Synthesis of nearly spherical AlN particles by an in-situ nitriding combustion route

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Abstract: Spherical AlN powders with micrometer size have attracted great attention owing to their good fluidity and dispersity. However, the industrial preparation methods usually require high temperature and long soaking time, which lead to the high cost and limit the wide application of the products. Herein, nearly spherical AlN particles with the average size of 2.5 μm were successfully synthesized via an in-situ combustion synthesis method. The effect of N_2 pressure, NH_4Cl content and Al particle size on the combustion reaction procedure, phase composition and microstructure of the products was systematically investigated. The results showed that the decreased N_2 pressure, increased NH_4Cl content and Al particle size led to the decreasing of combustion temperature and speed, which further affected the morphology of the products. As a result, low N_2 pressure (0.2 MPa), a small amount

of NH_4Cl (0.5 wt%) and fine Al particles ($\sim 2.5\ \mu\text{m}$) contributed to a moderate combustion temperature and facilitated the formation of nearly spherical AlN particles. In addition, based on the gas-releasing assisted quenching experiments and thermo-kinetic analysis, a two-step growth mechanism for the nearly spherical AlN particles was rationally proposed. The present method shows the advantages of low cost and high efficiency for preparing nearly spherical AlN particles, which can be used as raw materials for electronic substrates and fillers for packaging materials.

Keywords: combustion synthesis, AlN, microstructure, growth mechanism

1. Introduction

AlN, as an important III-V semiconductor material, has attracted great attention because of its high thermal conductivity, high electrical resistance, wide band gap, low dielectric constant, and low thermal expansion coefficient [1,2]. Based on these excellent properties, it has good application prospects in terms of electronic substrates, packaging materials, heat sinks and field-emission devices [3-6]. Recently, spherical AlN particles with micrometer size have shown significant promise for applications in raw materials for electronic substrates and fillers for packaging materials owing to their good fluidity and dispersity [7,8]. Hence, many efforts have been devoted to synthesis spherical AlN particles, including direct nitridation [9], carbothermal reduction-nitridation [10] as well as other two-step chemical routes [11]. However, these methods usually require high temperature, long soaking time or expensive raw materials, which will increase the cost and limit the industrial applications. Therefore, it is imperative to further exploit new synthetic routes for preparing spherical AlN

particles.

Combustion synthesis (CS, also known as self-propagating high temperature synthesis (SHS)), is considered as a promising synthesis route to fabricate AlN powders because of its low processing cost, high energy efficiency and short reaction period [12–15]. However, because of the high thermal-gradient, high combustion temperature and fast reaction speed, the morphology of the AlN powders is difficult to control and various grain morphologies, such as whiskers, faceted particles, agglomerated particles are often observed [16–19], which impedes the CS process for wide application.

In previous studies, we have reported the synthesis of AlN nanowhiskers [20,21], porous-shell hollow spheres [22] and rod-like nanoparticles [23] with uniform morphologies by the CS method. The morphology of the products can be controlled through adjusting the CS parameters (such as diluent content and N₂ pressure) and introducing various additives (such as NH₄Cl, PTFE, and oxides). As a consequence, a “micro-reactor” can be in-situ formed at the original Al particle during the CS process, which provided an almost consistent environment for the growth of AlN crystal with uniform morphology in the products [24]. These results give us an inspiration for the synthesis of spherical AlN particles by CS route.

In this work, we developed an efficient CS route to directly prepare nearly spherical AlN particles by in-situ nitridation of spherical Al powders. The effect of combustion parameters including N₂ pressure, NH₄Cl content and Al particle size on the combustion reaction procedure, phase composition and microstructure of the

products was systematically investigated. Furthermore, the bylying growth mechanism for the nearly spherical AlN particles in the CS process was proposed by both experimental and thermo-kinetic analysis.

