CNT/Alumina-Composites as Electrically Conductive Ceramics

H. Kühl, C. Bechteler, R. Girmscheid, A. Rübling

CNT-reinforced alumina ceramics are an interesting option for the production of electrically conductive ceramics. It is shown that high electrical conductivity can be achieved with only 0,25 mass-% of CNTs in the alumina matrix. These small amounts added enable the production of dense ceramics with very good mechanical properties, although CNTs massively inhibit densification of the ceramics during the sintering process, especially at higher concentrations. The article also describes the manufacturing process, the mechanical and thermal properties achieved and possible applications.

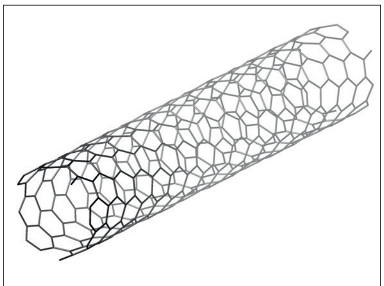

Fig. 1 Structural visualisation of a Single Wall Carbon Nanotube (SWCNT)

Ceramics are known for their outstanding hardness as well as temperature and chemical resistance, which exceed the properties of metals. A considerable disadvantage is the high brittleness, related to their low fracture toughness. Furthermore, lots of ceramics are electrical insulators, which make them suitable for spark plug and high voltage insulators as well as substrates or dielectric materials.

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The combination of the superior ceramic properties with electrical conductivity and improved fracture toughness has been investigated for decades. To enable electrical conductivity in an insulating ceramic, like alumina, an electrically conductive material has to be used as additive with a concentration exceeding the so-called percolation threshold. This is the minimum amount of electrically conductive component that must be introduced into the insulating ceramic so that the insulating property is lost and electrical conductivity dominates. Usually, such a transition happens at a very specific concentration, leading to an increase in conductivity often by over ten orders of magnitude. The concentration strongly depends on the geometry and orientation of the conducting particles. A percolation theory for spherical particles, reported by Zallen [1], mentions a critical concentration of 16 vol.-%. This theory was proven in ATN-ceramics, where spherical, electrically conductive TiN-particles are embedded in an alumina matrix [2, 3].

At the Technische Hochschule Nürnberg Georg-Simon-Ohm electrically conductive ceramics have been investigated for 20 years now. The development of ATN-ceramics has been the focus for a long time and changed towards CNT/alumina-ceramics during the last years, because of a BMBF-funded project in cooperation with Rauschert GmbH/DE.

CNTs (Carbon-Nanotubes) (Fig. 1) are concentric cylindrical carbon-monolayers/graphene layers based on hexagonal structured carbon atoms. Usually, CNTs show a diameter between 0,5–50 nm, dependent on the diameter of the inner layer and the number of layers. Compared to their length, which can be up to several centimetres, the diameter is very small, resulting in an extraordinarily high aspect ratio.

CNTs can appear as Single-Wall- (SWCNTs), Double-Wall- (DWCNTs) or Multi-Wall-CNTs (MWCNTs), which also defines their properties. Some of their properties are outstanding, such as a high electrical conductivity up to 10^7 S/m, the highest known thermal conductivity of all materials up to 6000 W/m·K (SWCNTs) or 3000 W/m·K (MWCNTs), respectively, exceeding even the thermal conductivity of diamond. The Young's modulus, dependent on the CNT-type, can reach 1000 GPa.

Experimental

In the context of this project, CNT/alumina-composites based on two different alumina powders (TM-DAR, Taimei Chemicals Co. Ltd./JP, and CT 3000 SG, Almatis GmbH/DE) were produced by pressureless sintering or hot-pressing with a CNT-content between 0–5 mass-%. Alumina as matrix material was used, because of the comparably low price and the well-known properties and processing techniques. CNTs in form of a water-based MWCNT-suspension were provided by Future Carbon GmbH/DE.

