The effect of graphite addition on thermal conductivity, microstructure, and electrochemical impedance spectroscopy of AlN ceramics

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Graphite/aluminum nitride (AlN) multiphase ceramics are pressureless sintered under 1850 °C using Dy2O3 and CaF2 as sintering additives. The effects of added graphite on microstructure, thermal conductivity, and electrochemical impedance spectroscopy of AlN ceramics were investigated. It was found that with 1wt% graphite addition the thermal conductivity of AlN in the through-plane can achieve 210 W/(m·K), which 25% higher than that of AlN without graphite. The graphite addition eliminates the oxygen impurity in AlN by a carbon reduction reaction in form of nanosized Dy2O3 particles. From electrochemical impedance spectroscopy manifested that the activation energy ($E_{a,g}$) of samples in grains is increased from 0.784 to 1.112 eV, suggesting that the concentrations of defects and impurities of Graphite/AlN multiphase ceramics are lower than those of monophase AlN ceramics.

Introduction

With the development of integrated circuits, power modules, energy units, and advanced package structures, the volume of the electronic component keeps getting smaller leading to an improvement heat density of devices [1, 2]. Higher thermal conductivity materials attract attention to solving the heat dissipation problem of Electronic component devices [3, 4]. AlN ceramics are deemed to be an up-and-coming candidate for the application of high temperature structural materials in electronic devices because of high thermal conductivity, good matching of thermal expansion coefficient to that of silicon, excellent dielectric property and mechanical properties [5–10]. The thermal conductivity of AlN ceramics is closely related to the content of oxygen impurities in the powder. The effect of oxygen impurities on AlN samples was researched by Slack et al. [10–13], which could be described by the following equation:

$$\text{Al}_2\text{O}_3 \rightarrow_{3\text{AlN}} 2\text{Al}_{\text{Al}} + 3\text{O}_N + V_{\text{Al}}^{'''} \quad (1)$$

The oxygen atom is incorporated into the AlN lattice to replace the N atom, forming aluminum vacancies. It has been widely recognized that phonon conduction is the thermal conduction mechanism of AlN [14–17]. The movement of phonons is influenced by the scattering of aluminum vacancies [18–20]. Therefore, the thermal conductivity of AlN samples is greatly limited by aluminum vacancies.

Doping sintering additives is considered to be an effective approaching that can fabricate high thermal conductivity AlN ceramics. Non-oxide additives, alkaline earth oxides and rare earth oxides are commonly adopted to be sintering additives for AlN ceramics [21–23]. In general, sintering additives mainly improve the thermal conductivity of AlN ceramics through two ways: During the sintering process, sintering additives can promote the densification of AlN ceramics by forming a liquid phase. Due to the reaction with sintering additives, oxygen impurities are fixed at the grain boundary as interphase newly formed [24, 25]. The amount of aluminum vacancy decreases when the diffusion behavior of oxygen impurities into the AlN lattice is restrained [26, 27].

Unfortunately, common sintering additives can prevent oxygen impurities from diffusing into the AlN lattice, but it does not reduce the oxygen content of the AlN ceramics. The excessive grain boundary phase might enhance the relative contact area between the grain boundary phase and the AlN grains. This
situation would bring about declining of the thermal conductivity of the AlN sample [28–30]. The secondary annealing method is often used to anneal the AlN samples for reducing the oxygen content in the AlN ceramics and eliminating the influence of the grain boundary on the thermal properties of the AlN ceramics [31–33]. Watari et al. found that the thermal conductivity of the AlN samples was effectively enhanced by heat treatment using the graphite furnace [34, 35]. The reduction atmosphere was produced in the graphite furnace at a high temperature. The oxygen content and thermal conductivity of the samples were improved by the carbothermal reduction, which was further confirmed by Koji [36] et al., Kim et al. [37] and Jiang et al. [38].

