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Electrically conductive alumina–carbon nanocomposites prepared by Spark Plasma Sintering

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Abstract

Carbon nanotubes (CNTs) and carbon black were added to alumina to convert it into a good electrical conductor. Alumina–CNT and alumina–carbon black nanocomposites were fabricated by Spark Plasma Sintering (SPS). The electrical conductivity of alumina–CNT nanocomposites was found to be four times higher as compared to alumina–carbon black nanocomposites due to the fibrous nature and high aspect ratio of CNTs. The electrical conductivity of alumina–CNT nanocomposite increased with increasing grain size due to increasing density of CNTs at the grain boundaries. This effect was not observed for alumina–carbon black nanocomposite due to the particulate geometry of the carbon black.

Keywords: Nanocomposites; Electrical conductivity; Al_2O_3; Carbon; Spark Plasma Sintering (SPS)

1. Introduction

Carbon nanotube (CNT) is one of the recently discovered fullerene forms of carbon. Since 1991,[1] CNT reinforced nanocomposites have been the focus of intense global research. The excitement for CNTs originates from their unique and unrivalled mechanical, thermal and electrical properties. CNTs are potential reinforcements for ceramic matrices in microelectronics, microwave and medical devices, batteries, solid oxide fuel cells, chemical sensors, gas turbine engines, high-temperature reactors and structural components that are exposed to high temperatures and aggressive environments.[2]

The addition of small amounts of CNTs to a ceramic that is an insulator can make it a good conductor.[3–8] Rul et al.[7] uniaxially hot-pressed CNT–$MgAl_2O_4$ and reported a percolation threshold of 0.64 vol%. To date, this is the lowest percolation threshold reported. This percolation threshold is more than 20 times smaller than that of micron scale, two-phase, particulate composites, and this low value has been attributed to the large aspect ratio (100–10,000) of CNTs.[9]

In order to preserve structural integrity of CNTs, Spark Plasma Sintering (SPS) was used to sinter alumina–carbon nanocomposites. SPS is a variant of hot pressing, which involves the rapid heating of graphite dies by pulsed DC electric currents. This rapid heating rate (up to 600 °C/min) and high pressure (up to 1 GPa)[10] are the main feature of SPS. During SPS, the detailed mechanism of enhanced densification is unclear. It has been suggested that the direct current pulse could generate several effects such as spark plasma, spark impact, Joule heating, and electrical field diffusion.[11,12]

In this paper, we compare the electrical conductivity of alumina–CNT nanocomposite and alumina–carbon black nanocomposites sintered by SPS at different temperatures. We also discuss the effect of grain size on the electrical conductivity of the alumina–CNT nanocomposites.

2. Experimental details

Multi-wall CNTs (NC-7000 by Nanocyl Inc., Belgium: average outer diameter 9.5 nm; lengths of up to 1.5 μm; and density 1.7 gcm^{-3}) were dispersed in dimethylformadie, DMF using high power sonication for 2 h and then hand-mixed with alumina nanopowder (Sigma–Aldrich, UK: gamma phase; particle size <50 nm; surface area 35–43 $m^2\,g^{-1}$; melting point 2040 °C; and density 3.97 g cm^{-3}) for 2 min. In our previous work [13], DMF was found to be a much more effective dispersant than ethanol for making stable, homogeneous CNT and composite dispersions. The liquid mixture was rotation ball milled for 8 h. It was then dried at 75 °C for 12 h on a heating plate in air, followed by in a

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vacuum oven at 100 °C for 3 days. The dried agglomerated mixture was ground and sieved at 250 mesh and then placed again in the vacuum oven at 100 °C for another 4 days to thoroughly extract the solvent. Alumina and nanocomposite pellets (diameter 20 mm and thickness 2 mm) were prepared by SPS in a HPD 25/1 (FCT Systeme, Germany) furnace. A pressure of 100 MPa was applied concurrently with the heating (rate 300 °C min^{-1}) and released at the end of the sintering period, which was 3 min for all of the samples. The carbon black nanocomposites were prepared in the same way as the ceramic–CNT nanocomposites. Carbon black (Printex L6: particle size 18 nm and density 1.8 g cm^{-3}) was supplied by Evonik Degussa GmbH.

All of the sintered samples were ground using SiC paper down to 4000 grit. The density of the ground samples was measured using the Archimedes' method. Field emission scanning electron microscopy (FE-SEM) was used to observe fractured surfaces in order to determine the grain sizes. The fractured and polished surfaces were coated with a very thin layer of gold and transferred to an FE-SEM (JEOL JSM-6300, 10 kV, working distance 13–15 mm) for examination. Grain sizes were measured with the aid of the software (Image tool for Windows, version 3.00, developed by UTSHCSA, USA). A minimum of 200 readings was taken to measure the grain sizes of each material. High-resolution transmission electron microscopy (HR-TEM) was carried on JEOL 2010 (LaB_6 filament, 200 kV). The electron transparent nanocomposite films (thickness < 100 nm) were prepared by mechanical grinding, polishing, dimpling and focused ion milling. The electrical conductivities of the samples were measured with a high-sensitivity digital micro-ohmmeter (Keithley 580) using the two-point method on silver electroded specimens (3 mm × 3 mm × 3 mm) prepared using a diamond cutting machine.

