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Journal of the European Ceramic Society 30 (2010) 2525–2531

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Boehmite derived surface functionalized carbon nanotube-reinforced macroporous alumina ceramics

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Received 11 February 2010; received in revised form 23 March 2010; accepted 12 April 2010
Available online 23 May 2010

Abstract

Carbon nanotube (CNT)-reinforced macroporous alumina ceramics with tailored porosity were fabricated using hydrothermally synthesized (200 °C for 2 h) boehmite–CNT starting composite powders. Multi-wall CNTs were first mixed with a mixture of chemicals suitable to synthesize stoichiometric boehmite powders and then put in an autoclave. During hydrothermal synthesis, the formation of fine particles of boehmite was accompanied by the functionalization of CNTs. Subsequently, CNT–boehmite powders were used to produce bulk ceramics and sintering took place in a vacuum furnace at 1450 °C for 3 h for the formation of CNT-reinforced alumina ceramics. The pore network in various dimensions occurred as a consequence of the reconstructive transformation and dehydration of boehmite during the transformation to alumina. FEG-SEM and TEM analysis were used to determine the CNT distribution in the matrix, the morphology and size of particles, as well as the visual properties of the pores. The final macroporous alumina ceramics can be considered to be ideal for the separation and filtration of contaminants in liquid or air environment.

Keywords: Al_2O_3; Carbon nanotube; Nanocomposites; Porous ceramics

1. Introduction

Industrialization and increasing population make pollution free natural resources difficult to access; therefore the removal of chemicals and biological contaminants in water and air is getting crucial. The contaminants, such as bacteria, viruses, pollens and heavy metals are commonly seen in air or water.[1,2] For the treatment of water and air, filtration is part of the applied methods that involve the adsorption of the contaminants by van der Waals, electrostatic and hydrophobic attractions and the presence of a barrier to their movement due to the small pores.[3] The most important contaminants in natural sources are viruses and bacteria which have diameters of about 10–500 nm and 0.5–5 μm, respectively. Thus fine pore sizes for filters are needed for the effective removal of contaminants.[4]

Polymer, metal and ceramic based filters are being used for removing chemical and biological contaminants.[5] The main advantages of having porous ceramics are their durability, resistance to chemical attacks, high pressure resistance and thermal stability. In addition, low cost and mass production of porous ceramic filters can be achieved and long term usage can be maintained.

There are several ways to fabricate macroporous ceramics such as the replica technique,[6] the sacrificial template method[6] and direct foaming.[6]

As a reinforcement material for porous ceramics, CNT incorporation might be useful to obtain additional adsorption effect. A CNT can be considered to be a rolled up sheet of graphite, of the order of nanometers in diameter and several microns in length so it can be regarded as a nanowire having large surface area. CNTs consist of sp^2 bonded carbon atoms; unlike graphite, the curvature of the CNTs causes the π orbitals to slightly delocalize outside the tubes.[7] This makes the nanotubes chemically and biologically more active than graphite.[7] An individual CNT can have two adsorption regions which are inner spaces and sidewalls.[2] CNTs reactivity and large surface areas make them a feasible choice for reinforcement of porous ceramics used for filtration to enhance the adsorption capabilities.

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doi:10.1016/j.jeurceramsoc.2010.04.020

On the other hand alumina is one of the most important oxides as it can be used as a filter material and can be obtained by thermal treatment of boehmite. During the thermal treatment, boehmite transforms into different transitional alumina phases (γ, δ, θ) having different arrangement of anions and cations[8]:

$$\gamma\text{-AlOOH} \xrightarrow{400\,^{\circ}\text{C}} \gamma\text{-Al}_2\text{O}_3 \xrightarrow{800\,^{\circ}\text{C}} \delta\text{-Al}_2\text{O}_3 \xrightarrow{1000\,^{\circ}\text{C}} \theta\text{-Al}_2\text{O}_3 \xrightarrow{1200\,^{\circ}\text{C}} \alpha\text{-Al}_2\text{O}_3 \quad (1)$$

In boehmite, the oxygen sublattice has cubic packing. γ, δ and θ aluminas have face centered cubic arrangements of oxygen anions with the aluminum cations arranged in different octahedral and tetrahedral positions.[8] The oxygen anion arrangement in alpha alumina is hexagonal close packed and 2/3 of the octahedral sites contain cations.[9] During the thermal treatment, atoms rearrange to form transition aluminas and finally alpha alumina a process accompanied by the large amount of dehydration. The reconstructive transformations and dehydration lead to pore formation in boehmite derived aluminas. Morphology, particle size of boehmite and heat treatment conditions substantially effect the porosity of the final phase.

