

Effect of AlN content on the properties and microstructure of pressureless-sintered Al₂O₃-AlN composites

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Aluminium oxide (Al₂O₃)-aluminium nitride (AlN) composites were prepared at 1500-1600 °C by pressureless sintering. The main raw materials used were AlN and Al₂O₃, and appropriate amounts of TiO₂-Y₂O₃-CaO-La₂O₃ quaternary sintering aids were added. The effects of different AlN contents and sintering temperatures on the bulk density, bending strength, Rockwell hardness, thermal conductivity, and other properties of Al₂O₃-based ceramics were studied. The phase composition and microstructure of the samples were analysed with an X-ray diffractometer and scanning electron microscope. Results showed that the Al₂O₃-AlN composites had excellent overall performance in terms of a flexural strength of 295.7 MPa, a Rockwell hardness of 61.5 HRA, and a thermal conductivity of 38.8 W/(m·K) (at 25 °C) after pressureless sintering at 1600 °C for 3 h with 10 wt% AlN content. These properties met the requirements of high-power ceramic LED lamp holders. The Al₂O₃-10 wt%AlN composites sintered at 1600 °C had a dense microstructure, tight bonding among grains, and few pores, which explained the excellent performance of the samples.

Key words: AlN, Al₂O₃ ceramics, Pressureless sintering, Thermal conductivity, Microstructure.

Introduction

Al₂O₃ ceramics have excellent physical and chemical properties, such as high strength, hardness, insulation resistance, and corrosion resistance. These ceramics also have the advantages of abundant raw-material sources, low cost, and relatively mature processing and manufacturing technologies. However, the broad application prospects of these ceramics in electronics, electrical appliances, machinery, chemicals, textiles, automobiles, metallurgy and aerospace are limited by their low toughness and thermal conductivity [1-2]. Meanwhile, AlN ceramics have a high thermal conductivity (theoretical thermal conductivity = 319 W/(m·K); actual value = 260 W/(m·K) equivalent to 10-15 times that of Al₂O₃ ceramics). AlN ceramics also have reliable electrical insulation (bulk resistivity > 10¹⁴ Ω·cm), low dielectric constant (about 8.8 at 1 MHz), thermal expansion coefficient matching that of silicon (4.6 × 10⁻⁶ K⁻¹ at 20-500 °C), nontoxicity, and other excellent physical properties. These features enable their extensive use as support substrates in integrated circuits and electronic components, heat-dissipating LED substrates, and electronic substrates for high-temperature semiconductor packages [3-5]. However, single AlN ceramics have low mechanical strength and high

production cost. When AlN and Al₂O₃ are combined to prepare Al₂O₃-AlN composites, their superior performance can be combined to realise their complementary advantages. Al₂O₃ can improve the high-temperature oxidation resistance and mechanical strength of AlN ceramics, whereas AlN can improve the thermal conductivity and high-temperature strength of Al₂O₃ ceramics. Therefore, using suitable methods of preparing Al₂O₃-AlN composites with overall excellent performance, extensive applications in the above-mentioned fields can be achieved.

Hot-press sintering or spark plasma sintering (SPS) technology for fabricating Al₂O₃-AlN composites is extensively researched. For example, Chen et al. [6-7] prepared Al₂O₃-AlN composites through hot-press sintering by using AlN and Al₂O₃ powders as raw materials and Y₂O₃ as a sintering aid. They studied the effects of sintering temperature and Al₂O₃ content on sintering properties, strength, thermal conductivity, dielectric properties, and microstructure. Sahin et al. [8] prepared AlON ceramics by SPS method at 1400 and 1650 °C under N₂ gas flow using Al₂O₃ and AlN powders as raw materials. Li et al. [9] prepared AlON ceramics through SPS method by using Al₂O₃, AlN, and different contents of Y₂O₃ as raw materials and then analysed the ceramics' properties and reaction mechanism. Li et al. [10] prepared Al₂O₃-AlN composites through hot-press sintering at 1600 °C by using high-purity Al₂O₃ and AlN as the main raw materials, adding a certain amount of nano-Al₂O₃ powder. They studied the composites'