After dispersing alumina particles in water, the CNT-suspension was added to generate

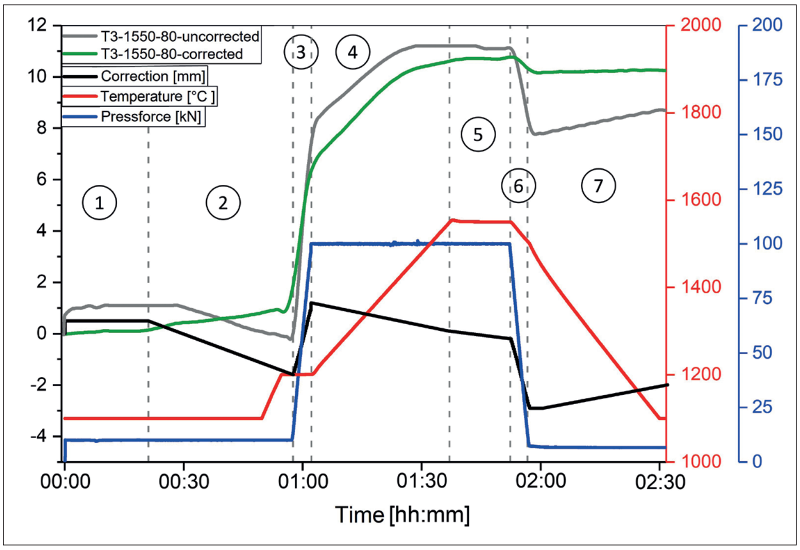

Fig. 2 Hot-pressing process with corresponding process steps including press-force (blue), temperature (red), correction (black), uncorrected (grey) and corrected densification profile (green) of the CNT/Al_2O_3-composite

a homogeneous slurry, which was frozen in liquid nitrogen, freeze-dried and sieved to produce appropriate granules. For pressureless sintering, disks were pressed by uniaxial die pressing, debinded and sintered in argon atmosphere.

Hot-pressing was conducted by debinding the granules before densification in a graphite die under varying pressure and temperature in argon.

Developing an optimal debinding process was one of the most challenging tasks during the project. On one side the organic additives had to be removed without any residue, on the other side, the CNTs must not be thermally deteriorated. Even the hot press route required debinding, because the CNT-suspension included high amounts of organic dispersants, which had to be removed to enable good densification during sintering. To achieve complete burn-out of the organics, debinding in air at the highest possible temperature was conducted because debinding in an inert atmosphere would have led to carbon residues in the material.

The intensive research showed that, dependent on the alumina powder, varying debinding temperatures are necessary to enable complete burn-out of the organics without deteriorating the CNTs [4].

An exemplification of a conducted hot-pressing process is shown in Fig. 2 for hot-pressing under 80 kN at 1550 °C. The pressure was applied during the heating process at a temperature of 1200 °C. By means of an integrated dilatometer, it was possible to monitor and optimise the densification process. Therefore, a correction (black curve) was measured showing the thermal and elastic deformation of the die. This correction was used to correct the measured dilatometer curve (grey curve), leading to the actual densification profile of the material (green curve).

The visualised hot-press procedure, shown in Fig. 2, can be separated in seven steps:

1: Evacuation, purging with argon
2: Heating up to 1200 °C (pyrometer measurement from 1100 °C)
3: Applying pressure
4: Heating under pressure
5: Dwell time
6: Reducing pressure
7: Cool-down.

Results

Fig. 3 a shows the achieved relative densities dependent on the applied pressure and the CNT-content for TM-DAR-based composite ceramics. Fig. 3 b summarises the relative densities of TM-DAR (T) and CT 3000 SG (C) based ceramics dependent on CNT-content and sinter temperature (1450 °C or 1550 °C) under 80 MPa applied pressure. It can be seen that CNTs drastically impede the densification of the composites. If pressureless sintering is conducted, dense ceramics (>95 % RD) are achievable for 0,25 mass-% and 0,5 mass-% CNTs respectively. Hot-pressing under 80 MPa enables the production