Techniques of synthesizing boehmite include hydrothermal (HS),[10] sol–gel[11] and hydrolysis of aluminum.[12] Among these techniques, HS is the most suitable technique for production of pure and fine crystals with narrow size distribution; control over shape can be maintained easily.[13] HS refers to any chemical reaction taking place in the presence of a solvent (aqueous or non-aqueous) above room temperature and with a pressure greater than 1 atm.[13]

The process of carbon nanotube reinforcement in composites involves two critical problems which must be overcome to achieve enhanced properties. CNTs tend to agglomerate due to the van der Waals attractions between the sidewalls; the matrix–CNT interface connections must be provided for better properties.[14] These problems cannot be achieved by conventional powder mixing techniques and sintering processes, such as pressureless sintering, hot pressing and hot isostatic pressing (HIP).[15] The process called functionalization is required which is the attachment of functional groups (carboxyl or other oxygen-containing groups) to the sidewalls of the nanotubes to change the interaction characteristics of the nanotubes and to make them hydrophilic so that they can easily be dispersed in liquid environment due to elimination of non-wetting properties of CNT surfaces.[14] CNTs are hydrophobic in unfunctionalized state but hydrophilic CNTs are capable of supplying enhanced surface interactions with biological contaminants.[2] Concentrated nitric acid and sulphuric acid solutions are commonly used for the functionalization of CNTs but this method introduces high amount of defects on CNTs which causes damage and loss of structure.[14]

In the present work, the functionalization of CNTs without causing any structural damage is achieved during hydrothermal synthesis of boehmite. It is also shown that hydrothermal synthesis is a rapid way of synthesizing nano-boehmite powders mixed with CNTs; converted to a sintered body using pressureless sintering at 1450 °C for 3 h. The final macroporous alumina ceramics are considered to be ideal for filtration purposes.

2. Experimental work

To prepare 1 wt.% CNT-reinforced porous alumina matrix ceramics, basic aluminum acetate was used as a starting material for the boehmite production. 20 g of aluminum acetate and 0.063 g multi-wall CNTs (20 nm in diameter and 10–25 μm in length, Thomas Swan Co. Ltd, UK) were added to 380 ml deionized water; subsequently 15 ml ammonia solution added dropwise. 0.1 wt.% alpha alumina was added to the mixture of the starting materials before the hydrothermal synthesis. The modifiers, such as alpha alumina act as a seed and lower the transformation temperature of the final α-alumina and prevent the formation of vermicular structure due to phase transformation of boehmite. The pH of the suspension was adjusted by addition of ammonia and the pH value was kept above 9. The mixture was then placed in a Teflon lined autoclave which had a reaction chamber having 500 ml of volume (Berrgof, Germany). Approximately 80% volume of the chamber was filled and hydrothermal synthesis took place at 200 °C for 2 h (the pressure of the reaction was 1 MPa). Subsequently, the processed sol was vacuum filtered 4 times to remove the impurities and dried in an oven at 110 °C for 4 h. The obtained powders were used to make pellets (10 mm in diameter and 3 mm in thickness) by die pressing using an applied pressure of 124.8 MPa. A tube furnace was used for the calcinations of CNT–boehmite and boehmite pellets. An inert atmosphere was supplied by N_2 gas due to the high tendency of the CNTs to oxidation at elevated temperatures and the reaction took place at 1450 °C for 3 h.

The morphology, size of particles, the interactions between CNTs and boehmite particles and also the size and morphology of pores were determined by means of SEM and TEM analysis. The CNT distribution and effect of the functionalization to the structure of CNTs were also examined. Density analyses were conducted to determine the percentage of the porosity and the amount of the agglomeration of CNTs. FT-IR spectrometry was used for the phase identification and determination of the functional groups.

