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Alumina/MWCNTs composites by aqueous slip casting and pressureless sintering

Martin Michálek[a,*], Katarína Bodišová[b], Monika Michálková[b], Jaroslav Sedláček[a], Dušan Galusek[a]

[a] *Vitrum Laugaricio—Joint Glass Centre of the IIC SAS, TnU AD, FChPT STU and RONA, j.s.c., Trenčín, Slovakia*
[b] *Slovak Academy of Sciences, Institute of Inorganic Chemistry, Bratislava, Slovakia*

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Abstract

Slip casting of stabilized aqueous suspensions followed by pressureless sintering was used for preparation of dense Al_2O_3/MWCNTs composites. The suspensions were stabilized by commercial polyelectrolyte dispersant Darvan C–N. In order to increase the stability, the pH value of the suspension was adjusted to ~10. At this pH the highest ζ-potential values of the alumina powder and of the MWCNTs functionalised in boiling nitric acid were achieved. Two different agents, namely ammonium hydroxide and sodium hydroxide, were used for the pH adjustment. Their influence on the viscosity of suspensions and on consolidation and densification behaviour of the Al_2O_3/MWCNT composites was evaluated. The effect of ammonium hydroxide was more pronounced, as confirmed by lower viscosity of the suspension, higher sintered density, and fine-grained microstructure of the sintered composites. The Al_2O_3/t-MWCNTs composites with 0.1 wt% of the MWCNTs, with 99.9% relative density, the mean size of alumina grains ~1 μm, and homogeneously distributed carbon nanotubes were prepared by the pressureless sintering at 1500 °C.

Keywords: Microstructure; Al_2O_3/MWCNTs composites; Viscosity; Zeta potential

1. Introduction

Slip casting is a technique commonly used for the preparation of ceramics composites. Careful control of processing conditions and high stability of the composite suspensions are essential for its successful application in ceramic processing. The preparation of well dispersed and stabilized suspensions with high solid loading is prerequisite for achievement of high density and good mechanical properties of the sintered composites.

The term "colloid" is used when the particles of at least one component of the system, such as suspension of submicron particles of a ceramic powder in aqueous, or non-aqueous liquid, have the dimensions in the range between 0.1 and 1 μm. The surface area, and hence, the interphase energies, in such systems are high, and the interparticle forces play an important role. Dominance of the attractive van der Waals forces in such systems often results in the agglomeration of colloidal particles, which prevents formation of stable suspensions. In order to suppress agglomeration, electrostatic, steric or electrosteric repulsive forces must be introduced into the system. The electrostatic repulsion is explained by the DLVO theory [1]. The surface charge is influenced by the pH value of the suspension. The charge is highest in the close vicinity of the particle surface, and decreases exponentially with the distance from the particle. Adjustment of the pH alone is therefore often sufficient for successful stabilisation of the suspension. The stable alumina/zirconia suspensions were prepared by Requena et al. through the pH adjustment of the system [2]. At the pH=4 the surface of both the alumina and zirconia powders are charged positively, and the stability of the system can be easily controlled. The steric repulsion forces can be introduced by the addition of

*Corresponding author. Tel.: +421 2 59410 443.
E-mail addresses: uachkigo@savba.sk, martin.michalek@savba.sk (M. Michálek).

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a suitable polymer. The polymer chains are attached at the surface of ceramic particles in the suspension. Two mechanisms, which prevent agglomeration are in operation:

(1) the molecules of the polymer adsorbed at the surfaces of two adjoining particles limit their configuration space. The particles then cannot get close enough for the attractive van der Waals forces to prevail; and
(2) if the particles are pressed together by an external force, an increase of the stress energy is observed, arising from overlapping of the polymer chains attached to the particle surfaces.

In order to stabilise the ceramic suspensions with high solid loading both electrostatic and steric repulsion forces are usually applied through the use of polyelectrolytes [3]. These usually contain hydrocarbon chains with polar ionic part, which facilitates additional electrostatic repulsion [4]. Common polyelectrolytes used for the stabilisation of ceramics suspensions include polyacrylic acid (PAA) [5,6], salts of polymethacrylic acid (e.g. Darvan C) [7], alkali free carboxylic acid-based dispersants (e.g. Dolapix CE 64) [8], polyethylenimine PEI [9] or ammonium polymethylmetacrylate e.g. (Darvan C–N) [10]. Proper control of the colloidal chemistry leads to stable homogenously dispersed suspensions with high solid loading. The interactions among the particles and the stability of the suspension can be evaluated by rheological measurements. Low viscosity of the suspension together with high solid loading usually facilitates preparation of the green compacts with high relative density.

