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RESEARCH ARTICLE

Electrical and thermal conductivity of CNT/alumina-nanocomposite ceramics

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Abstract

In the present work, carbon nanotube (CNT)-reinforced alumina nanocomposite ceramics were investigated about their electrical and, for the first time in such detail, thermal conductivity. Therefore, two different alumina powders with varying CNT-contents were processed by pressureless sintering and hot pressing to achieve CNT/alumina composite ceramics with varying porosity and CNT-content between 0 and 5 wt.% CNTs. A significant influence of the grain size on percolation threshold of the electrical conductivity was detected. The coarser CT 3000 SG-based ceramic showed a threshold of <0.25 wt.%, which is the lowest reported threshold in literature. Pore orientation in the hot-pressed materials shows a significant influence on the electrical and thermal conductivity of the composite, causing anisotropic properties. Both, electrical and thermal conductivity are higher parallel to the pore structure and perpendicular to the press-direction, respectively, with electrical conductivity being up to three times and thermal conductivity up to 30% higher parallel to the pore structure. Unlike electrical conductivity, thermal conductivity decreases significantly with increasing CNT-content. As two influences, CNT-content and porosity, interact, each of them was analyzed separately in order to measure the isolated influence of CNT-content on thermal conductivity at constant porosity. It was shown, that thermal conductivity decreases considerably with increasing CNT-content even at constant porosity, because of a disturbed crystal structure due to a finer grain structure with more grain boundaries. This behavior is contrary to the expected, and sometimes reported, effect of CNTs. The combination of an increasing CNT-content and the related increase in porosity causes a strongly decreasing thermal conductivity of the material from 35 W/m•K for pure alumina to 10 W/m•K for alumina with 5 wt.% CNTs. The presented results in this and other previously published investigations from the authors show that CNT/alumina-nanocomposites have the potential of combining outstanding mechanical properties and electrical conductivity, which can be used as high performance electrically conductive ceramic material for a wide range of applications.

KEYWORDS
alumina, carbon nanotube, electrical properties, nanocomposite, thermal properties

1 | INTRODUCTION

Ceramic materials generally exceed the properties of metals in terms of hardness, wear-resistance, temperature, and chemical resistance. An important disadvantage of ceramic materials, caused by their distinct hardness and brittleness, is the expensive and time-consuming post-processing after sintering. Electrical discharge machining (EDM) is one possibility for postprocessing, but electrical conductivity of the ceramic material is required. In this perspective electrical insulation can be seen as a disadvantage. Furthermore, in some applications, electrical conductivity is desirable, for example, where electrical charge dissipation is necessary or if electrical currents have to be transferred in a very demanding environment.

One possibility for combining mechanical properties of ceramic materials with electrical conductivity is the production of composites. Beside metallic particles, carbon nanotubes (CNTs) were used as a second phase in CNT/ceramic-composites because of their outstanding mechanical properties and exceptional electrical conductivity[1–4]. Furthermore, the high aspect ratio of CNTs is the reason why a small amount of CNTs, 20 times lower than spherical metallic particles[5], is sufficient to form a connected network of CNTs in the insulating ceramic matrix. Al_2O_3, as matrix material, is highly interesting because it combines good mechanical properties, chemical and temperature resistance, relatively high thermal conductivity and comparatively low price. Because of that, the combination of Al_2O_3 as a matrix material and CNTs as reinforcing second phase might enable the production of a material with outstanding mechanical properties and high electrical and thermal conductivity.

As a consequence of the mentioned aspects, Al_2O_3 as a matrix material for CNT/ceramic-composites was intensively researched in the last decades, including a variety of more or less extensive production methods. Some of the reported results show improved mechanical properties, whereas others do not show such considerable improvements. These discrepancies in mechanical properties are caused by different production methods, pretreatments, but also varying raw materials, applied measurement techniques, and evaluation processes, as it was shown, investigated, and discussed by the authors in previous publications[6,7].

Beside the numerous investigations about the influence of CNTs on mechanical properties, electrical properties of CNT/Al_2O_3-nanocomposites were investigated by a few research groups. Even if there are not that many reported investigations about the electrical properties of CNT/ceramic-composites[8–13] significant differences regarding the influence and the grade of improvement of the electrical conductivity, caused by the addition of CNTs, are reported.

As already mentioned for mechanical properties, varying production processes, raw materials, and applied measurement procedures might also be the reason for such significant discrepancies between the reported electrical properties. For instance, varying characterization methods for electrical properties, like two- or four-point measurement or impedance spectroscopy, can cause such a considerable deviation of the results. The percolation threshold as one important electrical parameter can be used as an exemplification for this problem. The characteristically percolation threshold is defined as the critical CNT-content, at which the electrical conductivity increases by several orders of magnitude and the electrical behavior changes from an electrically insulator to an electrically conductor.

In the context of investigations about CNT/ceramic-composites, Shi et al. reported a CNT-content of 0.64 vol.% double walled CNTs in $MgAl_2O_4$ as the characteristical percolation threshold[14]. Note that 0.79 vol.% as the percolation threshold of multi walled CNTs (MWCNTs) in alumina was reported by Ahmad et al.[5]. A CNT-content between 1.0 and 2.0 wt.% MWCNTs in yttria-stabilized tetragonal polycrystalline zirconia (3Y-TZP) as the point of percolation was reported by Rul et al.[15]. Based on these results, it can be seen that the type of CNTs (SWCNT or MWCNT), as well as matrix materials and production methods are important factors, which make the results hardly comparable.

The mentioned investigations show that the percolation threshold can vary strongly dependent on the used materials and the processing. Due to the lack of investigations about the influence of CNTs on the electrical properties of CNT/ceramic-nanocomposites, it is not possible to forecast, at which CNT-content a change in the electrical behavior occurs, or when the best combination of electrical and mechanical properties can be achieved.

Even less research was conducted about thermal properties of CNT/Al_2O_3-composites. Kumari et al. reported an 228 % increase in thermal conductivity for spark plasma sintered CNT/Al_2O_3-composites with 7.39 wt.% CNTs compared to pure alumina[16]. On the other side, Zhan and Sarkar[10,13] reported no improvement in thermal conductivity of their spark plasma sintered or pressureless sintered composites. Solely one result about the influence of the measured orientation on thermal diffusivity in SWCNT/Al_2O_3-composites, containing 10 vol.% SWCNTs, is provided by Zhan and co-workers[10], which leads to the question if an anisotropic behavior of the described properties is possible.

To enable a better interpretation of the results, common standard models for thermal conductivity in porous materials are used as fundamental theories. Beside the simplified *parallel* model, models and relations according to Maxwell-Eucken[17], Landauer[18], and Russell-Rayleigh[19,20] are considered. A more detailed description of the theoretical models can be found in the Supplementary Information.