3. Results and discussions

During the hydrothermal synthesis aluminum acetate decomposed to form boehmite and acetic acid as shown in the fallowing reaction:

$$\text{Al(OH)(C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{O} \rightarrow (\gamma\text{-AlOOH}) + 2\text{CH}_3\text{COOH} \quad (2)$$

The existence of acetic acid and its dissociation under hydrothermal synthesis enable the creation of carboxyl groups (COOH) which have a significant role on modification of surfaces of CNTs. The other oxygen-containing groups, such as hydroxyls effect the modification.

Boehmite has an orthorombic layered structure, consisting of layered deformed octahedras with aluminum ions near the cen-

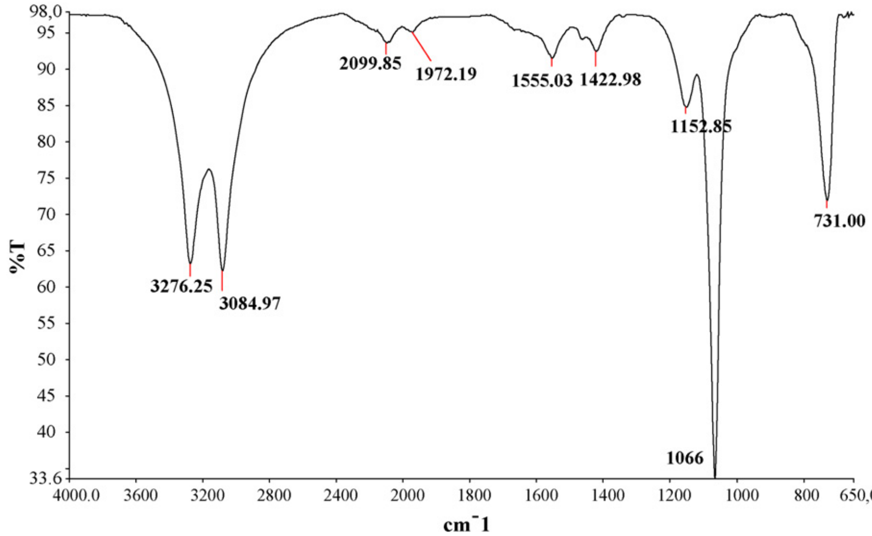

Fig. 1. The FT-IR spectrum of CNT/boehmite powder mixture.

ter. The layers are held together by hydrogen bonds between the hydroxyl ions. Boehmite has a tendency to grow in a preferred direction leading to formation of high aspect ratio crystals.[16] Hydrothermal synthesis was performed under basic conditions (>pH 9) to obtain crystals having fine sizes and low aspect ratio.

The specific volume of boehmite is 0.332 and for alumina this value is 0.251. Because of the difference in the specific volumes, boehmite derived alumina involves high amount of porosity when processed at low sintering temperatures[17] and to obtain high density products the sintering temperature must exceed 1600 °C for several hours. Alpha alumina was added to the structure prior to sintering process to regulate the porosity. Thus the experiments were carried out at 1450 °C for 3 h which is a relatively low temperature to obtain finer grain size and control the overall porosity.

The FT-IR spectrum of hydrothermally synthesized CNT/boehmite is given in Fig. 1. The absorption bands at 731, 1066, 1152, 1337, 1972, 2099, 3084, 3276 are agreed val-

