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Tape casting of AlN/glass composites for LTCC substrate

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AlN/glass composite is low-fired substrate material for microelectronic packaging material. In this work, AlN/glass sheets were prepared by tape casting process. The dispersion, stabilization and the rheological properties of the slurry were studied. The optimum drying condition and mechanisms of debinding were also investigated. The results showed that powder size influenced the optimum content of dispersant and the viscosity of slurry. The slurry for tape casting exhibited a typical shear-thinning behavior. Smooth green tape without cracking was acquired after it was dried at solvent atmosphere. The binder was fully burned out at 600°C at low heating speed. The lamination with uniform microstructure was achieved by hot-pressed at 900°C. © *2003 Kluwer Academic Publishers*

1. Introduction

Low Temperature Co-fired Ceramics (LTCC) technology offers significant benefits over the other established packing technologies due to high-density, high-radio-frequency, fast-digital applications requiring hermetically sealed packaging and good thermal management. Ceramic/glass substrates have been widely used in the microelectronic packaging industry to produce low-temperature sintering substrates (800°C–1000°C) which can be co-fired with high conductive metals such as copper, gold and sliver [1, 2]. In recent years, many LTCC systems were made up of Al_2O_3 and glass [3–5]. AlN ceramic is an excellent microelectronic package material due to its good dielectric properties and low thermal expansion, especially its high thermal conductivity, which is ten times as much as that of Al_2O_3 [6, 7]. Accordingly, it is possible that AlN/glass composites will be beneficial for improving thermal conductivity of LTCC.

As a convenient and low cost processing for making high-quality laminated materials, tape casting has been extensively studied to produce ceramic substrate [8–10]. However, the casting slurry is a complex system containing solvents, binders, plasticizers, dispersants and ceramic powders. Each component has a substantial effect on the fluid characteristics of slurry and then affects microstructure and densification behavior of the green sheets.

In this paper, AlN/glass composite sheets were prepared by tape casting. The effects of the components on the rheological behaviors and properties of green tapes were studied. The drying conditions and the binder burnout mechanisms of the green sheet were discussed in detail.

2. Experimental procedure

AlN powder and borosilicate glass powder were used as raw materials. The commercial AlN powder (Shenhai Nitride Co. Ltd. China) was synthesized by self-propagation high-temperature synthesis (SHS) method, with nominal particle size of 7.1 μm (grade A). Different grain sizes of AlN were acquired by controlling attrition-milling time. Borosilicate glass powder was milled to the same particle size as the different grade of AlN. AlN and glass powders were mixed with the weight ratio of 70:30. The binary solvent system, Ethanol (EtOH)/Butanone (MEK) (40:60) was employed. Triethyl phosphate (TEP), polyvinyl butyral (PVB), polyethylene glycol (PEG) and diethyl-o-phthalate (PHT) were introduced as dispersant, binder and plasticizers, respectively. The formulations of the slurries were shown in Table I.

The mixed powders, with TEP as dispersant, were firstly ball-milled for 24 h in EtOH/MEK solvent system with AlN ball. Binder and plasticizers were added to the slurries and milled for another 24 h. Then the tape was cast on a glass surface through the action of a blade that leveled the slurry. The tapes were dried at air and solvent atmosphere in order to compare the influences of different drying condition on the green sheet. The dried tapes were cut into 30 × 35 mm squares, then stacked and burned out. Finally, the green laminate of AlN/glass composites were hot-press sintered at nitrogen atmosphere at 900°, for 2 h.

The particle size was measured using sedimentation method (SICAS 4800). The shear viscosity of the suspension without binder and plasticizers was determined by rotating viscometer (NDJ-7). The rheological behavior of slurry was carried out on ARES-9A

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TABLE I The composition of the slurry

Materials	Function	Weight percent (wt%)
AlN and glass	Powders	35–40
EtOH (Ethanol)	Solvent	16–18
MEK (Butanone)	Solvent	32–36
TEP (Triethyl phosphate)	Dispersant	1.0–1.3
PVB (polyvinyl butyral)	Binder	4.1–5.8
PEG (polyethylene glycol)	Plasticizer	1.0–1.5
PHT (diethyl-o-phthalate)	Plasticizer	1.0–1.5

rheometer with 25 mm diameter parallel plates. Shear viscosity and stress were determined in a range of shear rates from 0 to 400 s^{-1}. The binder burnout processing was studied from room temperature to 600° at 10°/min in air (STA-429 thermal analyzer Netzsch. De.). The microstructures of green tapes, the sintered substrates and the particle shape were observed by SEM (EPMA-8705QHII). The density and open porosity were measured through Archimedes' principle.