Even if the influence of pores on the thermal conductivity can be seen as the most important influence, grain size (GS) and grain boundaries in ceramics are also influencing the conductivity of the solid material as described by Smith and co-workers[21]. Furthermore, a dependency of thermal grain boundary conductivity from relative density (RD) is mentioned by Smith. Note that >99.8 % pure and almost 100% dense alumina show a thermal conductivity of 35 W/mK, which decreases with increasing porosity. The thermal resistivity of grain boundaries in fully dense alumina is 1.3×10^{-8} m^2KW^{-1}, whereas grain boundary resistivity increases to 2.2×10^{-8} m^2KW^{-1} at 70% density. A possible explanation, given by Smith and co-workers, is related to the statistics of grain-boundary types in alumina and the crystallographic misorientation.[21]

The aim of the present research is the production of CNT/Al_2O_3-composites with improved mechanical properties, shown in previous publication[7], combined with improved electrical and thermal properties. Because of that, the following research investigates the influence of CNTs on the electrical properties of CNT/Al_2O_3-composites, such as percolation threshold and direct current (DC) conductivity. Furthermore, investigations about thermal conductivity of the composites and a variety of influences, like CNT-content and RD are conducted. Another issue, which is investigated in this publication, is the orientation of pores, generated during hot pressing, parallel and perpendicular to the hot press direction and their influence on electrical as well as thermal conductivity.

2 | MATERIALS AND METHODS

The detailed production and development process of the investigated samples and composites was reported in previous publications[6,7]. Based on the previously published results, the following characterizations were executed.

Particularly, RDs, microstructure, and mechanical properties were adopted from the previous publications and provide a basis for the following research about electrical and thermal properties of the produced CNT/Al_2O_3-nanocomposites. Figure 1 gives a short overview about the production process and previously published investigations.

For the production of the composites two different alumina powders, TMDAR (Taimei Chemicals, Japan), named as T, and CT 3000 SG (Almatis GmbH, Germany), named as C, and a CNT-suspension (Future Carbon GmbH, Germany) were used as raw materials for the production of the composites. More detailed information about the used materials can be found in the Supplementary Information.

In the following sections of the publication, the structure of the name, representing the corresponding composites, is A-1111-XXX. A represents the type of alumina (T or C), 1111 the hot press temperature in°C and XXX is used for additional information like measured direction.

2.1 | Microstructure

The investigations about microstructure and GS of the composites were conducted based on SEM (JCM-6000, JEOL GmbH) images of thermally etched and carbon coated samples. Thermal etching was executed in argon (Ar 4.8) for 30 min at 1500°C for CT 3000 SG-based composites and 30 min at 1400°C for TM-DAR-based composites. SEM images were converted into a suitable format for a digital microscope software (KEYENCE VHX-6000 version 2.8.0.110, software version 2.02), which enabled an automated calculation of the average GS including geometrical standard deviation (GSD). More than 150 grains of each composition were considered, and no correction factor was used for the GS because a comparable shape of the alumina grains in CT 3000 SG and TM-DAR was assumed.

2.2 | Electrical properties

If no other information is given, all samples for the investigation of the electrical properties were hot-pressed at 1550°C and 80 MPa applied pressure.

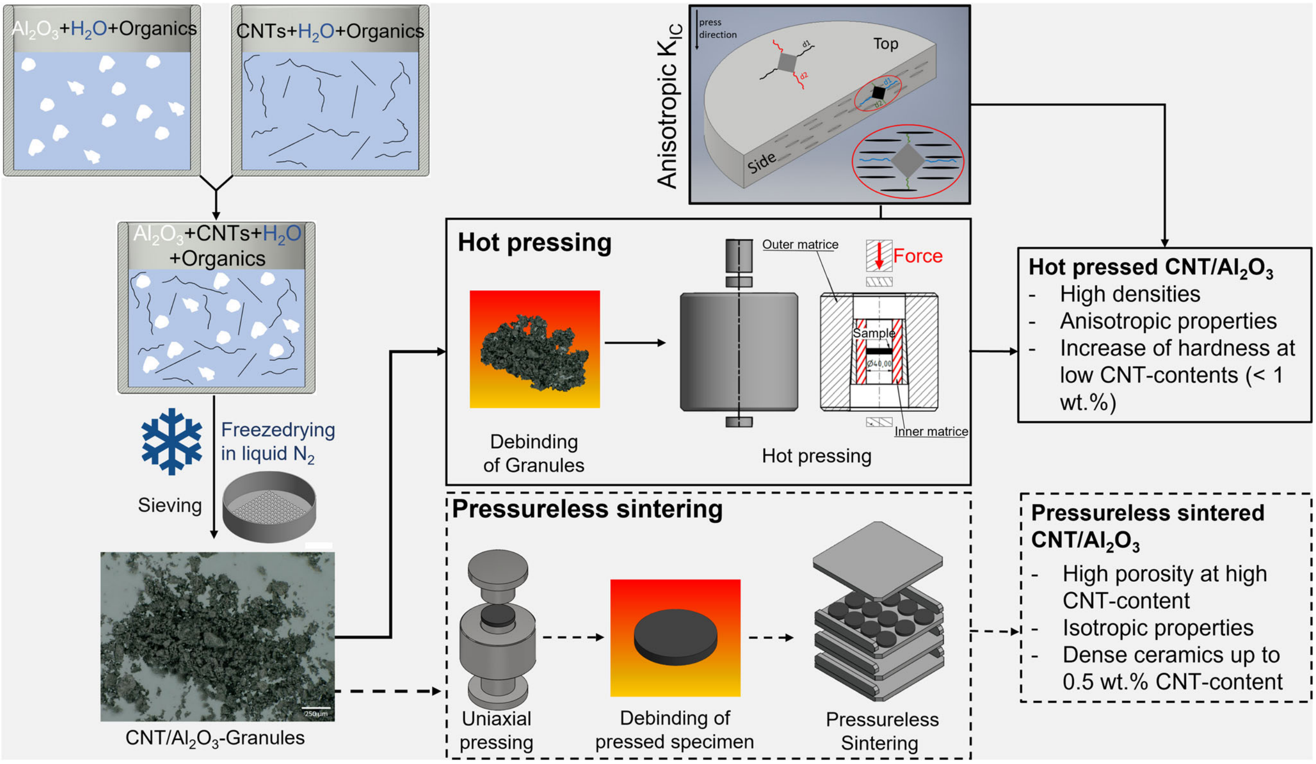

FIGURE 1 Production route and fundamental results of carbon nanotube (CNT)/Al_2O_3-composite ceramics[6,7]

The electrical conductivity of the composites was characterised by four-point measurements and can be seen as the DC conductivity (σ_{DC}). Prior to the conductivity measurements, the disk-shaped samples were ground and polished. For the orientation dependent characterisation samples were cut into cubes with a side length of 15 mm ±0.2 mm. All sides were ground and polished before the measurement to enable a reliable comparison between all the results. Subsequently, samples were stored in a drying chamber for at least 24 h to prohibit moisture or dirt on the characterised surfaces.