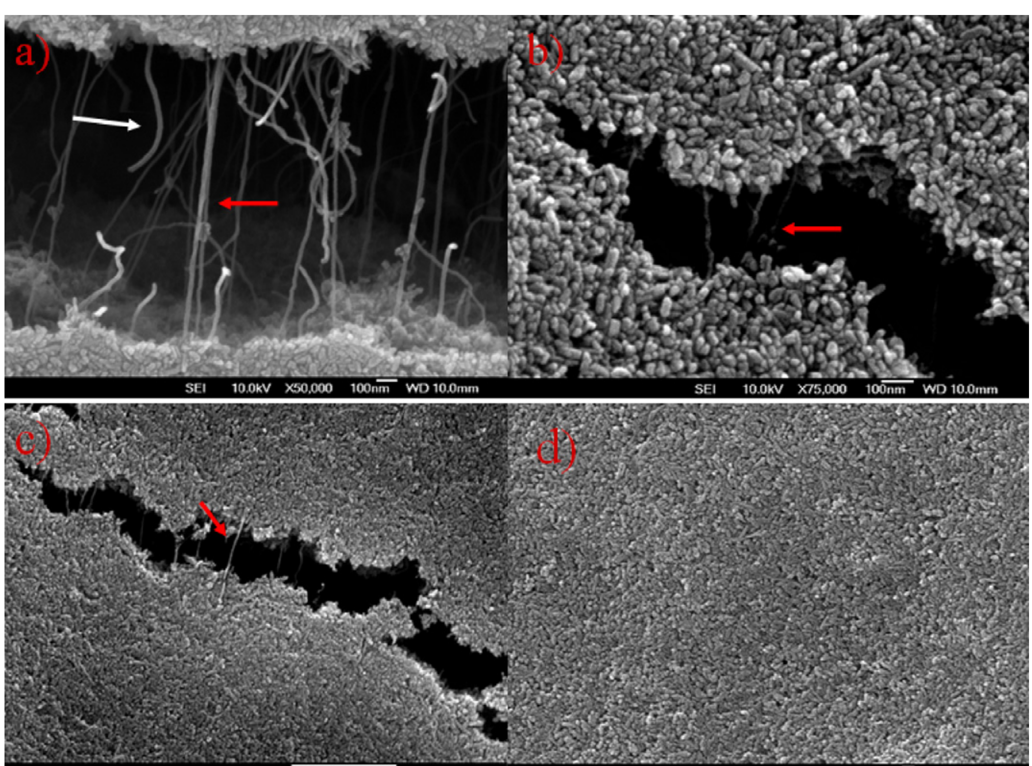

Fig. 2. FEG-SEM micrographs of un-sintered CNT/boehmite powder mixture showing the presence of: (a) cracking and bridging, (b) particle morphology of nano-boehmite powders with particle sizes ranging from 20 nm to 40 nm, (c) bridgings of CNTs, and (d) the densely packed boehmite crystals having regular shapes.

ues in literature for boehmite.[10] The other peaks at 1555.03, 1422.98 can be assigned to the deprotonated carboxyl groups (COO–) which have a crucial role on the functionalization of nanotubes.[18]

FEG-SEM micrographs of the CNT/reinforced boehmite are shown in Fig. 2. In Fig. 2a–c the location of existing CNTs along a microcrack is revealed. The arrow in Fig. 1a indicates the pull out of CNTs and the arrows in Fig. 2a–c are indicating the bridging of CNTs between the walls of the crack. There was no evidence for the agglomeration of CNTs acccording to SEM observations. The boehmite particles showing elliptical geometry, indicating low aspect ratio crystals, having regular shapes (Fig. 2a–d), and consequently the packing of the boehmite crystals is high (Fig. 2d).

The detail microstructural examination of synthesized boehmite/CNT powder mixture and transitional alumina was conducted using TEM technique to evaluate the fine details including particle size and shape. The TEM images of as synthesized CNT/boehmite powder mixture after hydrothermal processing are shown in Fig. 3a and b indicating that the boehmite particles synthesized have a particle shape of near hexagonal and particle size of 20–40 nm. Fig. 3a and b also shows that the surface functionalized CNTs are covered by boehmite particles due to presence of electrostatic attractions. The TEM micrograph of gamma alumina particles after the thermal treatment of boehmite at 550 °C for 1 h is shown in Fig. 3c indicating the presence of bigger particle sizes of about 40–60 nm due to crystal growth during thermal treatment and the change in particle shape from near hexagonal to platelet. The TEM micrograph shown in Fig. 3d indicates alpha alumina particles with increased particle size of about 200 nm obtained after the thermal treatment at 1200 °C for 1 h. It is important to mention that the carbon nanotubes are surrounded by boehmite particles due to the interaction of the opposite charges, this indicates the accomplishment of the functionalization and in addition, there was no presence of agglometation determined by TEM micrographs (see Fig. 3a and b). It is also found from Fig. 3c and d, that gamma alumina particles conserve the shapes of the boehmite particles; in contrast to boehmite, presence of the pores inside the particles can be seen which can be attributed to the large amount of dehydration during the transformation. It should also be noted from Fig. 3d