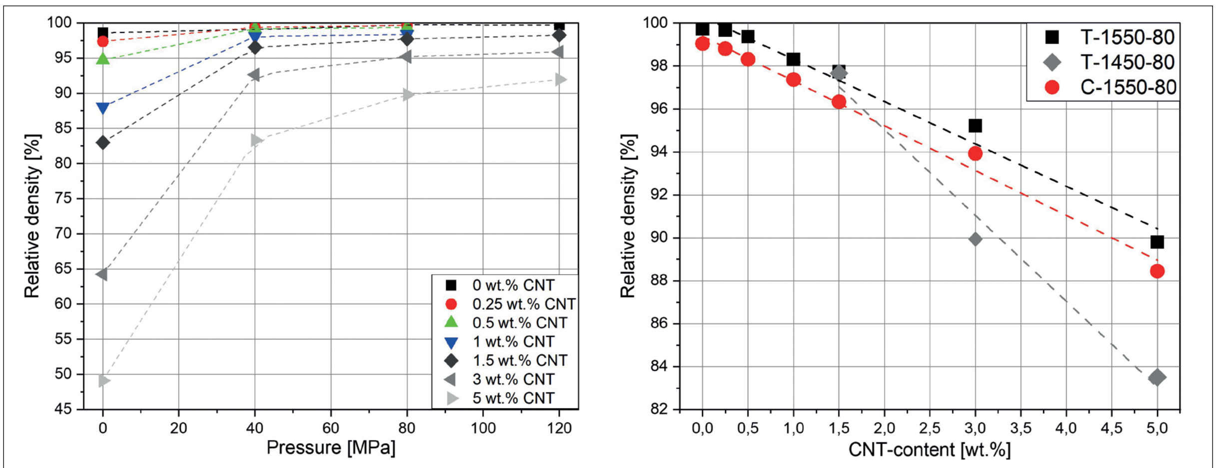

Fig. 3 a–b **Achieved relative densities dependent on the applied pressure and CNT-content in TM-DAR-based composites (a); and relative densities in dependency of CNT-content, sinter temperature and alumina matrix under constant pressure of 80 MPa (b)**

of dense CNT/alumina-composites up to 3 mass-% CNTs. TM-DAR-based composites lead to a higher density compared to CT 3000 SG-based composites produced under equal parameters.
Fig. 4 shows a SEM-image of CNTs in a pore of a 3 mass-% CNT-containing composite.
Mechanical properties, like hardness and fracture toughness, are presented in greater detail in [5]. Lower CNT-contents (up to 1 mass-%) increase hardness up to 20 %, whereas, higher CNT-contents lead to a reduction in hardness, which is probably related to the increasing porosity. Furthermore, hot-pressed specimens show a considerable anisotropy of pore geometry and distribution, leading to an anisotropic fracture toughness.
Highly interesting are the results of the electrical conductivity, characterised by four-point measurements, shown in Fig. 5 and published in greater detail in [6]. Even a very low CNT-content of 0,25 mass-% (≈ 0,5 vol.-%) leads to an electrical conductivity of over 1 S/m in CT 3000 SG-based composites. This points towards a percolation threshold of less than 0,25 mass-%, which is the lowest percolation threshold of CNT-reinforced ceramics presented in the literature and proves a very good homogenisation of the CNTs in the alumina matrix.
In addition to the electrical conductivity, thermal conductivity of the composites was investigated by a Laserflash Method (LFA). Because of the outstanding thermal conductivity in CNTs, which can be as high as 3000 W/m·K for MWCNTs, it could be assumed that the addition of CNTs into an alumina matrix will lead to an overall increase in thermal conductivity.

