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3-D micro-ceramic components from hydrothermally processed carbon nanotube–boehmite powders by electrophoretic deposition

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Abstract

Boehmite/multi-wall carbon nanotube (MWCNT) composite powders were prepared by hydrothermal processing. Starting chemical of aluminum acetate powders ($2Al(OH)(C_2H_3O_2)_2$) and MWCNTs were mixed for the formation of stoichiometric boehmite powders in an attempt to synthesize MWCNT-reinforced boehmite nano-powders via hydrothermal synthesis at 200 °C for 2 h. Kinetically stable suspensions of MWCNT–boehmite composite powders were prepared and subsequently electrophoretic deposition (EPD) was applied to obtain complex shape products in the form of micro-gears. It is shown that the EPD technique is a powerful tool to manufacture small components in a short time. Detail TEM observations also indicated that hydrothermal processing provides an ideal environment to obtain homogeneous mixtures of MWCNT–boehmite powders due to effective surface functionalization of MWCNTs under hydrothermal conditions.

Keywords: D. Al_2O_3; Carbon nanotube; Electrophoretic deposition; Micro-gears

1. Introduction

Micro-electro-mechanical systems (MEMS) have been attracting attention due to the industry requirements for reliable, fast and smaller devices [1]. Due to the need for high-performance and low-cost microcomponents used in MEMS devices, new and cost-effective fabrication technics are needed in recent decades [2]. Current fabrication technics for microcomponents, such as laser micromachining, micro-electro-discharge machining and focus ion beam are expensive and slow [1–4]. However, electrophoretic deposition can be a good candidate for microcomponent fabrication in a short time and low cost. Alumina based ceramics can be a better choice for microcomponents due to their very good corrosion resistance, low density, high thermal stability, high hardness resulting in a very low wear rate and high elasticity modulus providing rigidity. Carbon nanotubes are excellent reinforcement materials in order to improve toughness and also the electrical conductivity of alumina due to their outstanding mechanical properties and also remarkable electrical properties [5]. However there are two problems that have to be overcome to enhance the toughness of CNT-reinforced alumina composites. The first one is the difficulty of achieving homogenous dispersion of carbon nanotubes in the alumina matrix since CNTs have a tendency to agglomerate because of the van der Waals attractive forces between them and the second one is the poor bonding between the carbon nanotubes and the matrix [6]. To make the carbon nanotubes dispersible it is necessary to physically or chemically attach certain molecules (functionalization), or functional groups, to their sidewalls. One conventional functionalization method involving acid treatment (HNO_3 and H_2SO_4 mixture) is based on the formation of strong covalent bonds which introduce defects on the nanotubes; thus such an acid treatment has a harmful effect on the CNTs' mechanical and electrical properties. However hydrothermal synthesis provides favourable conditions for the functionalization of nanotubes during the ceramic powder processing. Moreover, unlike the acid treatment, hydrothermal synthesis does not give rise to high amount of defects on the nanotubes. Hydrothermal synthesis (HS) can be defined as the

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occurrence of any chemical reaction at temperatures greater than room temperature and pressures above 1 atm in a closed system in a liquid medium [7]. Under hydrothermal conditions, surface groups like carboxyles (–COOH) and hydroxyles (–OH) attach on to the surfaces of CNTs', which consequently functionalize them which results in good dispersion and the formation of stable suspensions. Hydrothermal synthesis was employed because of its ease of controlling the particle size and the morphology of the synthesized powders by adjusting the synthesis conditions, the possibility of low temperature synthesis and also its cost effectiveness [8].

Electrophoretic deposition (EPD) is achieved via the motion of charged particles dispersed in a liquid towards an electrode under an applied electric field (electrophoresis); deposit formation occurs by particle coagulation [9]. EPD can be applied to any solid that is available in the form of fine powder but, for successful results, suspension stability is a key requirement [10]. For the stability of suspensions according to the DLVO theory, the Coulombic repulsive forces must counteract the van der Waals attractive forces between the particles [11]. Thus it is necessary to alter the electrostatic double layer forces on the particle surfaces [9]. The methods for the stabilization of suspensions are the attachment of ions and the absorption of polymeric molecules onto particle surfaces (electrostatic and steric stabilization, respectively) [12]. Solid-loading, conductivity, particle size and morphology, dielectric constant and the zeta potential of the liquid medium must be taken into account to optimize the electrophoretic mobility and stability of the suspension. Usually aqueous suspensions are used for EPD as the high zeta potential of water increases the dissociating power and it provides high surface charge so higher deposition rates can be achieved [12]. But voltages higher than 4 V have the disadvantage of gas evolution on the electrodes due to the electrolysis of water. This obstacle can be prevented by using a membrane in front of the deposition electrode but it is not feasible to use membranes for complex shaped products and the second method is the use of palladium electrodes for cathodic EPD because of the hydrogen storage ability of palladium [13]. Non-aqueous solvents are superior in this respect to aqueous solvents because gas evolution can be avoided.

