

Preparation of Slurry for Tape Casting of AlN Ceramic Substrates

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Abstract

AlN ceramics are employed in a multitude of applications including large-scale integrated circuit (LIC) packaging substrates, electrostatic chucks, and transparent ceramics due to their excellent thermal conductivity, insulation and dielectric properties, robust corrosion resistance, and thermal expansion coefficient nearly identical to that of silicon. Tape casting is the optimal methodology for the fabrication of large-area, thin, and flat ceramics and components. However, the well-dispersed slurry with high solid loading is required to obtain the ceramic substrates with excellent properties by tape casting. Therefore, in this study, the effects of dispersant content, first ball milling time, binder content, and R value (plasticizer/binder) on the rheological properties of aluminum nitride slurry and casted sheet qualities were investigated. The results indicated that the optimal dispersant formulation was 1.1 wt%, the binder formulation was 2 wt%, the R value was 1.5, and the solid content was 60 wt%. The utilization of the aforementioned organic system enabled the preparation of AlN sheet exhibiting favorable morphology, high solid content, and flexibility.

Keywords: Tape casting; AlN; Slurry; Solid loading; Rheological property

1 Introduction

As the microelectronics and integrated circuit manufacturing field continue to higher integration, miniaturization, and higher reliability, the unit volume of the integrated block of electronic components work on the heat generated by a sharp increase in excessive heat emitting will inevitably produce irreversible damage to the electronic components on the substrate, or even lead to the burnt out of integrated block. Therefore, higher requirements on the thermal conductivity of electronic packaging substrates are put forwarded^[1-2]. Researchers have attempted to address this challenge by exploring emerging materials such as AlN^[3], SiC^[4], BeO^[5] and Si₃N₄^[6]. Among them, aluminum nitride (AlN) is an emerging ceramic material with a number of desirable properties, including high thermal conductivity, low dielectric constant and dielectric loss, high volume resistivity, good mechanical properties at room and elevated temperatures, and a coefficient of thermal expansion similar to that of silicon. Among these properties, the theoretical thermal conductivity of single-crystal AlN is up to 320 W m⁻¹ K⁻¹, which is several times higher than that of Al₂O₃ as the traditional

substrate material for electronic packages^[7]. Additionally, AlN is chemically stable and nontoxic compared with the highly toxic nature of BeO, which has attracted a wide range of attention^[8].

As the demand for electronic devices continues to evolve, the size and thickness of aluminum nitride substrates are becoming increasingly challenging. Consequently, the urgent need of a suitable casting method to accelerate the large-scale production of silicon nitride substrate materials has become apparent. Currently for the ceramic substrate casting preparation, there are mainly the following types, including dry pressure, injection, gel injection molding and tape casting^[9]. The use of dry pressure molding and injection molding is only suitable for thickness greater than 1mm thick pieces. For large size, thin-walled pieces, these two methods are difficult to avoid uneven material density due to uneven casting pressure, so the parts in the sintering process is very easy to deformation, or even cracking, leading to low production efficiency. For gel injection of ceramic substrates, although it can solve the problem of deformation and cracking in the sintering process of the blank, the gel injection of the blank needs a slow drying and debinding process. Therefore, this method is inefficient and unsuitable for mass production.

While tape casting is the best way to prepare large-area, thin, flat ceramics and components, it is more suitable for industrialized production owing to the degree of automation and high efficiency^[10].

Tape casting is a forming process for preparing the ceramic substrates that offers numerous advantages. It is highly automated, requires minimal equipment, and can be operated continuously. Based on the type of solvent used, tape casting can be divided into two categories: water-based tape casting and organic-based tape casting^[11]. The organic-based tape casting, also known as the traditional casting process, has been studied and applied for a longer period of time than the water-based system. Additionally, the application of ceramic substrate preparation has been relatively mature in the case of the organic-based tape casting system. The most commonly used solvents are toluene, xylene, ethanol, and trichloroethylene. Binary azeotropic solvents such as ethanol/toluene and ethanol/trichloroethylene are also commonly used in actual production^[12]. The organic-based tape casting offers numerous advantages due to its compatibility, volatility, low latent heat of evaporation, low surface tension, and ability to prevent the hydration of ceramic powders. These advantages include a wide range of additives, fast solvent volatilization, short drying times, and the ability to obtain ceramic sheets with uniform structures, small green body defects, high strengths, and good flexibility.