3. Results and discussion

The processing conditions and densities of the nanocomposites studied are given in Table 1. The DC electrical conductivities of alumina–CNT and alumina–carbon black nanocomposites are shown in Fig. 1. The conductivity mechanism of an individual CNT can be metallic or semiconducting, depending on the chirality of the CNT.[14] The conduction networks in CNT nanocomposites could involve fluctuation-assisted tunnelling[15] or variable range hopping[16] between the individual CNTs. The axial electrical conductivity of CNTs was reported to be extremely high, reaching 2×10^7 S/m,[17] comparable to that of silver, copper, gold and aluminium (10^7 S/m).[18] The higher electrical conductivity of alumina based CNT nanocomposites (Fig. 1) is the result of the large aspect ratio of CNTs (~150) as compared to that of carbon black (~1) (Fig. 2a). The CNTs and carbon black are located on the alumina grain boundaries (Fig. 2). The CNTs are well dispersed, while there was some agglomeration of the carbon black (Fig. 2). The large aspect ratio of CNTs resulted in an entangled network of conductive pathways (Fig. 3), which was missing in the alumina–carbon black nanocomposites (Fig. 2a). As compared to alumina–2 wt% carbon black (30 S/m), the electrical conductivity of alumina–2 wt% CNT nanocomposites is 125 S/m. The sintering conditions were the same for both materials. A larger CNT content resulted in higher electrical conductivity. The highest electrical conductivity observed in this study was 576 S/m for alumina–5 wt% CNTs. To date, this is the highest electrical conductivity observed for alumina–CNT nanocomposites where multi-wall CNTs were used.[9,19–22] The increased electrical conductivity is attributed to the presence of undamaged CNTs, due to the utilization of SPS technique, which allowed lower sintering temperatures and shorter sintering times.

The addition of CNT for improving electrical conductivity of ceramics is widely appreciated (Table 2). However, to date, there is no publication that reports the dependence of the electrical conductivity of ceramic based CNT nanocomposites on grain size. Fig. 4 shows the electrical conductivity of alumina–carbon nanocomposites as a function of grain size. Tailoring electrical conductivity by changing grain size could be useful for many applications. Ceramics with tailorable electrical conductivity have many industrial applications, such as, static charge dissipation, lightning protection, ceramic heaters, elec-

Table 1
Processing conditions and densities of alumina–carbon nanocomposites.

Filler	wt%	Sintering conditions	% theoretical density
Carbon black	2	1400 °C/100 MPa/3 min	~84
Carbon black	2	1600 °C/100 MPa/3 min	~98
Carbon black	2	1800 °C/100 MPa/3 min	>99
CNT	2	1200 °C/100 MPa/3 min	~77
CNT	2	1400 °C/100 MPa/3 min	~88
CNT	2	1600 °C/100 MPa/3 min	~98
CNT	2	1800 °C/100 MPa/3 min	>99
CNT	3.5	1000 °C/100 MPa/3 min	~67
CNT	3.5	1100 °C/100 MPa/3 min	~85
CNT	3.5	1200 °C/100 MPa/3 min	~98
CNT	3.5	1400 °C/100 MPa/3 min	>99
CNT	3.5	1600 °C/100 MPa/3 min	>99
CNT	3.5	1800 °C/100 MPa/3 min	>99
CNT	5	1200 °C/100 MPa/3 min	>99
CNT	5	1600 °C/100 MPa/3 min	>99
CNT	5	1800 °C/100 MPa/3 min	>99

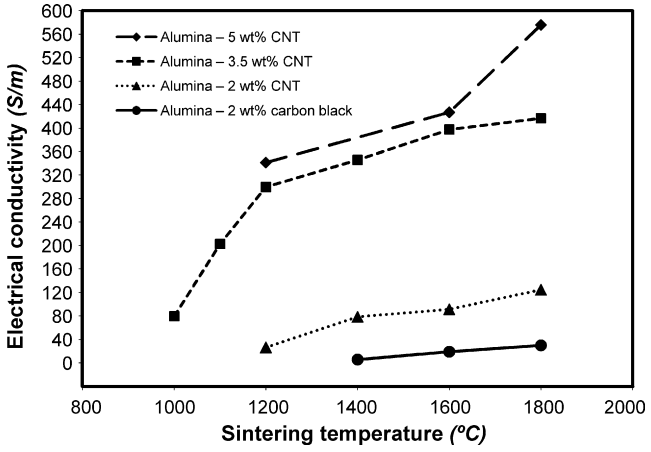

Fig. 1. Electrical conductivities of alumina–carbon nanocomposites. All nanocomposites were SPSed at 100 MPa for 3 min.

