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New approach for distribution of carbon nanotubes in alumina matrix

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Abstract

Alumina–carbon nanotubes composites were studied with respect to obtain the homogeneous distribution of nanotubes within the alumina matrix. Disaggregation and uniform dispersion of carbon nanotubes in alumina matrix are crucial requirements for improvement fracture toughness and also electrical conductivity of these composites. New approach comprises functionalisation MWCNTs by acid treatment, stabilisation of alumina/MWCNT dispersion with subsequent freezing has been used, which resulted in formation of granulated homogenous mixture. The ceramic composites were prepared by hot pressing at 1550 °C using these mixtures. Microstructural analysis as well as electrical conductivity measurements has been used for observation of distribution of nanotubes within composites. Electrical conductivity, as an indicator of homogeneity of conductive network distribution, increases from 6 to 1140 S/m when compared the conventional process and approach presented in this work at the same volume fraction of MWCNTs 10 vol.%.

Keywords: Al_2O_3; Carbon nanotubes; Freeze granulation; Microstructure; Electrical conductivity

1. Introduction

Alumina based ceramics have been used in industrial sectors at high temperatures due to their intrinsic thermal stability, good corrosion resistance, high temperature mechanical strength and low density. However, alumina ceramics are known to exhibit low fracture toughness since plastic deformation in ceramics is very limited. Carbon nanotubes (CNTs), in the form of multi-wall (MWCNT) and single-wall (SWCNT), since their discover by Iijima[1,2] and Bethune,[3] are interesting materials due to their extraordinary mechanical properties, e.g. Young's modulus in the range of TPa,[4–9] bending strength approx. 14.2 ± 8 GPa,[7] tensile strength of outermost layer of MWCNTs in the range of 11–63 GPa[9] and flexibility.[8] According to this, CNTs seem to be a very promising material for reinforcing of ceramics, metals and polymers. Mechanical properties of CNTs strongly depend on their structure and defects.

Moreover, the CNTs exhibit also extraordinary functional properties, such as thermal conductivity in the range of 2500–6000 W/m K along the tube axis of isolated multi-wall or single-wall carbon nanotube is much higher in comparison with conventional materials, e.g. thermal conductivity of Cu is 400 W/m K.[10–14] Except the thermal conductivity, electrical conductivity seems to be also very interesting. Electrical conductivity for single-wall carbon nanotubes was measured by four probe technique and it is on the order 10^6 S/m.[15] Ando et al. measured electrical conductivity of individual MWCNTs using a two-probe method with micro-manipulation system and they reported values on the order 10^5 S/m.[16] According to these superior properties of CNTs, these seem to be a promising material for the reinforcement of ceramics, especially of alumina, however also for improving functional properties.

Despite the intense effort in the field of alumina–CNTs composite, there is still key problem in homogeneous dispersion or distribution of carbon nanotubes in the alumina matrix. In order to obtain a homogeneous distribution of CNTs in ceramic matrix, several approaches have been developed. Conventional powder processing in which raw CNTs and ceramic powder are mixed together followed by ultrasound agitation and/or ball milling.[17] Molecular level mixing process which involves mixing of functionalised CNTs and metal ions homogeneously in an aqueous solution at a molecular level.[18] Colloidal heterocoagulation method was used for homogeneous distribution of CNTs in ceramic powder which was reached by adjusting

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surface properties of CNTs and ceramic powder and make them bind together with attractive electrostatic forces.[19,20] The in situ synthesis of CNTs on ceramic powders, where CNTs have been directly grown on the ceramic particles by CCVD method.[21,22] Another approach which is used in order to disperse CNTs uniformly is using of surfactants like sodium dodecyl sulphate or dimethylformamide with common interactions of ultrasound agitation.[23–25] In this work we used novel approach which comprises acid treatment of multi-wall carbon nanotubes, dispergation of as-treated MWCNTs in aqueous solution of sodium dodecyl sulphate by ultrasound agitation in order to reach a stable and homogeneous suspension in which MWCNTs are individually isolated. This stable suspension of CNTs and alumina powder was sprayed into the liquid nitrogen in order to preserve this state and reach granulated alumina–MWCNT powder with homogeneous distribution of MWCNTs. Finally, as prepared granulates where densified by hot pressing and evolution of microstructures as well as electrical conductivity were studied.