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mechanical properties, fracture toughness, density, and other properties. However, these sintering technologies require high operation costs, demonstrate low production efficiency, and produce sintered samples with simple shapes only. The latter significantly hinders the mass production of large-size and complicated-shape components. The use of pressureless sintering process can yield large and complex ceramic products with low production cost and easily achievable large-scale industrial production. Accordingly, pressureless sintering is considered as one of the most promising sintering methods of ceramic-material sintering. Boey et al. [11] studied a system comprising Al₂O₃, 20% AlN, and 5% Y₂O₃ and found that AlON formed only at ≥ 1700 °C. Due to the low thermal conductivity of AlON, its formation is detrimental to the thermal conductivity of Al₂O₃-AlN composites to which it is introduced. Therefore, the key to preparing Al₂O₃-AlN composites is to sinter at low temperatures and thus avoid AlON formation whilst ensuring high density. Maghsoudipour et al. [12-13] prepared AlN-AlON composites by pressureless sintering at 1750-1950 °C, studied their sintering and oxidation behaviours, and found that AlON forms at >1650 °C sintering temperature. In the abovementioned studies, the sintering temperatures mostly exceed 1650 °C, and AlON new phases are easily generated in the system, which is unfavourable to the thermal conductivity of the composites. Additionally, reports on the effect of AlN content on the sintering, mechanical, and thermal properties of Al₂O₃-AlN composites are few.

In the present work, Al₂O₃-AlN composites containing different AlN ratios were prepared at 1500-1600 °C by pressureless sintering. The raw materials used were commercial Al₂O₃ and AlN powders, and appropriate amounts of TiO₂-Y₂O₃-CaO-La₂O₃ quaternary sintering aids were added. The effects of AlN content and sintering temperature on the bulk density, bending strength, hardness, thermal conductivity, and other properties of the sintered materials were discussed. The composition and microstructure of the sintered body were analysed, and the sintering mechanism of the prepared ceramic material was discussed.

Experimental

α -Al₂O₃ powders (2.8 μ m average size and $>99.7\%$ mass percentage; Changsha Huake Special Ceramics Co., Ltd.) and AlN powders (0.5 μ m average size and $>99.5\%$ mass percentage; Shanghai Chaowei Nano Technology Co., Ltd.) were used as the main raw materials. TiO₂-Y₂O₃-CaO-La₂O₃ powders were used as sintering aids. The relative proportion of the initial powder is shown in Table 1. A certain amount of the above raw materials was weighed according to the experimental formulation table and then placed in a mill jar. A certain amount of absolute ethanol was added to the mill jar as dispersion medium. Alumina

Table 1. Compositions of starting powders.

Sample	Al ₂ O ₃ /wt%	AlN/wt%	Y ₂ O ₃ /wt%	CaO/wt%	TiO ₂ /wt%	La ₂ O ₃ /wt%
#1	88.0	5.0	2.5	2.0	1.5	1.0
#2	83.0	10.0	2.5	2.0	1.5	1.0
#3	78.0	15.0	2.5	2.0	1.5	1.0
#4	73.0	20.0	2.5	2.0	1.5	1.0
#5	63.0	30.0	2.5	2.0	1.5	1.0

ceramic balls were used as grinding media, and the mixture was ball milled for 4 h in a planetary ball mill. The slurry was collected and dried in a vacuum-drying oven at 80 °C for 24 h, after which the powder was sifted through a 60 mesh sieve. A certain amount of a poly(vinyl alcohol) (PVA) solution with a mass percentage concentration of 5 wt% was added as a binder. The powder was uniformly mixed with the PVA solution, and the uniformly mixed powder was crushed in a sealed bag for 24 h before being manually granulated through a 30-mesh sieve. The granulated powder was moulded under 100 MPa into a ceramic green body, which was dried at 110 °C for 12 h and then placed in a tube atmosphere furnace. Under flowing nitrogen atmosphere (purity $\geq 99.99\%$; nitrogen flow rate = 1.5 L/min), the temperature was initially increased to 550 °C at a heating rate of 2 °C/min and kept for 2 h to remove organic substances. After raising the temperature to 1500, 1550, and 1600 °C at a heating rate of 10 °C/min held for 3 h, the ceramic sample was naturally cooled to room temperature.