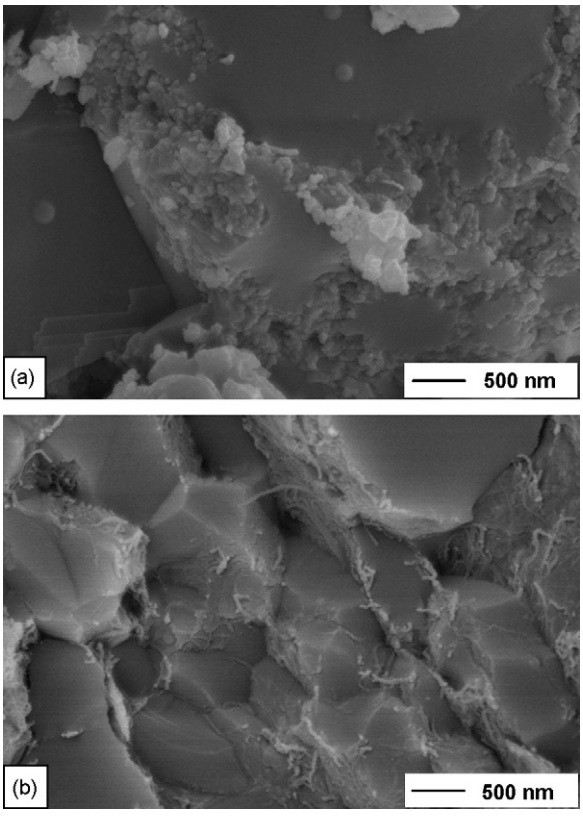

Fig. 2. FE-SEM images of fractured surfaces of sintered nanocomposites processed at 1800 °C for 3 min under a pressure of 100 MPa: (a) alumina–2 wt% carbon black nanocomposite and (b) alumina–2 wt% CNT nanocomposite.

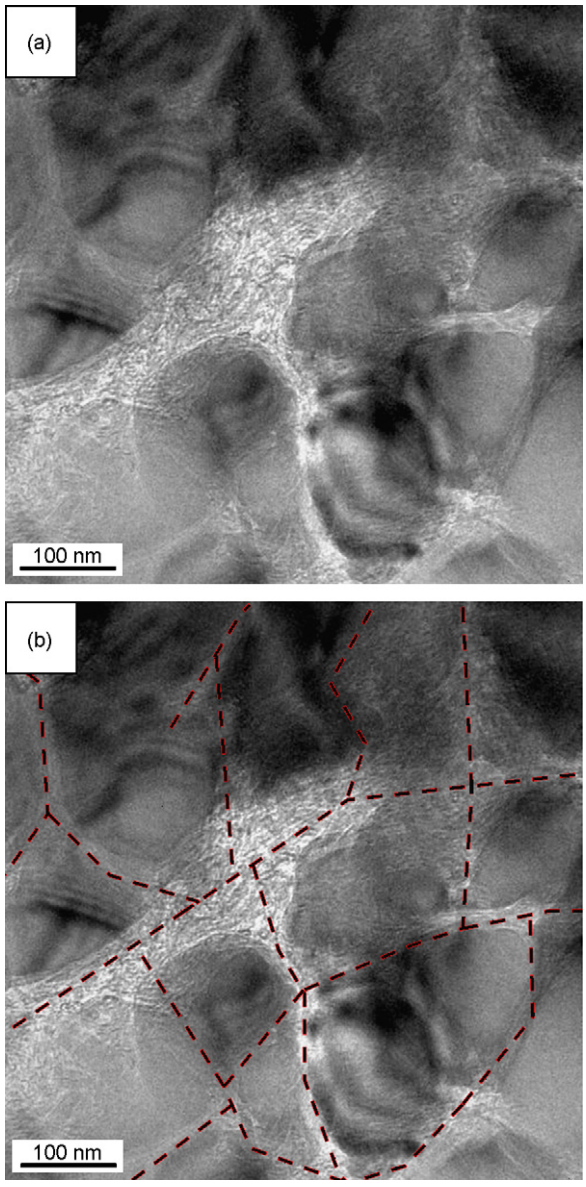

Fig. 3. HR-TEM image of alumina–5 wt% CNT nanocomposite: (a) CNTs around grains and (b) percolating network highlighted.

tric discharge machining (EDM), electromagnetic interference (EMI) shielding in electronic, mechanical, structural, chemical, and vacuum applications.[23] In particular, alumina with added electrically conductive fillers has been used to fabricate substrates for handling semiconductor wafers that require static protection.[23]