2. Experimental

Multi-wall carbon nanotubes (MWCNTs) with outer diameter of 8–15 nm, length of 50 μm and content of metal catalyst particles was approximately 0.7 wt.% (Chengdu Organic Chemicals Co. Ltd., China) were stirred and ultrasonicated in a mixture of concentrated sulphuric and nitric acids (both p.a. quality) at a volume ratio of 3:1 for 7 h. Afterwards, the CNTs were filtered from this mixture and thoroughly washed by distilled water to be acid-free and then finally dried at 80 °C overnight. Water based dispersion of as treated MWCNTs have been prepared with addition of stabilising agent of sodium dodecyl sulphate (SDS, Alfa Aesar GmbH, Germany). The weight ratio of SDS and MWCNTs was 1.5:1. Centrifugation has been done to remove excess of water in order to reach suspension with suitable content of solid which is necessary for freeze granulation. Alumina powder (Martoxid MR-70) was added into the stabilised dispersion of MWCNT in order to prepare mixtures with various content of nanotubes in the range of 2.5–10 vol.%. Finally, the mixture was ball milled for 24 h with temporary dispersants and binders (Dolapix ET 85, Zusoplast WE8, Optapix AC 95) in total amount of 3 wt.% of alumina powder. Obtained dispersions were rapidly frozen in liquid nitrogen (LS-2, PowderPro AB, Sweden) and subsequently lyophilised (Unicryo MC2L, UniEquip Laborgerätebau- und Vertriebs GmbH, Germany) to dry the granulate. Granulate powder was sieved through a 300 μm microscreen and fraction below 300 μm was used. Prepared granulates were than heated at 400 °C for 45 min in air in order to remove rest of organic additives without damaging of CNTs. Alumina–CNTs composites were then densified by hot pressing at 1550 °C for 1 h and load of 30 MPa under inert atmosphere of argon. Final dimensions of prepared samples were 20 mm in diameter with thickness of approximately 3–4 mm. Densities of ceramic composites were measured using Archimedes method by weighing in water. Relative densities were calculated using a volumetric rule of mixtures based on densities of 3.97 g/cm^3 for Al_2O_3 a 2.0 g/cm^3 for MWCNTs.

Vickers hardness (HV) and fracture toughness (K_{1c}) were determined by indentation method and measured by hardness tester LECO LV 100 (FutureTech Corp, USA). The fracture toughness was calculated from the minimum of 10 indentations carried out at the load of 98.1 N. The Vickers hardness was evaluated adopting an indentation load of 9.81 N. Dwell-time of 10 s was applied at the maximum load in both cases. Fracture toughness was calculated from length of radial cracks extending from the corners of the indents by the method described by Anstis.[26]

Electrical resistivity was measured by 4-point method using compensated RLC bridge. Scanning electron microscopy (EVO 40HV, Carl Zeiss, Germany) was used for microstructural analysis of prepared powder mixture as well as final composite bodies; grain size of alumina matrix was estimated by the linear interception method. Raman spectra of raw as well as acid treated MWCNTs were recorded using Micro-Raman spectrometer (Horiba HR800, Germany) equipped with an Ar laser (irradiation wavelength 633 nm). Gaussian curve fitting of the Raman bands (OriginPro 8.1 Software) was applied for the evaluation of intensity of D-band and G-band. Zeta potential of MWCNTs and alumina dispersions has been measured at various pH in the range of 2–11 (Zetasizer Nano Malvern Instruments Ltd., United Kingdom). Microstructural evolution and MWCNTs distribution within the alumina matrix was compared with composite counterparts prepared by conventional powder processing and densified under the same condition.