In this study, under hydrothermal conditions boehmite and MWCNT-reinforced boehmite powder mixtures were synthesized. Powders were seeded with 0.1% alpha alumina powders in order to obtain a densified ceramic matrix during the sintering at relatively low temperatures. Calcined boehmite powders at different temperatures and CNT-reinforced boehmite powders (as synthesized) were used to obtain stable suspensions for EPD. Then, micro-gears, which can be used in many applications, such as micro-electro-mechanical systems (MEMS) were produced by means of electrophoretic deposition.

2. Experimental work

2.1. Hydrothermal synthesis

20 g alumina acetate powders ($2Al(OH)(C_2H_3O_2)_2$) and 0.06354 g MWCNTs (average diameter 20–25 nm and 10–25 μm in length) were mixed and the mixture was vigorously stirred in 380 g distilled water. 17 ml 25% ammonia solution (NH_3) was then added to the mixture to adjust the pH above 9 in order to obtain fine boehmite particles. The reason for the addition of such quantity of MWCNTs in the mixture was the aim of obtaining 1%-reinforced final structure which was going to be in the form of CNT-reinforced alumina (Al_2O_3) after the heat treatment. The resultant mixture was transferred into a teflon lined autoclave approximately filling 80% of the 500 ml total volume and the hydrothermal synthesis was performed at 200 °C for 2 h in a high pressure autoclave (see Fig. 1). The pressure of the autoclave was approximately 1 MPa. The autoclave was then cooled to room temperature naturally. The resultant solution was vacuum filtered for four times to remove water soluble impurities. Then, the filtered solution was dried in an autoclave at 110 °C. Finally CNT-reinforced boehmite and boehmite ceramic powders were obtained. To obtain γ-alumina powders, synthesized boehmite was calcined at 550 °C for 1 h in an electric furnace and to obtain alpha alumina, the boehmite powders were seeded by addition of 0.1 wt.% alpha alumina followed by thermal treatment, taking place in an electric furnace at 1200 °C for 1 h. The aim of seeding was to lower the transformation temperate of α-alumina.

2.2. Suspension preparation, EPD and mold design

The suspensions containing MWCNT/boehmite, gamma alumina and alpha alumina powders were prepared for EPD experiments using butanol as dispersion media (butanol allows crack-free deposit formation during the drying process and also confers the high stability especially for boehmite and CNT/boehmite suspensions). 1.5 g CNT/boehmite powders were mixed with 50 ml butanol and polyethyleneimine (PEI) was used as a dispersant. Suspensions were ball-milled with zirconia balls for 3 h to break the agglomerates and then ultrasonicated for 15 min. Finally the suspension was left to rest for 1 day. The pH of the suspensions was not manipulated due to the sufficient pH distance from the IEP of the CNT/boehmite suspension. The EPD experiments were conducted using a cell which is composed of two electrodes and a DC power supply, similar to that shown in the schematic presentation of EPD cell in Fig. 2. The distance between the electrodes was 20 mm and a DC voltage was applied in the range of 30–100 V. The deposition time varied from 1 to 10 min. Before the deposition, the deposition electrodes were shielded with non-conductive molds. Molds were placed in front of the deposition electrode (see Fig. 3). The gaps in the molds allowed deposition to take place towards the gap. During the process, charged particles moved through the gaps and deposited on the electrode and took the shape of the mold cavity (see Fig. 3). The obtained deposits were dried horizontally at room temperature. Because of the higher tendency of boehmite derived gamma and alpha alumina powders to sedimentation, high solid-loadings could not be used with these powders. Solid-loading was kept between 1 and 5 wt.% for all experiments and the course of the process parameters was identical to that used for the boehmite deposition explained above except the 15 min of rest for