The sintered ceramic sample was cut, ground, and polished, and then its bulk density was measured by the Archimedes method. A universal material performance tester was used to test the flexural strength of the sintered samples. The sample size was processed into 3 mm \times 4 mm \times 36 mm strips. The spans of the specimens were 20 mm, and the loading speed was 0.5 mm/min. The hardness of the sintered samples was determined with a HRS-150 digital Rockwell hardness tester. The thermal conductivity of the samples at room temperature (25 °C) was measured using a DRL-III thermal conductivity meter. X-ray diffraction (XRD) was performed on a TD-3500 X-ray diffractometer to analyse the phase composition of the mixed precursor powder and ceramic sintered bodies. Scanning electron microscopy (SEM) was conducted on a Quanta FEG 250 scanning electron microscope to observe their fracture morphology.

Results and Discussion

Fig. 1 shows the bulk density of ceramic samples containing different amounts of AlN sintered at 1500-1600 °C for 3 h. The bulk density of samples with the same formulation gradually increases with increased sintering temperature. At the same time, the sintered

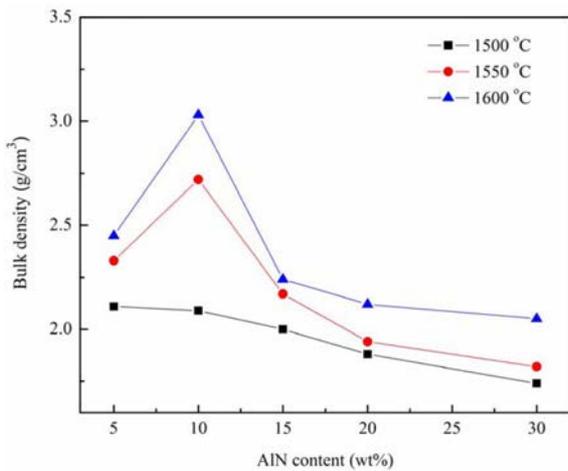


Fig. 1. Bulk density of ceramic specimens sintered at 1500-1600 °C for 3 h with different AlN contents.

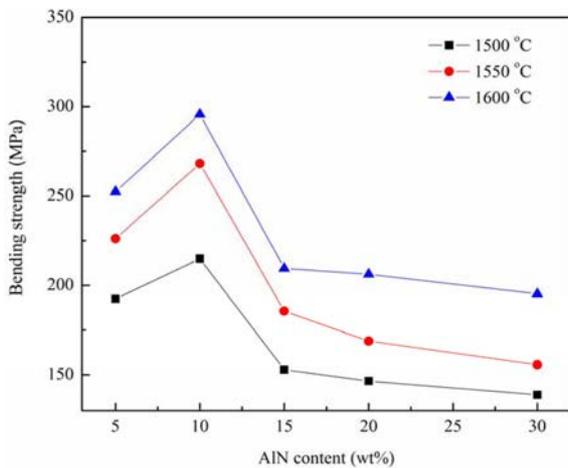


Fig. 2. Flexural strength of different formulation specimens stored at 1500-1600 °C for 3 h.