3. Results and discussion

Raman spectroscopy was used for characterisation CNTs, because this technique is very sensitive to structural disorder. Any changes in the ratios of I_D/I_G would be a good indicator of effectiveness of functionalisation. Raman spectra of raw and functionalised MWCNTs were measured. The representative features of MWCNTs in the Raman spectra are the so-called disorder induced D-band at approx. 1350 cm^{-1}, the G-band at approx. 1582 cm^{-1} due to in-plane stretching of sp^2 carbon and D*-band at approx. 2600 cm^{-1} which represent the overtone of disorder. Chemical functionalisation of MWCNTs leads to changes in the intensity and and/or width of these bands. From Raman spectra is clearly seen that D-band intensity was increased in the modified MWCNTs compared to raw MWCNTs. The intensity ratio ($I_D/I_G = 2.76$) at D-band and G-band for the modified MWCNTs exceeded those of raw MWCNTs ($I_D/I_G = 2.47$). This result indicates that some of sp^2 carbon atoms were converted to sp^3 carbon atoms at the surface of the MWCNTs after the acid treatment in H_2SO_4/HNO_3.[27] Based on Raman measurements of raw and functionalised MWCNTs, Fig. 1 we assume that density of defects at the surface increases after acid treatment. An indicator of this statement is the different ratio of intensity I_D/I_G peaks for functionalised and as received MWCNTs, respectively.

Zeta potential of raw and acid treated MWCNTs, as well as of alumina was measured in water or solution with sodium dodecyl sulphate in order to reveal the area of dispersion stability, Fig. 2. Acid treatment of MWCNTs results in negative charging of nanotubes and thus to shift of isoelectric point (IEP) from pH

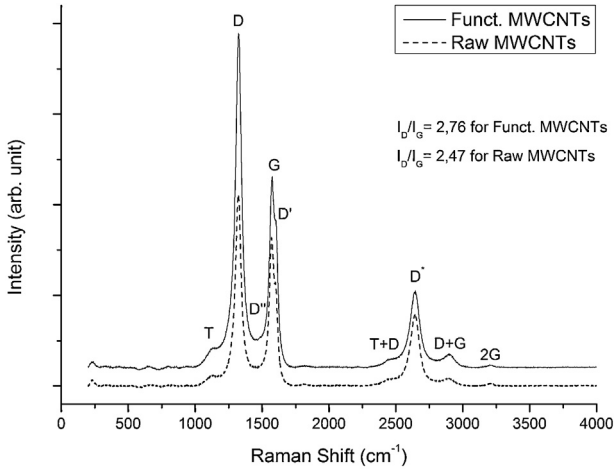

Fig. 1. Raman spectra of raw and functionalised CNTs.

3.5 for as received MWCNT to below pH 2. The effect of acid treatment is quite known, as changes wetting behaviour from hydrophobic to hydrophilic and moreover, removes the rest of catalyst particles and amorphous carbon.

Thus the CNT bundles are deagglomerated and individual nanotubes can be negatively charged due to the formation of carboxylic and oxygen containing groups.[28,29] Further addition of SDS results in a stable dispersion over the whole range of pH, where zeta potential is more or less constant at −55 mV due to the effective charging of adsorbed molecules of anionic surfactant. Moreover, common interaction of SDS and ultrasound agitation leads to obtaining individually isolated MWCNTs which are stable in suspension.[30] Similarly, the effect of negative charging after SDS adsorption has been observed by measuring zeta potential of alumina dispersion at each pH value, with the highest value of zeta potential at pH 10.8. Therefore, the pH of final dispersions of MWCNTs and alumina were adjusted to this value in order to receive a stable mixture prior to freeze drying step.

Stable dispersion was sprayed subsequently into the liquid nitrogen and resulted to formation of granules with broad range of size distribution up to 150 μm in diameter, Fig. 3a. The detail microstructural analysis of freeze dried granules of composite mixtures does not reveals any presence of MWCNTs bundles, only the individual separated nanotubes were observed between the alumina grains, even at highest nanotubes loading of 10 vol.% in the composite, Fig. 3b. The freezing step seems to be very important as the separation of nanotubes and alumina particles does not occur and it was possible to retain the homogeneity of the aqueous suspension in the powder mixture and thus in the consolidated bodies.