2. Materials and method

2.1 Materials

Four types of spherical Al powders with different particle sizes ($d_{50} = 2.5 \mu\text{m}$, $5 \mu\text{m}$, $10 \mu\text{m}$ and $25 \mu\text{m}$, respectively; purity > 99.9%; Henan Yuanyang Powder Technology Co., Ltd, China) were used as reactant materials. The morphologies of the spherical Al powders and their particle size distributions are shown Fig. 1. AlN powder (particle size: $\sim 2.5 \mu\text{m}$; purity > 99.5%; self-prepared by the same procedure in this work) was adopted as the diluent, and NH_4Cl (purity > 99.5%, Sinopharm Chemical Reagent Co., Ltd, China) was chosen as the reaction controlling agent.

Fig. 1 Morphologies of the spherical Al powders and their particle size distributions:

(a), (e) $d_{50} = 2.5 \mu\text{m}$; (b), (f) $d_{50} = 5 \mu\text{m}$; (c), (g) $d_{50} = 10 \mu\text{m}$; (d), (h) $d_{50} = 25 \mu\text{m}$

2.2 Sample preparation

In the CS procedure, Al and AlN powders were mixed with a molar ratio of 4:6, which was chosen to achieve pure AlN product [25]. Additionally, different amount of NH_4Cl (0, 0.5, 1 wt%) was also added. The raw powders were lightly mixed by a

mortar for 20 minutes, and sieved through 150-mesh to disperse any large agglomerates. Then, 50 g of the powder mixture was poured into a porous graphite crucible and ignited at high purity N₂ atmosphere (99.999%) with different gas pressures (0.2, 0.5, 0.8 and 1.0 MPa). The samples prepared by different combustion parameters can be briefly denoted as P1.0N0R2.5, P0.8N0R2.5, P0.5N0R2.5, P0.2N0R2.5, P0.2N0.5R2.5, P0.2N1.0R2.5, P0.2N0.5R5, P0.2N0.5R10 and P0.2N0.5R25, respectively, which are illustrated detailly in [Table 1](#). The combustion temperature and speed were measured by W-Re thermocouples. After the combustion reactions, all of the as-fabricated AlN products were loose like dry cakes, which were dry milled for 30 minutes by a mortar and sieved through 150-mesh to obtain the dispersed powder products.

Table. 1 Experimental parameters for the CS of AlN powders

Sample name	N ₂ pressure (MPa)	NH ₄ Cl content (wt%)	Al particle size (μm)	Maximal combustion temperature (K)	Combustion speed (mm·s ⁻¹)
P1.0N0R2.5	1.0	0	2.5	2536.15	0.31
P0.8N0R2.5	0.8	0	2.5	2344.15	0.24
P0.5N0R2.5	0.5	0	2.5	2255.15	0.20
P0.2N0R2.5	0.2	0	2.5	2196.15	0.19
P0.2N0.5R2.5	0.2	0.5	2.5	2150.15	0.16
P0.2N1.0R2.5	0.2	1.0	2.5	1967.15	0.14
P0.2N0.5R5	0.2	0.5	5	1997.15	0.12
P0.2N0.5R10	0.2	0.5	10	1893.15	0.10
P0.2N0.5R25	0.2	0.5	25	1810.15	0.09

A gas-releasing assisted quenching method [\[26,27\]](#) was employed to disclose the growth mechanism for the nearly spherical AlN particles. The difference between this

method and the above CS experiments lies in that N_2 was quickly released from the chamber when the combustion wave was passing through the sample. Because the residual N_2 was not enough to sustain the combustion reaction, the afterburning was inhibited and the combustion was quenched. By this means, the detailed information of the combustion reaction can be obtained.

2.3 Characterization

The phase composition of the as-synthesized products was examined by X-ray diffraction (XRD; X'Pert Pro, Holland) with $Cu\ K\alpha$ radiation. Granulometric distribution of raw Al powders and the as-synthesized AlN powders was characterized using a laser diffraction analyser (Mastersizer 2000, Malvern, England), and the morphology of the powders was observed by field emission scanning electron microscopy (FE-SEM; SU6600, Japan) equipped with energy dispersive spectrometer (EDS). Samples for SEM observations and EDS analysis were coated with thin films of sputtered gold to increase the electrical conductivity. The focused ion beam (FIB) micromachining technique was used to slit the representative particles in different zone of the quenched samples and the cross-section morphology of the particles was observed by FE-SEM.