Large potential of the ceramic composites with carbon nanotubes (CNT) led in recent years to extensive research aimed at incorporation of the nanotubes into various ceramic matrices [9,11,12]. The addition of the CNT is expected to improve mechanical and functional (e.g. electrical) properties of the composites. However, preparation of the CNT-containing ceramics is complicated by the difficulties related to incorporation and homogenous dispersion of the highly agglomerated CNT in the ceramic matrix. It is associated also with the decrease of the driving force of sintering, and the problems associated with densification of the composite. The CNT-containing ceramic composites are usually prepared by pressure-assisted sintering techniques, such as hot pressing HP [13], pressureless sintering combined with hot isostatic pressing (sinter-HIP techniques) [14] or by spark plasma sintering [15,16]. The applicability of the mentioned techniques at the industrial scale is limited by high production costs, and the problems associated with fabrication of the parts with complex shapes.

Present work deals with the preparation of the dense alumina/MWCNT composites by the pressureless sintering. Special attention is paid to preparation of the composite green bodies by slip casting. The effect of the addition of the dispersant Darvan C-N (ammonium polymethylmetacrylate) in combination with various pH modifying agents, such as NaOH [17,18] and NH_4OH [7,10], is studied and discussed. Determination of the ζ-potential, the evaluation of rheological properties of the suspensions, and measurement of the relative density of consolidated green bodies are used as the measure for evaluation of the efficiency of different agents with respect to preparation of the dense composites with homogeneously distributed CNT.

2. Experimental

2.1. Materials

For the preparation of the alumina matrix the α-alumina powder Taimicron TM-DAR (Taimei Chemicals Co., Ltd., Tokyo, purity 99.995%, the mean particle size 150 nm, the specific surface area 13.7 $m^2 g^{-1}$) was used. Ammonium polymethylmetacrylate (Darvan C–N, R.T. Vanderbilt Company, Inc., Norwalk, USA) was used as a dispersant. Commercially available multi walled carbon nanotubes (MWCNTs, Chengdu Organic Chemicals Co., Ltd., China, the length ~25 μm, the diameter in the range 7–15 nm, synthesised by chemical vapour deposition) were also used. Alkali aqueous solutions (1 M NaOH and 25% NH_4OH, both p.a., Sigma Aldrich Co., Germany) were used for the pH adjustment of the suspensions.

2.2. Processing

For the preparation of the stabilized alumina/0.1 wt% MWCNTs suspensions, and of the pure alumina reference suspension the processing conditions were slightly different. Schematic depiction of the processes is shown in the Fig. 1. The pure alumina reference suspension was prepared by mixing of the appropriate amounts of distilled water with the commercial dispersant Darvan C–N (the amount of dispersant was fixed to 2.2 wt% with respect to the weight of the solid [10]) with the alumina powder. After the addition of 50 wt% of the powder the suspension was mixed thoroughly, the pH value was adjusted by the addition of the NaOH or NH_4OH solution, and then the rest of the powder was added. The mixture was further homogenised by milling the suspension for 24 h on rollers in polyethylene jar with high purity alumina milling balls.

For the composite suspensions, the MWCNTs were functionalized by heating the as-received (raw) MWCNT (r-MWCNT) for 8 h in the concentrated (65%) HNO_3 at 80 °C. CH_x, C–OH, C═O and N–C═O groups are formed at the surface of the CNT under the applied conditions, at the ratio of 76%, 13%, 4.2% and 6.2%, respectively [19]. The functionalisation reduces the hydrophobic nature of the CNT. The treated (t-MWCNTs) were dispersed in distilled water by ultrasonification (Ultrasonificator SONOPLUS, HD 3200, MS 73 micro needle, BANDELIN electronic GmbH & Co.KG, 93 W input power, the amplitude 45%, 10 min). The t-MWCNTs were added into the suspension after the first 50 wt% of the

