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Processing and properties of alumina–carbon nano fibre ceramic composites using standard ceramic technology

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Abstract

Multi-wall carbon nano fibres (MWCNFs) offer an alternative to multi-wall carbon nanotubes (MWCNTs) as conductive reinforcing phases in ceramic composites. The main differences being their lower cost and larger dimensions. Alumina (Al_2O_3) composite materials with up to 12.5 vol.% content of carbon nano fibres (CNFs) have been produced using standard ceramic processing technology and additives. A detailed description of the milling and dispersion procedure, which produces a homogenous dispersion of the CNFs in the Al_2O_3 microstructure is presented. Dense hot pressed ceramic–CNF composites produced thereof have been characterized for electrical and thermal conductivity, three point bending strength and microstructure. The composites show that a critical flaw size is introduced with the CNFs and the decrease in strength does not vary with increasing CNF content. The composites show a near linear increase in electrical conductivity as a function of CNF content. A slight decrease in the thermal conductivity with increasing CNF content was also observed.

Keywords: A. Suspensions; B. Nanocomposites; C. Electrical conductivity; D. Al_2O_3; Carbon nano fibres

1. Introduction

The high aspect ratio (length to radius ratio) and high electrical as well as thermal conductivity of CNTs makes them excellent reinforcing phases for producing electrically conducting ceramic composites. A two phase equi-axed particle mixture of conducting and insulating particles becomes conductive when the volume fraction of the conducting phase exceeds a theoretical minimum 'percolation threshold' of 16% [1], which is the minimum amount to give a continuous path across the microstructure. In practice in some ceramic systems this value can be higher when grain boundary phases exist and also when grain sizes are extremely large. When the conducting phase consists of long thin particles, the possibilities of an interconnecting contact increases, this may reduce the percolation threshold so that conduction occurs at a much lower content, in ceramics reinforced with CNTs, percolation can occur at less than 1 vol.% [2]. Electrically conductive CNT ceramic composites have potential for a wide range of applications as new functional materials for gas sensors, MEMs, microelectronics, field emission devices, sensor based devices, etc. if their structural integrity is retained [3].

Technical ceramics (e.g. silicon nitride, zirconia, silicon carbide, Al_2O_3, etc.) have a combination of high strength, high Young's moduli, chemical and thermal stability, but a relatively low fracture toughness. Incorporating carbon nanotubes into a ceramic matrix might be expected to produce a composite with both high strength and toughness for use at temperatures upto ~800 °C (decomposition temperature of the CNTs in air). However, achieving a homogeneous dispersion of CNTs in a ceramic matrix whilst achieving full density with no microscopic pores, with strong bonding between CNTs and the matrix presents rather more of a challenge than incorporating CNTs into a polymer [4,5]. CNTs have been introduced into

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different ceramic matrices including silica based nanocomposites [6], yttria-stabilized zirconia (Y-TZP) [7–9], silicon nitride [10] and also Al_2O_3 [11,12] primarily to successfully produce conductive ceramics, but with limited success in improving the mechanical properties. In Al_2O_3–MWCNT composites the improvements in strength are limited to a low content of CNTs (below 4 vol.%) with higher content leading to significant decreases. There are also a few cases of observed increases in fracture toughness but these are normally measured by indentation based methods [13,14]. The indentation fracture toughness technique has been shown to be inappropriate for ceramics and also for CNT composites [15,16]. Often the preparation of CNT–ceramic composites uses processes or chemicals not commonly used in the ceramic industries, e.g. special dispersants, specific washing of the CNTs to remove surface species or sintering by SPS.

In the current work we use processing technology, and materials and chemicals which are readily used at an industrial level. A cheaper alternative to MWCNTs is MWCNFs. The cost of MWCNFs currently starts from approximately 200 €/kg. These have similar properties to CNTs but are larger in size (MWCNTs have typical diameters of 5–40 nm and MWCNFs have diameters up to 600 nm). Al_2O_3 is the most widely used technical ceramic material owing to its relatively high hardness (15–22 GPa), good oxidation resistance, chemical stability, relative ease of processing and sintering as well as its cost and availability [17]. Al_2O_3 is an electrical insulator and is one of the most widely known and studied ceramic materials. Al_2O_3 has been used for over 30 years in biomedical implants, high purity Al_2O_3 is biocompatible and is often used for hip replacement prosthesis. An electrically conductive biocompatible ceramic would offer a new material for conductive electrodes for use in human implantation. Currently metallic electrodes are used for a range of electrodes, including electrodes for brain and muscle simulation and for heart pace making. These metallic electrodes are susceptible to fibrosis in the human body, ceramic biomaterials have been shown to be more biocompatible than metals. Conductive Al_2O_3–CNF composites were developed in this work, these will be later characterized in a future article for biocompatibility.