For the four-point measurements a device with a pin-distance of 1.5 mm was used (PSP, Loresta-Series, NH Technology GmbH). A measurement current of 10 mA was applied by a 6220 Precision Current Source (Keithley Instruments, Ohio) and controlled by a Prologix GPIB Configurator software. The applied contact force between the pins and the sample was constant and controlled by the measurement device. Every position was measured 20 times and the corresponding voltage was recorded by a 2182A Nanovoltmeter (Keithley Instruments, Ohio). Each of the 20 measurements is based on three separated measurements, which were automatically executed with a change in polarity in-between the single measurements to prevent any influence of the polarity or electrical charging on the measured voltages. The average value of the measured voltages was used to calculate the resistivity and conductivity by Ohmťs law, including correction factors referring to Smits[22].

If the detectable voltage exceeded the measurable range of the device, an *overflow* was detected. If so, the conductivity of the composite was assumed as 10^{-13} S/m. This value represents the limit of the measurement device and can be seen as an approximation but should not be considered as absolute value.

Two orientations, *SIDE* and *TOP*, were investigated to detect the influence of the orientation, which was generated during hot-pressing (HP) of the samples. The orientation of the originally disk-shaped sample is shown in Figure 1. The schematical setup for the four-point measurements, with the two investigated directions, is visualised in Figure 2. The introduced nomenclature (Figure 2) will be used throughout the publication to describe the measured parameter in the corresponding direction.

2.3 | Thermal properties

The thermal conductivity (λ) of the produced CNT/TM-DAR-composites was measured by a laser flash system (LFA 457 MicroFlash, Netzsch GmbH, Germany). A neodym-glass laser and a laser-voltage of 1538 V was used. A laser expansion of 12.7 mm was applied by 100 % transmission of the laser-system. Each sample was measured

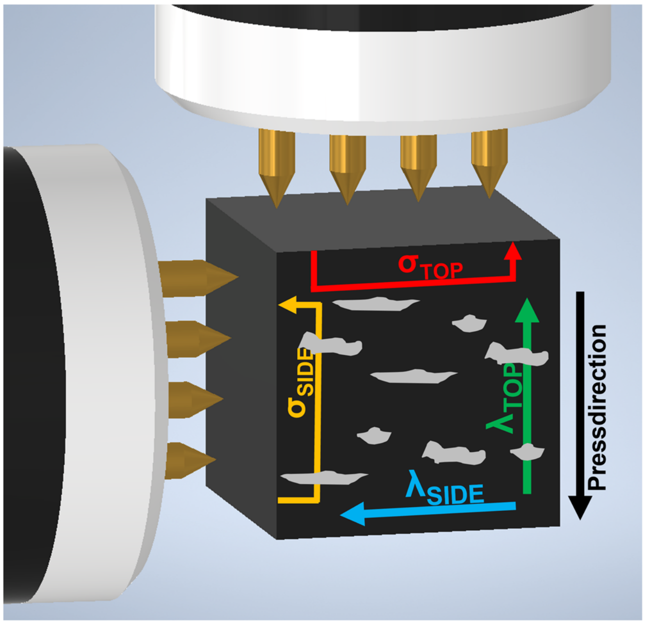

FIGURE 2 Setup for four-point measurements, including description of the two different measurement directions (SIDE and TOP) of the electrical (σ) and thermal conductivity (λ), dependent on the hot-press direction. The grey areas symbolize pores in the composite.

five times and the average value was calculated to define the thermal conductivity of each material by the following equation.

$$\lambda = a \cdot \rho \cdot c_p$$

λ is the thermal conductivity, a is the temperature conductivity measured by the LFA, ρ represents the density measured by Archimedes method and c_p is the thermal capacity, measured by LFA and compared to a sapphire standard. Furthermore, the radiation-model in the software was used to correct the measured values.

For the measurements, squared samples, side length of 8 mm and 2 mm height, were cut from the hot-pressed disks before grinding and polishing. Sample coating with graphite spray (Cramolin Graphite, ITW LLC Co) on both sides was executed before the measurements were conducted in air at room temperature.

3 | RESULTS

3.1 | RDs

As already mentioned, RDs of the samples were presented in a previous publication[7]. Because of the strong influence of the densities on the following characterisations and properties, the densities are depicted in Figure 3. More

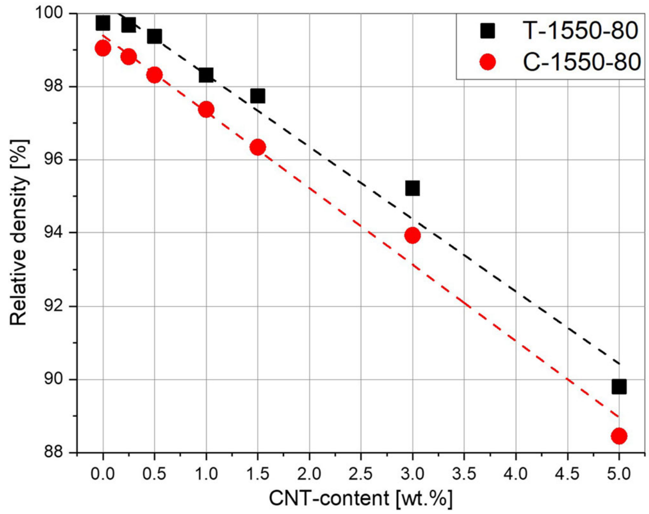

FIGURE 3 Relative densities of hot-pressed composites (1550°C and 80 MPa) dependent on carbon nanotube (CNT)-content and alumina matrix

details about the achieved densities can be found in the Supplementary Material.

3.2 | Microstructure

The following Figure 4 shows the taken SEM images of the thermally etched microstructures at appropriate magnifications, dependent on the GS of the microstructure. Figure 4A–D shows the microstructure of TM-DAR-based composites with a comparable density of 98.5 % ±0.3 %, which were hot pressed at varying pressures and varying CNT-contents. Figure 4E,F shows CT 3000 SG and TM-DAR-based composites with 0.25 wt.% CNTs.