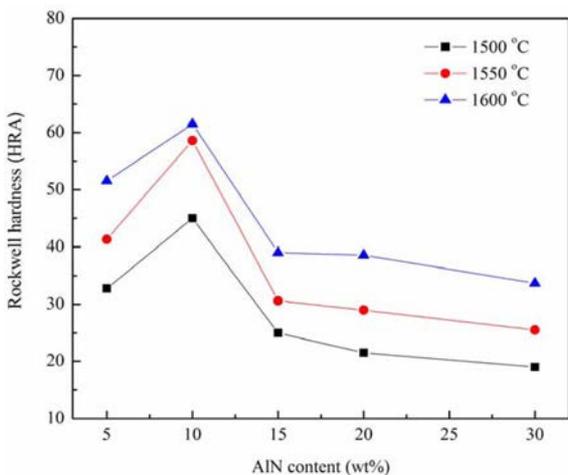


Fig. 3. Rockwell hardness of sintered specimens containing different AlN contents.

body sample initially increases and then decreases with increased AlN content at the same sintering temperature. When the amount of AlN in the formulation raw

material is 5 wt% (corresponding to sample #1), the bulk density of the sintered body sintered at 1600 °C is relatively low, i.e., 2.45 g/cm³. This finding may be due to the following: 1) the theoretical density of AlN is 3.26 g/cm³, which is smaller than that of Al₂O₃ (3.99 g/cm³); and 2) the micropores inside the AlN powder particles added to the system increase in number, thereby loosening the structure. Both factors lead to decreased bulk density of the sintered body sample. With further increased of AlN addition amount to 10 wt% (corresponding to sample #2), some solid-solution AlON products form due to the reaction of AlN and Al₂O₃ in the system (which improves the material's compactness), and the bulk density of the sintered body sample increases to 3.03 g/cm³. However, with further increased AlN content to >15 wt%, AlON grains significantly grow and grain size increases due to the increased AlON content in the system at high temperatures. The increase in the size of large-sized AlON grains decreases the bulk density of the ceramic sintered body [14].

Fig. 2 shows the flexural strength of sintered specimens with different AlN contents. The flexural strength of ceramic samples shows a similar variation with bulk density with varied amounts of AlN and sintering temperature. When the amount of AlN is 5wt%, the ceramic sample sintered at 1600 °C has a small bending strength of 252.4 MPa. The bending strength of the ceramic sample increases to 295.7 MPa when the amount of AlN is 10 wt%. The introduction of AlN has a significant dispersion strengthening effect on the Al₂O₃ ceramic matrix. In the composites, the toughening and reinforcing effects of the second-phase particles mainly originate from the difference in thermal expansion coefficient and elastic modulus between the reinforcing particles and matrix material. The difference in elastic moduli causes the material to undergo microscopic stress redistribution when subjected to external forces. The difference in the thermal expansion coefficient of the composites creates a residual stress field in the second-phase particle and its surrounding matrix, causing the split crack to diverge, deflect, and dissipate more energy in the process [7, 15]. Given that the thermal expansion coefficient of second-phase AlN (4.3×10^{-6} – 4.5×10^{-6} K⁻¹) is much smaller than that of the Al₂O₃ ceramic substrate (6.8×10^{-6} K⁻¹), a residual stress field is generated in the multiphase ceramics. When the crack propagates to the stress field, it cracks form in the material to diverge and deflect along the grain boundary, increase the crack propagation path, and correspondingly consume the energy of crack propagation, which can prevent further crack propagation to a certain extent. When the amount of AlN in the composite material exceeds 15 wt%, AlON formation increases in the system at high temperatures. AlON grains significantly grow at high temperatures and the crystal grains enlarge, resulting in gradually decreased flexural strength of the ceramic sintered body.

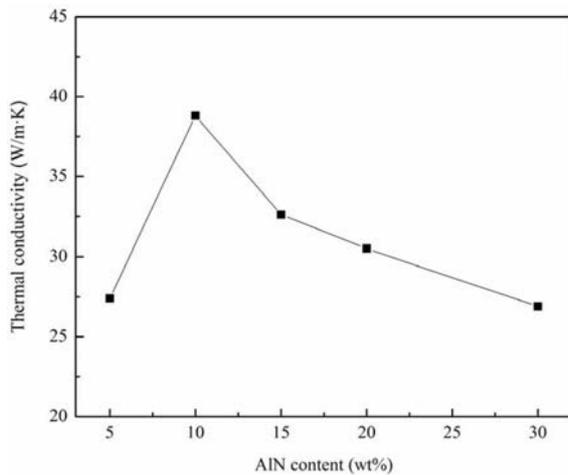


Fig. 4. Thermal conductivity of ceramic specimens sintered at 1600 °C for 3 h.