3. Results and discussion

3.1 Effects of combustion parameters on the reaction procedure

The combustion temperature-time curves of the samples prepared by different combustion parameters are shown in [Fig. 2](#). Once the combustion reaction is triggered, the temperature increases rapidly close to its apex in several seconds and then slowly

decreases after the combustion wave passes by. With the decrease of N_2 pressure from 1.0 MPa to 0.2 MPa, the maximal combustion temperature decreases from 2536.15 K (P1.0N0.5R2.5) to 2196.15 K (P0.2N0.5R2.5) and the corresponding combustion speed reduces from 0.31 to 0.19 $\text{mm}\cdot\text{s}^{-1}$. This indicates that higher N_2 pressure makes the combustion reaction more drastic since there are more active molecules per unit volume and the collision probability between Al and N_2 molecules increases.

Besides, the combustion temperature and speed can be influenced by the amount of NH_4Cl additive because it absorbs sufficient heat from the reaction system through sublimation and dissociation [28]. Hence, as the content of NH_4Cl additive increases, the combustion temperature and speed sharply decrease (see Fig. 2 and Table 1). Compared with the sample without NH_4Cl additive (P0.2N0R2.5), the maximal combustion temperature and speed of sample P0.2N1.0R2.5 decrease by 229 K and 0.05 $\text{mm}\cdot\text{s}^{-1}$, respectively.

Fig. 2 Combustion temperature-time curves of the samples synthesized by different combustion parameters

Al particle size also affects the combustion temperature and speed. On condition that other combustion parameters are the same, as the Al particle size increases from

~2.5 μm (P0.2N0.5R2.5) to ~25 μm (P0.2N0.5R25), the combustion temperature and speed decrease from 2150.15 K to 1810.15 K and from 0.16 $\text{mm}\cdot\text{s}^{-1}$ to 0.09 $\text{mm}\cdot\text{s}^{-1}$, respectively. This is mainly caused by the reduced surface area of Al particles, which further leads to the decreased contact area between Al and N_2 molecules. Therefore, the reaction procedure can be well controlled by adjusting the combustion parameters.

3.2 Effects of combustion parameters on the phase composition

Fig. 3 shows the XRD patterns of the samples prepared by different combustion parameters. For the samples of P0.2N0R2.5, P0.2N1.0R2.5 and P0.2N0.5R25, all the diffraction peaks in the XRD patterns can be indexed to the AlN crystal (JCPDS No.25-1133) with hexagonal wurtzite structure. The sharp diffraction peaks indicate the good crystallinity of the products. Besides, no characteristic peaks of impurities are detected in the patterns, which demonstrates that the AlN products with high purity can be obtained by using different Al powders as the reactant at relatively low N_2 pressure (0.2 MPa) and the addition of NH_4Cl does not affect the phase composition of the products [29]. The fabricated AlN products with high purity can be attributed to the strong exothermic reaction between Al and N_2 (Eq. (1)), which ensures the sufficient nitridation of Al powders.

Fig. 3 XRD patterns of the synthesized AlN powders: (a) P0.2N0R2.5; (b) P0.2N1.0R2.5; (c) P0.2N0.5R25

3.3 Effects of combustion parameters on the morphology

Representative SEM images of the samples synthesized by different combustion parameters are displayed in Fig. 4. Apparently, when the N_2 pressure ≥ 0.8 MPa, large agglomerates are observed in the product of P1.0N0R2.5 and P0.8N0R2.5 (Figs. 4 (a) and (b)). The AlN particles are all bonded by the sintering necks, which can be mainly ascribed to the high combustion temperature (see Fig. 2). With the decrease of N_2 pressure, the combustion temperature decreases and the sintering of AlN particles weakens. As a result, the morphology of the products (P0.5N0R2.5 and P0.2N0R2.5) becomes more uniform and the percentage of nearly spherical particles with the grain size of ~ 2.5 μm increases gradually (Figs. 4 (c) and (d)). However, most of the particles are still bonded together by the sintering necks because the maximal combustion temperature is still higher than 2173.15 K (see Fig. 2).