In this work, different concentrations of CNFs (2.5, 5, 7.5, 10 and 12.5 vol.% of CNF, respectively) were introduced into an Al_2O_3 matrix in order to obtain composites with high electrical conductivity. Sintering is carried out by hot pressing as SPS which gives better densification of ceramic–CNTs is still mostly used on a research level. Due to the difficulties with dispersion of CNFs in a ceramic suspension the focus of this work is in the preparation of the ceramic suspension in two different ways, using two different dispersing agents. One dispersant used, is specifically for the dispersion of the CNFs whilst the other is normally used to aid dispersion of ceramic oxide powders in water. Both types of dispersants have been used for many years in the ceramic, polymer and detergent industries. Here we investigate the effect of using both dispersants together on the dispersion of CNFs in an Al_2O_3 slurry. Densified ceramic composites with up to 12.5 vol.% CNF content were characterized for electrical and thermal conductivity, bending strength and microstructure.

2. Experimental

The starting materials used were; Al_2O_3 grade CT3000 SG (from Alcoa, Germany) which is a mid price, semi-reactive, high purity grade with a d_{50} of 0.7 μm and BET of 7.5 m^2/g. MWCNFs grade HTF150FF-LHT (from Electrovac Austria) with an outer diameter ranging from 50 to 600 nm and lengths of a few to several 10 s of micron long were used. TEM images of these CNFs have already been presented in previous work [18,19]. For dispersion of the CNFs, DBSA (dodecylbenzene sulphonic acid soft type, 90%, dodecyl maranil from ABCR GmbH, Germany) was used. Whilst, Darvan C–N an ammonium based polyacrylate (from R.T. Vanderbilt Company, Inc., Norwalk, USA) was used as an anionic dispersant for the Al_2O_3. Millipore™ water which has a resistivity of 18.2 MΩ cm was used in the preparation of all compositions.

Ceramic slurries/suspensions were prepared from the ceramic powder and CNFs by three different methods outlined in Table 1. Parameters investigated included the milling sequence, milling times and the stage at which dispersants and materials were added. The goals were to get good homogenization of the suspension (CNF and Al_2O_3 powders together) and to make a suspension which could be easily spray dried and give a high yield of spray dried powder granulates. Milling was carried out in PET bottles on a roll mill with 30 rpm, the bottles were filled to 50 vol.% with 3 mm diameter Y-TZP balls. Three different milling procedures investigated are summarised in Table 1 for the preparation of a composition with 7.5 vol.% CNF content, the results corresponding with these methods will be shown later.

After milling, the suspensions were characterized for particle size using laser light scattering (with a Coulter LS230, Beckmann Coulter, USA). The suspensions were sieved (90 μm) to remove any remaining large agglomerates from the

Table 1
Summary of milling methods investigated for a composition of Al_2O_3 with 7.5 vol.% CNF. The percentages given in the table are in wt.%.

	Method 1	Method 2	Method 3
Bottle size	250 ml	500 ml	250 ml
Step 1	47.7% Millipore water + 4.2% DBSA (mill 1 min)	84.5% Millipore water + 1.2% DBSA (mill 1 min)	48.5% Millipore water + 0.6% Darvan C–N (mill 1 min)
Step 2	1.6% CNF (mill 10 min)	0.5% CNF (mill 10 min)	47.3% Al_2O_3 (mill 1 h)
Step 3	46.5% Al_2O_3 (mill 17 h)	13.8% Al_2O_3 (mill 17 h)	1.9 DBSA (mill 1 min)
Step 4	–	–	1.7% CNF (mill 17 h)

Table 2
The different compositions of powder produced for investigation, with the spray dryer output as a percentage of the starting powder.

vol.% CNF [%]	H_2O [ml]	Al_2O_3 [g]	CNF [g]	DBSA [g]	Darvan C–N [g]	Output Method 2 [%]	Output Method 3 [%]	HP Temp [°C]
0	420	100	–	–	–	**34**	–	1450
0	50	48.8	–	–	0.67	–	**41.8**	1450
2.5	550	102	1.158	3.5	–	**48.5**	–	1500
2.5	100	102	1.158	1.5	1.26	–	**46.6**	1500
5	550	100.23	2.315	6.15	–	**34.13**	–	1550
5	100	100	2.315	3	1.27	–	**42.6**	1550
7.5	650	97.6	3.473	8.8	–	**24.62**	–	1600
7.5	100	97.6	3.473	4	1.25	–	**41.4**	1600
10	650	95	4.631	11.45	–	**17.2**	–	1620
10	100	94.96	4.631	4	1.23	–	**47.2**	1620
12.5	100	92.32	5.789	4	1.21	–	**35.7**	1650

slip prior to spray drying. Spray drying was carried out using a laboratory spray dryer (Büchi model 190, BÜCHI Labortechnik AG, Switzerland), with an outlet temperature of 85–105 °C. Spray drying was performed in an extractor with a nanoparticle filter. The following compositions of materials listed in Table 2 were prepared and the spray dryer output is listed. The amount of DBSA was changed for each suspension with the CNF content, whilst the amount of Darvan C–N used for each composition is related to the specific surface area of alumina used.

After spray drying ~5 g of powder (for 1 dense specimen) was filled into boron nitride coated graphite dies of 22 mm diameter for hot pressing. Hot pressing was performed in an argon atmosphere, in the first step the temperature was increased to 1200 °C and a load of 13 MPa was applied over a period of 10 min. The samples were then heated to a sintering temperature of between 1500 and 1650 °C depending on the CNF content (see Table 2). The heating rate was 20 °C/min, with a dwell time of 30 min and a cooling rate of 20 °C/min. The dwell temperature was increased with increasing CNF content since it is known that CNFs and CNTs hinder densification.