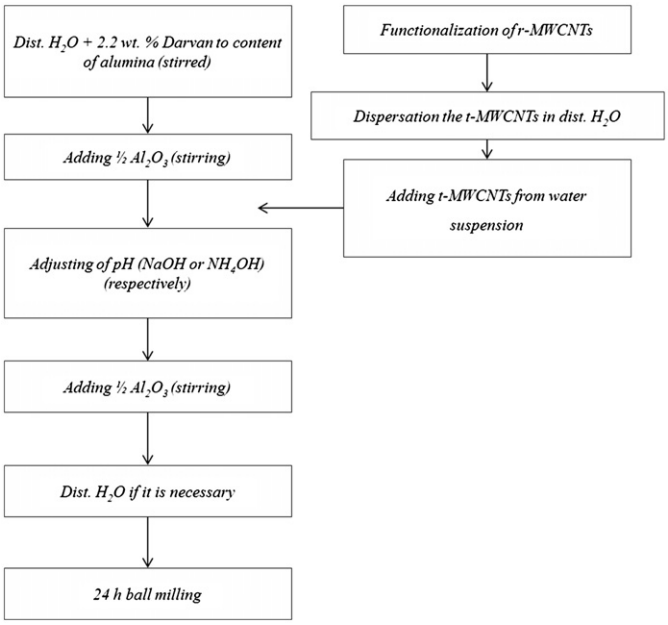

Fig. 1. The flow chart of preparation of the pure Al_2O_3 reference and composite Al_2O_3/t-MWCNTs suspensions.

Al_2O_3 powder. Then the pH was adjusted, the rest of the Al_2O_3 powder was added, and the composite suspension was homogenised under the same conditions as the reference alumina suspension. After the homogenisation the suspension was de-aired by careful evacuation.

The ζ-potential was measured by the instrument Zetasizer Nano (Malvern Instruments Ltd. Enigma Business Park, Grovewood Road, Malvern, Worcestershire, UK), in diluted suspensions (solid loading 0.1 wt%). The pH values of the suspensions were measured by a pH metre (Mettler-Toledo GmbH, Analytical, Sonnenbergstrasse 74, CH-8603 Schwerzenbach, Switzerland). The viscosity measurements were carried out with the use of the rheometer (Haake RheoStress 600, Haake Mars, Thermo Scientific) after de-airing of the suspension. The measurements were performed at constant temperature (23 °C) in the interval of shear rates between 1 and 1000 min^{-1}.

The green bodies in the form of pellets 12 mm in diameter and 6 mm thick were prepared by slip casting of the prepared suspensions into Teflon® dishes. The cast pellets were dried in two steps: firstly at room temperature for 72 h in closed plastic box, then at 150 °C for 5 h in drying oven. The relative density of the green bodies was determined by the Archimedean method in mercury.

The green bodies were sintered at 1500 °C for 2 h, without external pressure, in Ar protective atmosphere to prevent oxidation of the CNT. The relative densities (RD) of the sintered pellets were measured by the Archimedean method in water. The microstructure was examined by scanning electron microscopy (SEM; Zeiss EVO 40 HV, Germany, and JEOL 7600f, JEOL, Japan) on fracture surfaces of the sintered composites. The mean size of alumina grains in the sintered samples was determined by the linear intercept method, measuring at least 200 intercepts (software LINCE, TU Darmstadt, Germany), and using the correction factor 1.56 according to [20]. The hardness Hv and fracture toughness K_{1c} were measured by the Vickers indentation method with the use of the hardness tester LECO LV-100 (FutureTech Corp, USA). Ten indents were made in each sample. The loads of 10 N and 100 N were used for determination of Hv and K_{1c}, respectively.

The hardness was calculated from Eq. (1)

$$Hv = \frac{1.8544P}{d^2} \quad (1)$$

The fracture toughness was calculated by Eq. (2)

$$K_{1C} = 0.0889\left[\frac{P\,Hv}{4c}\right]^{1/2} \quad (2)$$

where P is the applied load (N), Hv is the hardness measured at the load of 10 N, c is the average crack length (m), and d is the average length of the two diagonals of the indent (m) made at the load of 100 N [21].

3. Results and discussion

3.1. ζ-Potential

The electrical surface charge (ζ-potential) of colloid particles is the main indicator of the stability of the suspension through the action of electrostatic forces in polar solvents. The pH dependence of the ζ-potential in water solutions of pure alumina particles compared with the alumina stabilised by the addition of 2.2 wt% of the dispersant Darvan C–N is shown in the Fig. 2a. The pH values were adjusted by incremental addition of the 0.1 M HCl and 1 M NaOH solutions.

