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

Gurdial Blugan [a,*], Monika Michalkova [b], Miroslav Hnatko [b], Pavol Šajgalík [b], Tiziano Minghetti [c], Christian Schelle [c], Thomas Graule [a], Jakob Kuebler [a]

[a] Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for High Performance Ceramics, Ueberlandstrasse 129, 8600 Duebendorf, Switzerland

[b] Slovak Academy of Sciences, Institute of Inorganic Chemistry, Dúbravská Cesta 9, 845 36 Bratislava, Slovak Republic

[c] RUAG Technology, CH-6460 Altdorf, Switzerland

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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

* Corresponding author.
E-mail address: gurdial.blugan@empa.ch (G. Blugan).

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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)