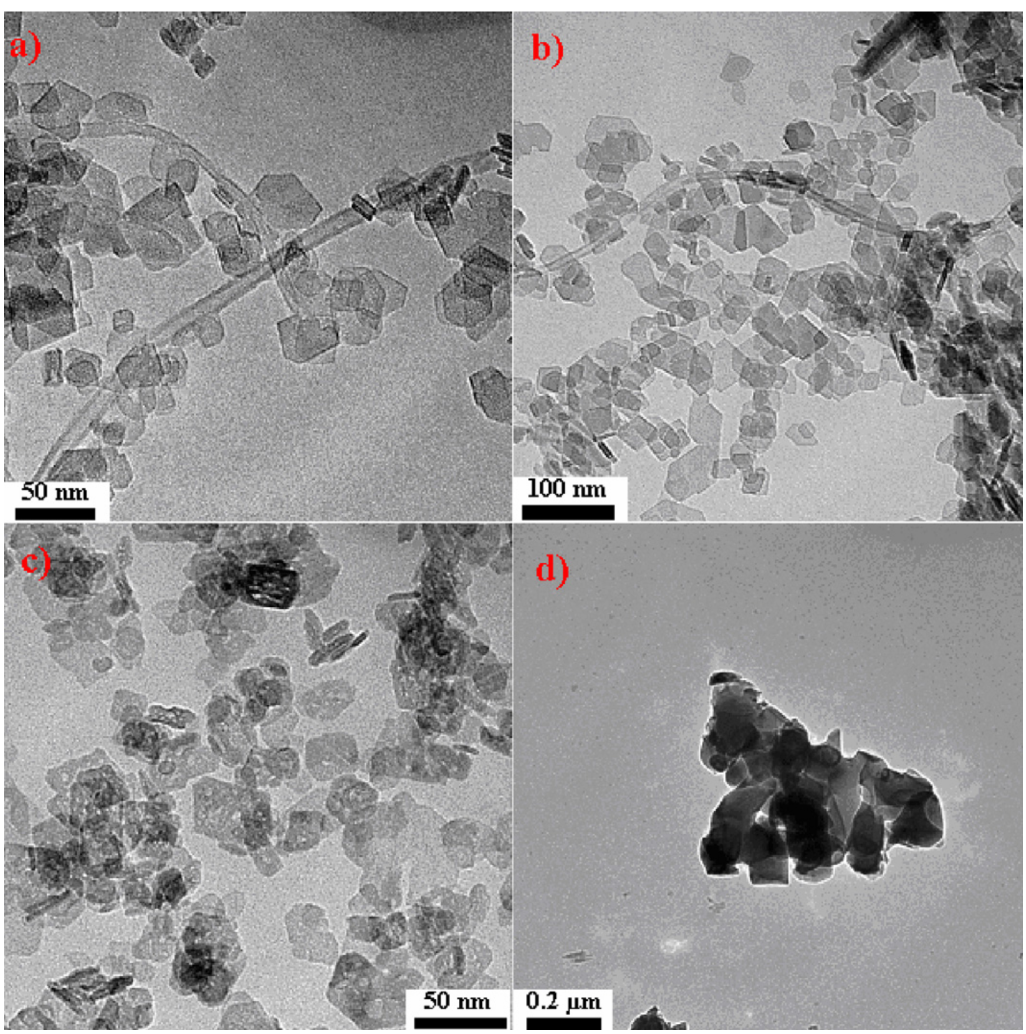

Fig. 3. The TEM images of as synthesized CNT/boehmite composite particles (a and b), gamma alumina synthesized after the thermal treatment at 550 °C for 1 h (c) and alpha alumina obtained after the calcination at 1200 °C for 1 h (d). Note the presence of pores within the gamma alumina powders (c) and alpha alumina (d).

