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Preparation of aluminum nitride green sheets by aqueous tape casting

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Abstract

Aluminum nitride green sheets were prepared by aqueous tape casting. The characteristics of a treated AlN were studied in aqueous ball-milling media. The oxygen content picked up with the increase of ball-milling time. It was noted that the oxygen content of AlN powder with the dispersant DP270 was lower than that of AlN powder without the dispersant DP270. The isoelectric points of the treated AlN with and without DP270 were, respectively, at pH 3.35 and pH 3.90. The dispersant DP270 not only efficiently dispersed AlN powder in water to form a stable suspension, but also formed a coat onto AlN surface to limit hydrolysis of the AlN powder. The tape casting slurry exhibited a typical shear-thinning behavior. Aqueous AlN green tape had a smooth surface and a narrow pore size distribution. Its relative density was 52.6%. No other crystalline phase was detected by XRD except for AlN and sintering aid yttria in AlN green sheet.

Keywords: A. Tape casting; B. X-ray methods; C. Mechanical properties; AlN

1. Introduction

Aluminum nitride (AlN) has received much interest in the area of high density package because of its high thermal conductivity, high electrical resistivity, low dielectric constant, no toxicity and its thermal expansion coefficient (TEC) close to that of silicon [1]. However, one of the difficulties associated with AlN is the reaction between AlN and water. Many works have reported the mechanisms and kinetics of the hydrolysis reaction of aluminum nitride [2–6], which has been used to improve the hydrophobic nature of AlN. Both organic long-chain molecules and inorganic aid have been used as a surface-modifier of AlN [7–10]. Different surface treatment had a significant effect on the characteristics of AlN powder in water.

Tape casting has been proved its efficiency for the fabrication of thin ceramic substrates for electronic applications [11–13]. In the past, organic solvents were favored to prepare ceramic slurries for tape casting due to their low boiling points, low latent heat of evaporation and low surface tension. However, environmental and health concerns with the use of organic solvents has been the catalyst for the efforts to develop aqueous tape casting [14–16]. An added benefit is the cost reduction involved with the use of water. The typical aqueous tape casting is made of slurry preparation and tape casting. The stable slurry are composed of ceramic powder dispersed in water, dispersant, binder, plasticizer and other surfactant [17–19]. D. Hotza et al. [20] reported aqueous tape casting of AlN. They showed that there was no need for a dispersant in AlN slurries. These results were possibly related to the surface-treated method. The hydrophobic mechanisms were different for AlN powders treated with stearic acid and with phosphoric acid. Stearic acid has hydrophobic function groups, which could be beneficial to the dispersion of AlN powders in water.

In this work, AlN powders were anti-hydrolysis treated by phosphoric acid and its characteristics were investigated in aqueous balling media. The slurry properties of aqueous tape casting AlN were discussed in details. AlN green sheets were prepared by aqueous tape casting.

2. Experimental procedures

2.1. Starting materials

The AlN powder used in this study was synthesized by self-propagation high temperature synthesis method and

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anti-hydrolysis treated simultaneously by phosphoric acid. The formation of impermeable, water-insoluble phosphate on the AlN surface could prevent AlN powder from hydrolysis [4,7]. The average diameter of the powder is 1.7 μm. The content of oxygen and nitrogen are 1.44 and 32.31 wt.%, respectively. The deionized water (pH 5.60–6.0) was employed as solvent. The pH value of slurry was adjusted by analytical grade HCl and NaOH. DP270 (a kind of ester of polyacrylate, provided by Rhodia Co., France) and PVA124 (Kuraray Chemical Co., Japan, 10 wt.% emulsion) were used as dispersant, binder, respectively. Analytically pure glycerol was chosen as a plasticizer. All organic additives are soluble in water. Yttria (99.99%) was selected as sintering aid. The contents of organic components in this experiment were expressed in weight percent with respect to the AlN powder.

2.2. AlN powder characteristics in water and slurry properties

The AlN slurries (20 g AlN powder + 20 g deionized water) were milled with 40 g AlN balls in polyethylene jar. DP270 was added to the slurries as controlled test. The pH value was tested every 12 h. After milling for 72 h, the slurries were centrifuged to separate the powder from water solvent, and then the sedimented powders were dried at microwave oven for oxygen content analysis (TCH600, LECO Co.).

The zeta potential of slurries was measured by Zetaplus Analyzer (Brookhaven Instruments Corp.). The slurries were prepared by dispersing AlN powders (0.01 vol.%) in 0.001 mol/l NaCl, which was used to adjust ionic strength. The pH value was adjusted by adding HCl (0.01, 0.1, 1 M) or NaOH (0.01, 0.1, 1 M). The slurries were mixed ultrasonically before the tests to ensure that only the mobility of single particle was measured.