3. Results and discussions

3.1. Effect of particle size on dispersion

The average particle size of AlN powder is listed in Table II. Fig. 1 shows SEM micrographs of B grade AlN powder. The milled AlN powder was spheric and uniform. The aggregates formed by spheric particles were easy to break down during ball milling, which was beneficial to prepare compact sheet and to increase the strength of the green tape.

In tape-casting processing, particle size and its specific surface area can have effects on the content of organic additives, the stability of the slurry and the quality of the tapes. Usually, it was easy to obtain dense tape with fine powders. If the powder size was as large as grade A, the suspension was unstable and uneven. When the powder was as fine as grade D, the slurry was too viscous and required more surfactant. Therefore the proper particle size was helpful to get stable and uniform slurry. In this work, the powders of B (1.7 μm) and C (0.82 μm) grade were chosen.

TABLE II Average particle size of AlN powder

Grade A	Grade B	Grade C	Grade D
7.1 μm	1.7 μm	0.82 μm	0.29 μm

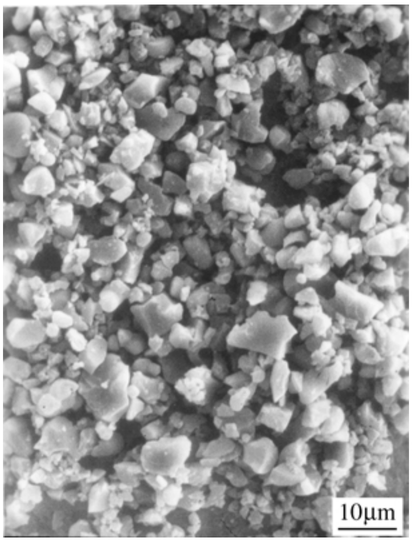

Figure 1 The SEM micrographs of B grade AlN powder.

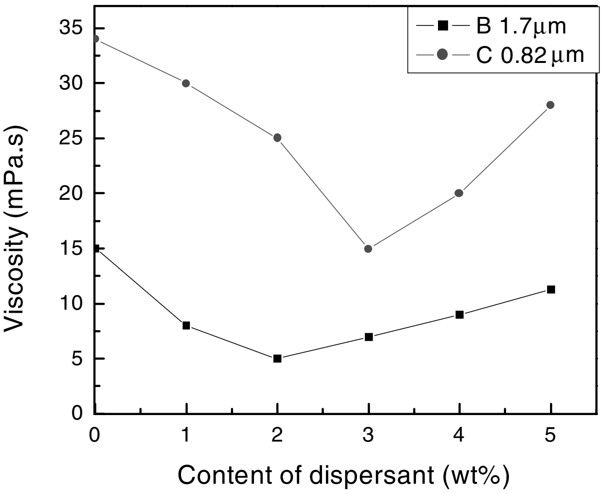

Figure 2 The viscosity of slurry with different dispersant content.

Fig. 2 shows the viscosity of slurry with B and C grade powders. With the same proportion of powder and solvent, the relation between the apparent viscosity and content of dispersant (TEP) was non-linear. When the content of dispersant was low, the powder was agglomerated and the viscosity was high. However, when the dispersant was excessive, the redundant surfactant formed bridge between the particles and then caused the increasing viscosity. Consequently, there should be a minimum value in the viscosity curve with a certain dispersant percentage, which named optimum weight percentage of dispersant (D_{opti}).

In addition, D_{opti} was changed with different particles size. According to the two curves in Fig. 2, the D_{opti} were 2 wt% and 3 wt% for B and C grade powders respectively. In organic slurry, the dispersion mechanism is Steric stabilization [11, 12]. The effective dispersant was amphipathic, with polar group and oleophilic group. The hydrophilic group was absorbed and fixed on the particle surface, and at the same time the oleophilic group was dissolved in the organic solvent. Hence, the particles were distributed in the slurry evenly and stably. When the particle was small, the specific surface area increased and the D_{opti} increased.