The sintered discs were then prepared for characterization by diamond grinding. Circular discs were used for density measurements (by Archimedes principle), electrical resistivity by the four point Van der Pauw method [20] and thermal diffusivity by laser flash method. Small bars of approximately 1.7 mm × 2 mm × 20 mm were prepared by grinding and polishing to measure the three point bending strength. In addition the carbon content of the powders and some of the sintered specimens were measured using TGA/DTA and by combustion analysis (using an ELTRA CS800), both in air.

3. Results and discussion

3.1. Processing

The preparation of CNT/CNF ceramic composites by powder preparation methods (dry or wet methods) and hot pressing is known to be especially difficult with regards to homogeneous distribution of the CNTs and densification [5,21]. In the current work the goal was to validate production of CNF–Al_2O_3 composites by an industrially ready production route. Darvan C–N is an ammonium polymethacrylate salt often used as a dispersant for steric stabilization of slurries and slips during ceramic processing [22,23]. The amount of Darvan C–N used was based on the surface area of Al_2O_3 powder in the different compositions. The DBSA is a liquid soap which is often used in the production of detergents and also as a surfactant in water based polymer emulsions for dispersion of micro and nanoparticles [24,25]. In addition, DBSA has also been used as a dispersant for CNFs in water based ceramic slips [7,18,19].

Suspensions with a CNF vol. content of 7.5% prepared by the different methods are shown in Fig. 1. For the calculation of the particle sizes in the suspensions by laser light scattering an Al_2O_3 model was selected. In Fig. 1a the suspension from Method 1 without Darvan C–N is a thick slip with high viscosity and a considerable amount of foam, this suspension was difficult to spray dry. Fig. 1b shows that the addition of the extra water in Method 2 produces a thinner slip. However, the sieving of this suspension shows that many large and small bundles of CNFs exist after the milling procedure. In Fig. 1c the addition of the Darvan C–N and the change in the milling procedure of Method 3 breaks down these agglomerated bundles, also the darker colour of the slip indicates more CNFs are homogeneously dispersed in this suspension. These results clearly show a beneficial effect due to the addition of Darvan C–N. The spray dried powder produced from Method 3 is also darker.

Fig. 2 shows the particle size analysis from the suspensions prepared by the three different methods. The suspension from Method 1 has mostly agglomerates greater than 10 μm, in the suspension from Method 2 there is now a higher amount of dispersed particles (350 nm) and also many agglomerates. These agglomerates are smaller than in the first suspension. The suspension from Method 3 shows a real dispersed system, containing two peaks. These peaks match those for pure Al_2O_3 as shown in Fig. 3. Fig. 3 shows the particle size analysis for different compositions, these indicate that the CNFs as fibres, bundles and clusters are dispersed to a similar range as the pure Al_2O_3 particles (submicron).

From our experiments the addition of the Darvan C–N plays a more important role than the milling sequence (the milling sequence change alone does not improve the dispersion). The