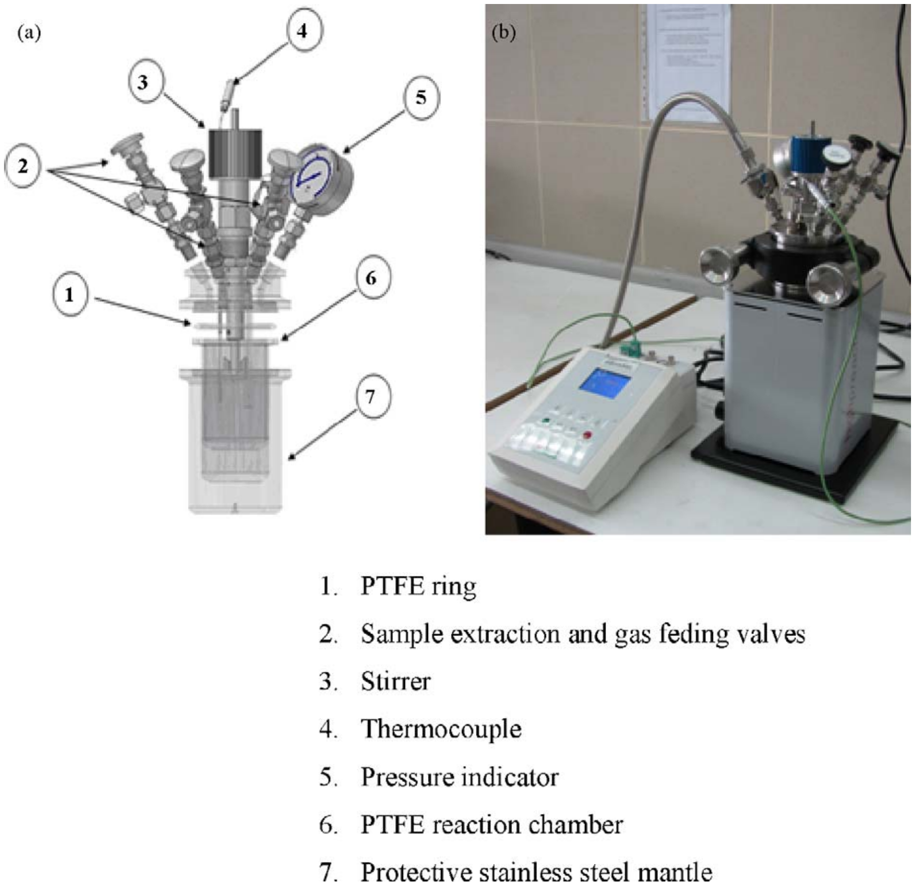

Fig. 1. (a) Shematic presentation and (b) real image of the high pressure autoclave used for MWCNT-reinforced boehmite and boehmite synthesis. (1) PTFE ring; (2) sample extraction and gas feding valves; (3) stirrer; (4) thermocouple; (5) pressure indicator; (6) PTFE reaction chamber; (7) protective stainless steel mantle.

sedimentation of alumina powders before the EPD step. The initial pH of the suspensions was adjusted to be 3.

The non-conductive molds that were going to be used for shielding the deposition electrode were designed in solidworks (Fig. 3a). The design files were then used by a rapid prototyping machine and different shape polymer molds were obtained (Fig. 3b). Because of the interaction tendency of the molds with the alcohols, the molds can not be used more than once or twice so some experiments were carried out with hand-made polymer molds (Fig. 3c) and gear shape metal substrates covered by polymers to prevent unwanted parts to be deposited (Fig. 3d).

2.3. Characterization

The boehmite powders are subjected to DTA (differential thermal analysis) and TG (thermogravimetric analysis) in order to determine the phase transformation temperatures and the corresponding weight loss. For the phase identification of boehmite and calcined boehmite processed at different temperatures, XRD (Cu Kα radiation) was used. To determine the functional groups and also the phase identification, FT-IR spectroscopy was used. FEG-SEM was used to determine the morphology and the grain size of the deposits of CNT/boehmite and also the toughening effect of the CNTs' in the boehmite

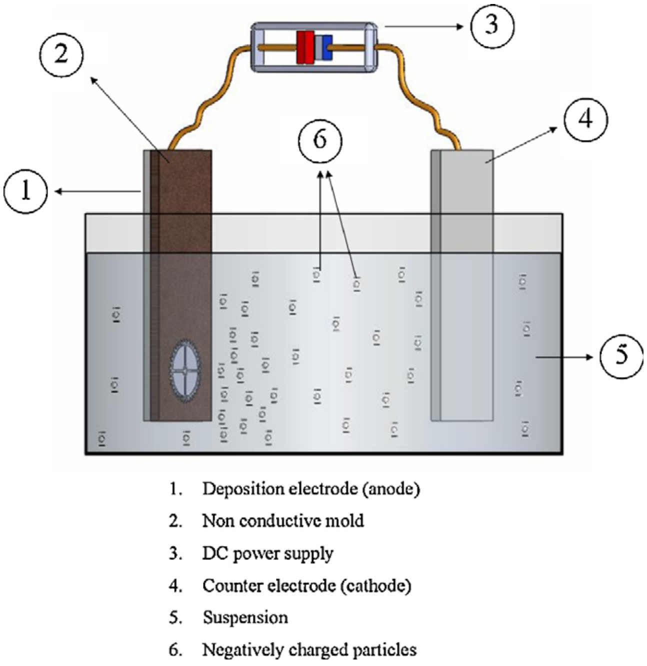

Fig. 2. Shematic presentation of EPD cell used to fabricate micro-gears. (1) Deposition electrode (anode); (2) non-conductive mold; (3) DC power supply; (4) counter electrode (cathode); (5) suspension; (6) negatively charged particles.