3.2. Rheological properties of slurry

Fig. 3 shows shear viscosity and shear stress of slurry as a function of shear rate. Hysteresis loop was found for the slurry. The existence of loops indicated that there were a structure of favorable particle arrangement in the slurry and the slurry was thixotropic. The slurries need take time to recover their original state. In the hysteresis loop experiment, the structure was broken down during

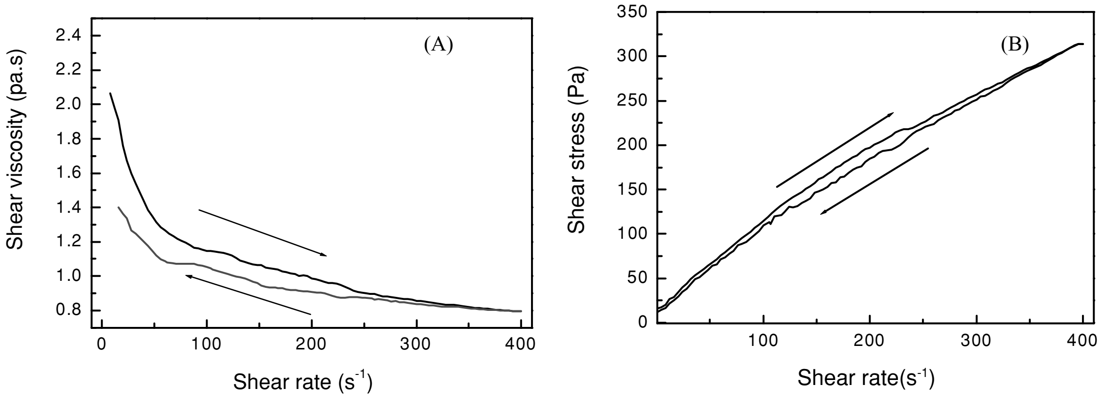

Figure 3 Rheology curve of the slurry (A) Shear viscosity curve and (B) Shear stress curve.

the increase in shear rate level (up curve). The structure would build up as the shear rate decreased (down curve). As the structure build-up was fast, the structure that existed at each shear rate (in the down curve) was close to the structure at the highest shear rate. Clearly, different structure could exist at the same shear rate level as a result of different histories. Moreover, shear viscosity decreased with the increase in shear rate. It suggested that the slurry was non-Newtonian with shear-thinning behavior.

3.3. Effects of atmosphere on drying

Drying involves a complex interplay of several kinetic processes, including evaporation, viscous deformation of the film, flow of fluid in the pores and diffusion [13, 14]. The green tape was cracked when the evaporating rate of solvent was too fast (shown in Fig. 4). The solvent was evaporated rapidly at open air, so organic additives cannot fill up the blank of solvent. The uneven microstructure was caused by rapid shrinkage. High porosities existed on the surface of the green tape. The microstructure of tape dried at solvent atmosphere was rather uniform (Fig. 5). A few interlock pores existed in the tape. In this condition, the solvent was removed at low speed and the shrinkage was relaxed. The surface of tape was smooth and the structure was more uniform. Hence, it was probable to obtain good quantity green tape by providing suitable solvent atmosphere of drying.

3.4. Thermal analysis of tape

The organic additives, such as dispersant, binder, and plasticizers, remained in the tape after drying. They should be removed before sintering. Fig. 6 shows the TGA and DSC curves of AlN/glass green tape. The weight loss occurred at about 80°C due to the residual solvents evaporation. The main weight loss occured at 270°–370°C. There was an endothermic peak at about 280°C on the DSC curve corresponding to volatilization of the plasticizers. The binder (PVB) was degraded and burned out gradually at 300°–600°C. In air, the organic additives can be degraded and oxidized into carbon oxides and water, as well as other small organic molecules. Without oxygen, organic substances would only be degraded into small molecules step by step. Some small organic molecules could not be oxidized and a small amount of carbon was kept in the green tape. If the carbon content was likely less than 1.0 wt%, the sintering character and properties of substrates were