Prepared composite granulated powder was heated at 400 °C for 45 min in air in order to remove rest of organic additives without damaging of CNTs. As treated granulated powder was hot pressed at 1550 °C for 1 h under the pressure of 30 MPa in an argon atmosphere. The real content of carbon for granulated powders which were heated at 400 °C in air and sintered composites was measured by Carbon/Sulphur Combustion Analyser (Horiba Ltd., Japan) (Table 1).

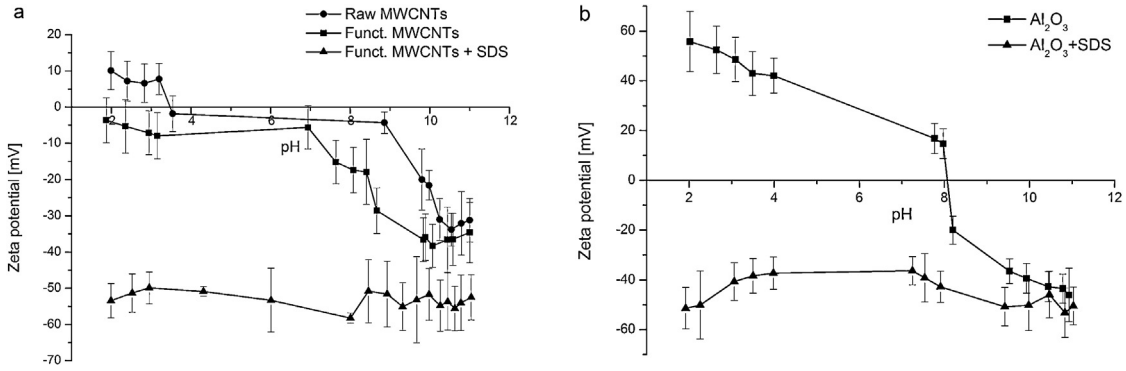

Fig. 2. Zeta potential of (a) raw MWCNTs, functionalised MWCNTs with/without SDS and zeta potential of (b) alumina with/without SDS.

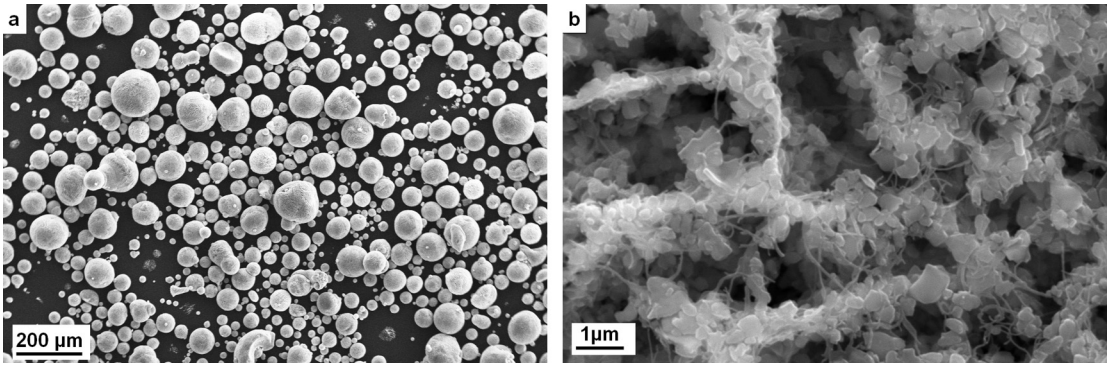

Fig. 3. SEM images of (a) granulated alumina/CNT composite powder and (b) detail of granule surface with distribution of MWCNTs and alumina grains.

Table 1
Analysis of carbon content in granulated powder heated at 400 °C and sintered composites.