For alumina–CNT nanocomposites, the electrical conductivity increased significantly with increasing grain size (Fig. 4). The grain size was modified by changing the sintering temperatures (Fig. 1). Increasing grain size resulted in decreasing grain boundary area. In large grained nanocomposites where fillers are of a fibrous nature, higher electrical conductivity is due to the increased number of conductive paths. However, due to the particulate nature of carbon black and some agglomeration (Fig. 5), this behaviour was not observed for the alumina–carbon black nanocomposites (Fig. 2a). The electrical conductivity also increases, but to a lesser extent. With the growth of the alumina grains (Fig. 2), the particulates or agglomerates of carbon black became more isolated (Fig. 5). Due to the good dispersion,

Table 2
Electrical conductivity of some of the ceramic–CNT nanocomposites.

Group	Year	Ceramic matrix	Processing method	Filler type[a]	Electrical conductivity (S/m)	Percentage improvement
Hirota et al.[3]	2007	Alumina	SPS	5 wt% CNF	588	10^{20}
Balazsi et al.[4]	2006	Silicon nitride	Hot pressing	5 wt% MWNT	130	10^{16}
Shi and Liang[5]	2006	Yttria stabilized zirconia	SPS	10 wt% MWNT	65	10^{16}
Guo et al.[6]	2007	Silica	SPS	7.8 wt% MWNT	64.5	10^{16}
Rul et al.[7]	2004	Magnesium aluminate	Hot pressing	12.2 wt% (SWNT + MWNT)	853	10^{14}
Boccaccini et al.[8]	2007	Borosilicate glass	Hot pressing	10 wt% MWNT	7.7	10^{5}

[a] CNF: carbon nanofibre, MWNT: multi-wall carbon nanotube and SWNT: single wall carbon nanotube.

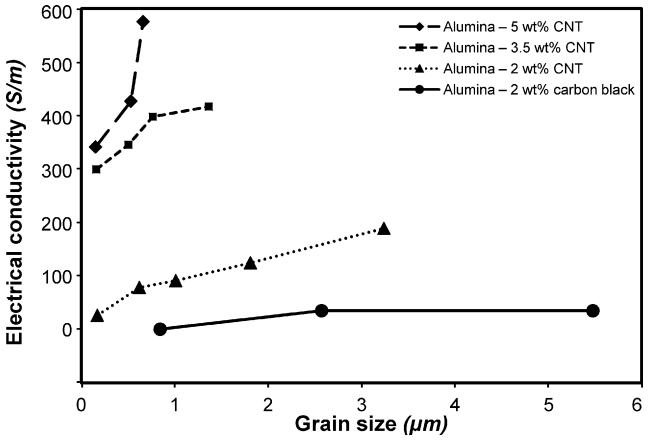

Fig. 4. Electrical conductivities of alumina–carbon nanocomposites as a function of grain size.

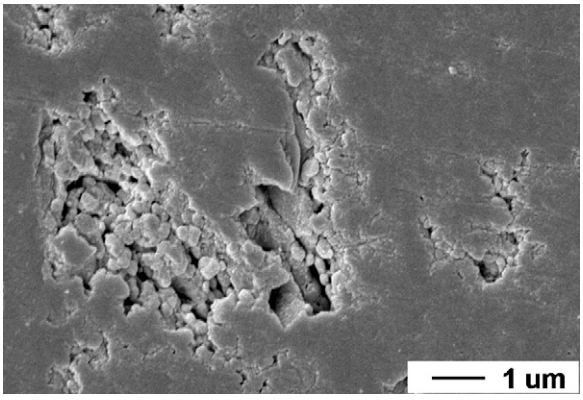

Fig. 5. FE-SEM image of polished surface of alumina–2 wt% carbon black nanocomposite processed at 1800 °C for 3 min under a pressure of 100 MPa. Polishing plucked out agglomerates of carbon black from the surface.

fibrous nature and high aspect ratio of CNT, such isolation is not possible, which resulted in higher electrical conductivity for the alumina–CNT nanocomposite.

4. Conclusion

The increasing availability of nanopowders and nanotubes combined with new processing techniques is enabling the development of new materials. This was illustrated by electrically conductive ceramic–CNT composites. SPS allows the sintering of alumina–carbon nanocomposites in very short times (3 min) without damaging the CNTs. The electrical conductivity of alumina–CNT nanocomposites is four times higher as compared to alumina–carbon black nanocomposites due to the fibrous nature and high aspect ratio of CNTs. The conductive network structure allowed the percolation of CNTs at low volume fractions and thus increased the electrical conductivity compared to alumina–carbon black nanocomposites. The electrical conductivity of alumina–CNT nanocomposite increased with decreasing grain boundary area due to the increased number of CNTs conductive paths. This could be used to tailor the electrical conductivity of ceramics for desired applications.

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