The detected GS, including processing parameters, RD, GS, and GSD, are summarized in Table 1. A decrease in GS by approximately eight times, from 2.15 μm for pure TMDAR to 0.26 μm for TM-DAR including 1.5 wt.% CNTs, was detected in composites with a varying CNT-content and a comparable RD. The addition of 0.25 wt.% CNTs in TM-DAR led to a decrease in GS by four times. The measured GS in the coarser CT 3000 SG composite, containing 0.25 wt.% CNTs, is 1.5 times bigger compared to the finer TM-DAR composite including the same amount of CNTs.

3.3 | Electrical conductivity

Electrical conductivity of the CNT/alumina-composites was measured in dependency of CNT-content and alumina matrix. The following σ_{TOP}-measurements were conducted after polishing and drying the samples. Figure 5 shows the electrical conductivities for TM-DAR-(T) and

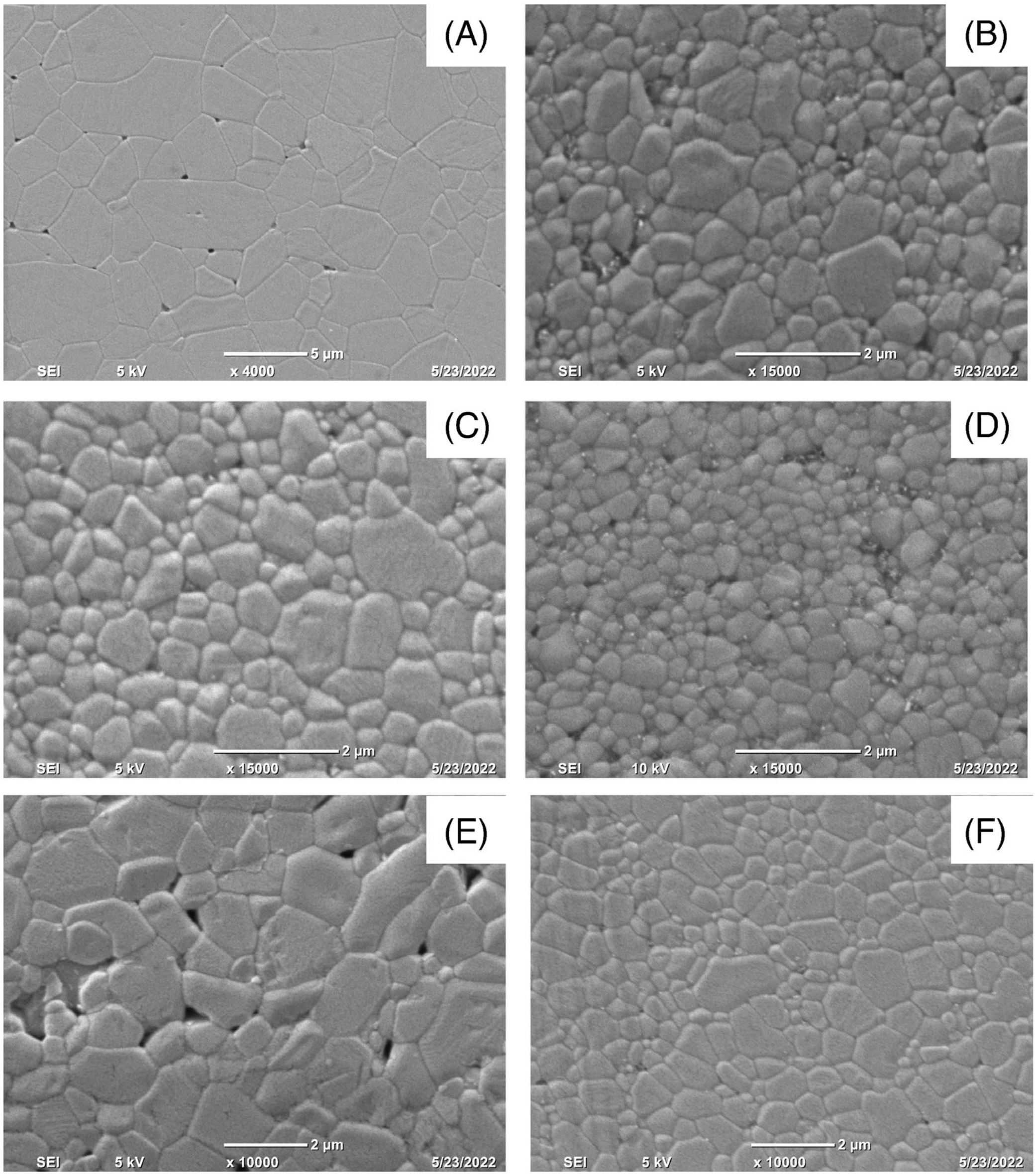

FIGURE 4 (A–D) Microstructure of TM-DAR-based composites hot-pressed at varying pressures resulting in a comparable density of 98.5% ±0.3% in all of the depicted composites (A–D). (A) 0 (B) 0.5 (C) 1.0, and (D) 1.5 wt.% carbon nanotubes (CNTs), for details, see Table 1. (E and F) Microstructure of (E) CT 3000 SG- and (F) TM-DAR-based composites including 0.25 wt.% CNTs.

TABLE 1 Detected grain size (GS) including geometrical standard deviation (GSD) of the produced composites, dependent on matrix material and CNT-content. Microstructures 1–4 are depicted in Figure 4A–D, microstructures 5–6 in Figure 4E,F

Matrix	CNT-Cont. (wt.%)	HP pressure (MPa)	RD (%)	GS (μm)	GSD
TM-DAR	0	0	98.8	2.15	1.75
TM-DAR	0.5	25	98.4	0.40	1.65
TM-DAR	1.0	80	98.3	0.36	1.62
TM-DAR	1.5	120	98.4	0.26	1.48
CT 3000 SG	0.25	80	98.8	0.78	1.62
TM-DAR	0.25	80	99.7	0.53	1.63

Abbreviations: CNT, carbon nanotube; RD, relative density.