Compared with traditional ceramics, multiphase ceramics have unique properties and applications due to the integrating advantages of every composite phase [39], such as Yang et al. [40] fabricated Si₃N₄/SiC multiphase ceramics with different sintering additives and found the SiC crystal grains that existed in the β-Si₃N₄ grain boundary can avoid overgrowth of β-Si₃N₄ grains and enhance the flexural strength of the sample. Carbon materials have good thermal and electric properties, high temperature stability, and reduce properties leading to extensively the addition in the multiphase materials, and adjusted properties of materials [41]. Besides, the research about graphite as additives used in multiphase ceramics has also made some progress. For example, Sun et al. [42] indicate that graphene effectively adjusted the dielectric properties of graphene-silicon carbide ceramics. The microstructure, phase compositions, and mechanical properties of Si₃N₄/SiC multiphase ceramics are also changed by graphene [43].

In the present work, the graphite/AlN multiphase ceramics with high thermal conductivity were fabricated by pressureless sintering with aid of Dy₂O₃ and CaF₂. The experimental results indicate that addition of graphite can reduce the oxygen content and aluminum vacancy concentration, purify the lattice and grain boundary, resulting in an obvious enhancement of thermal conductivity of the AlN sample. Moreover, the electrochemical impedance spectroscopy of the graphite/AlN multiphase ceramics were characterized to study the relevant mechanism of thermal conductivity of AIN ceramics under the condition of graphite.

**Results and discussion**

**Phase compositions evolution of AIN/graphite ceramics**

The AlN was exhaustively researched by XRD. Figure 1 shows the XRD diffraction pattern of samples sintered at 1850 °C for 2 h and 12 h. All samples have the hexagonal AlN phase as the master phase, matching a purple vertical line that represents the standard PDF card of JCPDS#25–1133. The grain boundary phase of samples sintering for 2 h mainly was constituted of Dy₃Al₅O₁₂ (DAG phase). Sintering at 1850 °C for 12 h, the second phase of the graphite-free AlN sample transformed to Dy₂O₃ and Dy₄Al₂O₉ (DAM phase), but only the Dy₂O₃ phase existed in the graphite-doped AlN sample. During the preparation period of the AlN ceramic, the Dy₂O₃ first reacted with the Al₂O₃ layer on the AlN surface to form the DAG phase. The DAG phase gradually converted into the DAM phase during the

![Figure 1: XRD patterns of Graphite/AIN multiphase ceramics: (a) the sample C₅ sintered at 1850 °C for 2 h; (b) the sample C₅ sintered at 1850 °C for 2 h; (c) the sample C₅ sintered at 1850 °C for 12 h; (d) the sample C₅ sintered at 1850 °C for 12 h.](image-url)
long-term holding temperature process. Lastly, the DAM was reduced to the Dy$_2$O$_3$ phase by the graphite. The reaction equations are noticed as 2, 3, 4, and 5 [29]. All samples were sintered in a graphite resistance furnace in this experiment. Hence, some Dy$_2$O$_3$ phases are also found in the graphite-free AlN sample.

$$3\text{Dy}_2\text{O}_3 + 5\text{Al}_2\text{O}_3 \rightarrow 2\text{Dy}_3\text{Al}_5\text{O}_{12} \text{(DAG)}$$ (2)

$$\text{Dy}_3\text{Al}_5\text{O}_{12} + \text{Dy}_2\text{O}_3 \rightarrow 5\text{DyAlO}_3 \text{(DAM)}$$ (3)

$$2\text{DyAlO}_3 + \text{Dy}_2\text{O}_3 \rightarrow \text{Dy}_4\text{Al}_2\text{O}_9 \text{(DAP)}$$ (4)

$$\text{Dy}_4\text{Al}_2\text{O}_9 + 3\text{C} + \text{N}_2 \rightarrow 2\text{Dy}_2\text{O}_3 + 2\text{AlN} + 3\text{CO} \uparrow$$ (5)

The secondary phase of graphite/AlN ceramic is constituted of rare-earth (Dy) compounds and graphite due to the non-volatile properties of their on the high temperature [6, 32, 35]. The compounds of the Ca element will be volatilized in the ceramic sintering process [13, 28] and hardly found in the XRD pattern. The secondary phase of the sample can be changed using the reduced property of graphite at a high temperature [34, 43].