In order to improve the dispersity of nearly spherical AlN particles, NH_4Cl was added to the reaction system. It is observed that a small amount of NH_4Cl (0.5 wt%) facilitates the formation of AlN powders with uniform morphology, as shown in the

SEM image of sample P0.2N0.5R2.5 (Fig. 4(e)). However, some fibrous particles are formed in the product P0.2N1.0R2.5 (Fig. 4(f)) when the NH_4Cl content further increases to 1 wt%. This can be ascribed to the catalysis of NH_4Cl , which promotes the growth of one dimensional AlN structures by vapor-solid (VS) mechanism [30].

The effect of Al particle size on the morphology of the products was also investigated. With the increase of Al particle size, hemispheric particles with core-shell structure appear in P0.20.5R5 and P0.2N0.5R10 samples, where the shells consist of small stacked granules and the cores are filled with large granules (Figs. 4 (g) and (h)). This morphology can be ascribed to the high N_2 permeability and high supersaturation of the Al vapor [31]. When the Al particle size further increases to $\sim 25\text{ }\mu\text{m}$, the morphology of the product becomes more complicated, including core-shell structure, granules with different particle size and whisker-like morphology, as shown in Fig. 4(i). The formation of AlN whiskers can be attributed to the lower saturated pressure of Al vapor than the critical vapor pressure of uniform nucleation [32,33]. Above all, nearly spherical AlN particles can be synthesized only by adopting Al powder with small particle size, proper N_2 pressure and NH_4Cl content to maintain moderate combustion temperature and speed.

Fig. 4 SEM images of the samples synthesized by different combustion parameters: (a) P1.0N0R2.5; (b) P0.8N0R2.5; (c) P0.5N0R2.5; (d) P0.2N0R2.5; (e) P0.2N0.5R2.5; (f) P0.2N1.0R2.5; (g) P0.2N0.5R5; (h) P0.2N0.5R10; (i) P0.2N0.5R25

3.4 Characterization of the nearly spherical AlN particles

Fig. 5(a) shows the low-magnification SEM image of the sample P0.2N0.5R2.5, where most of the AlN particles exhibit nearly spherical morphology with good dispersity. The size distribution of these particles is shown in Fig. 5(b) and the d_{50} is about 2.5 μm , which is similar to that of the original Al particles, as shown in Figs. 1(a) and (e). Because of the similar shape and size, one can notice that the nearly spherical AlN particles could be evolved from the original Al particles. The high-magnification SEM image of a single particle is shown in Fig. 5(c). It can be clearly observed that the particle is endowed with nearly spherical shape. In addition, some steps appear on the surface of the AlN particle, illustrating that the VS

mechanism plays an important role in the growth of AlN grains [34].

Fig. 5 (a) Low-magnification SEM image, (b) particle size distribution, (c) high-magnification SEM image and (d) EDS analysis of the nearly spherical AlN particles

However, because of the lack of liquid phase and short soaking time at high-temperature in the CS process, it is difficult to form a perfect spherical particle. Fig. 5(d) shows the chemical composition of the nearly spherical AlN particle confirmed by the EDS analysis. As observed, only peaks of Al, N and O are detected. The atomic ratio of Al and N is nearly to the stoichiometric proportion of 1:1, indicating the sufficient nitridation of Al during the CS process. Meanwhile, the small amount of oxygen originates mainly from the essential oxide layer of the AlN powders.

3.5 Growth mechanism for the nearly spherical particles

Fig. 6 XRD patterns of the quenched sample P0.2N0.5R2.5 in different reaction regions: (a) preheated region, (b) initial-combustion region, (c) middle-combustion region, (d) post-combustion region, and (e) complete-combustion region

In order to investigate the phase transformation and morphology evolution of the nearly spherical AlN particles, a gas-releasing assisted quenching method was performed for the sample P0.2N0.5R2.5. Fig. 6 shows the XRD patterns of the quenched sample in different regions. It can be seen that both of Al and AlN peaks are detected in the preheated region (Fig. 6(a)), initial-combustion region (Fig. 6(b)), middle-combustion region (Fig. 6(c)) and post-combustion region (Fig. 6(d)). The peak intensity of Al in these regions gradually decreases, while that of AlN gradually increases. This indicates that Al is gradually nitrided to AlN as the combustion wave passes. Therefore, only a small amount of Al is detected in the post-combustion region and complete AlN product is obtained in the complete-combustion region (Fig. 6(e)).