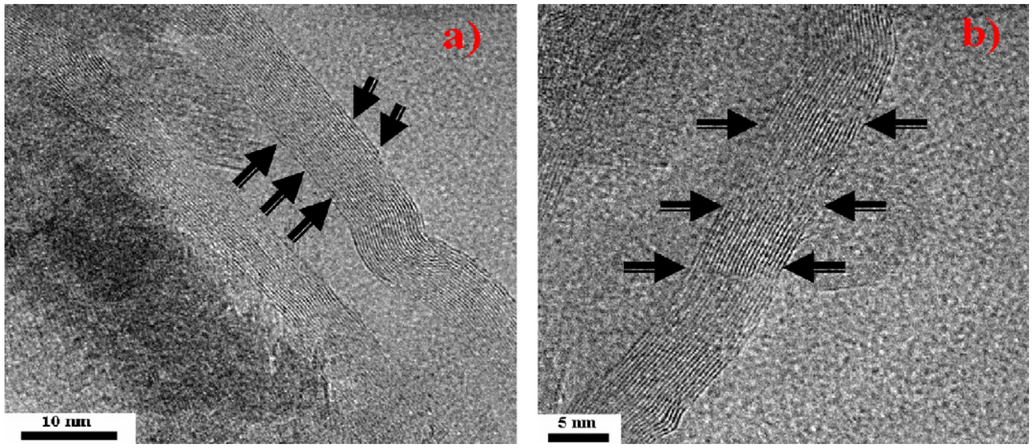

Fig. 4. The TEM micrographs of surface functionalized CNTs during HS: lower magnification (a) and higher magnification (b). Both micrographs show that the sidewalls of nanotubes remaining intact after functionalization.

that alpha alumina particles have bigger size and contains some intra-granular pores.

High resolution TEM of CNTs was studied to state the effect of the functionalization performed under hydrothermal conditions as shown in Fig. 4. The intense investigations by means of TEM analysis revealed that there were no harmful consequences or any damage to CNTs during hydrothermal functionalization. As clearly seen in Fig. 4a and b, the sidewalls of nanotubes remain intact. This is considered to be quite significant to obtain surface-defect free CNTs so that better mechanical, optical and electrical properties can be obtained when the CNTs are added to composite system.

Bulk ceramics were prepared by sintering at 1450 °C for 3 h and the fractured surfaces were analyzed by FEG-SEM as shown in Fig. 5. In Fig. 5a, the general porosity content of the fractured surface can easily be seen. In Fig. 5b the pores showing various dimensions ranging from slightly below 100 nm to approximately 1 μm are determined. In Fig. 5c and d, the presence of CNTs are clearly seen and pull out of carbon nanotubes at fracture surface is evident from the micrograph shown in Fig. 5d. Overall, the results presented in Figs. 4 and 5 show that there is no evidence of loss of structure or damage on the functionalized CNTs during the process introduced in the present work.