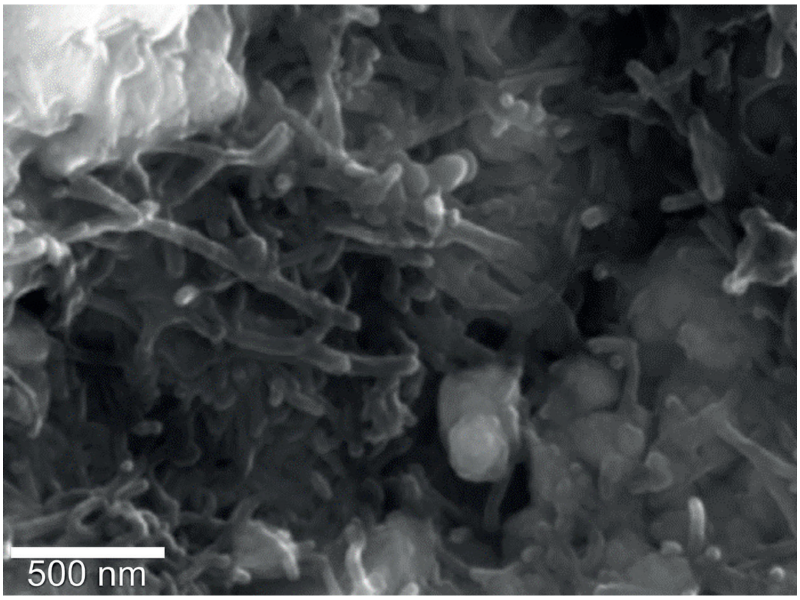

Fig. 4 CNTs in a CNT/Al_2O_3-composite

Since the CNTs lead to a reduction in relative density of the ceramic influencing the thermal conductivity in a negative way, samples with a constant CNT content (3 mass-%) and different densities (produced with different pressures) and samples with a constant density (98,5 % RD) and different CNT content were produced in order to be able to determine the isolated influence of the CNTs without being distorted by different porosities. The investigations showed that the CNTs lead to a significant reduction in thermal conductivity even at constant relative density (Fig. 6), which disagrees with the previously mentioned assumption.
The reason for this phenomenon was found by SEM-characterisation of the microstructure showing a considerable fining of the grains in the microstructure caused by CNTs. Such a grain fining leads to an increase in the number of grain boundaries considerably impeding thermal conductivity through the material. These results as well as the anisotropic behaviour of the electrical and thermal conductivity are intensively reported in [6].

Summary

CNT-reinforced alumina ceramics can be a highly interesting material for the produc-

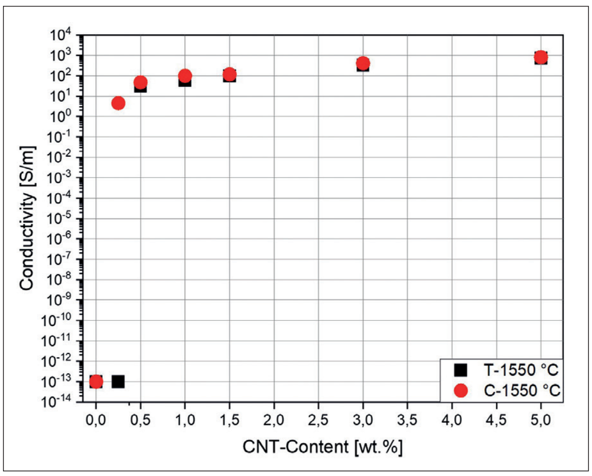

Fig. 5 Electrical conductivity dependent on CNT-content and alumina matrix

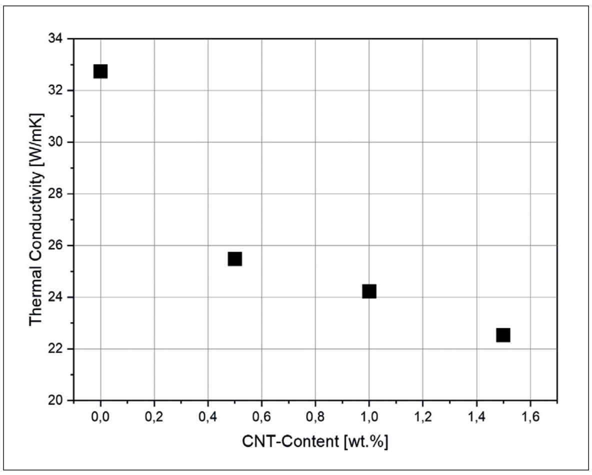

Fig. 6 Thermal conductivity dependent on CNT-content at constant relative density

tion of electrically conducting ceramics. One particular reason is the very low amount of CNTs (0,25 mass-%), which is necessary to change the insulating to an electrically conducting behaviour. Such low CNT-contents enable the production of dense ceramics with accordingly good mechanical properties under appropriate effort. These composites could be used to realise interesting applications. For instance, elimination of electrical charges in combination with very high hardness and wear resistance or ceramic ignitors or as electrode material in critical environments. Also, the possibility of Electrode Discharge Machining (EDM) is a big advantage provided by electrically conductive ceramic composites.

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