**The effect of graphite addition on the thermal conductivity of AlN ceramics**

The Dy$_2$O$_3$ and CaF$_2$ as the sintering aids can improve the sample's relative density and thermal conductivity from Fig. 2. Our previous work has studied the specific efficacy of those sintering aids in the AlN sintering process [44]. The influence of graphite and holding time on the thermal conductivities of graphite/AlN multiphase ceramics is further explored in this work. As shown in Fig. 2(b), the thermal conductivity of graphite/AlN ceramics first increases and then decreases as holding time extended.

The sample at sintered 12 h has the highest thermal conductivity. Besides, the thermal conductivity of samples is effectively improved by doping graphite. For example, the thermal conductivity of ceramics sintered at 1850 °C for 12 h was enhanced from 169 W/(m·K) to 210 W/(m·K) when 1 wt% graphite was added in samples.

The AlN ceramics with 0 wt%, 0.1 wt%, 0.5 wt%, 1 wt%, 1.5 wt%, and 2 wt% graphite was sintered at 1850 °C for 12 h. Sintering additives are obviously enhanced the relative density and thermal conductivity of AlN compared to the sample of none sintering additives. The effects of the graphite incorporation on the density and thermal conductivity of samples are displayed in Fig. 3. It was clear that the relative densities of graphite/AlN ceramics kept almost theoretical value when the contents of graphite were less than 1.5 wt%. In contrast, it decreased drastically to 92% when graphite content attained...
2.0 wt%. Meanwhile, the thermal conductivity of graphite/AlN raised to 210 W/(m·K) when graphite addition attained 1 wt%, followed by a sharp decline to 125 W/(m·K) as the graphite content reached 2 wt%.

The microstructure of AlN/graphite ceramics

Figure 4(a) to (l) showed the microstructure and grain size of the addition of different content graphite to the sample. The sintering additives and alumina formed the second phase randomly distributed at the grain boundary in the graphite-free AlN as the grain boundary phase [Fig. 4(a)]. The grain size is increased with 0.1 wt% graphite addition in Fig. 4(b) and (h). This result may be due to the small amount of graphite reducing the pinning effect of the sintering additives [45]. As known in Fig. 4(b), (h) to Fig. 4(d), (j), the grain boundary phase is gradually replaced by graphite, and the grain size of the sample is reduced, with the ratio increase of graphite in the AlN ceramic. Excessive graphite forms a large number of agglomerations and pores in the AlN ceramic, causing a detrimental effect on the grain growth and ceramics densification [Fig. 4(e), (k), (f), (l)]. Therefore, the appropriate amount of graphite can eliminate the grain boundary phase and improve the thermal conductivity in the sintering process of aluminum nitride ceramics. However, graphite agglomeration is observed in the AlN ceramics with graphite content further enhanced, resulting in the sharp decrease of the thermal conductivity and relative density of AlN samples. This phenomenon is because graphite powder might be negative to the densification process of AlN because of harmfully affecting material diffusion in the AlN sintering process. The optimal content of graphite in the AlN samples was 1 wt%. The sample has the highest thermal conductivity and relative density at this time.

The element evolution of the graphite-doped sample was observed from ESD mapping image (See Supplementary Materials file for details). The grain boundary phase was mainly composed of the hardly volatile secondary phase formed by Dy₂O₃ and Al₂O₃. In general, the equation for the reaction of Dy₂O₃ with Al₂O₃ was shown in Eq. 6:

\[
\frac{y}{2} \text{Dy}_2\text{O}_3 + \frac{x}{2} \text{Al}_2\text{O}_3 \rightarrow \text{Al}_x\text{Dy}_y\text{O}_{3(x+y)/2}
\]

(6)

Al₂DyₓO₃ₙ₋ₓ/₂ is the dysprosium aluminate produced by the reaction of Dy₂O₃ with Al₂O₃, such as Dy₃Al₅O₁₂(DAG), Dy₄Al₂O₉(DAM), and DyAlO₃(DAP). The graphite can decrease the content of oxygen impurities by reverting the Al₂DyₓO₃ₙ₋ₓ/₂ phase. In the preparation of ceramics, oxygen impurities were formed the grain boundary by combining with Dy₂O₃ or dissolved in the AlN lattice producing Al vacancies. The aluminum vacancies are closely linked with the oxygen impurities amount and have an essential effect on the thermal conductivity. The graphite can effectively improve the thermal conductivity of AlN ceramics by the carbothermal reduction reaction at the grain boundary.