Apparent viscosity of the slurries was measured by the rotary viscometer (Model NDJ-7, Shanghai Balance Instrument Plant). Shear dependent behavior was tested with Model SR5 (Rheometric Scientific, Inc., Piscataway. NJ).

2.3. Tape casting and characteristics of green tape

According to the basic requirements for tape casting of ceramic powders [21], the optimum content of organic additives, including dispersant, binder and plasticizer, were determined. AlN powders, Y_2O_3 and deionized water, with optimum content of dispersant were first mixed in polyethylene jar with AlN ball for 12 h. The optimum content of binder and plasticizers were added, and then, the slurry was mixed for another 24 h. Subsequently, the slurries were vacuumed and simultaneously stirred in cage-contained stirrer for1 h. The optimal composition of tape casting slurry was listed in Table 1. Tape casting was performed on a table top tape caster (Eph Engineering, Inc., Orem, UT, USA) with a moving blade on a glass slab. Drying was conducted at 25 °C and 65% relative humidity. The density and pore size distribution of the green sheets were measured by mercury porosimetry (Model PoreSizer 9320, Micromeritics Instrument Corp., Norcross, A). The phase composition of green sheet was detected by XRD.

Table 1
Slurry formulation of aqueous tape casting AlN

Material	Function	Content (wt.%)
Aluminum nitride	Ceramic powders	51.49
Yttria	Sintering aid	1.55
Water	Solvent	17.16
DP270	Dispersant	0.20
PVA124 emulsion (10 wt.%)	Binder	25.74
Glycerol	Plasticizers	3.86

3. Results and discussions

3.1. Characteristics of the treated AlN in aqueous media

pH variation of two aqueous AlN suspensions as a function of ball-milling time was shown in Fig. 1. It could be seen that pH values of two aqueous suspensions gradually ascend with the increase of ball-milling time. It was noted that no ammonia was smelled though the PH values of suspensions had a notable increase. The suspension without dispersant DP270 exhibited a notable rise in pH value, increasing from the initial 5.96 to 9.92. In contrast, the suspension retaining 0.4 wt.% DP270 showed a smaller increase in pH. Its final PH value was 9.37, which was lower 0.55 pH unit than that of the suspension without dispersant DP270.

Fig. 2 shows the oxygen content of AlN powders with and without DP270 after different ball-milling time. It can be seen that the oxygen content picked up with the increase of ball-milling time. It indicated that milling ball destroyed the coating of AlN. However, it was noted that the oxygen content of AlN powder with DP270 was lower than that of AlN

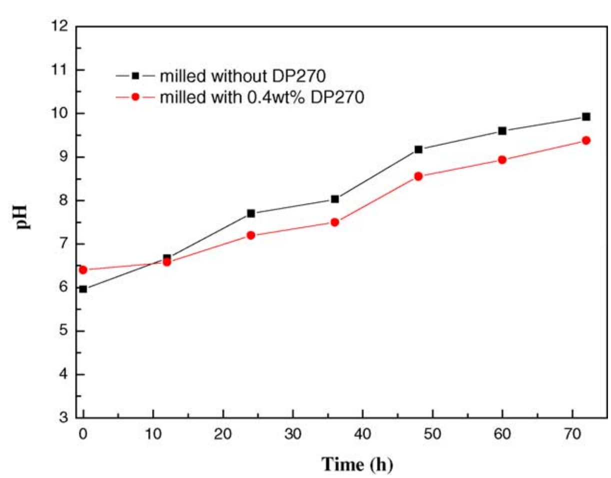

Fig. 1. pH changes of two aqueous AlN suspensions as a function of ball-milling time.

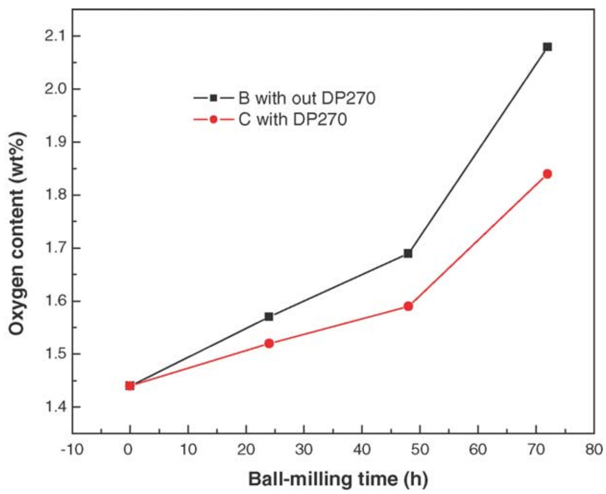

Fig. 2. Oxygen content of the treated AlN powder as a function of ball-milling time.