The isoelectric point (iep) of the pure alumina reference was found to be at the $pH_{iep} \sim 7$, which is in good agreement with the range of iep values reported for α-Al_2O_3 in the literature ($pH_{iep} \sim 7$–9.5) [22]. The addition of the polyelectrolyte dispersant Darvan C–N markedly influenced the behaviour of the suspension. The iep was shifted to the acidic side, with the ζ-potential equal to zero at $pH_{iep} \sim 3$. The addition of the dispersant also increased the surface charge of the alumina particles in comparison to the system without the dispersant. While in the suspension without the dispersant the maximum surface charge −37 mV was achieved at pH = 11, the addition of the polyelectrolyte nearly doubled it, to −64 mV at pH = 10. These results are similar to those reported by Lyckfeldt et al. [23]. Singh et al. [7] came to similar conclusions when using Darvan C, and attributed the effect to the presence of the COO^- groups adsorbed at the surface of alumina particles, as the result of dissociation of the dispersant in the solution.

The results of determination of the ζ-potential in the raw and functionalised MWCNT are summarised in Fig. 2b. As mentioned above, the raw MWCNTs (r-MWCNTs)

were treated with HNO_3 in order to form COO^- and OH^- groups at their surface. The hydrophobic nature of the raw multi-wall carbon nanotubes can be thus partly eliminated. They become hydrophilic, and can be more readily distributed in aqueous environments. Although the ζ-potential can only be with confidence employed as the measure of the surface charge of spherical particles, it gives some hints also on the stability of suspension of the carbon nanotubes. The isoelectric point of the raw MWCNTs was achieved at the pH ~8. The maximum surface charge was achieved either in the acidic environment (+33.5 mV at the pH=3.5) or in strongly basic region (−32.5 mV at the pH=10.6). The treatment of r-MWCNTs in the 65% HNO_3 shifted the isoelectric point to the pH value ~2.

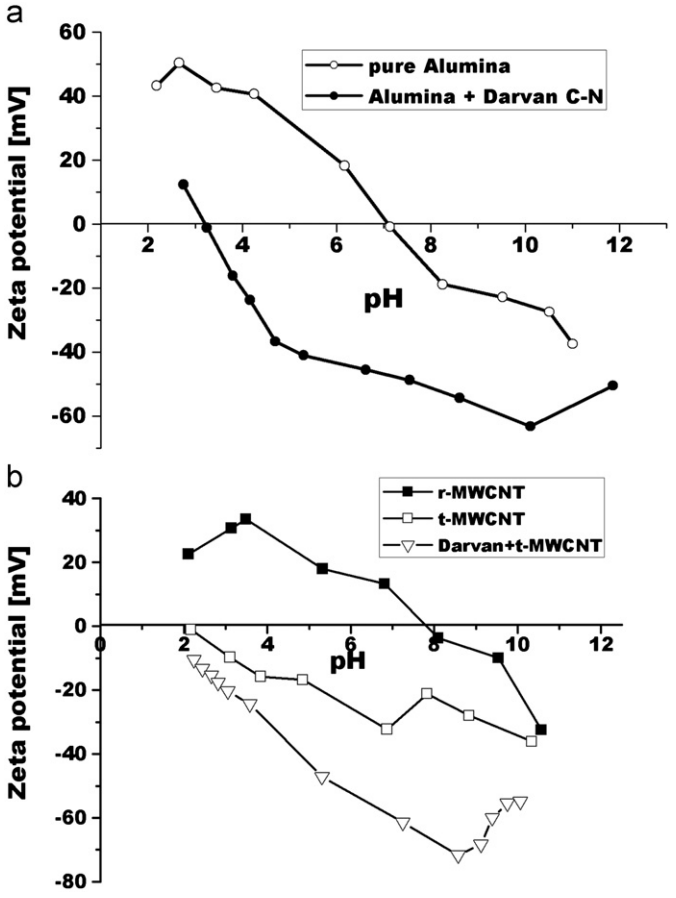

Fig. 2. The dependence of ζ-potential on the pH value in the suspensions of pure alumina powder with and without the dispersant Darvan C–N (a), and of the raw and treated MWCNT (b).