Figure 4: The microstructure and grain sizes evolution of different graphite content AlN sample sintered at 1850 °C for 12 h: (a) and (g): C₀; (b) and (h): C₀.1; (c) and (i): C₀.5; (d) and (j): C₁; (e) and (k): C₁.5; (f) and (l): C₂.
The phase contains Ca element hardly found in the AlN samples because of CaF$_2$ and Ca$_x$Al$_{y}$O$_z$ (such as CaAl$_6$O$_7$, CaAl$_{12}$O$_{19}$, and CaAl$_2$O$_3$) will be volatile from the AlN ceramics in the sintering process [7, 35]. The XRD pattern result indicates that the compound containing the Ca element has not existed in the sample. The element distributes situation (See Supplementary Materials file for EDS mapping images) of the samples C$_0$ and C$_1$ are verified the conclusion of XRD patterns. The compound about Ca element is hardly detected by XRD and EDS.

To further investigate the influence of graphite on the microstructure and element distribution of grain boundary, the grain boundary of AlN ceramics is characterized by TEM and EDS. Figure 5(a) shows the grain boundary area containing graphite. The FIB technique fabricates the AlN HRTEM (High-resolution transmission electron microscopy) foil which is employed for the TEM test. The specific microstructure is discovered in Fig. 5(b). In particular, the bright white area in Fig. 5(b) center is hollow, which may have been produced in the process of AlN foil fabricated using FIB. The EDS line scan characterizes the element distribution at the grain boundary. The element distribution situation along with two lines is found to be similar. In Fig. 5(c), the element on both sides is mainly

**Figure 5:** Element distribution in the grain boundary of the sample C$_1$ sintered at 1850 °C for 12 h: (a) the SEM of AlN/C grain boundary; (b) the TEM of AlN/Graphite grain boundary; (c) the all element distribution; (d) the special element distribution details at the green area in the (c).
aluminum and nitride, and the element of the middle area is carbon. The detailed distribution about oxygen, dysprosium, and calcium elements at the grain boundary between graphite and AlN grains is observed in Fig. 5(d). The Ca element is hardly found at the grain boundary. Scanning from left to right along the line in Fig. 5(d), the enrichment region of the O element was first observed in the grain boundary. Besides, the enriched area of the Dy element is found.

The O enrichment region was closer to the AlN grains, and the Dy enrichment region was more adjacent to the graphite. During the AlN sintering period, the $\text{Al}_x\text{Dy}_y\text{O}_{3(x+y)/2}$ was first formed by the reaction between $\text{Dy}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$. Then $\text{Al}_x\text{Dy}_y\text{O}_{3(x+y)/2}$ was reduced by the graphite. The carbothermal reduction reaction reduces the oxygen content around the graphite. Thus, the O and Dy enriched areas have some differences. The nearer it was to graphite, the smaller the content of the O element, which has the existing step concentration in the grain boundary. During the sintering process, oxygen impurities diffused towards the grain boundary and produced a grain boundary phase with $\text{Dy}_2\text{O}_3$. The grain boundary phase was finally reduced by graphite at the grain boundary through the carbothermal reduction reaction, cutting down the amounts of oxygen impurities. Therefore, graphite can reduce the oxygen impurities at the grain boundary, purify the lattice and grain boundaries, and improve thermal conductivity.