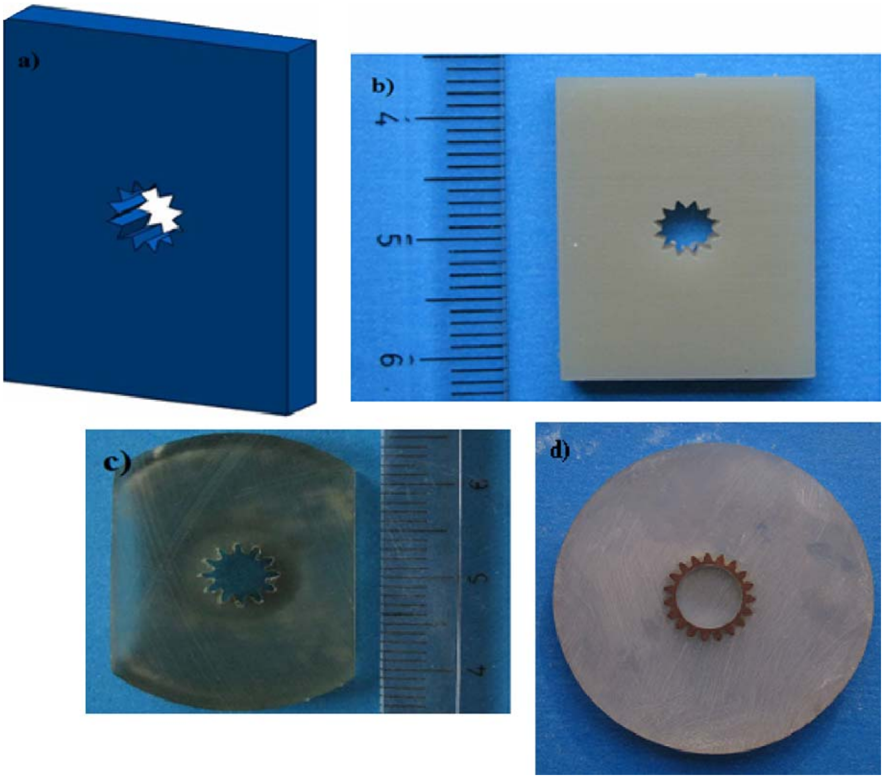

Fig. 3. Solidwork designs of the mold (a), the mold prepared by rapid prototyping machine (b), one example of polymer-based molds (c), and gear shape metal substrate (d).

matrix. The particle sizes of boehmite and CNT/boehmite were analysed by laser particle size analyser. The surface area measurements were obtained by means of BET method. The shape and size of boehmite as well as MWCNT–boehmite interactions were observed using TEM.

3. Results and discussions

The thermogravimetric and differential thermal analysis results of hydrothermally synthesized boehmite are shown in Fig. 4. The first mass losses of approximately 8% up to 100 °C and after 200 °C is assigned to desorbsion of physically absorbed water. The second mass loss between 400 and 500 °C can be attributed to the conversion of boehmite into gamma alumina as well as the removal of lattice water. The further peaks (640 and 1000 °C) can be assigned to the transformation of metastable alumina phases. Overall, Fig. 4 shows the presence of characteristic boehmite powder.

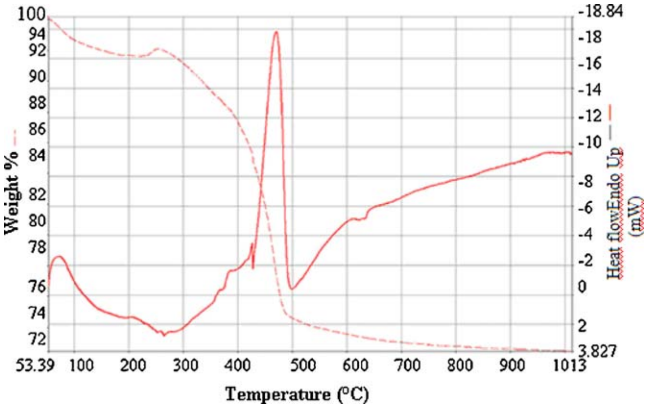

Fig. 4. DTA and TG curves of hydrothermally synthesized boehmite.

Fig. 5 shows the X-ray diffraction patterns of samples after calcination at 950 °C for 1 h (Fig. 5a), at 550 °C for 1 h (Fig. 5b) and after HS (Fig. 5c). The patterns of boehmite (JCPDS Card no. 21–1307), gamma alumina (JCPDS Card no. 29–0063) and theta alumina (JCPDS Card no. 35–0121) match the Standard patterns. No residual peak is observed.