The shift is attributed to the presence of anionic groups at the surface of the nanotubes [24]. The highest negative surface charge was achieved in the same pH region as for the alumina powder with the added polyelectrolyte, i.e. −36.1 mV at pH=10.3. Higher values of the electrical surface charge resulting from the presence of anionic groups at the surface of the t-MWCNTs improved their dispersion, through elimination of the attractive van der Waals forces among the nanotubes. Addition of the Darvan C–N was favourable also in terms of the shift of the isoelectric point and the increase of the maximum absolute value of the ζ-potential of the t-MWCNTs. The surface charge was shifted to more negative values. The highest value of the ζ-potential was achieved at the pH=8.5. At pH ≥ 10, and in the presence of Darvan C–N, the surface charges of the alumina and the t-MWCNTs were similar.

3.2. Viscosity

The addition of the polyelectrolyte dispersant Darvan C–N increases the electro-steric repulsion of the alumina particles in the suspension in the alkaline region (Fig. 2a), [25]. The NaOH and NH_4OH solutions were therefore used for the adjustment of the pH of the reference alumina suspensions to ~10 in order to maximise the surface charge. The influence of the used pH-adjusting agent on the behaviour of the suspensions, sinterability, and the microstructure of the monolithic alumina references were investigated. Table 1 summarises basic characteristics of the prepared reference suspensions.

The rheological behaviour of the suspensions with high solid loading is an important indication of their capacity to yield ceramic green bodies with high relative density and sinterability. High solid loading and low viscosity are usually required in order to consolidate the green body by slip casting. The results of the viscosity measurements of the reference suspensions are shown in Fig. 3a. All suspensions exhibit pseudoplastic behaviour common to the colloidal systems with high solid loading [26]. If the pH was adjusted by the addition of NH_4OH, the electrostatic repulsive forces in the suspension increased, resulting in the lowest viscosity of the suspension at all applied shear rates. Favourable effect of the ammonium hydroxide in comparison to sodium hydroxide was attributed to the different sizes of their counter ions [27]. With the smaller Na^+ counter ions, stronger particle network is formed,

Table 1
Basic characteristics of pure Al_2O_3 reference suspensions.

Suspension	Dispersant	pH adjustment	pH	Solid loading (vol%)	Viscosity at 200 rpm (Pa s)
AD	Darvan C–N, 2.2 wt%	–	9.12	40	0.107
AD–Na		NaOH	10.14	40	0.107
AD–NH		NH_4OH	10.61	40	0.072
AD–NHc		NH_4OH	10.59	45.7	0.084

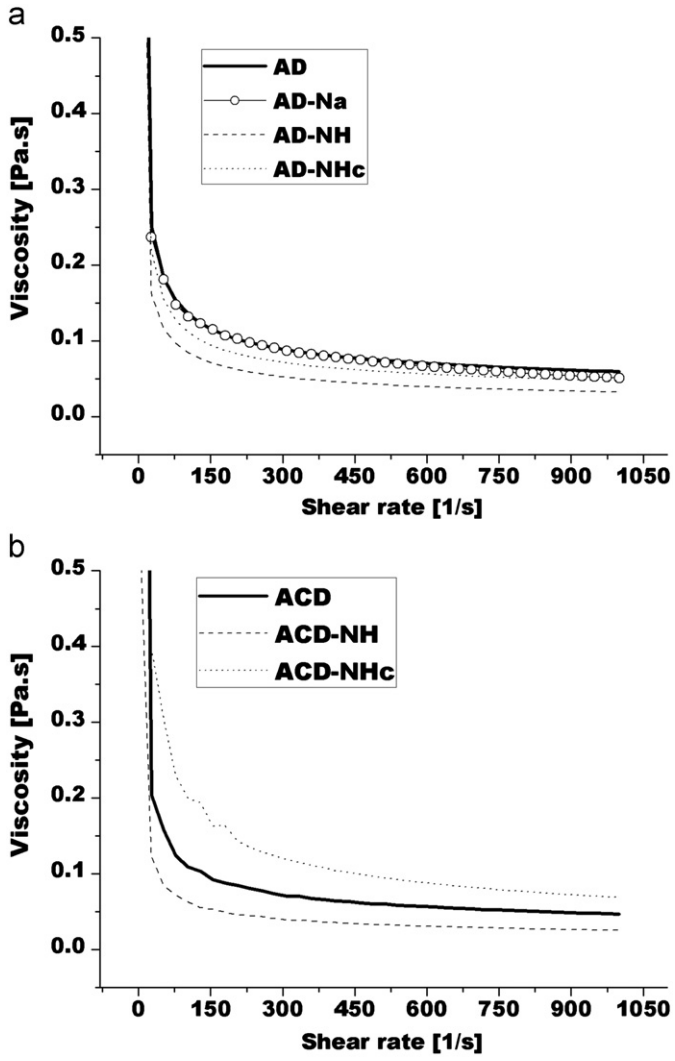

Fig. 3. The shear rate dependence of viscosity of prepared suspensions: pure Al_2O_3 reference suspensions (a), and Al_2O_3/MWCNT composite suspensions (b).