To further study the growth process from Al particles to nearly spherical AlN particles, SEM, EDS and FIB micromachining were carried out for the quenched sample in different regions. Fig. 7(a) shows the SEM image of a single particle in the preheated region. The particle has smooth surface with ball-like morphology, which is similar to that of the raw Al particle (Fig. 1(a)). XRD (Fig. 6(a)) and EDS results also indicate that this is an un-nitrided Al particle. In the initial-combustion region, the surface of the Al particle becomes rough since numerous island-like granules appear, as shown in Fig. 7(b). After slitting by FIB technique, the cross-sectional SEM image of the particle is obtained. EDS line-scan analysis of the major element distribution through the cross section of the particle reveals that the surface area mainly contains Al, N and O, whereas the core area is dominated by Al signal. Combining with the XRD result (Fig. 6(b)), the core and island-like granules on the surface can be identified as Al and AlN, respectively.

Fig. 7 (a) SEM image and EDS analysis of the particle in the preheated region; (b) SEM image, cross-sectional SEM image and EDS line-scan results of the particle in the initial-combustion region; (c), (d), (e) SEM image, cross-sectional SEM image of the particle and the corresponding EDS mapping results of Al and N in the middle-combustion region; post-combustion region, and complete-combustion region, respectively

In the middle-combustion region, the AlN granules on the surface of Al particle further grow and numerous gaps appear among the granules (Fig. 7(c)). According to the XRD pattern (Fig. 6(c)), cross-sectional morphology and EDS mapping results (Fig. 7(c)), the nitrided layer is thicker than that of the initial-combustion region, while the core area is mainly composed of Al. For the post-combustion region, since the combustion wave has just passed, a nearly completely nitrided hollow AlN particle with many granules and gaps on its crust is formed (Fig. 7(d)). This can be

confirmed by the XRD pattern in Fig. 6(d), where almost no diffraction peaks of Al can be observed. Besides, because of the high combustion temperature and speed, a small amount of Al vapor rushes out through the gaps among the AlN granules, which is then nitrided outside and hence the hollow sphere is formed [35]. Finally, the nearly spherical AlN particle is obtained in the complete-combustion region (Fig. 7(e)) and there are almost no residual pores or gaps in the particle. This could be mainly attributed to the in-situ sintering of AlN granules in the afterburning process because the maximal combustion temperature is higher than 2073.15 K.

According to the above analysis and discussion, a two-step growth mechanism, i.e. (1) nitridation of Al particle from the surface into the interior and (2) in-situ sintering of AlN granules, for the CS of nearly spherical AlN particles is reasonably proposed, as shown in Fig. 8. Firstly, the Al particle melts and reacts with N_2 gas at the surface of the particle to form numerous island-like AlN granules. Then, the N_2 gas diffuses through the surface gaps into the molten Al core and the nitridation process takes place from the particle's surface into the interior, which results in the thickening of nitrided layer. Subsequently, as the combustion wave propagates through the particle, the combustion temperature and speed rapidly rise, and a small amount of Al vapor rushes out from the gaps of the particle. Thus, the hollow particle is formed in the post-combustion region. When the combustion temperature further rises, the in-situ sintering of AlN granules occurs [36] and the nearly spherical AlN particle is finally obtained. Therefore, the maximal combustion temperature is an important factor for the formation of nearly spherical AlN particles. When the

combustion temperature is high enough, the sintering effect is intensive which benefits the densification of the AlN particle to form nearly spherical AlN particles. While at relatively low combustion temperature, the in-situ sintering of AlN granules is restrained and hollow spheres appear, as shown in the P0.2N0.5R5, P0.2N0.5R10 and P0.2N0.5R25 samples (Figs. 4(g)-(i)).