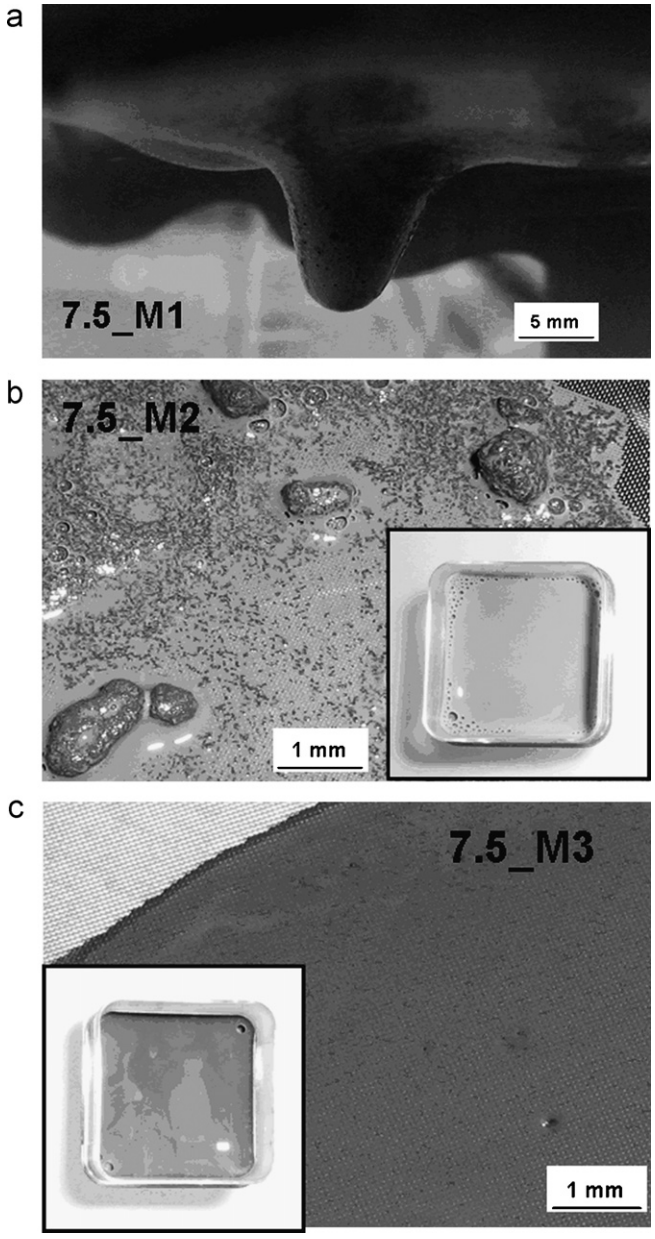

Fig. 1. (a) Suspension from Method 1 observed from below the sieve, (b) suspension from Method 2 showing CNF agglomerates and bundles collected by a 180 μm sieve and (c) suspension Method 3 after a 90 μm sieve showing an agglomerate free dark slip.

Darvan C–N coats the Al_2O_3 particles and leads to a sterically more stable slip for the addition of the CNFs. In addition to a better dispersion, the Darvan C–N also produces a suspension which is more time dependent stable. Sedimentation tests over 24 h showed that the suspension from Method 2 which has lower solids content and no dispersant for Al_2O_3 had faster sedimentation than the suspension from Method 3. The spray dryer output was in nearly all cases significantly higher from Method 3 (see Table 1). The addition of up to 10 vol.% CNFs allowed easy dispersion and spray drying of the slurry. However, at 12.5 vol.% content of CNFs the slurry was noticeably thicker and was at the limit of the spray drying

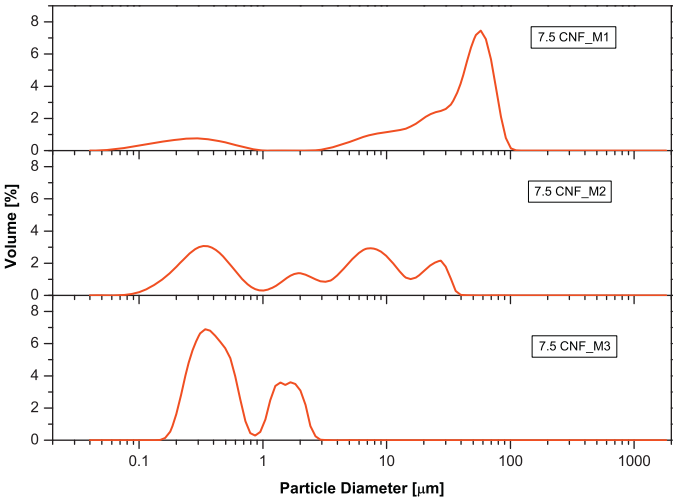

Fig. 2. Particle size distribution curves of the suspension with 7.5 vol.% CNF, dispersed by Methods 1, 2 and 3 from top to bottom.

equipment. Hence, 12.5 vol.% CNF addition in this Al_2O_3 is the limit with the current dispersion additives and process.

SEM of spray dried granulates was carried out to make observations on agglomeration of the CNFs after the spray drying process. Powders spray dried by both Methods 2 and 3 contained some bundles of CNFs. Some examples are shown in Fig. 4. The bundles were smaller than those observed in our previous work with ZrO_2 where no dispersant for the ceramic oxide powder was used [19]. Secondly it would appear that the bundles seem to be slightly smaller in the spray dried granulates from Method 3 and the fibres seem to be better individually dispersed.

3.2. Carbon content analyses

It is inevitable that some CNF content will be lost during processing and sintering. Two types of analyses were carried out to determine the content of the CNF fibres in the different

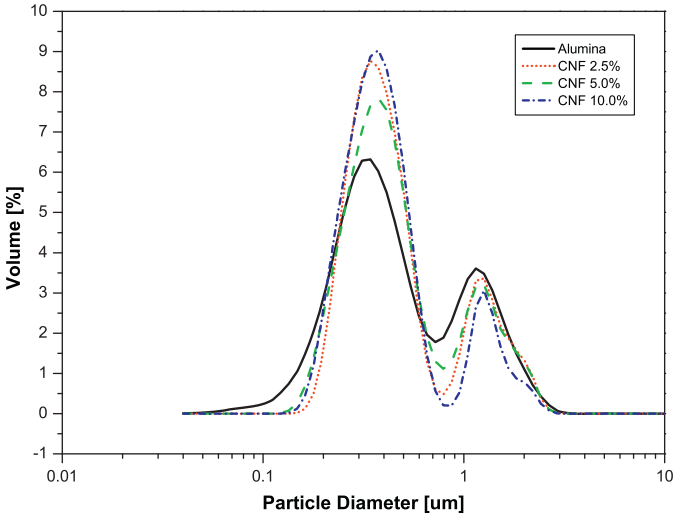

Fig. 3. Particle size analysis of suspensions with different CNF content prepared by the third method with Darvan C–N compared to pure Al_2O_3.