In recent years, tape casting has been employed with increasing frequency in new research fields such as biomaterials, supercapacitors, and metals. The expansion of tape casting, especially in the aforementioned fields, will become one of the most promising areas of researches in the coming years^[13]. The tape casting process was proposed by Howatt^[14] in 1947. The process involves the mixing and stirring of ball-milled raw materials with binder and plasticizer to create a uniform slurry. And then a uniform thickness sheet is formed, which is discharged and sintered to obtain the final product. The quality of the casting sheet produced by tape casting is largely contingent upon the characteristics of the slurry. This is because the slurry comprises a multitude of components, including powders, solvents, plasticizers, binders, and dispersants. Any alteration to the composition of the slurry will result in a corresponding change in viscosity and physical rheology. Furthermore, the individual components of the slurry will also exert an influence on one another^[15-16]. T. Chatter, E. Streicher, and colleagues^[17-19] prepared AlN substrates using the casting method and investigated the effects of organic components (binders, plasticizers) and their dosages on slurry and green body machinery. W. Yin et al.^[20, 22] conducted research on the preparation of AlN substrates by tape casting and discussed the primary factors influencing the viscosity of casting slurry. Their findings indicated that the viscosity of the slurry decreased as the solvent ratio increased, while it

increased as the plasticizer ratio decreased. Yao et al.^[23] conducted a study on the types of solvents, specifically xylene, butanol, isopropanol, n-propanol, and mixtures thereof (e.g., xylene + butanol, xylene + isopropanol, n-propanol + butanol, xylene + n-propanol, xylene + n-propanol). The results demonstrated that the mixed solvent xylene/isopropanol exhibited the most favorable wettability for AlN powder, while the slurry displayed the most optimal rheological properties, rendering it well-suited for tape casting. Liang et al.^[24, 25] prepared an AlN ceramic slurry using absolute ethanol as a solvent, polyvinyl butyral ester (PVB) as a binder, oleic acid as a dispersant, and glycerol as a plasticizer. Huang et al.^[26, 27] used an azeotropic mixture of dibutyl ketone and ethanol, while polyvinyl butyral ester (PVB) and butyl benzyl phthalate (BBP) were employed as binders and plasticizers, respectively, in the preparation of AlN slurries.

In addition to the individual formulations, the ball milling of the mixing process and the characterization of the fluid are also of great importance for the ceramic substrates. For systems with more wear-resistant components, the slurry is generally prepared by ball milling, and if there are special requirements, inert atmosphere or vacuum conditions may be required. However, vigorous agitation may disrupt the polymer chain of the binder, and both the binder and the dispersant need to be adsorbed on the surface of the ceramic powder, which is competitive^[28]. Therefore, the ball milling process needs to be divided into two steps. The purpose of the first step is to make the agglomeration of powder particles open and fully dispersed, and only powder particles, solvents and dispersants are included in the slurry, so that the dispersant can be fully adsorbed on the surface of powder particles. The second step is to add other additives to the slurry ball mill with the aim of homogenizing the slurry composition. After the ball mill is completed, there will also be a small amount of air and residue in the slurry, which requires degassing and filtration before it can be used for subsequent molding.

Fluids can be divided into several categories according to their viscosity as a function of the shear rate^[29]. The viscosity of pseudoplastic fluid decreases with the increase of shear rate, and the viscosity of plastic fluid increases with the increase of shear rate. In order to keep the thickness of the cast film with a smooth surface and a homogeneous microstructure, the slurry used for tape casting should be a pseudoplastic fluid. After the casting, the scraper will exert a shear stress on the slurry, and the viscosity of the slurry decreases under the action of shear stress, so that a uniform film can be formed on the substrate. When the scraper passes through the slurry, the shear stress disappears, the viscosity rises to the initial state, and the fluidity of the slurry becomes poor. And the composition of the casting film is kept uniform. In order to avoid the slurry remaining in a low viscosity state for a long time after the scraper has passed, the slurry should

not be thixotropic, i.e., the viscosity increases immediately after the stress is withdrawn.