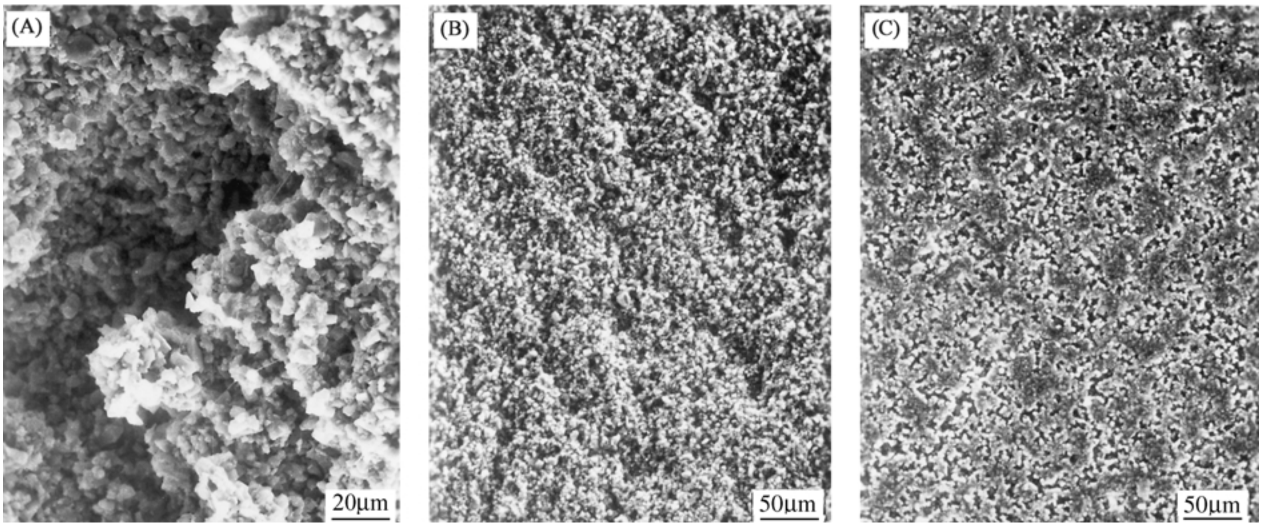

Figure 4 SEM micrograph of the green tape (drying in air) (A) Fracture surface, (B) Top surface, and (C) Bottom surface.

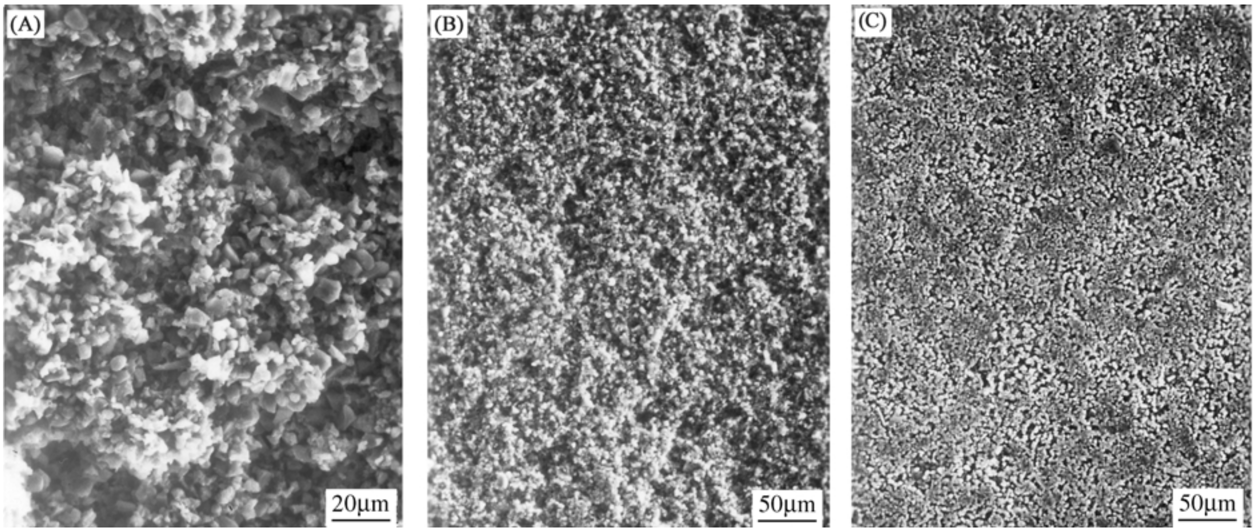

Figure 5 SEM micrograph of the green tape (drying in solvent atmosphere) (A) Fracture surface, (B) Top surface, and (C) Bottom surface.