To detect the functionalization of the carbon nanotubes as well as the phase identification, FT-IR analysis was performed on MWCNT/boehmite powder mixture as shown in Fig. 6. All the absorbsion bands at 3279, 3091, 2096, 1152, 815, 730 and 667 cm^{-1} are indicating the formation of boehmite [14,15]. The two strong absorption bands at 3279 cm^{-1} and 3091 cm^{-1} are assigned to the stretching bands of adsorbed water. The wavenumber at 1557 cm^{-1} is the bending mode of absorbed water. The peak at 1424 can be due to the absorption of $AlO(OH)^{\bullet}nH_2O$ network structure [16]. The peaks at 667, 730 and 815 cm^{-1} are due to the vibration mode of AlO_6 [15,17]. The peaks at 2096 and 1152 can be ascribed to the Al–O stretching and bending vibrations. The signal at 1738 cm^{-1} is characteristic of the carbonyl (C$\equiv$O) group joint with the OH groups in the system indicating the carboxylic acid group which has an essential effect on the funtionalization of CNTs.

The particle size analysis of the boehmite powders was measured using a laser particle size analyser. The particle size

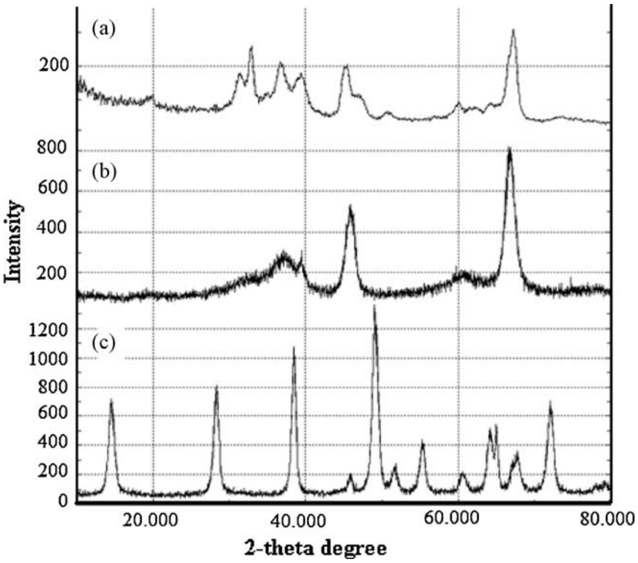

Fig. 5. XRD patterns of (a) theta alumina (JCPDS Card no. 35–0121, calcined boehmite at 950 °C for 1 h), (b) gamma alumina, (JCPDS Card no. 29–0063, calcined boehmite at 550 °C for 1 h) and (c) as synthesize boehmite (JCPDS Card no. 21–1307).

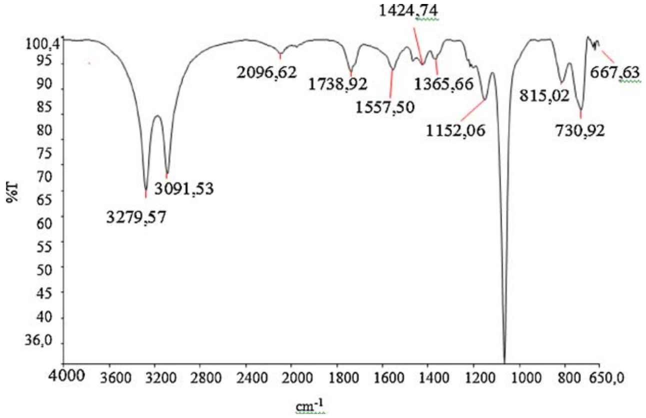

Fig. 6. FT-IR spectrum of synthesized MWCNT/boehmite powder.

measurement provides a reliable information about the degree of the agglomeration. The average particle size of boehmite is 9.71 μm (Fig. 7a) and CNT-reinforced boehmite is 14.30 μm (Fig. 7b). The surface area of boehmite and CNT/boehmite samples was measured by means of the BET method. The surface area of boehmite was 114.33 m^2/g and CNT/boehmite's was 101.85 m^2/g. The slight decrease in the surface area of the CNT/boehmite compared to boehmite is due to the presence of the CNTs. CNTs are long molecules so the small boehmite particles attach on to the surface of the molecules due to van der Waals attractive forces; consequently, the CNT–boehmite particle combinations' size is bigger. It can be concluded from Fig. 7 that there is a possibility of formation of big boehmite and MWCNT/boehmite agglomerates during particle size measurements. Therefore, in order to see the real particle size of hydrothermally synthesized boehmite and MWCNT/boehmite mixture, FEG-SEM (Field Emission Gun SEM) and TEM observation were conducted.