resulting in higher viscosity of the suspension. The use of larger counter ions like NH_4^+ enhances the repulsion forces, resulting in decrease of the viscosity [27]. The viscosity of the suspension AD–NH with 40 vol% of Al_2O_3 was low. The suspension with higher solid loading (45.7 vol% of Al_2O_3) was therefore prepared for comparison. At all shear rates the viscosity of the suspension AD-NHc was lower than the viscosity of the suspensions AD and AD–Na. The more concentrated suspensions were therefore used in further experiments.

Based on the results obtained for the reference alumina suspensions, the aqueous composite suspensions containing 0.1 wt% of the t-MWCNTs were prepared. The suspensions were prepared without the pH adjustment (sample ACD), or with the pH adjusted to ~10.5 by the addition of the NH_4OH solution (specimen ACD–NH). The highest solid loading 44 vol% of Al_2O_3 (sample ACD–NHc) was achieved. Table 2 summarises the information on the CNT-containing suspensions.

The viscosity measurements of the CNT-containing composite suspensions in Fig. 3b revealed the shear thinning behaviour similar to that observed in the reference Al_2O_3 suspensions. The addition of 0.1 wt% of the t-MWCNTs to the pure alumina suspensions with 40 vol% solid loading had no measurable influence on their rheological behaviour. The viscosity curves of the pure alumina suspension AD and of the composite suspension ACD were similar. The adjustment of the pH to ~10.4 in the composite suspension ACD–NH by the addition of the NH_4OH solution led to further decrease of the viscosity at all shear rates. This effect is attributed to the maximum repulsion among individual particles at pH~10.4. The increase of solid loading in the suspension ACD-NHc led to significant increase of the viscosity, as shown in Fig. 3b. In this case the high solid loading prevailed over the repulsive forces, and the MWCNTs with high aspect ratio impaired the flow properties of the suspension.

3.3. Sintering and microstructure

All samples were sintered for 2 h at 1500 °C in the atmosphere of argon, at the heating rate of 10 °C/min. The sintering temperature and dwell time were optimised in order to account for the densification retarding effect of the carbon nanotubes. In case of the pure alumina references the temperature and time applied exceeded by far those required for complete densification of the material. It could be therefore expected that under the applied conditions the measured densities were the highest possible, i.e. any residual porosity was present in the form of highly stable pores/defects, which could not be eliminated by pressureless sintering. This applies especially for the material prepared from the suspension AD–Na, where the presence of the Na^+ ions had negative impact both on the rheological behaviour of the suspension, and the densification of the material (Table 3).

Table 3 summarises the basic properties (green densities of the slip cast compacts, relative densities of the sintered alumina references and of the Al_2O_3–CNT composites, the mean size of alumina grains determined by the linear intercept method, hardness and fracture toughness of the composites) of all sintered materials. Only the reference materials prepared from the suspension AD–Na showed lower relative density (~98.5%), which was attributed both to the presence of defects in the green body and to densification retarding effect of the Na^+ ions. The fracture surfaces of the sintered alumina references are shown in the Fig. 4.

The densification retarding effect of the CNTs in ceramic matrices is well documented [28,29]. The effect was observed also in the composites prepared from the suspension ACD (Table 3), where the relative density of only ~97.5% was achieved. The result indicates insufficient dispersion of the CNTs, as demonstrated by the presence of CNT aggregates in the material (Fig. 5a and b). The aggregates acted as the defects, which could not be eliminated by pressureless sintering. The relative density exceeding 99% was achieved

Table 2
Basic characteristics of Al_2O_3/t-MWCTNs composite suspensions.

Suspension	Composition (wt%)	pH adjustment	pH	Solid loading (vol%)	Viscosity at 200 rpm (Pa s)
ACD	t-MWCNT 0.1wt%; Darvan C–N 2.2 wt%	–	9.17	40	0.107
ACD–NH		NH_4OH	10.42	40	0.05
ACD–NHc		NH_4OH	10.47	44	0.173

Table 3
Basic properties of green and sintered alumina references.