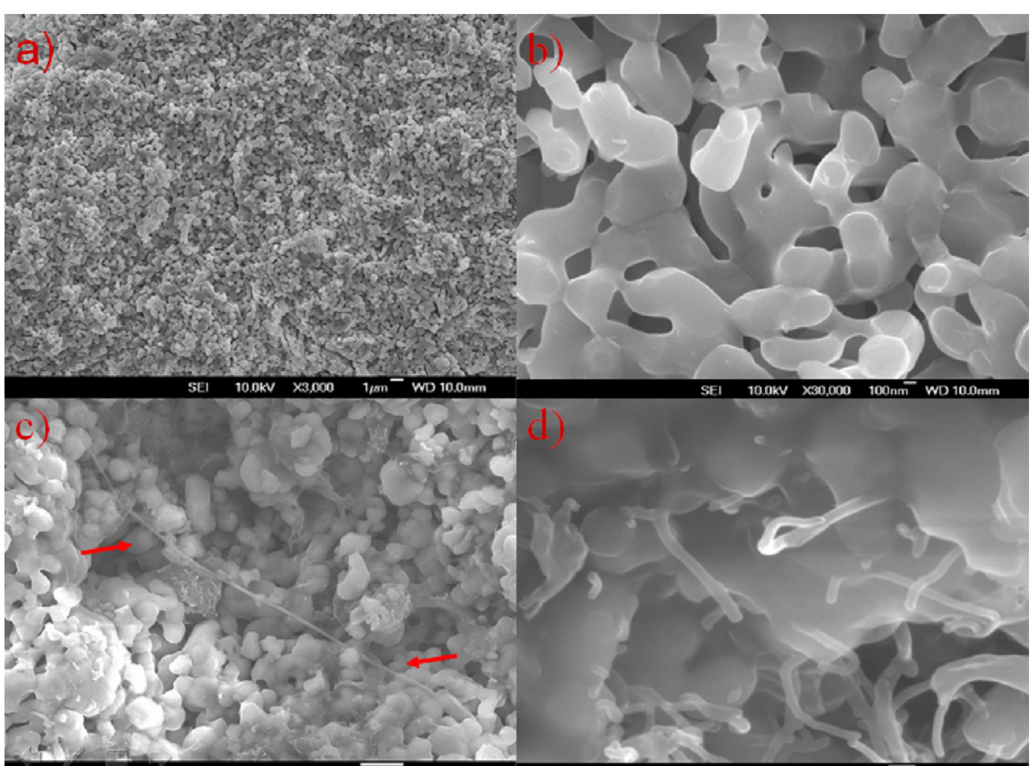

Fig. 5. SEM micrographs of fracture surfaces of the sintered CNT/alumina composites: (a) low magnification micrograph of porous ceramic, (b) the small and large pores in the structure, (c) general fracture surface indicating the porous nature of the alumina matrix and the location of carbon nanotube, and (d) pull out of CNTs.

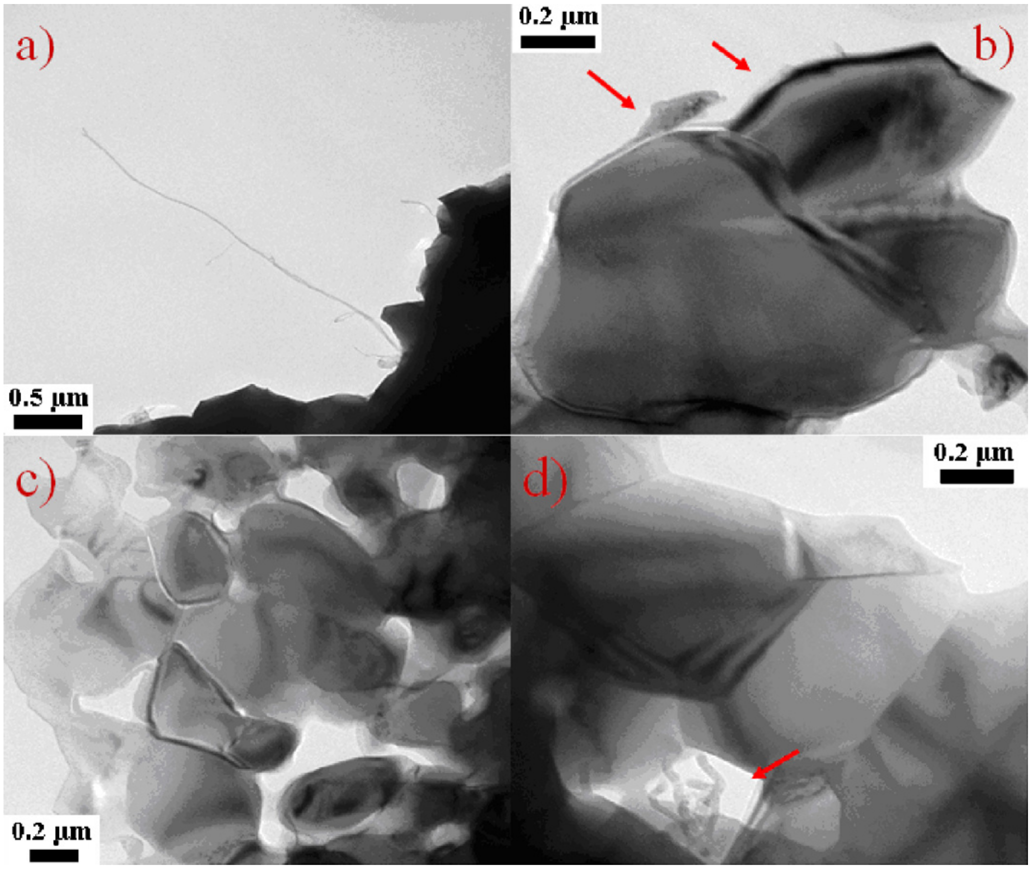

Fig. 6. The TEM images of sintered (1450 °C for 3 h) alumina/CNT ceramics: (a) long and short pull out of CNTs, (b) location of carbon nanotube along the grain boundaries of alumina as indicated by arrows, (c) alumina grains having grain sizes from 200 nm to 500 nm and the pores having various dimensions from 70 nm to 400 nm, and (d) shows the locations of the CNTs within a large pores.