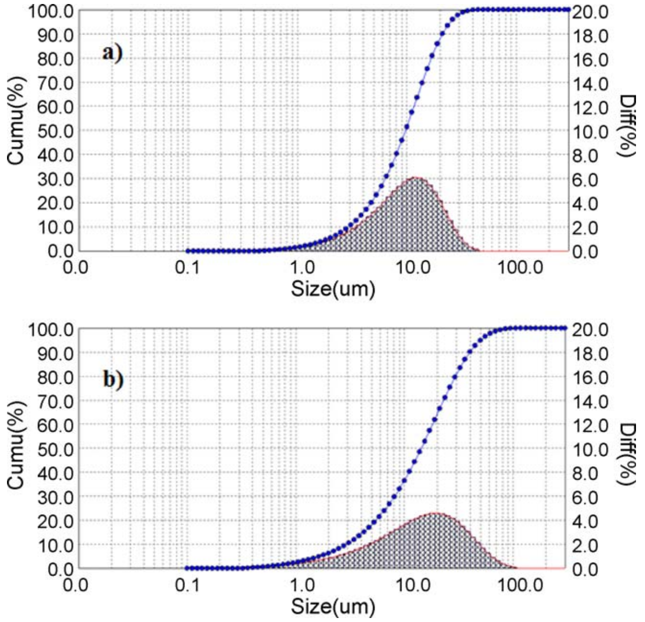

Fig. 7. The particle size distribution of hydrothermally synthesized boehmite in agglomerated form (a) and the MWCNT/boehmite mixture (b).

Different suspensions of methanol, ethanol, methyl ethyl ketone (MEK), isopropyl alcohol(Ipa), butanol and water were tested in order to determine the most stable suspension for use in EPD experiments. To obtain stable MWCNT/boehmite suspension with non-aqueous media isopropyl alcohol (ipa) and butanol were superior to other solvents. Thus ipa and butanol suspensions were selected to obtain better stability as the stability is an essential aspect for the formation of uniform deposits. During the drying process to obtain crack-free deposits, butanol was found to be a better choice for ipa.

Solid surface and the liquid determine the charge of the surface [18]. The charging mechanism is the adsorbtion of protons or hydroxyls on the surface of boehmite and alumina [11,18]:

$$\mathrm{Al{-}OH} + \mathrm{H}^{+} \Leftrightarrow \mathrm{Al{-}OH_2}^{+}$$

$$\mathrm{Al{-}OH} + \mathrm{OH}^{-} \Leftrightarrow \mathrm{Al{-}O}^{-} + \mathrm{H_2O}$$

Alcohols behave as proton donors, leaving the protons on the particle surface [11]. In butanol, the boehmite and alumina particles charge positively, having an initial pH of 5.5 for both ceramic powders. To obtain the stability of boehmite suspensions, polyethyleneimine (PEI) was used as a dispersant. PEI addition changes the pH and IEP of the suspension to higher levels. Thus for EPD experiments the pH of the suspensions has not been changed by the addition of acids or bases because of the sufficient distance from the IEP of the suspensions. The solid-loading was kept between 1% and 5% because for solid-loadings above 5%, the viscosity of the suspensions increases to undesired levels.

Monolithic alpha and gamma alumina suspensions were prepared with butanol. To adjust the pH of the alpha alumina suspension, HCl was used and the pH was adjusted to be 3 in EPD experiments for alpha alumina powders. PEI addition

Fig. 8. Photo images of MWCNT/boehmite mixture (a) and alpha alumina stable suspension with a 3 wt.% solid-loading (b).

substantially increases the stability of the suspensions but the thickness of the deposits decreases with the addition of PEI. This may be due to the increase in the electrical resistivity of the deposits which involve PEI.

In case of stability, stable suspensions of boehmite and accordingly CNT/boehmite with relatively high solid-loading without addition of dispersants can be obtained. Fig. 8 shows the prepared stable suspensions for EPD experiments containing MWCNT/boehmite particles (Fig. 8a) and alumina suspension (Fig. 8b) with a solid-loading of 3 wt.% in butanol.

In order to determine the particle size and morphology of the boehmite particles synthesized as well as CNT–boehmite interactions under hydrothermal conditions, detailed TEM observations are conducted as shown in Fig. 9.

Fig. 9a clearly shows that the synthesized boehmite particles under the hydrothermal conditions used in the present work are in cube shape with particle sizes of 30–40 nm. Fig. 9b shows that during hydrothermal processing, CNTs and boehmite particles are homogeneously mixed in the absence of big agglomerates. It is also evident from Fig. 9b that CNTs are covered by fine boehmite particles due to functionalization of CNTs during HS. The suspension microstructure shown in Fig. 9b is considered to be beneficial in obtaining higher densities during sintering as well as more homogeneous structure of CNT-reinforced alumina ceramics.