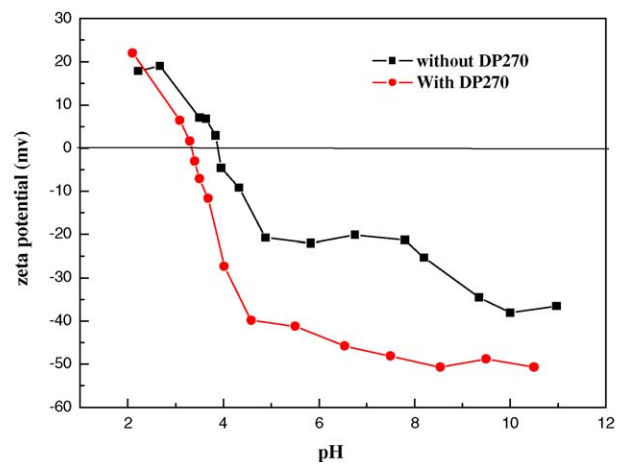

Fig. 4. The relationship between pH value and zeta potential.

powder without DP270. After 72 h ball-milling in aqueous media, the oxygen content of AlN powder with DP270 was 1.84 wt.%, which was lower than 2.08 wt.% of AlN powder without DP270. These results were ascribed to hydrolysis of the treated AlN. The kinetic scheme of AlN powder in aqueous ball-milling media is presented in Fig. 3. Ball-milling destroyed the coating of AlN powder, and thus new surface was exposed to water. For AlN powders with DP270, the destroyed surface quickly absorbed the long-chain polymer or the dissociated ionic of the dispersant to form steric or electrostatic coats, which effectually prevent continual hydrolysis of the AlN powder. In absence of dispersant DP270, it was easy for destroyed surface to react with water and high oxygen content was detected.

Fig. 4 shows the zeta potential of AlN suspensions with and without DP270. The isoelectric point (IEP) of AlN without DP270 was found at about pH 3.9. With the addition of DP270, the isoelectric points were located at about pH 3.35. The addition of DP270 made the IEP of AlN shift to the smaller pH value. Meantime, the absolute values of zeta potential markedly elevated. It could be explained by the chemical nature of dispersants DP270. The R-COO$^-$ dissociated from D270 could presumably adsorb onto the surface of AlN and make the AlN load the negative charge. The addition of DP270 made the AlN produce a high surface-charged density, which made the double electric layer become strong.

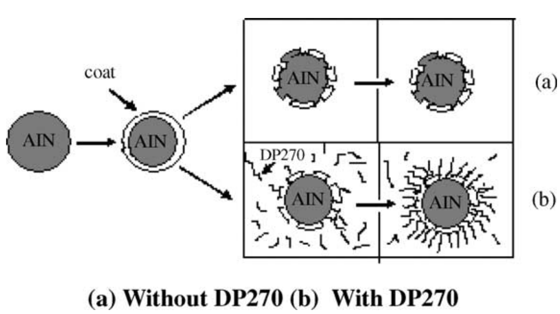

Fig. 3. Kinetic scheme of AlN powders in aqueous ball-milling media: (a) without DP270, (b) with DP270.

3.2. Properties of aqueous tape casting AlN slurries

Fig. 5 describes viscosity and sediment volume of AlN aqueous suspensions as a function of the dispersant DP270 content. At 0.4 wt.% content of the dispersant DP270, both the viscosity and the sediment volume of slurries reached minimum though there were different solid loading involved in the sedimentation and apparent viscosity experiments. These results indicated DP270 was efficient for the dispersing of AlN powders. For AlN powder treated by phosphoric acid, the dispersant DP270 could play a dual role. It not only efficiently dispersed AlN powder in water to form a stable suspension, but also formed a coat onto AlN surface to limit hydrolysis of the AlN powder.

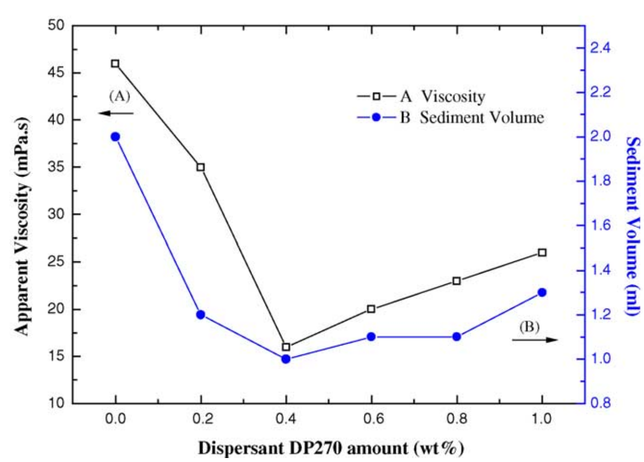

Fig. 5. Apparent viscosity at 350 s^{-1} and sediment volume of AlN slurry vs. dispersant DP270 amount (A) 67 wt.% solid loading (B) 5 wt.% solid loading.