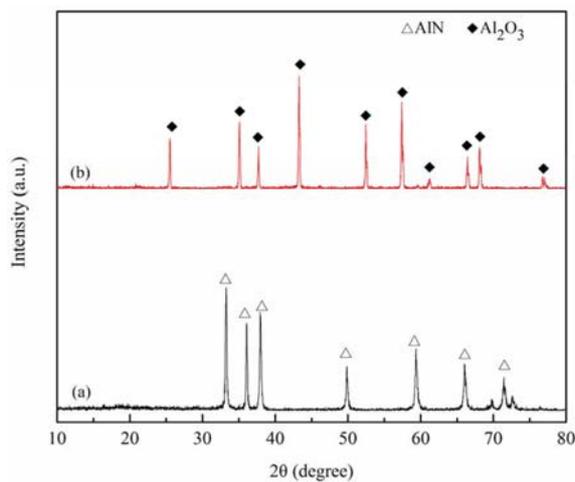


Fig. 5. XRD patterns of single aluminium nitride (a) and alumina (b) raw materials.

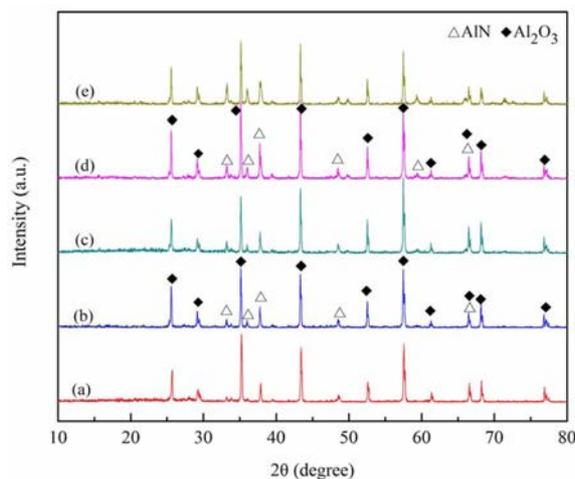


Fig. 6. XRD patterns of mixed precursor powders with different AlN contents: (a) 5 wt%, (b) 10 wt%, (c) 15 wt%, (d) 20 wt%, and (e) 30 wt%.

Fig. 3 shows the Rockwell hardness of sintered specimens containing different AlN contents. The

hardness of the ceramic sample varies similarly as the bending strength with altered AlN content and sintering temperature. The hardness of the ceramic sintered body initially increases and then decreases with increased AlN content in the system. When the addition amount of AlN is 10 wt%, the Rockwell hardness of the ceramic sintered body reaches the maximum value of 61.5 HRA. When the addition amount of AlN is increased to 20 wt% and 30 wt%, the Rockwell hardness of the ceramic sintered body decreases to 38.6 and 33.7 HRA, respectively. This change in hardness is related to two factors, namely, the hardness effect of the added phase AlN and the degree of densification of the composite. When the AlN content is less than 10wt%, the densification effect is the main factor affecting the hardness of the material, and when the addition amount of AlN exceeds 10wt%, the hardness effect of the added phase begins to become the main influencing factor. At this time, the hardness of Al₂O₃-AlN composites decreases with increased AlN content. Higher amounts of AlN also lead to more large-grained AlON particle in the multiphase ceramic system, thereby further reducing the hardness of the composite ceramic sintered body.