Sample	Content of CNTs [vol.%]	Content of CNTs [wt.%]	Content of C [wt.%] in granulated powder heated at 400 °C	Content of C [wt.%] in sintered bodies
A2.5CNT-FG	2.5	1.3	1.0120	0.9545
A5CNT-FG	5	2.6	2.2820	2.1770
A7.5CNT-FG	7.5	3.9	3.0265	2.8795
A10CNT-FG	10	5.2	4.3930	4.1715

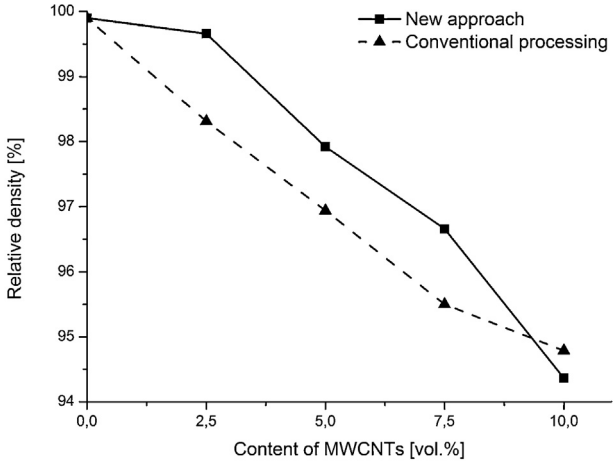

Fig. 4. Comparison of relative densities of composites prepared by conventional and new approach.

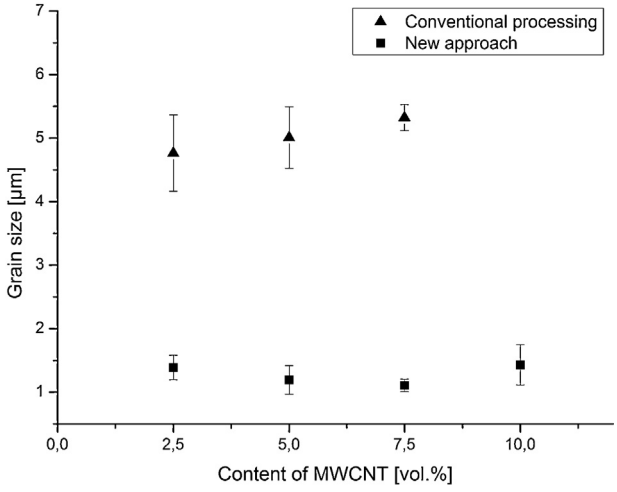

Fig. 5. Grain size of alumina in alumina–CNT composites prepared by conventional and freeze granulation process.

Relative density of alumina–MWCNT composites decrease with increasing content of carbon nanotubes, Fig. 4, due to the presence of CNTs on grain boundaries which hinder densification by retarding the grain movement and flowing of the matrix. Decreasing of densities of ceramic composites with MWCNT are in good agreement with previous reports.[31–33] With increasing content of carbon nanotubes increase the probability of presence of CNT agglomerates especially in composites prepared by conventional processing. In all samples prepared by approach used in this work were observed very good distribution of MWCNTs in alumina matrix (Fig. 7), some agglomerates were observed only in composite with the highest content of MWCNTs (Fig. 7d).

The evolution of microstructure of alumina/MWCNTs composites with relative density above 94% has been studied with respect to distribution of nanotubes within matrix, presence of microstructural defects as well as to alumina grain growth. Detail observation of fracture surfaces of composites prepared by conventional ball milling of alumina powder and carbon nanotubes revealed the presence of MWCNTs agglomerates surrounded by large alumina grains with average size of approximately 4–5.5 μm. Grain size of alumina with 10 vol.% of MWCNTs was not possible to determine correctly due to agglomerates of MWCNTs. Contrary to this, the microstructure of composites prepared from freeze dried granulate was much finer, average grain size of alumina particles in these composites were in the range of 1–1.5 μm, Fig. 5.