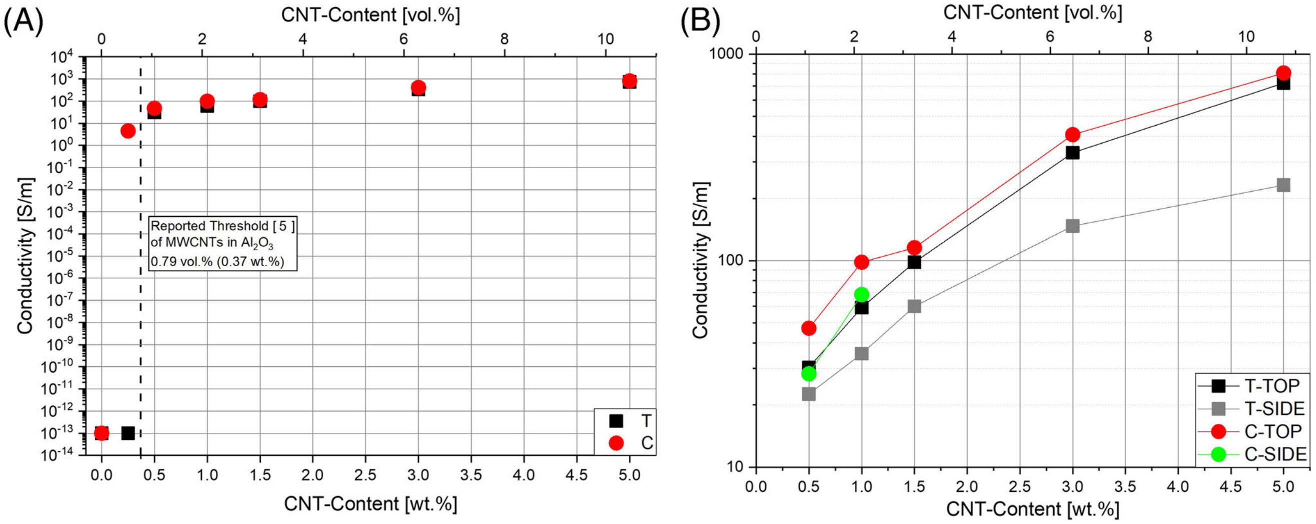

FIGURE 5 (A) Electrical conductivity (σ_{TOP}) of the hot-pressed carbon nanotube (CNT)/alumina-composites in dependency of CNT-content and alumina matrix, measured on TOP surface of the samples. (B) Electrical conductivity in dependency of the measured direction (σ_{TOP}, σ_{SIDE}), CNT-content, and alumina matrix

CT 3000 SG-(C)-based composites, which were hot pressed at 1550°C with 80 MPa.

In Figure 5A, the percolation threshold referring to Ahmad and co-workers[5] is visualized at a CNT-content of 0.79 vol.% (≈0.37 wt.%). This particular percolation threshold was chosen from literature because it was detected for MWCNT/alumina-composites and is the most appropriate value for comparing the results of this research to others.

For both alumina materials without CNTs (0 wt.%), the resistance is too high to be measured, and the electrical conductivity is assumed as 10^{-13} S/m. If the CNT-content increases to 0.25 wt.%, the CT 3000 SG-based composite shows an increase in electrical conductivity by several orders of magnitude compared to pure CT 3000 SG, whereas the comparable TMDAR-based composite does not show any increase in conductivity. At a CNT-content of 0.5 wt.%, TM-DAR-based composites show a several orders of magnitude higher electrical conductivity compared to pure alumina. Even if both composites changed their behavior from an insulating material to an electrically conductive material at a CNT-content of 0.25 wt.% and 0.5 wt.%, respectively, the conductivity of TM-DAR-composites for all CNT-contents is slightly lower than it is in CT 3000 SG-composites.

In addition to σ_{TOP} (Figure 5A), the conductivity of the composites was also measured in press-direction (σ_{SIDE}). For TM-DAR-based composites CNT-contents in the range between 0.5 wt.% and 5 wt.% were characterized.

CT 3000 SG-based composites were investigated at CNT-contents between 0.5 wt.% and 1 wt.%. The comparison of the direction-dependent results is depicted in Figure 5B. It can be seen that for both alumina matrices σ_{TOP} -values are considerably higher than σ_{SIDE}-values. Furthermore, it can be detected that the discrepancy between the two directions increases with increasing CNT-contents, but in both directions CT 3000 SG-based composites (C) show a higher conductivity than TM-DAR-composites (T).

3.4 | Thermal conductivity

In the following section, the thermal conductivities (λ) of the investigated CNT/TM-DAR-composites are summarized. Separated diagrams will be shown to enable the isolated detection of varying influences, such as CNT-content, RD, and anisotropy. In some of the figures, two diagrams are shown beside each other. In these related diagrams different colors symbolize different composites, whereby one color represents the same composite in both.

The thermal conductivity λ_{TOP} of the equally hot-pressed samples (1550°C, 80 MPa), dependent on CNT-content (Figure 6A) and RD (Figure 6B) is shown. Pure and dense (99.82 % RD) TM-DAR shows a thermal conductivity of approximately 35 W/mK, which is comparable to literature values. A significant decrease in thermal conductivity at increasing CNT-contents can be detected. As all samples were produced under the same HP-conditions, RD decreases with increasing CNT-contents. So, there are two interacting influences on thermal conductivity: CNT-content and RD. To enable the separation of these influences, further characterizations were conducted.

The isolated influence of the RD is shown in Figure 7, which depicts λ_{TOP} of compositions with a constant CNT-content of 3 wt.%. The samples were produced under varying pressures during pressureless sintering (0 MPa at 1550°C) or hot pressing (40, 80 or 120 MPa at 1550°C),

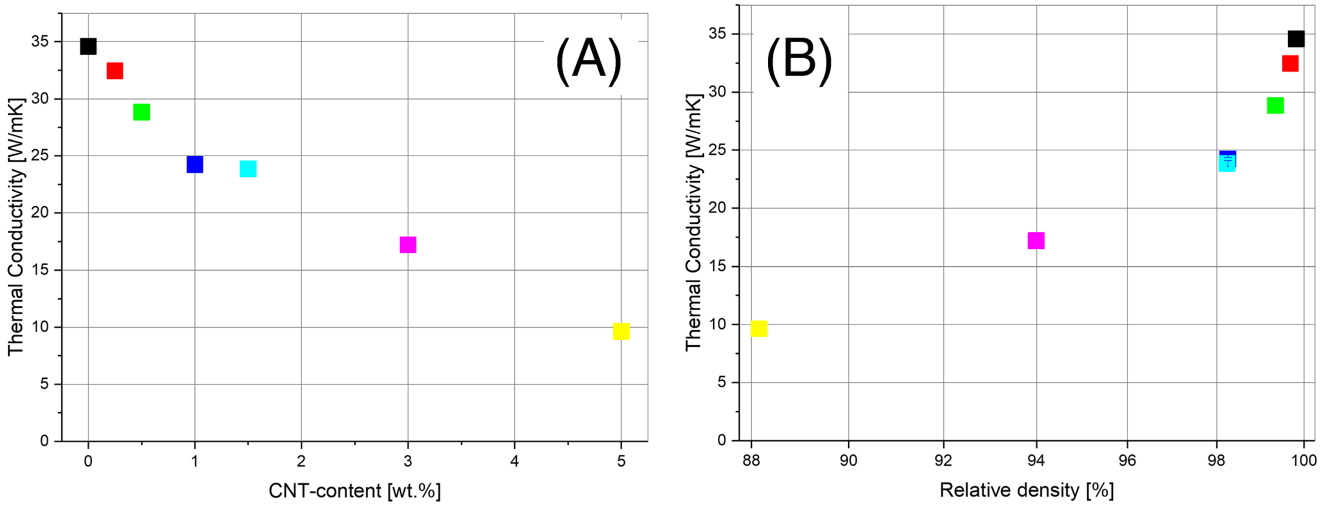

FIGURE 6 Thermal conductivity (λ_{TOP}) of equally hot-pressed carbon nanotube (CNT)/alumina-composites in dependency of the (A) CNT-content and (B) relative density.