The composition of casting slurries includes the used raw powders, solvents, dispersants, binders, plasticizers, and other additives. Each of these components exerts an important influence on the performance of the slurry, and the interactions among the individual components within the slurry are also significant. The complexity presents a significant challenge to the study of tape casting slurries. Consequently, it is essential to conduct further in-depth research and exploration of tape casting technology. In this study, aluminum nitride was used as the main raw material, and toluene and anhydrous ethanol were used as the binary solvents. Toluene was able to dissolve all the solutes and reduced the drying speed, which could reduce the volatilization, decrease the viscosity and increase the solid content. Fish oil, polyvinyl butyral and dibutyl phthalate were used as dispersants, binders and plasticizers, respectively, for the preparation of aluminum nitride ceramic substrates.

2 Experimental

2.1 Starting materials

Aluminum nitride powders (average particle size: 1 μm), calcium fluoride powder and yttrium oxide powder were used as sintering additives, and toluene and absolute ethanol were selected as solvent systems. Herring oil (Cas:8002-5-4, Shanghai Macklin Biochemical Co., Ltd., China) was used as a dispersant, and polyvinyl butyral (PVB, Cas:63148-65-2, Shanghai Macklin Biochemical Co., Ltd., China) and dibutyl phthalate (DBP, Cas:84-74-2, Shanghai Macklin Biochemical Co., Ltd., China) were used as binders and plasticizers, respectively.

2.2 Experimental process

The preparation method of AlN slurries was as follows. Firstly, mixed powders were prepared according to the molar ratio of AlN, CaF₂ and Y₂O₃ of 92:3:5. Toluene and absolute ethanol were used to prepare non-aqueous solvents according to the mass ratio of 1/1. Then, the mixed powders were added into the solvent, and they were ball-milled for 1-4 h. Dispersant, binder (PVB) and plasticizer (DBP) were added to further be milled for 12 h. The height of the scraper was controlled at 200 ~ 300 μm . The casting speed was 0.3 $\text{cm}\cdot\text{s}^{-1}$. The tape sheets were dried at 27.5 $^{\circ}\text{C}$ for 12 h to obtain the final samples.

2.3 Characterization

The viscosity of the slurries was quantified using a viscometer (NDJ-8S), and the dispersibility of the slurries was evaluated through the sedimentation method. Prior to the addition of the binder PVB, it is necessary to prepare a

precast colloid with toluene and absolute ethanol solvent in advance, which show a colorless, transparent, and clear solution at 90 $^{\circ}\text{C}$ in an oil bath before using.

3 Results & Discussion

In the tape casting process, the viscosity of the slurries is a crucial parameter influencing the quality of the tape sheet. And it, as an essential rheological property, is a quantifiable characteristic that reflects the friction or viscosity within the slurry^[30]. The viscosities are affected synergistically by multiple factors, including powder particle properties, slurry composition, mixed ball mill dispersion time, temperature, etc. The R-value (ratio of plasticizer to binder) is an indicator that reflecting the effect of these factors on the dispersion or viscosity of AlN slurries.

3.1 Effect of dispersant content on the properties of AlN slurries

Figure 1 shows the viscosity of the slurries with different contents of dispersant (0~2.6 wt%) after the first ball milling for 3h, in which the solid content of slurries is 57.8 wt%. The viscosity of slurries decreases with the increase of dispersant content. Since the dispersant is adsorbed on the surface of the particles, the spatial stability hinders the agglomeration among the particles and enhances the fluidity of the slurries^[30]. As the dispersant content increases from 0 to 2.6 wt%, the viscosity of slurries first decreases and then increases.