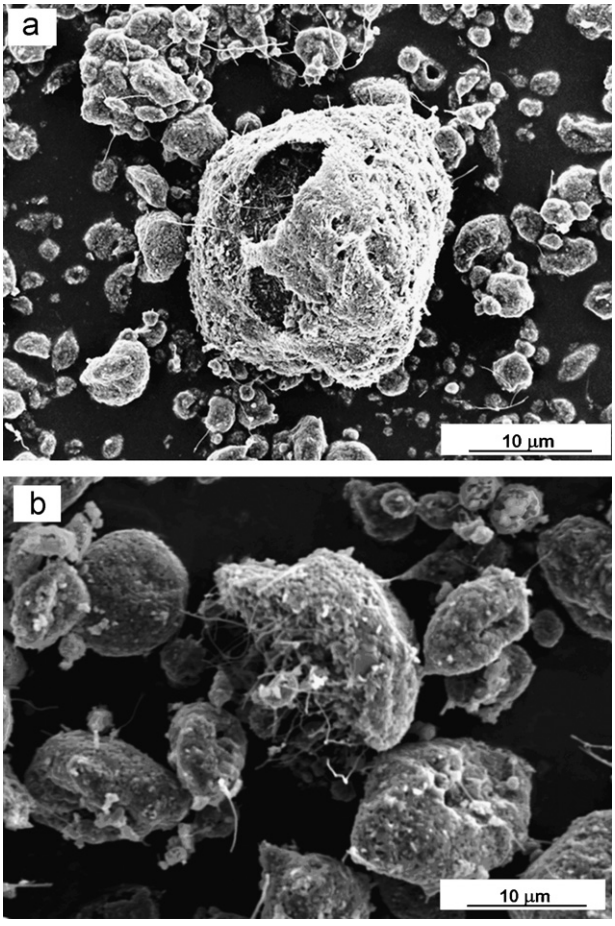

Fig. 4. SEM of Al_2O_3–CNF spray dried powder granulates prepared from dispersion and milling by (a) Method 2 and (b) Method 3 respectively.

compositions after the spray drying of the suspensions. Firstly TGA/DTA was performed. The curves for the composition of alumina with 10 vol.% CNF content are shown in Fig. 5 with and without the addition of Darvan C–N. The peaks corresponding to the burnout of the DBSA (between 400 and 500 °C) and Darvan C–N (at ~200 °C) are clearly visible. The oxidation of the CNFs starts at approximately 650 °C and no significant mass change is observed after 800 °C. The results are presented as mass change and show that with the addition of the Darvan C–N, the mass of CNF lost after the 650 °C increases from ~2.9% to ~4.5%, resulting from an increase in CNF content due to the better processing. The results were converted into vol.% for the different compositions and are summarized in Fig. 6a. In general a small loss of CNFs can often be observed compared to the starting composition. The results indicate that with the use of Darvan C–N a higher CNF content remains in the spray dried powder than the compositions without Darvan C–N. The only exception to an otherwise near linear trend was for the composition with 7.5 vol.% of CNF. This had a lower CNF content relative to the other mixes and was due to a slightly different milling procedure. The milling was carried out in a 250 ml bottle with loading greater than 50% (130 ml of water); normally the loading is approximately 30% when using a 500 ml bottle. This effectively reduced the efficiency of the milling process and the CNF fibres were not properly dispersed in the suspension and subsequently in the spray dried powder, giving a content of approximately 5 vol.%. Ball milling is a complex process and classical theory for ceramics suggests milling with ~50 vol.% of the mill full of media and ~40 vol.% of slip [26]. Hence, it is clear that milling of CNFs is an even more complex process, than for normal ceramic slips.

The second measurement technique by combustion analysis of the material also measures the amount of carbon as a mass change with temperature, the results are presented in Fig. 6b. The results are similar to those observed with the TGA/DTA. A measurement was also made on a sample that was sintered and then crushed back into a powder. The results indicate that with 10 vol.% CNF starting composition, less than 1 vol.% of CNFs

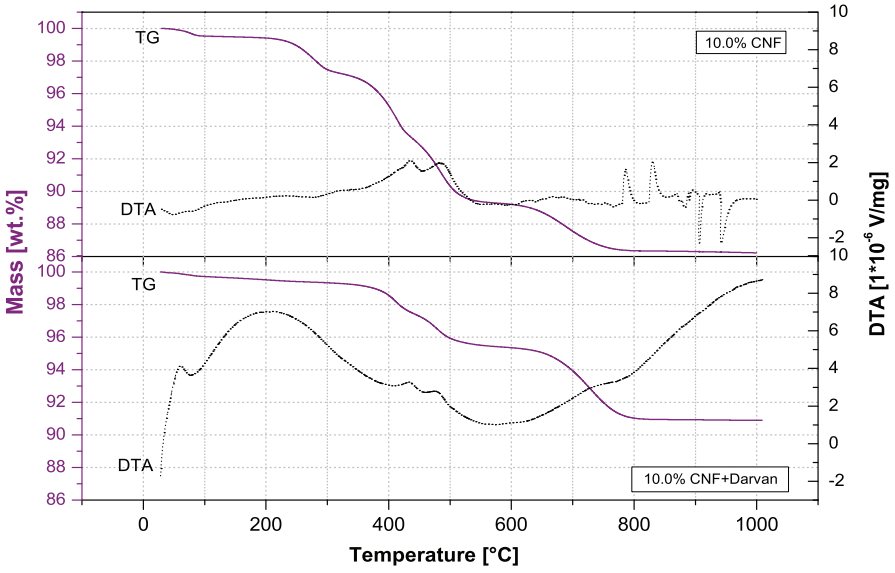

Fig. 5. TGA/DTA of Al_2O_3–10 vol.% CNT composite powder processed with and without Darvan C–N.