Moreover, the distribution of MWCNTs within these samples was more homogeneous when compared to the conventional

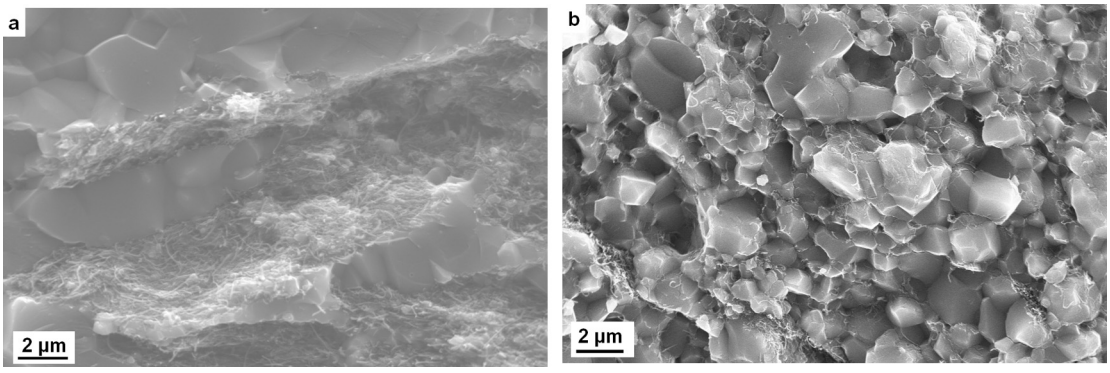

Fig. 6. Comparison of fracture surfaces of composite with 10 vol.% MWCNTs which was prepared by (a) conventional process and (b) freeze granulation.