Sample	Green density (%)	Mean grain size (μm)	Sintered density (%)	Hv (GPa)	K_{1c} (MPa $m^{1/2}$)
AD	55 ± 0.9	1 ± 0.1	99.9 ± 0.02	16.3 ± 0.2	5.4 ± 0.2
AD–Na	54 ± 2	1.34 ± 0.07	98.5 ± 0.03	13.8 ± 0.2	5.3 ± 0.1
AD–NHc	54 ± 0.5	1 ± 0.1	99.9 ± 0.02	15.8 ± 0.3	5.7 ± 0.2
ACD	53 ± 1.0	1 ± 0.1	97.5 ± 0.3	15.0 ± 0.4	5.3 ± 0.2
ACD–NH	55 ± 0.4	1.1 ± 0.1	99.1 ± 0.2	14.9 ± 0.5	5.4 ± 0.2
ACD–NHc	55 ± 0.6	1 ± 0.1	99.8 ± 0.2	15.1 ± 0.2	5.4 ± 0.2

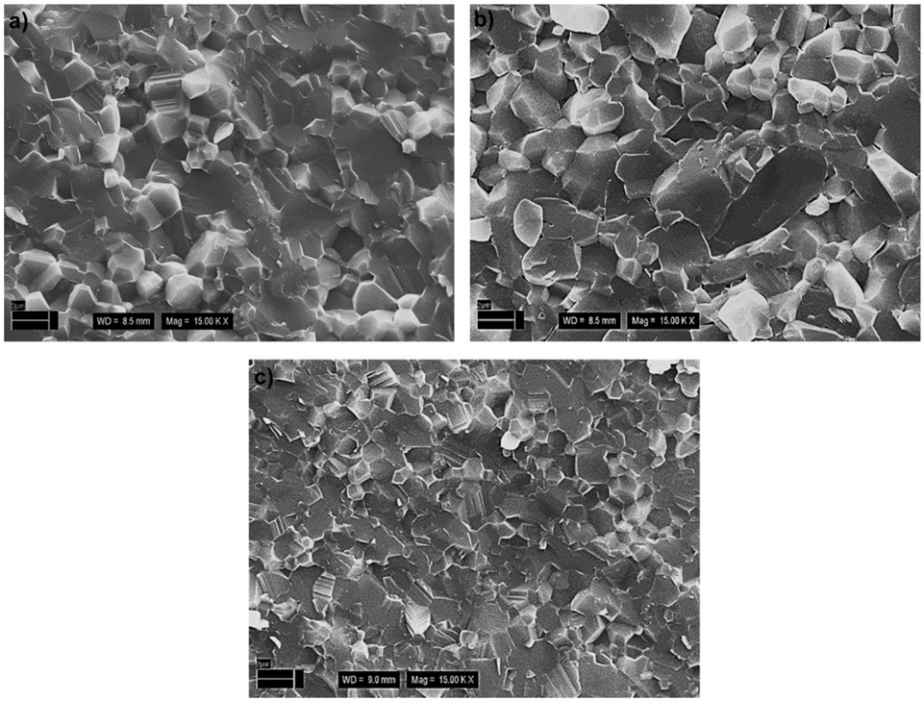

Fig. 4. SEM micrographs of pure alumina references after sintering at 1500 °C prepared from the suspensions (a) AD, (b) AD–Na, and (c) AD–NHc.

in the composites prepared from the suspensions ACD–NH and ACD–NHc with the solid loading of 40 and 44 vol%, respectively (Fig. 5c and d). High stability and sufficient deagglomeration of both the alumina powder particles and the MWCNTs were achieved through the combined effect of the polyelectrolyte dispersant Darvan C–N and the adjustment of the pH by the addition of ammonium hydroxide. The mean size of alumina grains (~1 μm) in the composites was comparable to those obtained in the alumina references (Fig. 5).

The Vickers indentation test yielded preliminary information on the influence of the MWCNT addition on mechanical properties of the composite (Table 3). The fracture toughness of the pure alumina reference was comparable to that measured in the composites ~5.4 MPa $m^{1/2}$. The incorporation of the t-MWCNT resulted in decrease of hardness. The lowest hardness in the AD–Na sample ~13.7 GPa is attributed to heterogenous microstructure and low relative density.