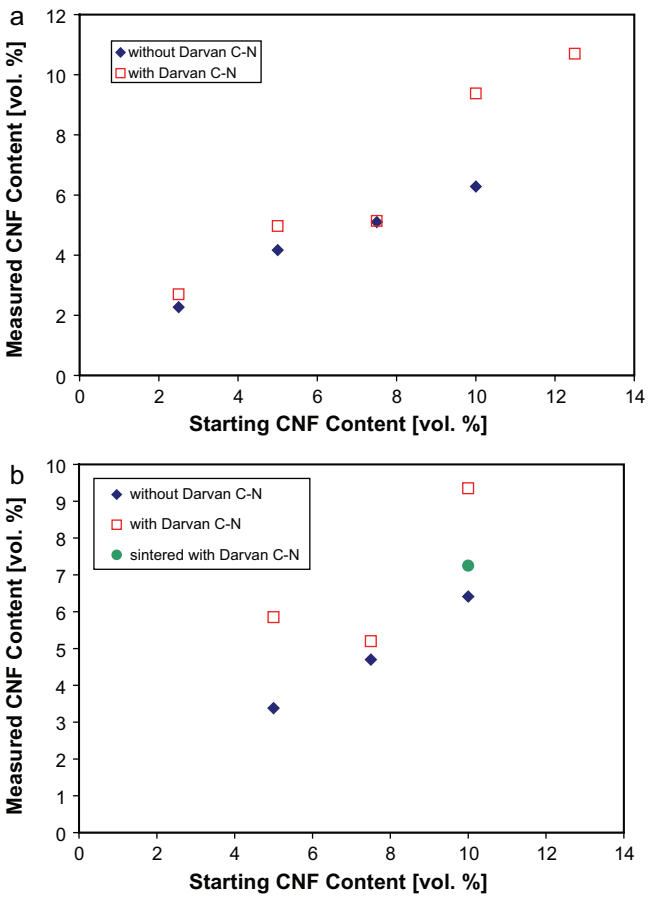

Fig. 6. (a) Summary of TGA/DTA results showing the CNF content as a function of original starting content and (b) CNF content for a limited number of compositions measured by combustion analysis.

is lost during the processing and 2 vol.% CNF is lost during the hot pressing, even though it is carried out in an inert argon atmosphere.

3.3. Electrical, mechanical and thermal properties

The density results indicated that all compositions after hot pressing achieved density higher than 98.8% of the theoretical density based on the starting compositions. After initial trials the hot pressing pressure was reduced from 30 MPa to 13 MPa as this was found to give good densification without excessive growth of the Al_2O_3 grains. The electrical conductivity results of the Van der Pauw measurements are shown in Fig. 7. Three measurements were made per composition. The results show a clear dependence on the CNF content. The relationship is near linear with the exception of the specimens with 7.5 vol.% content of CNF. This exception can be explained due to the difference in the milling process which was described in the previous section and led to a lower amount of CNFs (approximately 5 vol.%) being present in this composite. Simple two point electrical measurements were also made on samples in the green state (these were approximately 50% dense) which were pressed into discs using a uni-axial press, this showed that percolation in the green state occurred with a

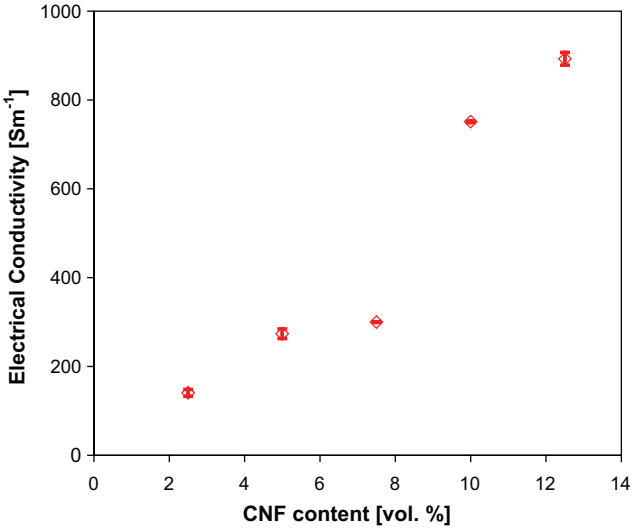

Fig. 7. Dependence of four point electrical conductivity on the CNF content in the sintered Al_2O_3–CNF composites.

CNF content of 7.5 vol.%. The electrical conductivity values achieved are similar to those obtained by other researchers where more expensive MWCNTs have been introduced into Al_2O_3 matrices [27].