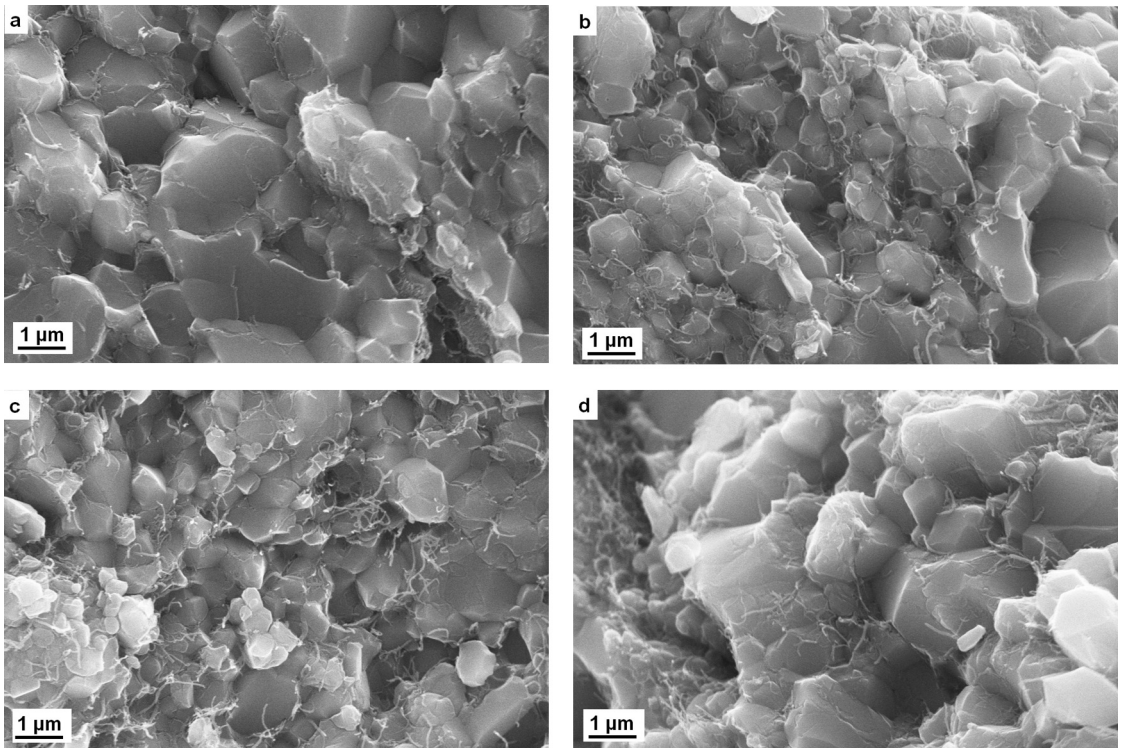

Fig. 7. Fracture surfaces of composites with different content of MWCNTs: (a) 2.5 vol.%, (b) 5 vol.%, (c) 7.5 vol.%, (d) 10 vol.% prepared by new approach.

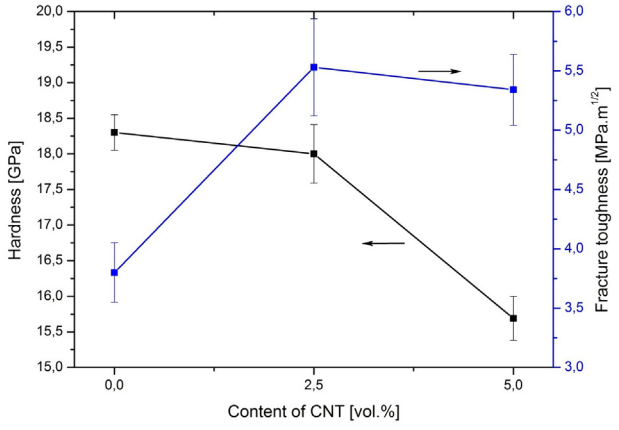

Fig. 8. Vickers hardness and fracture toughness of composites prepared by new approach.

counterparts, Fig. 6. Refinement of alumina grains probably results from better distribution of MWCNTs in matrix, where homogeneous localisation of carbon nanotubes on the grain boundary effectively hinder the grain growth. Grain growth of the ceramic component in the nanocomposites can be supressed by presence of carbon nanofibers as was corroborated by Borrell et al.[34] We assume the change of fracture mechanism from intergranular to transgranular observed on fracture surfaces (Fig. 6b) should be ascribed to the presence of homogeneously distributed CNTs on grain boundaries and thus to their effect to the crack propagation.

Vickers hardness and fracture toughness were measured only for composites with 2.5 and 5 vol.% of MWCNTs, Fig. 8. Composites with higher amount of MWCNT, i.e. 7.5 and 10 vol.%, were not tested as the measurements could be affected by the

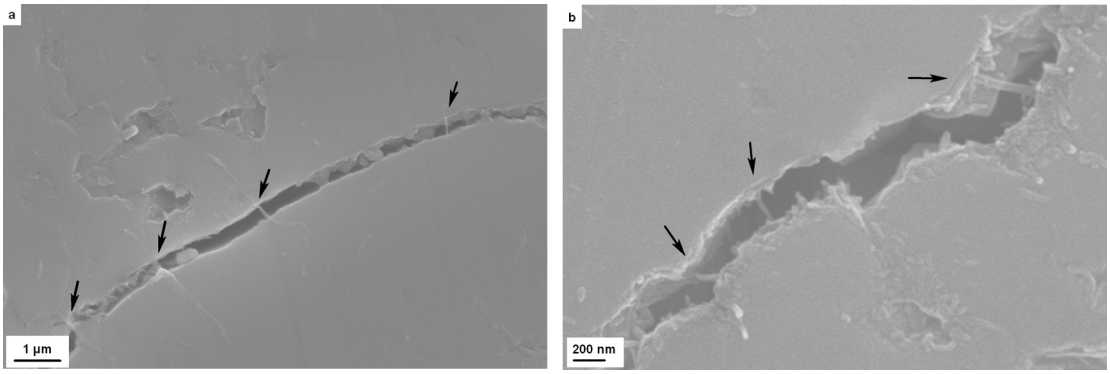

Fig. 9. Toughening mechanism observed in composites with 5 vol.% of MWCNTs prepared by new approach: (a) CNTs bridging of cracks, (b) CNTs bridging and pull out.