Fig. 4 shows the thermal conductivity of ceramic samples containing different amounts of AlN at 1600 °C for 3 h. With increased amount of AlN, the thermal conductivity of ceramic samples initially increases and then decreases. When the amount of AlN is 5-30 wt%, the thermal conductivity of the ceramic sample is between 26.9-38.8 W/(m·K). When the amount of AlN is 5 wt%, the thermal conductivity of the ceramic sample is 27.4 W/(m·K); When the amount of AlN is increased to 10 wt%, the thermal conductivity of the ceramic sample reaches the maximum value of 38.8 W/(m·K). This is mainly due to the fact that adding a certain amount of AlN (theoretical thermal conductivity = 319 W/(m·K)) to the system significantly affects the thermal conductivity of Al₂O₃ ceramics [16-17]. When the amount of AlN exceeds 15wt%, the thermal conductivity of Al₂O₃ ceramics begins to decrease mainly due to the reaction of AlN and Al₂O₃ in the system that forms AlON. AlON has a low thermal conductivity (theoretical thermal conductivity = 10 W/(m·K)), and the newly formed large AlON grains hinder the contact and overlap between small AlN grains, thereby reducing the thermal conductivity of the multiphase ceramic material [11]. When the amount of AlN is increased to 30 wt%, the thermal conductivity of the ceramic sample drops to 26.9 W/(m·K).

Fig. 5 shows the XRD analysis results of single AlN and Al₂O₃ raw materials. The characteristic diffraction peaks of the two raw materials well agree with the standard cards of AlN and Al₂O₃, respectively. Few impurity peaks are observed in the two spectra, indicating that AlN and Al₂O₃ raw materials are high purity and meet the requirements of experimental

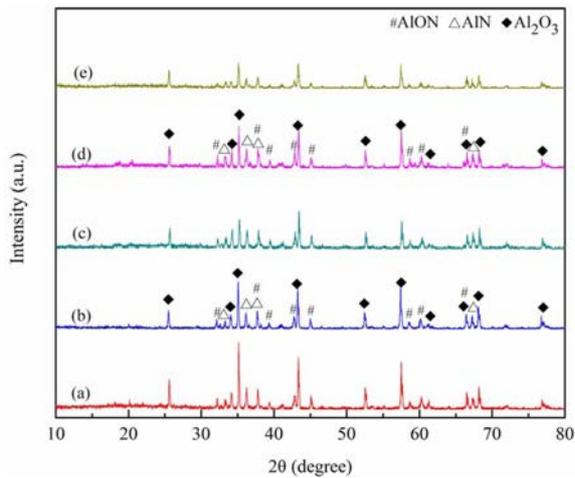


Fig. 7. XRD patterns of sintered samples at 1600 °C for 3 h with different AlN contents: (a) 5 wt%, (b) 10 wt%, (c) 15 wt%, (d) 20 wt%, and (e) 30 wt%.

studies. Fig. 6 shows the XRD pattern of the mixed precursor powders with different AlN contents. Fig. 6(a) shows weak AlN characteristic diffraction peaks in addition to the strong Al_2O_3 characteristic diffraction peaks in the XRD pattern. The diffraction peaks of $\text{TiO}_2\text{-Y}_2\text{O}_3\text{-CaO-La}_2\text{O}_3$ quaternary sintering aids in the XRD pattern are not obvious, which may be due to the low amount of quaternary sintering aids or their partly amorphous property. Comparing Figs. 6(a) with 6(e) reveals that with increased AlN content in the mixed raw materials, the diffraction peaks of AlN in the XRD pattern gradually increase. Fig. 7 shows the XRD pattern of ceramic samples obtained at 1600 °C for 3 h. Comparing Figs. 7(a) with 7(e) shows that in addition to the strong Al_2O_3 and AlN diffraction peaks in the sintered sample, relatively weak AION diffraction peaks exist, indicating that under the experimental conditions, part of the AlN and Al_2O_3 in the system