Thermal diffusivity tests were carried out at temperatures up to 800 °C and from this the thermal conductivities of the materials were determined. The results as a function of CNF content and test temperature are shown in Fig. 8. It appears that the addition of CNFs reduces the thermal conductivity slightly with increasing CNF content. There may be two possible explanations. Firstly, the test is carried out parallel to the hot pressing direction and most of the CNFs are aligned perpendicular to the hot pressing direction. It is known for MWCNTs that thermal conductivity across the fibre diameter is considerably lower than along the fibre length. A second possible explanation is that although density measurements indicate that 99% of theoretical density has been achieved, the

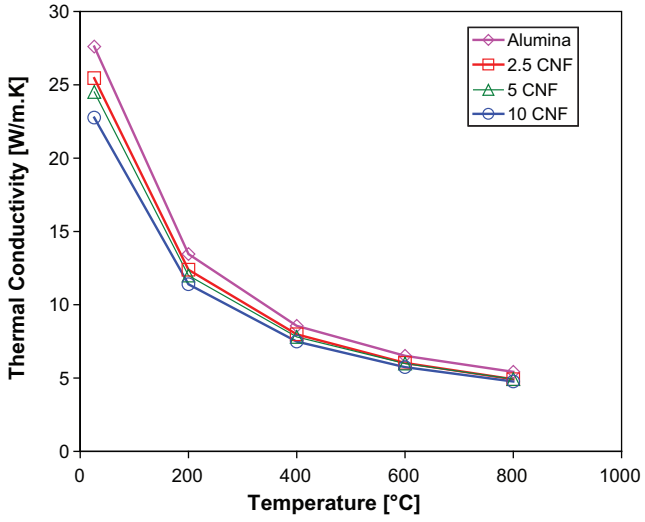

Fig. 8. Thermal conductivity measurements for different compositions measured from room temperature to 800 °C.

introduction of the CNF into the Al_2O_3 leads to microscopic pores and defects which lead to the observed reduction of the thermal conductivity. The results support a previous study by Kumari et al. in Al_2O_3–CNT composites, which showed similar results and only achieved an increase in thermal conductivity when sintering composites at considerably higher temperatures [28]. Kumari et al. synthesized CNT–Al_2O_3 nanocomposite using spark plasma sintering (SPS) methods in order to increase the sintering kinetics. The properties were highly dependent on the CNT content, bulk density, and SPS conditions. A maximum thermal diffusivity of 13.98 mm^2/s at 25 °C, an approximate 60% increase over that of pure Al_2O_3, was obtained in a 7.39 wt.% CNT–Al_2O_3 nanocomposite SPSed at 1550 °C. A maximum heat capacity of 3.76 J/g K at 100 °C, a 318% increase of that of Al_2O_3, was obtained in the 19.1 wt.% CNT–Al_2O_3 nanocomposite SPSed at 1450 °C, and a maximum thermal conductivity of 90.4 W/m K at 100 °C, about 228% increase of that of pure Al_2O_3, was achieved in the 7.39 wt.% CNT–Al_2O_3 nanocomposite sintered at 1550 °C. It is clear that SPS offers better densification than hot pressing and the possibilities of different materials properties. In addition graphitization of the CNFs or CNTs during hot pressing is also known to be detrimental to achieving improved thermal conductivity [5]. Our carbon analysis showed that CNFs are lost during the hot pressing, this could also be by a graphitization process. In thermal conductivity measurements of other hot pressed ceramics it has been shown that thermal diffusivity and conductivity is dependent on microstructural differences induced by differences in the hot pressing directions [29]. These microstructural properties include grain size and shape, properties of the grain boundary phases and defects in the lattice structure [30,31].

Flexural strength tests were carried out in 3 point bending mode, the specimens were much smaller than used in the standard test methods (3 mm × 4 mm × 45 mm). The results are therefore useful for comparative purpose to see the effect of the CNF addition on the strength of Al_2O_3, the results are presented in Fig. 9. It can be seen that due to the effects of the low sample volume a really high value of strength has been achieved for pure Al_2O_3 which decreases significantly with the addition of CNFs. To give a realistic value of strength in comparison to values measured with standard size test bars, the values were adjusted with a Weibull modulus of 5. These recalculated results are included in Fig. 9.

A critical flaw size is the size of a defect or flaw in the microstructure that will cause failure at a particular level. What the strength results show is that the introduction of the CNF into the alumina matrix decreases the strength by approximately 40%. However, further additions of CNF up to 12.5 vol.% do not decrease the strength further (taking into consideration the scatter of data). This would indicate that the bundles of CNF which act as the fracture origin in the composites all have a similar size range (critical flaw size) and that the dispersion of the CNFs in the different compositions up to 12.5 vol.% is similar.