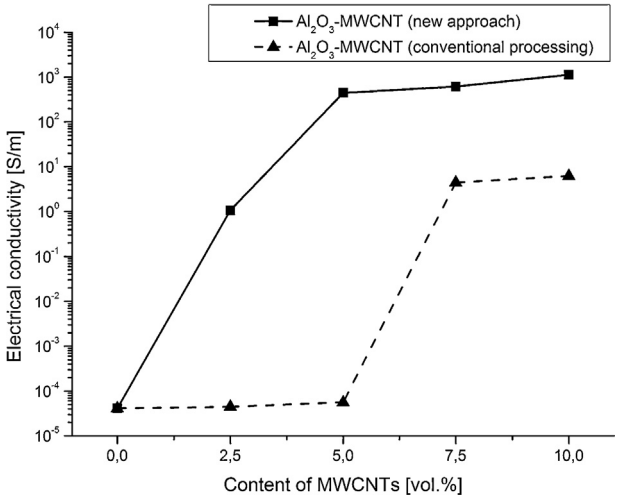

Fig. 10. Comparison of electrical conductivity of alumina–CNT composites prepared by conventional process and new approach.

porosity. Vickers hardness decreases with increasing content of CNTs due to fact that carbon nanotubes has lower hardness than alumina. Fracture toughness of these composites increases significantly already by addition of 2.5 vol.% of MWCNTs and seems to remains at the same level by increasing of MWCNT content (5 vol.%). This is probably due to fact that carbon nanotubes are very well distributed in matrix and toughening mechanisms: CNTs bridging of cracks and pull out were observed by SEM, Fig. 9a and b.

Four-probe DC measurement of electrical properties showed an increase of specific electric conductivity for all studied compositions prepared by presented approach compared to that conventionally prepared, e.g. at the same volume fraction of CNTs 5 vol.% the conductivity increases from 5.62×10^{-5} to 448 S/m, Fig. 10. This confirmed the formation interconnected network of nanotubes as a consequence of their good distribution within the alumina matrix.

The highest electrical conductivity which we reached is 1140 S/m for alumina composites with 10 vol.% of MWCNTs prepared by new approach. According to our knowledge, up to date this is the highest electrical conductivity for alumina–MWCNTs composites (Table 2).

Table 2
Comparison of electrical conductivities of alumina–MWCNTs composites.

Ceramic matrix	MWCNT content [vol.%]	Electrical conductivity [S/m]	References
Al_2O_3	0–7.6	12.2	[35]
Al_2O_3	0.6	2.5	[36]
Al_2O_3	0.9–3.7	65.3	[37]
Al_2O_3	1.66–15.3	3.5	[38]
Al_2O_3	2	2.7×10^{-1}	[39]
Al_2O_3	4.65	210	[40]
Al_2O_3	6.1	6.2×10^{-2}	[41]
Al_2O_3	6.1–15.3	576	[42]
Al_2O_3	2.5–10	1140	Present work

4. Conclusion

Multi-wall carbon nanotubes are attractive materials for reinforcement (toughening) and also improvement of electrical conductivity of ceramics. The most important prerequisite for improvement fracture toughness and electrical conductivity of ceramics is uniform distribution of carbon nanotubes in ceramic matrix. This work focuses on new approach for preparation of alumina composites with homogeneously distributed MWCNTs. This approach results in a granulated powder in which MWCNTs were homogeneously distributed and individually isolated and thus to more homogeneous ceramic composites. The preliminary results of mechanical properties, microstructural evolution and electrical properties seem to be very promising. From comparison of fracture surfaces of composites prepared by conventional and this new process is clearly seen significant differences in microstructure, especially in the distribution of nanotubes, grain size and presence of agglomerates. Fracture toughness increases due to toughening mechanisms (e.g. CNTs bridging of cracks and CNTs pull out). Electrical conductivity, as indicator of creation conductive network, increases significantly also due to better distribution.

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