The microstructure of the AlN with the addition of 1 wt% graphite was observed by TEM. The morphology and structure of grain and grain boundary of AlN ceramics were observed by HRTEM from Fig. 6. A large amount of flake graphite existed between AlN grains, which was further confirmed as the graphite-2H by the SAED (selected area electron diffraction) pattern, according to Fig. 6(c). The structure and crystal lattice of graphite were hexagonal structure and $P_6_3mc$ (194), respectively. The standard card PDF corresponding with graphite-2H is PDF#04–006-5764. The SAED pattern of AlN grain was also observed from Fig. 6(b). The structure and crystal lattice of AlN were hexagonal structure and $P_6_3mc$ (186), respectively. The standard card PDF corresponding with AlN-Wurtzite is PDF#04–003-5900.

Figure 6(a) shows a high-resolution grain boundary image. This area consisted of three parts. The lattice image of the left crystal phase was that of graphite, the interplanar spacing was 0.333 nm, and the direction was along the (100) crystal plane. The right lattice image was AlN phase, the interplanar spacing was 0.248 nm, and the direction was along the (002) crystal plane. There were also some thin amorphous layers between the graphite particles and the AlN grains [Fig. 6(a)] green dotted line region). A small number of nanocrystals were discovered in this amorphous layer, as shown in the red dotted line region of Fig. 6(a). The lattice image of the nanocrystal grains indicated $\text{Dy}_2\text{O}_3$, the interplanar spacing was 0.266 nm and 0.229 nm, and the direction was index as the (400) and (332) crystal plane, respectively.

Graphite is not only transformed the secondary phase of the sample but also has a key role to affect the relative density, thermal conductivity, element content and microstructure at
the grain and grain boundary [5, 14, 26]. The speed of grain growth and grain boundary migration is controlled using graphite by changed matter diffusion and element concentration at the grain boundary, during the AlN sintering process [12, 20]. This is important to fabricate fully densified ceramics. The thermal conductivity of AlN ceramic is related to grain boundary phase [30, 36] and the oxygen impurity content [15, 33, 46]. The grain boundary phase and oxygen impurity will be eliminated by graphite using a reduced reaction [22, 30, 37]. The sample has high relative density, excellent thermal conductivity (210 W/(m·K)), and low oxygen impurity content with 1 wt% graphite addition.

The mechanism of graphite addition influencing the properties of AlN ceramics

The mechanism that graphite improved the thermal conductivity of AlN ceramic was discussed in Fig. 7. The content of $V_{\text{Al}}''$ has a significant effect on thermal conductivity. The $V_{\text{Al}}''$ was produced by oxygen doping to AlN lattice. With the use of sintering additive in the ceramic preparation process, the oxygen impurities were formed grain boundary phase with sintering additives and hardly diffused into the AlN lattice. However, the grain boundary has a lower thermal conductivity than AlN. The defects might exist in the grain boundary in the process of grain boundary phase production. The grain boundary phase also has

![Figure 7: The schematic diagram of microstructural evolution of AlN ceramics: (a) without graphite and (b) with graphite.](image-url)
a disadvantage to the thermal conductivity increase of the sample. The grain boundary phase and defects were eliminated using graphite by the carbothermal reduction reaction [33, 34, 37], as shown in Fig. 7(b). According to previously researched, the oxygen impurity in the AlN ceramic was discharged as the modality of CO by the cycle of $Dy_2O_3 \rightarrow DAG \rightarrow DAM \rightarrow Dy_2O_3$.

The influence of graphite addition on the impedance spectroscopy of AlN ceramics

The impedance spectroscopy of the AlN sample was measured in a frequency of 0.1 Hz ~ 1 MHz in temperature ranging from 350 to 650 °C (Fig. 8). The different regions of the samples (AlN grains, grain boundaries, and electrodes) were associated with varying RC elements from the impedance spectroscopy. The impedance data of AlN was fitted employing the equivalent circuits containing two parallel R|CPE and an CPE, according to arcs of $Z'–Z''$ plots and brickwork layer model [13, 46]. $R_g$ and $R_{gb}$ represent the resistance of AlN grain and AlN grain boundary. CPEg and CPEgb are the capacitance with non-ideal behavior to accurately represent the behavior of AlN grain regions and AlN grain boundary. CPEe is the capacitance with non-ideal behavior related to electrodes [47]. $Z_{CPE}$ is given Eq. (7) [28, 37, 49]:

$$Z_{CPE} = \frac{1}{(j\omega)^n Y_0}$$  \hspace{1cm} (7)

where $n$ is an empirical exponent that varied from 0 to 1. The value of $n$ for the ideal resistor and capacitor is 0 and 1, respectively.

