy* 2006;6(2):124-130
179. Balani K, Anderson R, Laha T, Andara M, Tercero J, Crumpler E, Agarwal A. *Biomaterials* 2007;28(4):618-624.
180. Bai JB, Vignes J-L, Fournier T, Michel D. A novel method for preparing preforms of porous Alumina and carbon nanotubes by CVD. *Adv Eng Mater* 2002;4(9):701-703.
181. Sun J, Iwasa M, Nakayama T, Niihara K, Gao L, Jin X. Pressureless sintering of alumina carbon nanotubes composites in air atmosphere furnace and their mechanical properties. *J Ceram Soc Jpn* 2004;112(5):S403-S406[181] Unpublished results.
182. Kumari L, Zhang T, Du GH, Li WZ, Wang QW, Datye A, Wu KH. Thermal properties of CNT- $\text{Al}_2\text{O}_3$  nanocomposites. *Compos Sci Technol* 2008;68(9):2178-2183.
183. Park TJ, Banerjee S, Hemraj-Benny T, Wong S. Purification strategies and purity visualization technique for single-walled carbon nanotubes. *J Mater Chem* 2006;16(2):141-154.
184. Anstis GR, Chantikul P, Lawn BR, Marshall DB. A critical Evaluation of Indentation Techniques for Measuring Fracture Toughness: I. Direct Crack Measurements. *J Am Ceram Soc* 1981;64(9):533-538.
185. Olek M, Ostrander J, Jurga S, Mohwald H, Kotov N, Kempa K, Giersing M. Layer-by-layer assembled composites from multiwall carbon nanotubes with different morphologies. *Nano Lett* 2004;4(10):1889-1895.
186. Estili M, Kawasaki A, Sakamoto H, Mekuchi Y, Kuno M, Tsukada T. The homogeneous dispersion of surfactantless, slightly disordered, crystalline, multiwalled carbon nanotubes in  $\alpha$ -alumina ceramics for structural reinforcement. *Acta Mater* 2008;56(15):4070-4079.
187. Wagner HD, Lourie O, Feldman Y, Tenne R. Stress-Induced Fragmentation of Multiwall Carbon Nanotubes in a Polymer Matrix. *Appl Phys Lett* 1998;72(2):188-190.
188. Zhu Y.-F, Shi L, Zhang Ch, Yang X.-Z, Liang J. Preparation and properties of alumina composites modified by electric field-induced alignment of carbon nanotubes. *Appl Phys* 2007;A89(3):761-767.
189. Kumar MS, Lee SH, Kim TY, Kim TH, Song SM, Yang JW, Nahm KS, Suh E.-K. *Solid State Electron* 2003;47(11):2075-2080.

190. Wei T, Fan Z, Luo G, Wei F, Zhao D, Fan J. The effect of carbon nanotubes microstructures on reinforcing properties of SWCNTs/alumina composite. *Mater Res Bull* 2008;43(10):2806-2809.
191. 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.
192. Kim BN, Wakayama S, Kawahara M. Characterization of 2-dimensional crack propagation behaviour simulation and analysis. *Int J Fracture* 1996;75(3): 247-259.
193. Evans AG. Perspective on the development of high-toughness ceramics. *J Am Ceram Soc* 1990;73(2):187-206.
194. Karihaloo BL. Contributions of t-m phase transformation to the toughening of ZTA. *J Am Ceram Soc* 1991;74(7):1703-1706.
195. Casellas D, Ràfols I, Llanes L, Anglada M. Fracture toughness of zirconia-alumina composites. *Int J Refract Met Hard Mater* 1999;17(1-3):11-20.
196. White AA, Best SM, Kinloch AA. Hydroxyapatite-carbon nanotube composites for biomedical applications: a review. *Int J Appl Ceram Technol* 2007;4(1):1-13.
197. Niihara K. New design concept of structural ceramic-ceramic nanocomposites. *J Ceram Soc Jpn* 1991;99(10):974-982.
198. Biswas K, Mukhopadhyay A, Basu B, Chattopadhyay K. Densification and microstructure development in spark plasma sintered WC-6 wt% ZrO<sub>2</sub> nanocomposites. *J Mater Res* 2007;22(6):1491-1501.
199. Zhan G.-D, Mukherjee AK. Carbon nanotube reinforced alumina-based ceramics with novel mechanical, electrical, and thermal properties. *Int J Appl Ceram Technol* 2004;1(2):161-171.
200. Thomson KE, Jiang D.-G, Ritchie RO, Mukherjee AK. A preservation study of carbon nanotubes in alumina-based nanocomposites via Raman spectroscopy and nuclear resonance. *Appl Phys A* 2007;89(3):651-654.
201. Yu MF, Yakobson BI, Ruoff RS. Controlled sliding and pullout of nested shells in individual multiwalled carbon nanotubes. *Phys Chem B* 2000;104(37): 8764-8767.
202. Akita S, Nakayama Y. Extraction of Inner Shell from Multiwall Carbon Nanotubes for Scanning Probe Microscope Tip. *Jpn J Appl Phys* 2003;42(6B):3933-3936.
203. Xia Z, Curtin WA. Pullout forces and friction in multiwall carbon nanotubes. *Phys Rev B* 2004;69(233408):4 pages.
204. Cumings J, Zetl A. Low-friction nanoscale linear bearing realized from multiwall carbon nanotubes. *Science* 2000;289(5479):602-604.
205. An JW, Jou DH, Lim DS. Tribological properties of hot-pressed alumina-CNT composites. *Wear* 2003;255(1-6):677-681.
206. Yamamoto G, Hashida T, Takagi T. Tribological properties of single-walled carbon nanotube solids. *J Nanosci Nanotechnol* 2008;8(5):2665-2670.
207. Kovalev S, Ohji T, Yamauchi Y, Sakai M. Grain boundary strength in non-cubic ceramic polycrystals with misfitting intragranular inclusions (nanocomposites). *J Mater Sci* 2000;35(6):1405-1412.

208. Choi SM, Awaji H. Nanocomposites-a new material design concept. *Sci Technol Adv Mater* 2005;6(1):2-10.
209. Todd RI, Bourke MAM, Borsa CE, Brook RJ. Neutron diffraction measurements of residual stresses in alumina/SiC nanocomposites. *Acta Mater* 1997; 45(4):1791-1800.
210. Evans AG, Charles EA. Fracture toughness determinations by indentation. *J Am Ceram Soc* 1976;59(7-8):371-372.
211. Pezzotti G, Munisso MC, Porporati AA, Lessnau K. On the role of oxygen vacancies and lattice strain in the tetragonal to monoclinic transformation in alumina/zirconia composites and improved environmental stability. *Biomaterials* 2010;31(27):6901-69088.
212. Xue B, Liu R, Huang W-Z, Zheng Y-F, Xu Z-D. Growth and characterization of bamboo-like multiwalled carbon nanotubes over Cu/Al<sub>2</sub>O<sub>3</sub> catalyst. *J Mater Sci* 2009; 44(15):4040-4046.