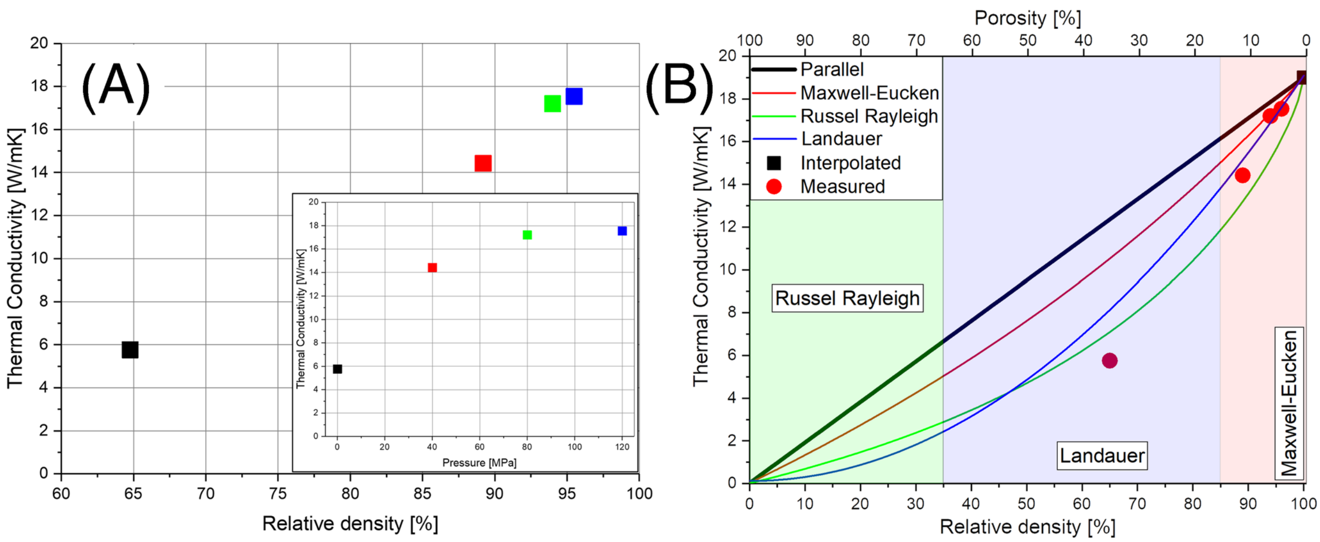

FIGURE 7 Thermal conductivity (λ_{TOP}) of carbon nanotube (CNT)/alumina-composites with a constant CNT-content of 3 wt.% dependent on (A) the relative density and the applied pressure (inserted diagram) during pressureless sintering (0 MPa) or hot pressing; (b) comparison of the measured thermal conductivity (λ_{TOP}) to different concepts of thermal conductivity in porous materials.

which resulted in varying densities. The main diagram in Figure 7A depicts λ_{TOP} in dependency of the RD. In the inserted diagram λ_{TOP} in dependency of the applied pressure is shown. A significant decrease in thermal conductivity with increasing porosity is the expected result.

Furthermore, a comparison between λ_{TOP} of the 3 wt.% CNT-content composites and the described concepts for thermal conductivity in porous materials is shown in Figure 7B. A thermal conductivity of 0.026 W/mK was assumed for pores and a thermal conductivity of 19 W/mK for the fully dense composite. The value for the fully dense composite with a 3 wt.% CNT-content was calculated by interpolation of the measured results. These two values were used for the calculation of the expected values for each of the depicted concepts. The best agreement between measured and predicted values, even if considerable deviations are detected, can be seen if the Landauer model[18], which describes thermal conductivity in materials with an open and connected porosity, is used.

To enable the detection of the isolated influence of CNTs on the thermal conductivity, without influence of RD, four composites with almost equal RDs (98.5 % ±0.3 %) were produced. Table 2 shows the CNT-content, production parameters and the achieved RDs of the samples. The detected λ_{TOP}-values are also included in Table 2 and visualized in Figure 8. It can be seen that the increase

TABLE 2 CNT-content, production parameters, and relative densities of CNT/TM-DAR-composites for the detection of the isolated influence of CNTs on the thermal conductivity (λ_{TOP}) of CNT/alumina-composites sintered at 1550°C

CNT-Cont. (wt.%)	HP pressure (MPa)	RD (%)	λ_{TOP} (W/mK)
0	0	98.8	32.7
0.5	25	98.4	25.5
1.0	80	98.3	24.2
1.5	120	98.4	22.5

Abbreviations: CNT, carbon nanotube; HP, hot-pressing; RD, relative density.

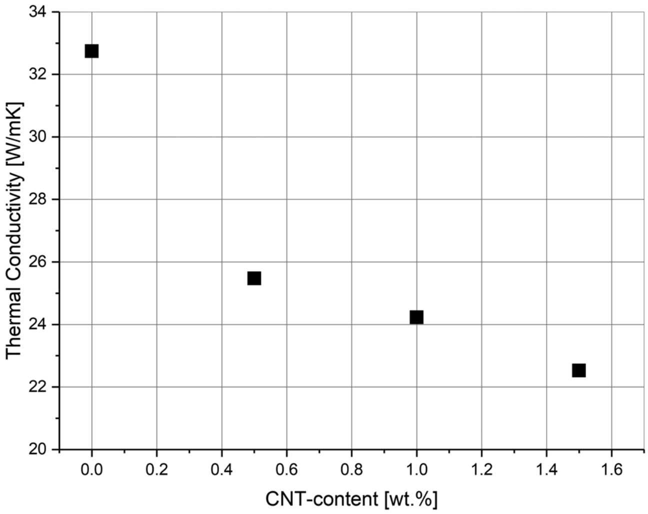

FIGURE 8 Thermal conductivity of carbon nanotube (CNT)/alumina-composites with a comparable relative density of 98.5 % (±0.3 %) and varying CNT-contents.

in CNT-content from 0 to 1.5 wt.% causes a significant decrease in thermal conductivity of the material, even if the RDs are almost equal.