Fig. 8 Schematic of the growth mechanism for nearly spherical AlN powders

3.6 Thermo-kinetic analysis

In order to confirm the above mechanism for the growth of nearly spherical AlN particles during the CS process, the thermo-kinetic analysis was carried out. Herein, it is assumed that Al vapor is nitrided to form AlN at a distance of:

$$L = \beta r \quad (2)$$

Where r is the radius of an Al particle (1.25 μm), β is a constant ($\beta \leq 1$). When the supply of N₂ is sufficient and the system is in equilibrium, the evaporation rate of Al particle is equal to the diffusion rate of N₂ gas. The evaporation flux (J) of Al vapor can be calculated by the following formula [37,38]:

$$J = \frac{P_1 / \sqrt{2\pi M_1 RT}}{1 + 2r^3 / (L^2 D) \times \sqrt{RT / (2\pi M_1)}} \quad (3)$$

Where M_1 is the molar weight of Al, R is the gas constant, T is the combustion temperature, D is the diffusion coefficient of the Al vapor in nitrogen, P_1 is the

equilibrium vapor pressure of Al vapor which rapidly increases with the combustion temperature ranging from 933 K to 2793 K and their relationship is as follows [39]:

$$\lg P_1 = -16380/T - \lg T + 11.44 \quad (4)$$

According to an empirical formula, D is determined by Eq. (5), in which C can be calculated from Eq. (6) [40]:

$$D = \frac{8.37 \times 10^{-3} T^{5/2}}{P_2 (V_1^{1/3} + V_2^{1/3})^2 (T + C)} \sqrt{\frac{1}{M_1} + \frac{1}{M_2}} \quad (5)$$

$$C = (1.504 - 3.43 \times 10^{-2} V_1 / V_2) \sqrt{T_1 T_2} \quad (6)$$

Where P_2 is the pressure of N_2 in the system, M_2 is the molar weight of N_2 , V_1 and V_2 are the molar volume of Al and N_2 at their boiling point, T_1 and T_2 are the boiling point of Al and N_2 , respectively. Besides, the time required for a spherical Al particle to completely vaporize and react with N_2 can be calculated from Eq. (7) [31]:

$$t = \frac{r \rho_{Al}}{J} \quad (7)$$

For the condition of preparing nearly spherical AlN particles ($P_2 = 0.2$ MPa, $T = 2150.35$ K), the calculated $C = 685.35$ K, $D = 2.68 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$ and $J \leq 0.048 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. According to Eq. (7), the time required for a spherical Al particle to be completely nitrided should be equal to or more than 0.070 s. The experimental results for sample P0.2N0.5R2.5 show that the time required for the combustion wave to travel across an Al particle is 0.016 s, which is in the same order of magnitude with the calculated result.

During the combustion reaction process, although the combustion wave has passed, the nitridation of one particle has not yet completed because of the post-combustion period. Thus, the time for an Al particle to be completely nitrided is

obviously longer than 0.016 s. Moreover, the equilibrium pressure of N_2 in the combustion system, which is inversely proportional to D (Eq. (5)), is actually lower than the gas pressure in the chamber. This phenomenon will make the calculated result (0.070 s) on the high side. Therefore, the thermo-kinetic results are possible to coincide with the experimental results.

However, when the Al particle size increases to $\sim 5\ \mu\text{m}$, $\sim 10\ \mu\text{m}$ and $\sim 25\ \mu\text{m}$, the Al particles can be in-situ nitride completely, but the combustion temperature are only 1997.15 K, 1893.15 K and 1810.15 K, respectively. Such low temperature is insufficient for the densification of AlN granules. Therefore, core-shell morphologies instead of solid particle with smooth surface are obtained in the products, as shown in Figs. 4(g)-(i).

4. Conclusions

In summary, nearly spherical AlN particles with the average size of $2.5\ \mu\text{m}$ were successfully synthesized by an in-situ nitriding combustion synthesis method using spherical Al powders as reactant. The combustion reaction procedure, which affected the morphology of the products, can be controlled by adjusting N_2 pressure, NH_4Cl content and Al particle size. As a result, high purity of AlN powders with nearly spherical morphology can be obtained by using low N_2 gas pressure (0.2 MPa), a small amount of NH_4Cl (0.5 wt%) and small Al particles ($2.5\ \mu\text{m}$). Moreover, based on the gas-releasing assisted quenching experiments and thermo-kinetic calculations, a two-step growth mechanism: (1) nitridation of Al particle from the surface into the interior and (2) in-situ sintering of intermediate AlN granules to form nearly spherical

particle was rationally proposed. The present process for synthesis of nearly spherical AlN particles is simple, productive, energy-saving and can be applied to produce raw materials for electronic substrates and fillers for packaging materials.