Fig. 10 shows the un-sintered micro-gears of CNT-reinforced boehmite (a and c) and alumina (powders were first calcined 1200 °C for 2 h to convert boehmite to alfa alumina and then EPD was performed) (b and d) obtained by EPD using an applied voltage of 100 V and a deposition time of 2 min (a and c) and 30 V for 1 min (b and d), respectively. Higher applied voltages are needed to form the gears due to higher particle size of CNT–boehmite clusters. Now, studies are underway to optimise the sintering conditions and determine the mechanical behaviour of the components manufactured.

As shown in Fig. 10, the micro-gears of CNT-reinforced boehmite and monolithic alumina are smaller than 1 cm and current experiments are dealing with manufacturing of smaller gears as small as 100 μm. No crack formation was observed on the surface of the gears after drying. The detailed microstructure of the gears shown in Fig. 10 is also analysed by FEG-SEM as shown in Fig. 11 in order to have an idea of possible toughening effects of CNTs added.

As shown in Fig. 11, the EPD-formed CNT/boehmite deposits are quite dense and free of large voids and pores. Two different toughening mechanisms, pull-out and bridging of CNTs can be seen from the micrographs shown in Fig. 11. Some CNTs pull-out from the matrix during the cracks' growth indicated by circles in Fig. 11a and the second is the bridging formed by bridging of the cracks between the walls of the crack indicated by arrows (Fig. 11b–d). The effectiveness of the toughening mechanisms proposed will be clearer after mechanical tests which are underway at the moment.

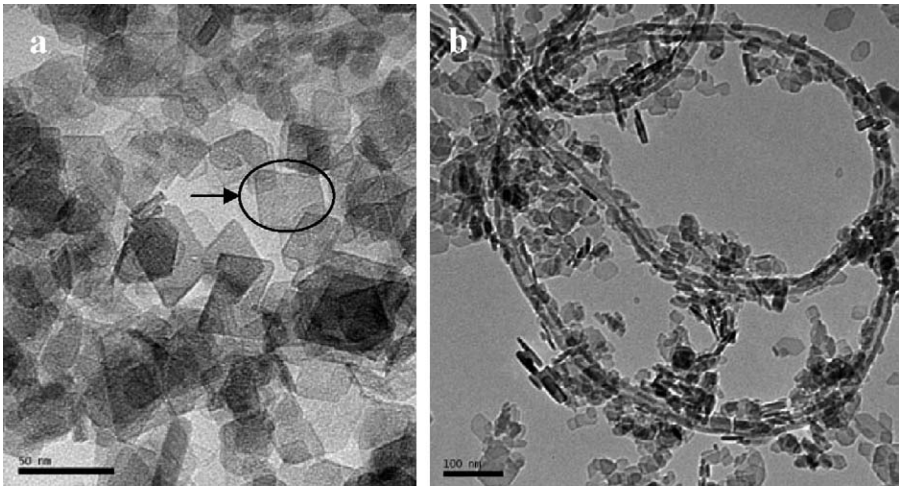

Fig. 9. TEM images of hydrothermally synthesized boehmite particles in cube shape with particle sizes of 30–40 nm (a) and CNT–boehmite interactions showing the coverage of CNTs by fine boehmite particles and the absence of large agglomerates (b).