Figure 9 shows the conductivity charged with the testing temperature which follows i the Arrhenius equation (Eq. 8). And the activation energy ($E_a$) of the AlN can be calculated from the slope of the curves in Fig. 9:

$$\sigma = \sigma_0 \exp \left(\frac{-E_a}{k_B T}\right)$$ \hspace{1cm} (8)

where $\sigma_0$ is the high-temperature limit of conductivity, $E_a$ is the activation energy, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature.

The grain conductivity ($\sigma_g$) and grain boundary conductivity ($\sigma_{gb}$) are calculated from Eqs. 9 and 10:

$$\sigma_g = 1/\rho_g = t/R_g \cdot S$$ \hspace{1cm} (9)

Figure 8: Complex impedance spectra ($Z'–Z''$) of the sample $C_0$ and $C_1$ sintered at 1850 °C for 12 h measured on: (a) 625 K; (b) 675 K; (c) 725 K; (d) 775 K.
where $S$ and $t$ are the effective electrode area and sample thickness, respectively.

The conductivity mechanism of the AlN grain at high temperature was considered as $V''_{Al}$ conductance [37, 46]. Oxygen impurities dissolved in the AlN lattice and $V''_{Al}$ formed at the same time, according to the defect reaction Eq. (1). The concentration of $V''_{Al}$ importantly affected the $E_a$ and thermal conductivity of the AlN sample. In the grain, the conductivity behavior of the AlN was closely related to the defects and impurities. In graphite/AlN ceramics, the $E_a$ value of the graphite/AlN ceramics is $E_{ag} = 1.112$ eV which is higher than that value ($E_{ag} = 0.784$ eV) of the pure AlN ceramics. Besides, the $E_{agb}$ of graphite/AlN ceramics in grain boundary is 0.608 eV, much smaller than the $E_{agb} = 1.123$ eV value of monolithic AlN ceramics.

Graphite is a common additive of multiphase materials due to its excellent electrical properties [41, 48]. The conductivity of the AlN is associated with the grain boundary phase and the $V''_{Al}$ at grain [28, 37]. The grain boundary phase is replaced with graphite in the graphite/AlN ceramic as previously discussed by SEM, XRD, and TEM. The grain boundary conductivity of graphite/AlN multiphase ceramic is rapidly improved due to the excellent conductivity properties of graphite. This phenomenon suggests that the graphite materials can effectively reduce the $V''_{Al}$ and oxygen impurities in AlN grain, purify grain boundary of AlN sample, thus improving the $E_a$ and thermal conductivity of the sample.

**Conclusion**

Graphite/AlN multiphase sample doped with 1 wt% $\text{Dy}_2\text{O}_3$, 1 wt% $\text{CaF}_2$, and graphite powder was sintered at 1850 °C under the flowing $\text{N}_2$ atmosphere. The sample has the optimal relative density (99.98%), thermal conductivity (210 W/m·K) and microstructure with 1 wt% graphite introducing. Oxygen impurities were discharged from the sample in the form of CO by $\text{Dy}_2\text{O}_3 \rightarrow \text{DAG} \rightarrow \text{DAM} \rightarrow \text{Dy}_2\text{O}_3$ periodic changes. The concentration variation of oxygen impurities and aluminum vacancies in AlN ceramics was further proved by $E_a$ value fitting from AC impedance spectroscopy. The graphite can effectively purify the lattice, clean the grain boundary of AlN ceramic, reduce the concentration of oxygen impurities and aluminum vacancies, and improve the thermal conductivity of the samples.