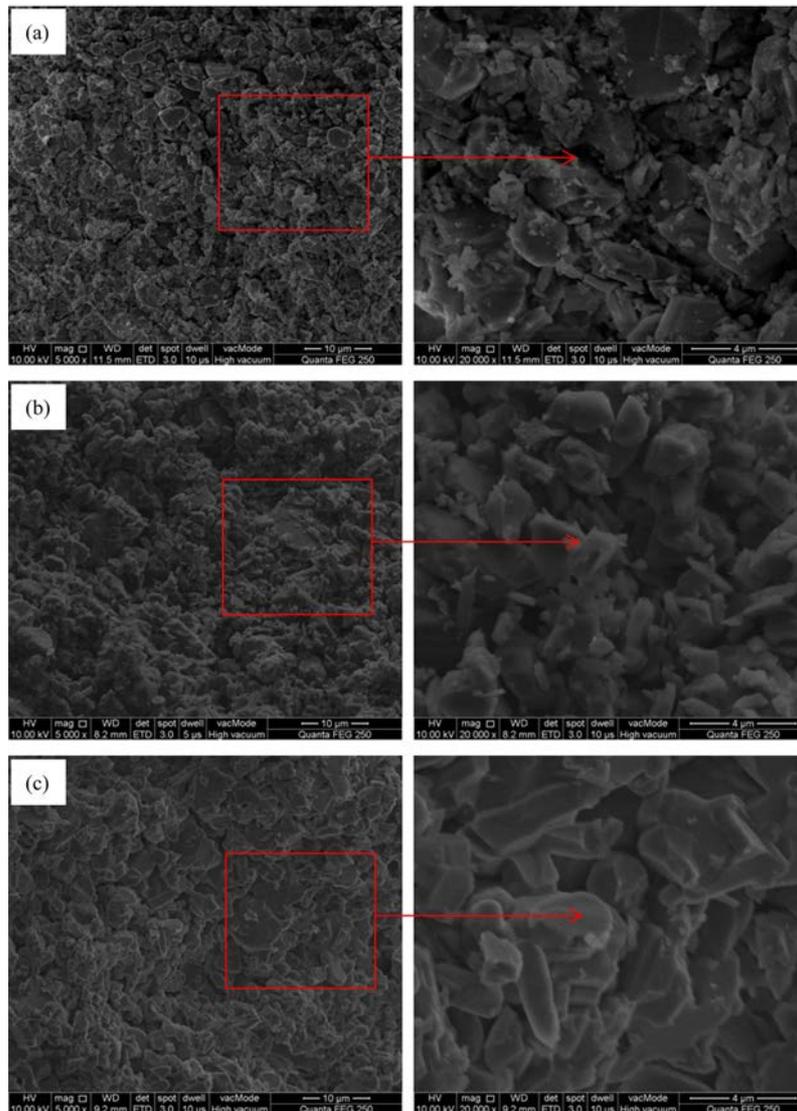


Fig. 8. SEM photographs of the ceramic samples obtained from Recipe 1 at different sintering temperatures for 3 h: (a) 1500 °C+3 h, (b) 1550 °C+3 h, and (c) 1600 °C+3 h.

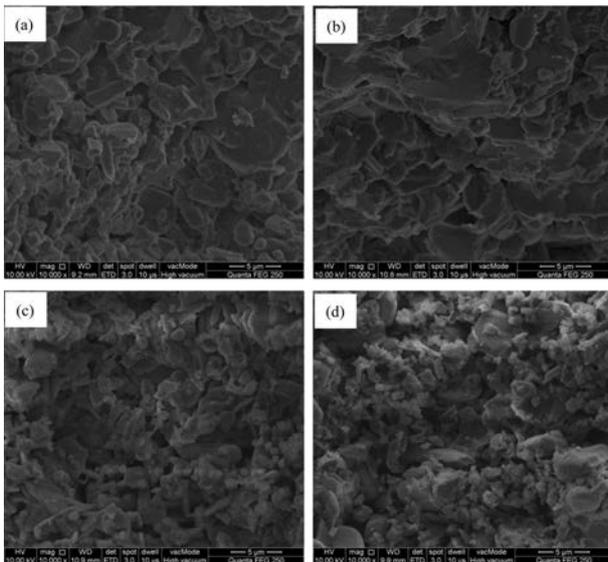


Fig. 9. SEM photographs of samples sintered at 1600 °C for 3 h with different AlN contents: (a) 5 wt%, (b) 10 wt%, (c) 15 wt%, and (d) 20 wt%.

react to produce a small amount of AlON product. This finding is consistent with the previous one on bulk density. The diffraction peaks of the TiO₂-Y₂O₃-CaO-La₂O₃ quaternary sintering aids in the ceramic sample sintered at 1600 °C for 3 h are still not obvious in the XRD pattern.