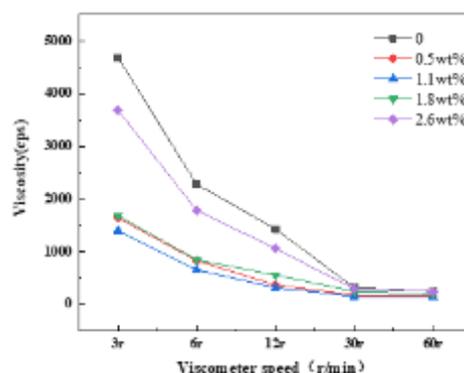


Figure 1 Effect of dispersant content on suspension viscosity

When the content is 1.1wt%, the viscosity has a lowest value. It is found that the excess dispersant content undergoes a cross-linking reaction among the particles, reducing the dispersion of the particles^[31]. Therefore, it is determined that 1.1 wt% dispersant is the optimal content.

3.2 Effect of ball milling time on the properties of AlN slurries

Figure 2 shows the viscosity of AlN slurries with different ball milling time at the dispersant content of 1.1wt%. It is found that the viscosity of the slurries

increases with the increase of ball milling time. The viscosity of the slurries increases because of the volatilization of the solvent in 0~4h. Meanwhile, it is seen that the viscosity of the slurries decreases with the increase of the shear rate, meaning that the prepared slurries exhibit typical pseudoplastic fluid characteristics^[32]. In the tape casting process, the scraper function is like a shearing process, and the shear thinning characteristics of the pseudoplastic fluid are very advantageous in the tape casting process. When the slurry passes through the scraper, the viscosity becomes small, which is conducive to the slurry passing through the scrape. After that, the shear rate becomes small and the viscosity of the slurry increases rapidly, which is beneficial for the forming of taped green sheets.

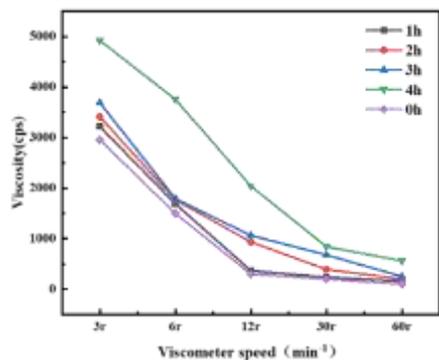


Figure 2 Changes in viscosity of slurries at different ball milling times

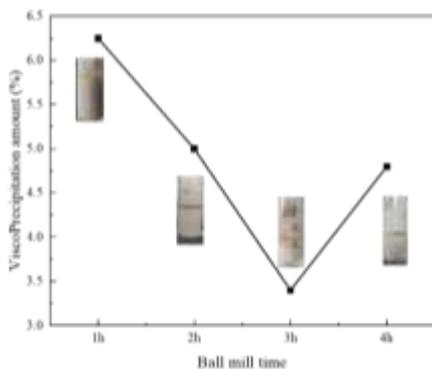


Figure 3 Comparison in the height of the upper precipitated liquid after standing for 1 h at different ball milling times

As shown in Figure 3, when the rotational speed of the planetary mill is 300r/min, as ball milling time increases from 1h to 3h, the height of the upper yellow liquid after resting 1h gradually decreases. At ball milling of 3h, the upper yellow liquid after resting 1h is least height. However, with the further increase of ball milling time, the precipitate height increases. These results show that too long ball milling time causes the instability of slurries. Therefore, appropriate ball milling time is required to obtain slurries with high performance.

3.3 Effect of binder content on AlN slurries w

In the manufacturing of ceramic green sheets,

binders are probably the most important additives in the overall system^[31].

Fig. 4 shows the viscosity variation of AlN slurries with different binder content, in which the solid content of the slurry is 46 wt.%, the dispersant content is 1.1 wt.%, the binder content ranges from (1.2~3.6) wt.%, and the mass ratio of plasticizer to binder is 1. With the increase of binder content, the viscosity of the slurry increases gradually. In order to obtain the maximum solid content, the binder should be selected as little as possible under the condition of maintaining a certain strength. Meanwhile, it is found that when the binder content is located at 1~1.5wt%, it has been demonstrated that the formed film exists micropores. When the binder content is 2.5wt%, the surface of the formed film is smooth. And when the binder content is 3.7wt%, the formed film is not easy to control the thickness, meanwhile, the high viscosity is not conducive to the subsequent increase of solid content. Therefore, the binder content of 2wt% is used for the preparation of slurries.