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References

- [1] Mussler BH. Aluminum nitride. *Am Ceram Soc Bull* 2000, **79**: 45-47.
- [2] Sheppard LM. Aluminum nitride: a versatile but challenging material. *Am Ceram Soc Bull* 1990, **69**: 1801-1812.
- [3] Yin S, Tseng KJ, Zhao J. Design of AlN-based micro-channel heat sink in direct bond copper for power electronics packaging. *Appl Therm Eng* 2013, **52**: 120-129.
- [4] Rutkowski PJ, Kata D. Thermal properties of AlN polycrystals obtained by pulse plasma sintering method. *J Adv Ceram* 2013, **2**:180-184.
- [5] Tondare VN, Balasubramanian C, Shende SV, *et al.* Field emission from open ended aluminum nitride nanotubes. *Appl Phys Lett* 2002, **80**: 4813-4815.
- [6] Lee ES, Lee SM, Shanefield DJ, *et al.* Enhanced thermal conductivity of

- polymer matrix composite via high solids loading of aluminum nitride in epoxy resin. *J Am Ceram Soc* 2008, **91**: 1169-1174.
- [7] Shang Q, Wang Z, Li J, *et al.* Gel-tape-casting of aluminum nitride ceramics. *J Adv Ceram* 2017, **6**: 67-72.
- [8] Suehiro T, Tatami J, Meguro T, *et al.* Morphology-retaining synthesis of AlN particles by gas reduction-nitridation. *Mater Lett* 2002, **57**: 910-913.
- [9] Ohashi M, Kawakami S, Yokogawa Y, *et al.* Spherical aluminum nitride fillers for heat-conducting plastic packages. *J Am Ceram Soc* 2005, **88**: 2615-2618.
- [10] Wang Q, Cui W, Ge Y, *et al.* Preparation of spherical AlN granules directly by carbothermal reduction–nitridation method. *J Am Ceram Soc* 2015, **98**: 392-397.
- [11] Wan J, Qiao X, Wu L, *et al.* Facile synthesis of monodisperse aluminum nitride microspheres. *J Sol Gel Sci Technol* 2015, **76**: 658-665.
- [12] Merzhanov AG, Borovinskaya IP. A new class of combustion processes. *Combust Sci Technol* 1975, **10**: 195-201.
- [13] Gromov AA, Chukhlomina LN. *Nitride ceramics - combustion synthesis, properties, and applications*. Germany: Wiley-VCH: Weinheim, 2014.
- [14] Zakorzhevskii VV, Borovinskaya IP, Sachkova NV. Combustion synthesis of aluminum nitride. *Inorg Mater* 2002, **38**: 1131-1140.
- [15] Zhang K, Yin D, He Z, *et al.* Combustion synthesis of Hf-doped zirconolite-rich composite waste forms and the aqueous durability, *J Adv Ceram*. 2019, **8**: 448-455.