Fig. 6 shows the TEM observations of the sintered CNTs/alumina ceramics. Long and short pull out of CNTs can be seen in Fig. 6a and a carbon nanotube is lying along the grain boundaries as indicated by arrows in Fig. 6b. As indicated in Fig. 6c alumina grains are in the length of between 200 nm and 500 nm and the pore sizes are in the range of 70–400 nm. In Fig. 6d, the location of the CNTs within a large pore is clearly evident. The crossing of CNTs in the pores might be useful for the reduction of the pore size and have a beneficial effect especially for increasing the adsorption capability; the pores supply space for the surfaces of carbon nanotubes to appear which is beneficial for the adsorption to occur; however the filter material can be clogged by carbon nanotubes, this problematic situation can be overcome by addition of relatively small amount of carbon nanotubes to prevent clogging. It is also important to note from the TEM image shown in Fig. 6b that some CNTs are actually located along the alumina grain boundaries which helps to prevent alumina grain growth during sintering. This also explains why the alumina grains are sub-micron size after sintering.

Density analysis was performed by Archimedes method. 3.97 g/cm^3 was used as the theoretical density for alumina. The density of monolithic alumina was measured to be 3.63 g/cm^3 and 3.16 g/cm^3 for the CNT/alumina. The relative densities of alumina and CNT/alumina were 91% and 80%, respectively. The difference between the densities of CNT/alumina and monolithic alumina is due to the presence of the CNT agglomeration which cannot be avoided below a certain level even with using high pressure sintering such as spark plasma sintering (SPS).[13]

Overall, it is shown in the present work that pressureless sintered (1450 °C for 3 h) carbon nanotube-reinforced alumina ceramic composites with tailored microstructure in terms of pore and grain size can be produced using hydrothermally synthesized nano-size boehmite particles mixed with CNTs before HS. First time in the present work it is also shown that surface functionalization of CNT surfaces can be achieved during HS without creating any surface defects. The manufacturing technique presented here offers a cost-effective technology to produce CNT-reinforced ceramics suitable for antimicrobial applications. Now further studies are underway to determine mechanical performance of the products and their antimicrobial behaviour.

4. Conclusion

CNT/reinforced boehmite ceramic composite powders were synthesized by means of hydrothermal synthesis. Fine particles of boehmite (40 nm) were obtained after hydrothermal synthesis. Die-pressed compacts were sintered at 1450 °C for 3 h in a N_2 gas atmosphere leading to the production alumina with

9% porosity and CNT-reinforced alumina with a porosity level of 20%. Both TEM and FEG-SEM observations revealed that functionalization of carbon nanotubes was accomplished under hydrothermal conditions. The sintered compacts contain tailored porosity sizes within the range of 70–400 nm and grain sizes of 200–500 nm.

The bridging of CNTs along the pores was observed by TEM analysis. This situation can have a beneficial effect on the reduction of the pore sizes to inhibit the permittivity of the contaminants but clogging phenomena may occur if the CNT content is too high. Incorporation of carbon nanotubes into porous alumina is expected to increase the adsorption capability of the ceramic composites. For a comprehensive understanding of the filtration properties of CNT-reinforced alumina ceramics; antibacterial and antiviral filtration capabilities and permeability properties are being investigated.

Acknowledgements

This work was funded by TUBITAK (The Scientific and Technological Research Council of Turkey) under the contract number 108T651. Assoc. Prof. Gültekin Göller from Istanbul Technical University and Özgür Duygulu from TUBITAK MAM are also acknowledged for the assistance with FEG-SEM and TEM studies, respectively.

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