Fig. 8 is the SEM photograph of the ceramic samples obtained from Recipe 1 at different sintering temperatures for 3 h. As the sintering temperature increases, the grain size of the sintered body as a whole gradually increases. Figure 8(a) shows that when the sintering temperature is 1500 °C, the sintered body sample has a loose structure as a whole, and many pores exist between the grains. When the sintering temperature is increased to 1550 °C, the pores in the sample are significantly reduced, the crystal grains are tightly bonded, and the density of the sample significantly increases (Fig. 8 (b)). When the sintering temperature reaches 1600 °C (Fig. 8(c)), grain growth in the sample is well developed, grain size is mostly 1-3 μm, crystal grains are tightly bound together, and the interface is clean. Consequently, the ceramic sample has a high density and mechanical properties, consistent with the previous analysis results. Fig. 9 shows the SEM images of the samples sintered at 1600 °C for 3 h with different AlN contents. The average grain size in the ceramic sample tends to decrease with increased amount of ultrafine AlN added to the system. When the added amounts of AlN are 10wt%, the sintered body samples have high density and few pores. Compared with that in Fig. 9(a), the sintered body sample in Fig. 9(b) has more tightly bonded crystal grains and fewer pores, thereby imparting various excellent properties to the ceramic sample. Generally, when Y₂O₃-CaO-La₂O₃ additives are used as sintering aids, the mechanism for accelerating sintering at

temperatures not higher than 1600 °C is that they generate a liquid phase at high temperatures and fill the gaps in Al₂O₃ and AlN sintered bodies. Literature shows that TiO₂ promotes the sintering of ceramic materials mainly by forming a solid solution with Al₂O₃, increasing the lattice distortion of Al₂O₃, and increasing the diffusion rate [18]. However, when the added amount of AlN continues to increase to 15 wt% and 20 wt%, the ceramic sample acquires a loose porous microstructure, which is mainly attributed to the formation of a small amount of AlON in the system and the increase in AlN particles that are difficult to sinter together [19].

Conclusions

(1) For the samples with the same formulation, bulk density gradually increases with increased sintering temperature. At the same sintering temperature, the bulk density of the sintered samples initially increases and then decreases with increased AlN content in the system. When the amount of AlN is 10 wt%, the ceramic sample sintered at 1600 °C has the highest performance in terms of bending strength, Rockwell hardness, and thermal conductivity (295.7 MPa, 61.5 HRA, and 38.8 W/(m·K), respectively).

(2) In addition to the strong Al₂O₃ and AlN diffraction peaks, the ceramic samples obtained at 1600 °C for 3 h also have relatively weak AlON diffraction peaks. The diffraction peaks of TiO₂-Y₂O₃-CaO-La₂O₃ quaternary sintering aids in the XRD pattern are not obvious, which may be due to the fact that the amount of the quaternary sintering aids is low or that part of the sintering aids has become amorphous.

(3) SEM analysis shows that the average grain size of the ceramic sample gradually decreases with increased ultrafine AlN content in the system. When the addition amount of AlN is 10 wt%, the sample sintered at 1600 °C has high density, tight bonding between crystal grains, and few pores, thereby conferring the ceramic sample with excellent properties. When the addition amount of AlN is increased to 15 wt% and 20 wt%, the ceramic sample acquires a loose microstructure, which is mainly attributed to the formation of a small amount of AlON in the system and the increase in AlN particles that are difficult to sinter.

Acknowledgements

This work is supported by the Natural Science Foundation of Hunan Province, China (Grant No. 2016JJ6047), the Planned Science and Technology Program of Hunan Province, China (Grant No. 2016TP1028), the Postdoctoral Scientific Research Fund of Central South University, China (Grant No. 161820) and the Science and Technology Innovation Project of Loudi City, China (Grant No. 2017).

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