- [16] Fu R, Chen K, Agathopoulos S, *et al.* Factors which affect the morphology of AlN particles made by self-propagating high-temperature synthesis (SHS). *J Cryst Growth* 2006, **296**: 97-103.
- [17] Jiang G, Zhuang H, Zhang J, *et al.* Morphologies and growth mechanisms of aluminum nitride whiskers by SHS method-Part I. *J Mater Sci* 2000, **35**: 57-62.
- [18] Jiang G, Zhuang H, Zhang J, *et al.* Morphologies and growth mechanisms of aluminum nitride whiskers by SHS method-Part II. *J Mater Sci* 2000, **35**: 63-69.
- [19] Moya JS, Iglesias JE, Limpo J, *et al.* Single crystal AlN fibers obtained by self-propagating high-temperature synthesis (SHS). *Scr Mater* 1997, **45**: 3089-3094.
- [20] Shi Z, Radwan M, Kiriwara S, *et al.* Morphology-controlled synthesis of quasi-aligned AlN nanowhiskers by combustion method: effect of NH₄Cl additive. *Ceram Int* 2009, **35**: 2727-2733.
- [21] Shi Z, Zhao C, Wang H, *et al.* Combustion synthesis of AlN nanowhiskers with different metallic catalysts. *Mater Lett* 2014, **128**: 156-159.
- [22] Shi Z, Yang W, Kang Y, *et al.* Synthesis of AlN porous-shell hollow spheres by a combustion route. *Ceram Int* 2013, **39**: 4663-4667.
- [23] Shi Z, Radwan M, Kiriwara S, *et al.* Combustion synthesis of rod-like AlN nanoparticles. *J Ceram Soc Japan* 2008, **116**: 975-979.
- [24] Shi Z, Miyamoto Y, Wang H. Combustion synthesis of aluminum nitride (AlN) powders with controlled grain morphologies. In *Nitride Ceramics: Combustion*

- Synthesis, Properties, and Applications*. Alexander AG, Liudmila NC, Eds. Germany: Wiley-VCH: Weinheim, 2015: 75-95.
- [25] Sakurai T, Yamada O, Miyamoto Y. Combustion synthesis of fine AlN powder and its reaction control. *Mater Sci Eng A* 2006, **415**: 40-44.
- [26] Shi Z, Radwan M, Kirihara S, *et al.* Formation and evolution of quasi-aligned AlN nanowhiskers by combustion synthesis. *J Alloy Compd* 2009, **476**: 360-365.
- [27] Wang H, Han J, Li Z, *et al.* Effect of additives on self-propagating high-temperature synthesis of AlN. *J Eur Ceram Soc* 2001, **21**: 2193-2198.
- [28] Rosenband V, Gany A. Activated self-propagating high-temperature synthesis of aluminum and titanium nitrides. *Exp Therm Fluid Sci* 2007, **31**: 461-467.
- [29] Radwan M, Bahgat M, El-Geassy AA. Formation of aluminium nitride whiskers by direct nitridation. *J Eur Ceram Soc* 2006, **26**: 2485-2488.
- [30] Radwan M, Miyamoto Y. Growth of quasi-aligned AlN nanofibers by nitriding combustion synthesis. *J Am Ceram Soc*. 2007, **90**: 2347-2351.
- [31] Chen K, Ge C, Li J, *et al.* Microstructure and thermokinetics analysis of combustion synthesized AlN. *J Mater Res* 1999, **14**: 1944–1948.
- [32] Evans CC. *Whiskers*. Britain: Mills & Boon, 1972.
- [33] Levitt AP. *Whisker technology*. America: John Wiley & Sons, 1970.
- [34] Bradshaw SM, Spicer JL. Combustion synthesis of aluminum nitride particles and whiskers. *J Am Ceram Soc* 1999, **82**: 2293-2300.
- [35] Lee J, Lee I, Kim D, *et al.* Effect of starting powder morphology on AlN

- prepared by combustion reaction. *J Mater Res* 2005, **20**: 659-665.
- [36] Russias J, Cardinal S, Esnouf C, *et al.* Hot pressed titanium nitride obtained from SHS starting powders: influence of a pre-sintering heat-treatment of the starting powders on the densification process. *J Eur Ceram Soc* 2007, **27**: 327-335.
- [37] Mukas'yan AS, Stepanov BV, Gal'chenko YA, *et al.* Mechanism of structure formation of silicon nitride with combustion of silicon in nitrogen. *Combust Explos Shock Waves* 1990, **26**: 39-45.
- [38] Ge Y, Cui W, Wang Q, *et al.* Microstructure and thermo-kinetics analysis in combustion synthesis of Si_3N_4 with high α -phase content. *J Am Ceram Soc* 2014, **98**: 263-268.
- [39] Liang YJ, Che YC, Liu XX. *Handbook of inorganic thermodynamic data*. China: North-East University Press, 1993.
- [40] Meng GY. *Chemical vapor deposition and non-organic new materials*. China: Science Press, 1984.