The SEM micrographs in Fig. 5c and d show the microstructure of the composites prepared from the suspensions ACD–NH and ACD–NHc. The t-MWCNTs in the alumina matrix were located mainly at the alumina/alumina grain boundaries. The applied temperature (1500 °C) was

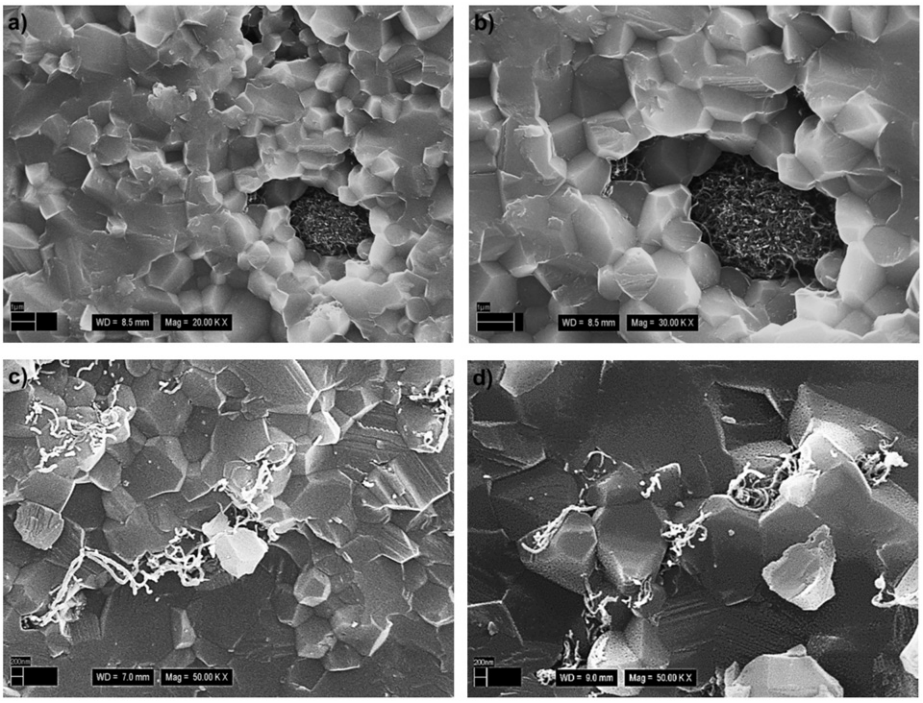

Fig. 5. SEM micrographs of alumina/MWCNT composites after sintering at 1500 °C prepared from the suspensions (a), and (b) ACD, (c) ACD–NH, and (d) ACD–NHc.

sufficient for nearly complete densification of the Al_2O_3/0.1 wt% MWCNT composite. No visible damage of the nanotubes due to sintering at 1500 °C was observed.

4. Conclusions

The alumina/t-MWCNT composites with 0.1 wt% of the MWCNT were prepared by pressureless sintering of the slip cast alumina–MWCNT green bodies. The suspensions were stabilised by combined action of the commercial polyelectrolyte dispersant Darvan C–N and the pH adjustment. The suspensions were optimised (the use of the polyelectrolyte dispersant, the pH adjustment by various agents, various levels of the solid loading) with the aim to obtain dense composites with homogeneously distributed MWCNT.

The surface charge, expressed in terms of the ζ-potential, of the Al_2O_3 stabilised by the addition of the commercial polyelectrolyte Darvan C–N, and of the treated MWCNTs reached the maximum values at pH ~ 10. Two different agents (the aqueous solutions of NaOH and NH_4OH) were therefore used for the pH adjustment, along with the dispersant.

The lowest viscosity of the reference alumina suspensions was achieved by adjusting the pH to ~10 by NH_4OH. The use of NaOH increased the viscosity of the suspension. The presence of Na^+ ions in the system impaired densification and enhanced the growth of alumina grains.

Dense composites with 0.1 wt% of the MWCNT (the relative density 99.8%) were prepared by pressureless sintering of the green bodies prepared by slip casting from the suspensions stabilised by the addition of the commercial polyelectrolyte dispersant Darvan C-N, and with the pH adjusted to ~10 by NH_4OH. The t-MWCNTs were well dispersed, and located at the alumina/alumina grain boundaries. No visible damage of the nanotubes by the process of sintering could be found. No evident improvement of the mechanical properties of the composites, namely fracture toughness and hardness, in comparison to the monolithic alumina reference was observed. The composites with higher content of MWCNT will be prepared in the next step, in order to evaluate the influence of the content of carbon nanotubes on mechanical properties and electrical conductivity of the composites.

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