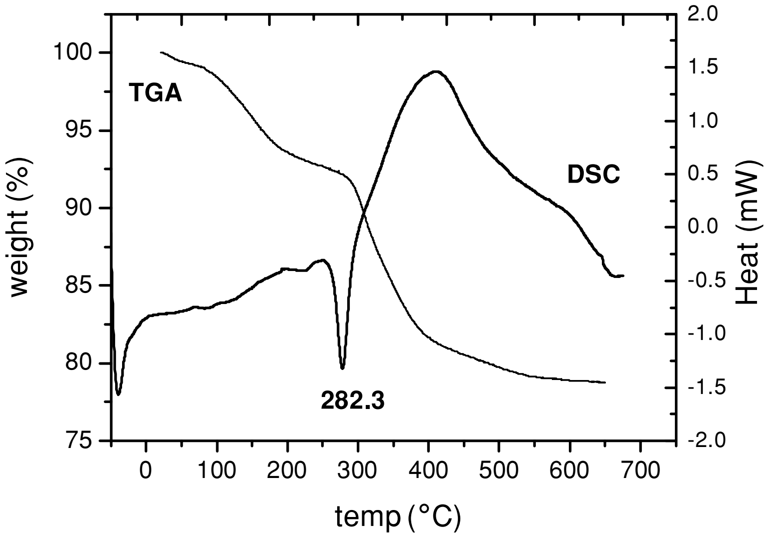

Figure 6 TGA and DSC curves of AlN/glass green tape.

influenced greatly. A certain amount of oxygen should be kept in the atmosphere before 600°C for oxidization of small organic molecules, but at higher temperature oxidization of AlN powder must be avoided. The heating rate was as low as 1°C per minute to decompose and oxidize the organic additives completely and to keep the tape flat and smooth. The carbon content in the green tape after burning out at 600°C in air is listed in Table III.

3.5. Microstructure of sintered composites substrate

Fig. 7 shows the microstructures of laminated composite hot-pressed at 900°C. Interface of the sheets disappeared after sintering (Fig. 7A). The surfaces were integrated together. The microstructure of the composite was uniform. The relative density was more than 98% and the open porosity was less than 0.5%. It was clear that the borosilicate glass showed a higher wettability

TABLE III Content of residual carbon in tape after debinding process at 600°C

Total carbon (wt%)	Free carbon (wt%)	Compound carbon (wt%)
0.49	0.15	0.34

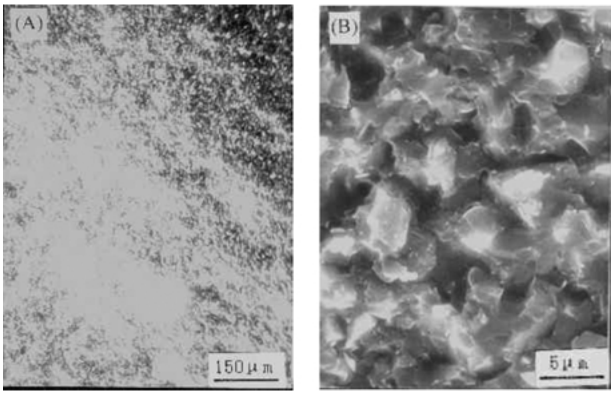

Figure 7 SEM micrographs of laminated composite hot-pressed at 900°C (A) The invisible interface of sheets and (B) the microstructure of the composites.

to the AlN particles at 900°C (Fig. 7B). Therefore, the borosilicate glass played an important role on low temperature sintering of the composite substrate.

4. Summary

The AlN/glass substrates were produced by tape casting processing. The influence factors of slurry characteristic and the tape quality were investigated. The optimum processing parameters were studied. The following conclusions can be summarized:

1. The powders granularity directly influenced the properties of slurry and the content of dispersant. The optimum dispersant content increased when the particle size decreased.
2. The slurry for tape casting exhibited shear-thinning behavior. The type of the slurry was non-Newtonian fluid.
3. Due to the evaporation of solvent was slow at solvent atmosphere, the dried tape was smooth and the cracking was avoidable.
4. According to thermal analysis, the binder was degraded and burned out at 300°–600°C. At low heating speed, the binder was removed completely and the tape kept flat and smooth.
5. The stacking sheets were hot-pressed at 900°C. The AlN/glass substrates were well sintered and its microstructure was uniform.

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