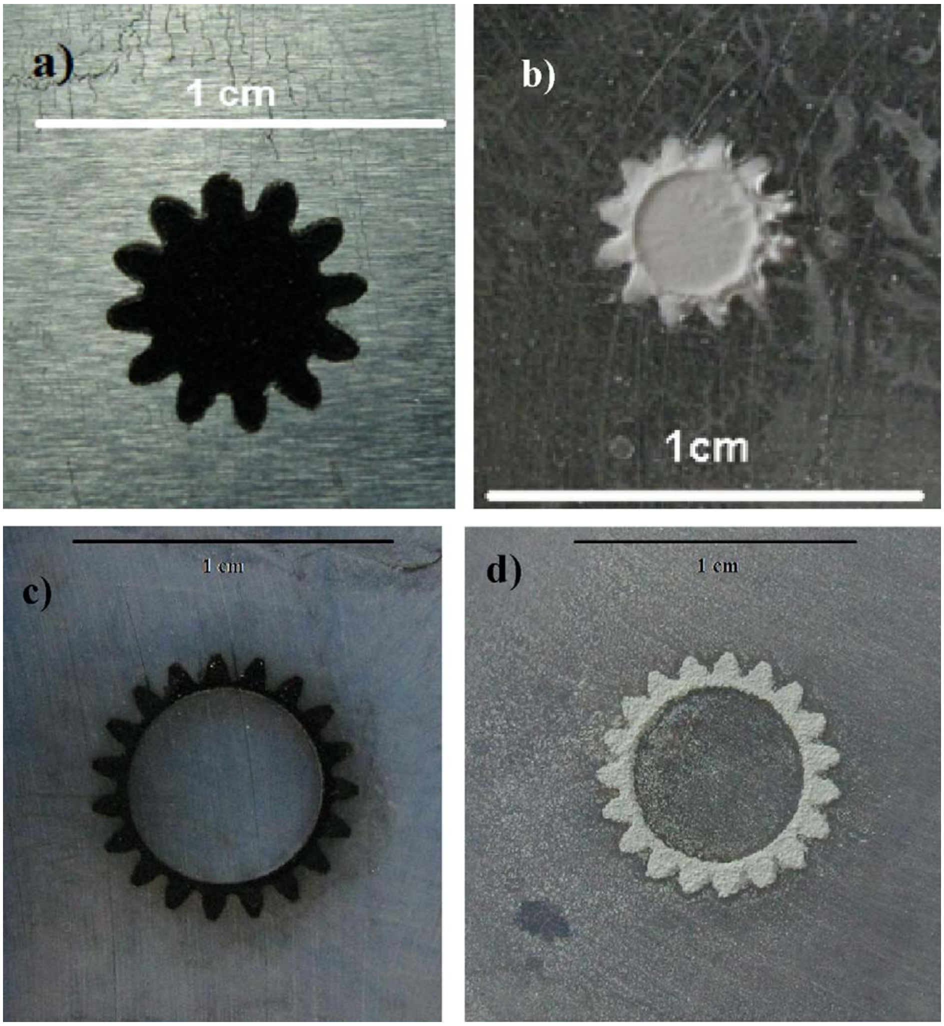

Fig. 10. Electrophoretically formed 1 wt.% CNT-reinforced boehmite (a,c) and alpha alumina (b,d) micro-gears before sintering.

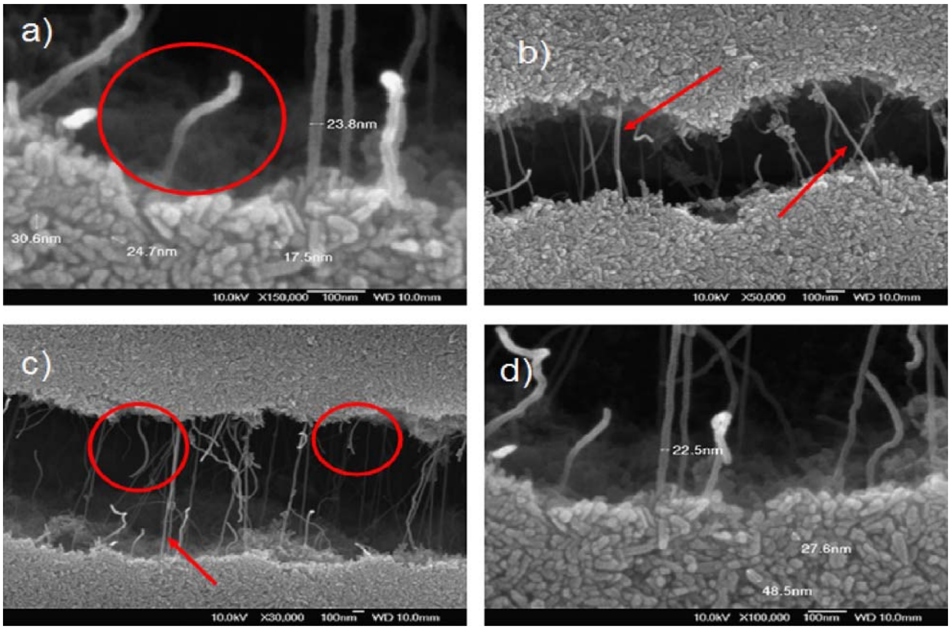

Fig. 11. SEM images of CNT-reinforced boehmite micro-gear shape deposits with different magnifications. The circles indicate the pull-out and the arrows indicate the bridging of CNTs (the cracks were created by applying a low level of tensile force).

4. Conclusion

A homogeneous mixture of CNT–boehmite particles is achieved using hydrothermal processing which also results in surface functionalization of CNTs. The TEM observations reveal that under hydrothermal conditions MWCNTs are covered by fine boehmite particles resulting in the formation of stable suspensions due to good dispersion. Complex shape micro-gears are successfully fabricated for the first time using electrophoretic deposition. It is also shown that the functionalization of carbon nanotubes could be provided by attachment of the functional groups under the hydrothermal conditions during the powder processing without implementing conventional functionalization steps which could harm the mechanical performance of CNTs.

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