As described in Figure 2, thermal conductivity was characterized in two directions, λ_{TOP} and λ_{SIDE}. Figure 9A shows the thermal conductivities dependent on the CNT-content and (B) RD for both directions. It is remarkable that in both diagrams all λ_{SIDE}-values are higher than λ_{TOP}. This tendency is independent of CNT-content or RD. Furthermore, the discrepancy between λ_{TOP} and λ_{SIDE} increases with an increasing CNT-content and decreasing RD. These results show an anisotropic behaviour of thermal conductivity in hot-pressed CNT/alumina-composites.

4 | DISCUSSION

Before the presented results about the electrical and thermal conductivity are discussed it should be noticed that in previous investigations, the debinding and sinter process of the investigated composites was intensively researched.

The previous investigations about the produced composites showed that different debinding temperatures, dependent on the alumina matrix, are necessary to prohibit a thermal degradation of the CNTs[6]. Because of the known influence and the adapted production process, it is assumed that the CNT-content in both alumina matrices is the same, and the composites can be reliably compared. In the following discussion the electrical properties will be discussed before the results for the investigated thermal conductivity are interpreted.

4.1 | Electrical properties

Like expected both of the investigated alumina ceramics did not show any electrical conductivity at room temperature if no CNTs were added. If the CNT-content increases to 0.25 wt.%, the electrical conductivity of the CT 3000 SG-based composite increases by several orders of magnitude, whereas the electrical conductivity of the TM-DAR-based composite is still too low and not measurable. This deviation of the electrical conductivity of the two composites points toward a deviating percolation threshold. Such a variation in the percolation threshold can hardly be caused by the production process because both composites were debinded at appropriate temperatures and hot pressed under the same conditions. Based on that, it can be assumed that the percolation threshold must be defined by the alumina powder and the final microstructure itself.

Referring to the datasheets of the manufacturer, CT 3000 SG, as the coarser alumina powder, has a surface area of 7.5 m^2/g and a particle size (D_{50}) of 0.5 μm. TM-DAR on the other side has a surface area of 15 m^2/g and a D_{50} of 0.15 μm. This deviation in primary particle size caused different GSs in the sintered material after HP. Evidence for this assumption is presented in the SEM-images in Figure 4E,F. The SEM-images show 1.5 times bigger grains in CT 3000 SG-composites compared to TM-DAR composites.

If CNTs are homogeneously distributed over the alumina particles, a considerably higher amount of CNTs is required to cover all TM-DAR grains compared to the amount of CNTs needed to cover the coarser CT 3000 SG grains. This phenomenon can be detected at a CNT-content of 0.25 wt.%. At this particular CNT-content no conductivity in TM-DAR-based composites is detectable because the amount of CNTs in this composite is insufficient to form a connected network and conduct the electrical charges through the insulating matrix. In CT 3000 SG, on the other hand, a connected network of CNTs can be formed at lower CNT-contents, which is responsible

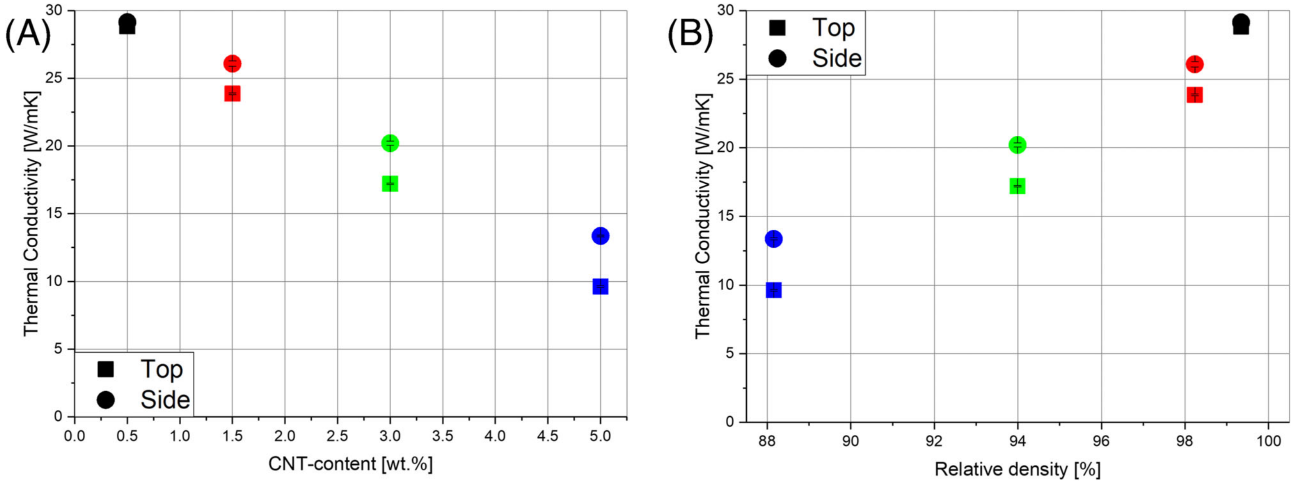

FIGURE 9 Thermal conductivity of carbon nanotube (CNT)/alumina-composites dependent on the measured direction (λ_{TOP}, λ_{SIDE}), for varying (A) CNT-contents and (B) relative densities.

for the transition of an insulating material to an electrical conductor, like it happens at the percolation threshold.

As far as we know, a particle-size dependency of percolation threshold in CNT/alumina-composites was not reported before and is an important parameter. The reason for its importance is the fact, that if an electrically conductive CNT/alumina-composite with optimal mechanical properties has to be produced, a high RD is essential, which is more likely at low CNT-contents, as previous investigations showed[7]. However, the CNT-content must be sufficient to reproducibly enable the formation of a connected CNT-network, which depends on the primary particle size and the resulting GS of the alumina ceramic, as shown in the presented results.

Compared to the illustrated percolation threshold of 0.37 wt.%, reported by Ahmad et al.[5], the produced CT 3000 SG-based composites show an even lower threshold. Furthermore, the detected percolation thresholds reported in this research, which are comparable to other reported values in the literature, prove that the CNT-content did not significantly decrease during the production process of the composites as it was assumed before, and, once more, the importance of an appropriate debinding and sintering process must be highlighted.