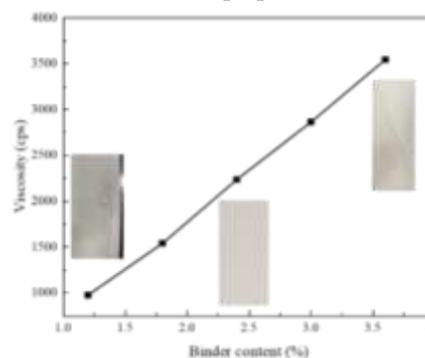


Figure 4 Effect of binder content on viscosity of AlN slurries

3.4 Effect of R-value on properties of AlN slurries

The R-value, i.e., the ratio of plasticizer to binder, is an important factor influencing the rheological properties of cast slurry and the properties of cast green materials. both of which

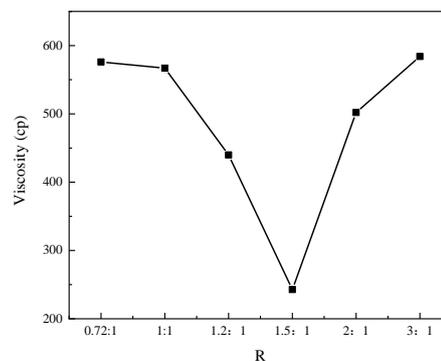


Figure 5 Effect of R value on the viscosity of AlN slurries

Make the cast sheets more flexible. In Figure 5, at the solid loading of 43wt%, binder content of 2wt%, and dispersant content of 1.1wt%, with the increase of R value from 0.72 to 1.5, the viscosity of slurries gradually

decreases. When the R value is 1.5, the lowest viscosity of slurries is obtained. With further increase of R, oppositely, the viscosity increases.

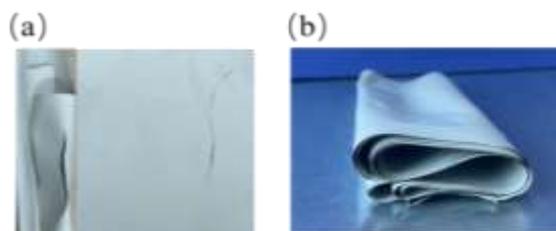


Figure 6 The photo images of formed tape sheets at the R value of (a) 0.72 and 1, (b) 1.5

In Figure 6a, when the R value is 0.72 and 1, the flexibility of the formed tape sheet is insufficient, causing it susceptible to cracking during the drying process. An appropriate R-value can reduce the viscosity of the slurry, thereby facilitating the forming of desired flexibility. As illustrated in Figure 6b, at an R-value of 1.5, the AlN green sheets exhibits optimal flexibility and a smooth surface. Accordingly, the R-value of 1.5 is selected for the subsequent experiments.

3.5 Effect of solids content on rheological properties of AlN slurries

The solid content of AlN slurries is crucial for the preparation of high density AlN ceramics. Therefore, it is necessary to prepare the slurries with high solid content as much as possible while ensuring the dispersion stability and low viscosity. As shown in Fig. 7, when the solid loading increases from 42 to 57wt.%, the viscosity of the slurry increases gradually. However, when the solid phase increases from 57 to 62wt.%, the viscosity value increase sharply, and the fluidity of the slurry become weak, which can not form the green film. The higher the solid content of the AlN slurry, higher density of the AlN ceramics can be obtained. Therefore, AlN slurries with solid loading of 60wt.% are selected to prepare the AlN ceramics.