**Methods**

**Raw materials**

Commercially available AlN powders (Grand E, Tokuyama Soda Co. Ltd., Japan) containing 0.85 wt% oxygen impurities are selected as the raw material. The content of alumina was estimated at 1.81 wt%. The average particle size and the specific surface of the powder are 0.8 μm and 3.4 m$^2$/g, respectively. Graphite powders (96.4%, Cabot Corp., America), whose average particle size is 18 nm, were mixed with the
AlN powder. The morphology of AlN powder and graphite is observed in supplementary materials file. The Dy$_2$O$_3$ (2.93 um, 99.99%, Sinopharm Chemical Reagent Co., Ltd., China) and CaF$_2$ (511.8 nm, 99.99%, Sinopharm Chemical Reagent Co., Ltd., China) were chosen as the binary sintering additives.

Fabrication of the graphite/ aluminum nitride (AlN) multiphase ceramics

The 1 wt% Dy$_2$O$_3$, 1 wt% CaF$_2$, and graphite were blended in the AlN powder. The contents of graphite are 0 wt%, 0.1 wt%, 0.5 wt%, 1 wt%, 1.5 wt% and 2 wt%, as shown Table 1. The absolute ethanol was poured into these powders and ball-milled for 12 h using the planetary ball mill (TENCAN Technology Co. Ltd., China) with alumina balls. After drying in vacuum, the mixed powders were compacted into a pellet of Ф17 mm and 5 mm thickness by uniaxially die pressing, followed by cold isostatic pressing at a pressure of 200 MPa. These samples are densified by pressureless-sintering under 1850 °C for 2–24 h in the flowing nitrogen atmosphere.

Characterizations

AlN ceramic discs were lapped and polished to 12.7 mm in diameter and 2 mm in thickness to measure thermal conductivity. The thermal conductivity of AlN ceramics was measured at room temperature (R.T.) using the Laser Flash Thermal Constants Analyzer (LFA-467, Netzsch, Selb, Germany). The relative densities were determined by the Archimedes method assuming that theoretical density (TD) of AlN ceramics is 3.26 g cm$^{-3}$. Crystalline phases of AlN samples were tested by X-ray diffractometer (XRD, D/MAX-2200, Rigaku, Japan) with a scanning rate of 4° min$^{-1}$. The polishing surface microstructures of the AlN ceramics were observed by the scanning electron microscope (Nova 600 Nanolab, FEI, USA). The normal SEM images were captured under BSE mode, the working distance of 3 mm, the voltage of 5 keV, and the probe current of 8 nA. The EDS patterns were obtained under the same working distance, the voltage of 20 keV, and the probe current of 20 nA. The TEM samples of AlN ceramics were fabricated by the dual-beam focused ion beam microscope (FIB, Nova 600 Nanolab, FEI, USA). The high resolution structural features about grain and grain boundary micromorphology were detected by the transmission electron microscope (TEM, F20 G2, FEI technai, USA). The element distribution at the grain boundary was analyzed with energy dispersive X-Ray spectroscopy (EDS, Oxford Instruments X-MaxN 80 T, Oxford, UK). Electrochemical impedance spectroscopy of the AlN sample was performed from 0.1 Hz to 1 MHz frequency range using Zahner-Elektrik IM6 workstation (Kronach, Germany) and the corresponding software Zahner Thales Z2.2.9. The testing temperature is ranged from R.T. to 700 °C.

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Data availability

The authors declare that all data supporting the findings of this study are available within this published article.

Declarations

Conflict of interest  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary Information

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| TABLE 1: Compositions of prepared AlN samples. |
|-----------------------------------------------|
| Sample composition (mass%)                     |
| Symbol | Dy$_2$O$_3$ | CaF$_2$ | Graphite | AlN |
|--------|-------------|---------|----------|-----|
| C$_0$  | 1           | 1       | 0        | 98  |
| C$_{0.1}$ | 1     | 1       | 0.1      | 97.9|
| C$_{0.5}$ | 1     | 1       | 0.5      | 97.5|
| C$_1$  | 1           | 1       | 1        | 97  |
| C$_{1.5}$ | 1    | 1       | 1.5      | 97.5|
| C$_2$  | 1           | 1       | 2        | 96  |
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