To our knowledge, the percolation threshold of the 0.25 wt.% CNT-containing CT 3000 SG-based composites, reported in this investigation, is the lowest detected percolation threshold in CNT/alumina-composites. This result is clear evidence for a homogeneous CNT-distribution in the produced composites. Furthermore, an increasing amount of pores decreases the conductivity of the CNT/alumina-composites because pores in general impede electrical conductivity. This effect was confirmed in the direction-dependency of the electrical conductivity. Based on the presented results, it can be seen that σ_{TOP}-values are exceeding σ_{SIDE}-values. This correlation is caused by the production process and the generated pore structure during hot pressing. Like depicted in Figure 2, the current in σ_{TOP}-measurements flows perpendicular to the press-direction and does not have to cross as many porous sections of the material as the σ_{SIDE}-current, leading to a higher conductivity in this direction.

4.2 | Thermal properties

As mentioned in the results section, thermal conductivity decreases with increasing CNT-content, which seems to be surprising because of the extraordinarily high thermal conductivity of CNTs. The reasons for this will be elaborated in the following paragraphs.

Figure 7 shows a decreasing thermal conductivity (λ_{TOP}) for increasing CNT-contents in composites, which were produced under equal conditions. It must be taken into account that two influences overlap, and it can hardly be said which one dominates. Nevertheless, pure and dense alumina showed a thermal conductivity of about 35 W/mK, which agrees to literature values and validates the measurement procedure and can be used as a reference.

λ_{TOP} for composites with a constant CNT-content of 3 wt.% CNTs and varying RDs show an improvement in the thermal conductivity if the RD increases. However, even at a density of more than 98% RD, a thermal conductivity of less than 18 W/mK was measured. This is rather surprising because pure and dense alumina shows a higher thermal conductivity of 35 W/mK. Based on that, it can be assumed that CNTs significantly decrease thermal conductivity in such composites. Also, the comparison to the described models about thermal conductivity in porous materials showed that the Landauer model could describe the behavior in the best way, however significant deviations between the measured values and the model are detected, which means that the porosity itself cannot explain the decrease in thermal conductivity. This assumption was proven by the investigation about the isolated influence of varying CNT-contents in composites with constant porosity, which confirmed a significant decrease in thermal conductivity at increasing CNT-contents.

Based on these results, it can be said that CNTs do not improve the thermal conductivity in our composites. One reason for the decrease in thermal conductivity at increasing amounts of CNTs is the disturbance of the alumina crystal structure by the embedded CNTs. Thermal conduction in pure alumina is caused by lattice vibrations which are conducted through the solid bulk material. These lattice vibrations can be scattered, reflected, or refracted at grain boundaries or other lattice defects, and, thereby, reduce thermal conductivity, even if the RD is constant. Evidence for such impeding mechanisms in the produced composites is provided in the SEM-images (Figure 4A–D), which show a considerable decrease by eight times in GS if 1.5 wt.% CNTs are embedded in the alumina matrix compared to pure alumina. An increase in CNT-content prevents grain growth even more and causes lower GSs and hence much more obstructive grain boundaries in composites with higher CNT-contents. Furthermore, even if single (MW) CNTs show high thermal conductivity, the connection points between CNTs are limiting their ability of electrical and thermal conduction.

The fact that an increasing CNT-content has the same effect on thermal conductivity as an increasing porosity, leads to an enforced influence and the disproportional decrease of thermal conductivity in CNT/alumina-composites compared to pure alumina, which explains the detected behavior shown in Figure 7.

Compared to the previously discussed λ_{TOP}-values, λ_{SIDE}-values show increased thermal conductivity in this direction. It is assumed that the GS in both directions is isotropic, and because of that the anisotropic influence of varying GS can be ignored. However, two direction-dependent influences might explain the detected behaviour, whereby one of them clearly dominates.

First, the pressure during hot pressing might lead to an orientation of CNTs in the composite. As proven in this investigation, CNTs conduct electrons, which can also be the reason for thermal conduction. Even if this fundamental mechanism is possible, previous investigations by the authors did not show a considerable orientation of the CNTs in the composite. Because of that, the influence of a potential CNT-orientation on the anisotropy of thermal conductivity can be neglected.

Second, during hot pressing an anisotropic pore-structure is generated in the composite as it was shown in greater detail in a previous publication[7]. Pores impede electrical as well as thermal conductivity, and, based on that, a pore orientation anisotropically influences the electrical conductivity of the produced composites but also the mechanical properties, as shown in this and previous investigations. Based on the gained knowledge about the anisotropic pore-structure, it is assumed that the anisotropic porosity is the most important influence when it comes to anisotropic thermal conduction in hot pressed CNT/alumina-composites.

5 | CONCLUSIONS

In this study, the electrical and thermal conductivity of CNT/alumina-composites were researched dependent on a variety of influences. The most important results are summarized in the following points.

1. The electrical conductivity of CNT/alumina-composites depends on the primary powder particle size and the following GS of the alumina matrix after sintering. Especially, the percolation threshold can vary for different alumina matrices because of the higher or lower amount of CNTs, necessary to form a connected CNT-network and thereby enable charge transfer through the insulating matrix. In this work, a percolation threshold of <0.25 wt.% of CNTs in CT 3000 SG-based composites was identified, which is the lowest in the literature of CNT/alumina-composites. Furthermore, the electrical conductivity of the composites is anisotropic due to an anisotropic pore structure. An increase in CNT-content increases the porosity and thereby enforces the anisotropic behavior in electrical conductivity.
2. Characterization of the isolated influence of CNT-content and porosity on thermal conductivity showed that for increasing CNT-contents at constant porosity, as well as for increasing porosity at constant CNT-content, a significant decrease in thermal conductivity occurs. A combination of both enforces the influence on the thermal conductivity even more and is present in the produced composites. It was found that an increase in CNT-content impedes grain growth and leads to finer GSs in composites with higher CNT-contents. The result of a finer GS is a disturbed crystal structure through grain boundaries, which causes a decrease in thermal conductivity of CNT/alumina-composites even at constant porosity. Also, an anisotropic thermal conductivity is detected for hot pressed CNT/alumina-composites in a way that the thermal conductivity parallel to the pores is significantly higher. The anisotropy of the thermal conductivity increases with

increasing CNT-contents and is rather caused by anisotropic pore structure than CNT-orientation.

The investigated CNT/alumina-composites provide a good possibility of combining outstanding mechanical properties with electrical conductivity. However, thermal conductivity decreases as soon as CNTs are embedded in the alumina matrix. Because of that, CNT/alumina-composites should be considered as modifiable high-performance materials for several applications, especially because low CNT-contents (<0.5 wt.%) are sufficient for high electrical conductivity, where very high densities with accordingly very good mechanical properties are achievable.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest that could be perceived as prejudicing the impartiality of the research reported.

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