SEM studies of fracture surfaces indicates that the causes of the failures were areas which are denser in CNF content and not due to the presence of large entangled CNF bundle(s) as shown

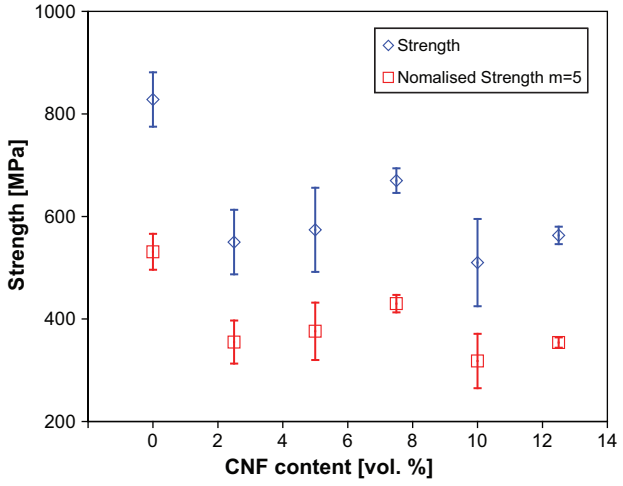

Fig. 9. Three point bending strength as a function of CNF content, adjustment of values considering volume of test samples using a Weibull modulus of 5.

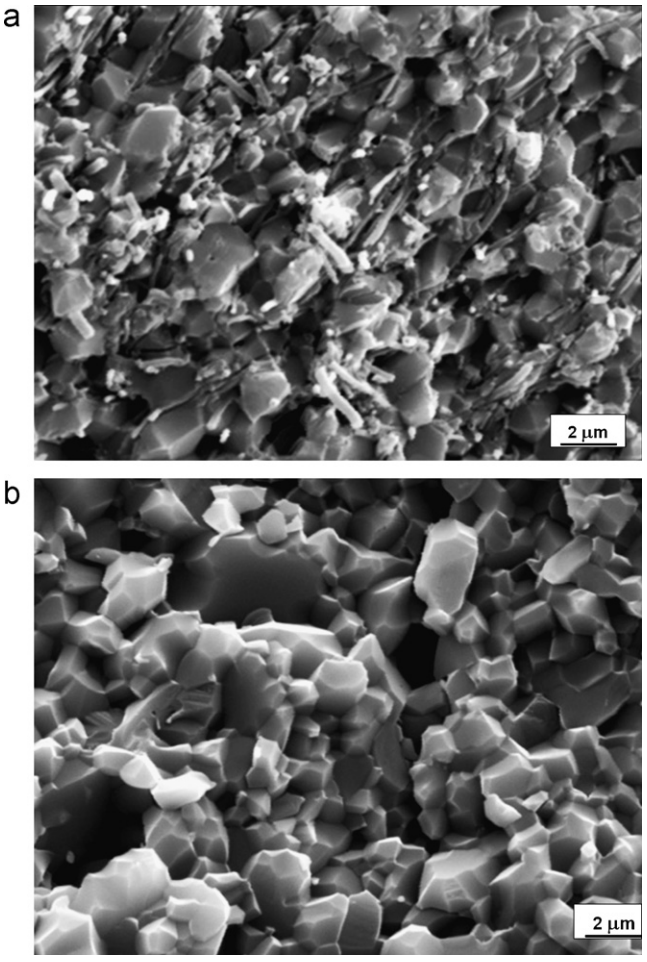

Fig. 10. (a) Fracture surface of Al_2O_3 + 10 vol.% CNF showing areas dense with dispersed CNFs but no large bundles and (b) fracture surface of hot pressed Al_2O_3 with larger grains.

in the fracture surface in Fig. 10a. From the fracture surfaces although there is some evidence of CNFs being pulled out (by random distribution), the short fibre ''pullout'' length makes it difficult to confirm any effect of these fibres on crack deflection, bridging or pullout as toughening mechanisms. SEM studies also show that the presence of the CNFs leads to a small reduction in the average grain size of the alumina as the CNFs hinder densification and the grain growth process. Average grain size for the alumina was ~2.9 μm (Fig. 10b) and varied from ~1.9 to 2.4 μm for the composites. The hindering of densification and grain growth by CNFs and CNTs has been previously reported in both hot pressing and SPS [7,12].

4. Conclusions

The work has shown the importance of designing a dispersion system for both the ceramic phase and the CNF when processing a composite of this type using traditional ceramic industrial technology, the only exception was an extraction system with a nanoparticle filter used when spray drying. It was possible to produce dense ceramics with good electrical conductivity. The following can be concluded:

- The use of Darvan C–N to disperse the Al_2O_3, makes a significant increase to the dispersion of the CNFs in the suspension and in the dense composites.
- The TGA/DTA and combustion analysis show that approximately 1 vol.% of CNFs is lost during the wet processing and spray drying. Also that Method 3 is the most efficient technique to stabilise the CNFs in the ceramic slurry and increase the CNF content in the final spray dried powders.
- The increase in CNF content leads to a near linear increase in electrical conductivity.
- The flexural strength decreases by approximately 40% when CNFs are introduced into the Al_2O_3 matrix.
- A small decrease in thermal conductivity was observed by the addition of the CNFs.
- Up to 10 vol.% CNF can be easily dispersed using the dispersion additives and process.

To summarize the ceramic/CNF processing of the best dispersion method, was as follows: Firstly the Darvan C–N was added to the water and milled for 1 min (for even distribution). Secondly the Al_2O_3 powder was added and the slurry milled for 1 h so that the Darvan C–N is evenly coated on all Al_2O_3 particles. Then the DBSA was added and milled for 1 min (for even distribution). Finally the CNFs were added and the complete suspension milled for a further 17 h.

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