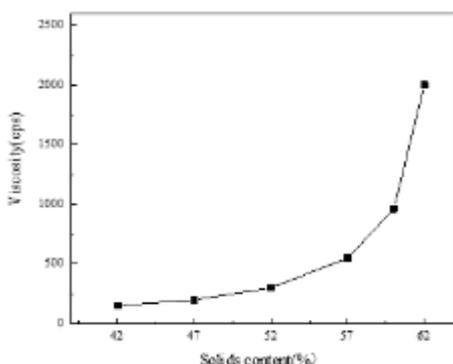


Figure 7 Effect of solids content on viscosity of AlN slurries

4 conclusions

In this paper, the effects of the dispersant, ball milling time, binder, plasticizer, and solid loading on the

properties of AlN ceramic slurries were researched. A 1.1wt% of fish oil as a dispersant for the slurry could yield a dispersion of AlN with good dispersion stability and low viscosity. The ball milling time of 3h was beneficial for the AlN slurry with best dispersion and low viscosity. Additionally, the binder content of 2wt% was used to prepare AlN slurries with high solid loading. Meanwhile, the viscosity of the slurry decreases first and then increases with the increase of the R value (plasticizer/binder), and the viscosity of the slurry reaches the lowest value when R=1.5. Finally, the slurries with the solid loading of 60wt% were chose to prepared the AlN ceramic sheets in future research.

References

- [1] R. Plieninger, M. Dittes, K. Pressel. Modern IC packaging trends and their reliability implications[J]. *Microelectronics Reliability*, 2006,46(9):1868-1873.
- [2] J. Baffett. Electronic systems packaging: future reliability challenges[J]. *Microelectronics Reliability*, 1998(38):1277-1286.
- [3] Hongjun N, Wei N, Libin M, et al. Research status and development trend of preparation technologies for high thermal conductivity AlN ceramic substrates [J]. *Modern Chemical Industry*, 2017, 37(07): 45-48.
- [4] Eom J H, Seo Y K, Kim Y W. Mechanical and thermal properties of pressureless sintered silicon carbide ceramics with Alumina-Yttria-Calcia[J]. *Journal of the American Ceramic Society*, 2016,99(5):1735-1741.
- [5] Akishin P G, Turnaev K S, Vaispapur Y V, et al. Composition of beryllium oxide ceramics [J]. *Refractories and Industrial Ceramics*, 2011,51(5):377-381.
- [6] Zhou Y, Hyuga H, Kusano D, et al. A Tough Silicon Nitride Ceramic with High Thermal Conductivity[J]. *Advanced Materials*, 2011,23(39):45-48.
- [7] Chung L S, Tsai I T, Huang C S. High Thermal Conductivity Ceramics from Combustion Synthesized AlN Powder through Microwave Sintering and Reheating [J]. *International Journal of Self-Propagating High-Temperature Synthesis*, 2012,21(1):45-50.
- [8] Sunil C Joshi, Y.C Lam, F.Y.C Boey & A.I.Y Tok. Power law fluids and Bingham plastics flow models for ceramic tape casting[J]. *Journal of Materials Processing Tech*, 2002(1-3),215-225.
- [9] Alain D. Moriana & Shujun Zhang. Lead-free textured piezoceramics using tape casting: A review[J]. *Journal of Materiomics*, 2018(4):277-303.
- [10] Qingdong H, Xudong L, Zhipeng X, et al. Development of the Environmental Friendly Non-Aqueous Tape Casting Process for High-Quality Si₃N₄ Ceramic Substrates[J]. *IOP Conference Series: Materials Science and Engineering*, 2019(678):012042-012042.
- [11] Zhao Pengbo, Zhao Xiaotong & Wang Hailong. Processing and Properties of Laminated ZrB₂-Mo₅SiB₂ Ceramic Composites Fabricated by Tape Casting and Hot Pressing Sintering[J]. *IOP Conference Series: Materials Science and*

- Engineering, 2019(10):012072-012072.
- [12] MORENO R. The role of slip additives in tape-casting technology. I: Solvents and dispersants[J]. American Ceramic Society Bulletin, 1992,71(10),1521-1531.
- [13] Hou Qingdong, Luo Xudong, Xie Zhipeng, et al. Development of the Environmental Friendly Non-Aqueous Tape Casting Process for High-Quality Si₃N₄ Ceramic Substrates[J]. IOP Conference Series: Materials Science and Engineering, 2019(15):012042-012042.
- [14] Jabbari M., Bulatova R., Tok A. I. Y., et al. Ceramic tape casting:A review of current methods and trends with emphasis on rheological behaviour and flow analysis[J]. Mater.Sci.Eng.B, 2016(212):39-61.
- [15] MESSING G L, FULLER E R, HAUSNER H. Ceramic powder science[M]. Columbus: American Ceramic Society, 1988.
- [16] ZHOU Jian-min, WANG Ya-dong, WANG Shuang-xi et al. Tape Casting Process for Fabricating Electronic Ceramic Substrate [J]. Bulletin of the Chinese Ceramic Society, 2010,29(5):1114-1118.
- [17] DESCAMPS M, MOREAU G, MASCART M, et al. Processing of aluminium nitride powder by the tape-casting process[J]. Journal of the European Ceramic Society, 1994,13(3):221-228.
- [18] STREICHER E, CHARTIER T, BOCH P. Influence of organic components on properties of tape-cast aluminum nitride substrates [J]. Ceramics International, 1990,16(4):247-252.
- [19] CHARTIER T, STREICHER E, BOCH P. Preparation and characterization of tape cast aluminum nitride substrates[J]. Journal of the European Ceramic Society, 1992,9(3):231-242.
- [20] WU Y, ZHOU H P, LIAO W G. Process of casting to make AlN ceramic substrates[J]. Electronic Components and Materials, 1996,15(1):20-23.
- [21] WU Y, LIAO W G. High thermal conductivity AlN substrates for low-temperature sintering were prepared by casting method[J]. Journal of Inorganic Materials, 1996,11(4):606-610.
- [22] WU Y, LIAO W G. Study on the viscosity of cast slurry for AlN substrate[J]. Electronic Components and Materials, 1996,15(6):21-24.
- [23] YAO Y J, QIU T. Study of cast forming pastes for aluminum nitride substrates[J]. Journal of Materials Science and Engineering, 2006,24(3):104-106.
- [24] CAO J. Study on the preparation of AlN ceramic substrates by casting method[J]. Journal of Inorganic Materials, 2001,16(2):269-276.
- [25] Liang Guangchuan, Liang Jinsheng, Liang Xiuhong, et al. A method for manufacturing aluminum nitride ceramic substrate with high thermal conductivity for integrated circuits using tape casting[P]. Tianjin:CN98125129.3,2002-07-03.
- [26] DONG H, ZHAOBO T, WEI C, et al. Effects of Y₂O₃ and yttrium aluminates as sintering additives on the thermal conductivity of AlN ceramic substrates[J]. Ceramics International, 2018,44(16):20556-20559.
- [27] HUANG D, LIU Z, HARRIS J, et al. High thermal conductive AlN substrate for heat dissipation in high-power LEDs [J]. Ceramics International, 2018,45(1):1412-1415.
- [28] HESSELINK, F. Th. Theory of the stabilization of dispersions by adsorbed macromolecules. I. Statistics of the change of some configurational properties of adsorbed macromolecules on the approach of an impenetrable interface[J]. The Journal of Physical Chemistry, 1971,75(1):65-71
- [29] Chartier T., Merle D., Besson J.L. Laminar ceramic composites[J]. J.Eur.Ceram.Soc. 1995,15(2):101-107.
- [30] Struble L, Sun G K. Viscosity of Portland cement paste as a function of concentration[J]. Advanced Cement Based Materials, 1995,2(2):62-69.
- [31] Bitterlich B., Jürgen G.H. Aqueous tape casting of silicon nitride[J]. J.Eur.Ceram.Soc. 2002,22(13):2427-2434.
- [32] F. P. M. A. A. Steady-state simulation of the film-casting process for Newtonian and viscoelastic fluids[J]. Journal of Non-Newtonian Fluid Mechanics, 2023(322):33-36.