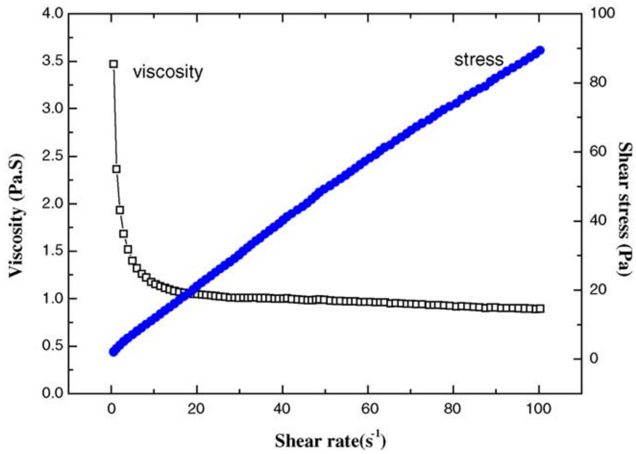

Fig. 6. Rheology curve of AlN tape casting slurry.

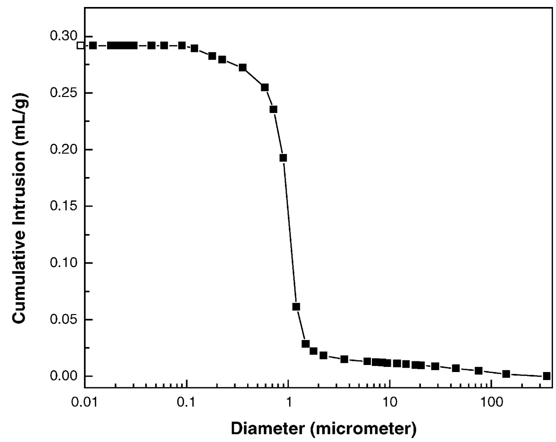

Fig. 7. Cumulative intrusion vs. pore diameter for aqueous AlN green sheet.

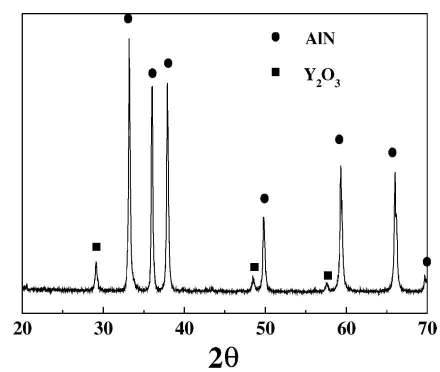

Fig. 8. XRD patterns for aqueous AlN green sheet.

The viscosity and shear stress of slurry with all components was measured at a continuous shear rate. As Fig. 6 shown, the viscosity of slurry was found to decrease with the increase in shear rate, giving rise to what is generally called 'shear-thinning' behavior. This behavior was ascribed to the attractive interaction of powder particles and the resultant formation of floc in the slurry. The shear rate brought about a more favorable arrangement of particles in the slurry. The tendency to form two-dimensional structure rather than a three-dimensional one was such favorable rearrangement. The shear-thinning behavior was expected in tape casting processing because it could reduce the mobility of constituents in the wet tape, preserves homogeneity and hinders uncontrolled flow of slurry.

3.3. Tape casting and drying of green sheets

According to the results of slurry-optimization experiments, the optimum formulation of slurry was determined, see Table 1. Before tape casting, the slurry was degassed in a closed vessel under vacuum to prevent the formation of bubbles in the cast tape. The tape casting speed was 12 cm min^{-1}. The gap between the moving doctor blade and the fixed glass plate was 0.5 mm, adjusted by the doctor blade with microscrews. For a slurry having constant rheological behavior, the thickness of the tape just after casting depended on the gap between the blade and the tape carrier, the speed of the doctor blade movement and the hydrostatic pressure in the casting head. The thickness of the final green sheet was determined by the drying shrinkage [22].

The drying is a complicated process and it is related to many factors such as surface tension, pore size, thickness of tapes and the organic additives [22]. The duration of drying was less critical in this work. The drying simply performed at room temperature, 25 °C and 65% relative humidity. After drying, the tape could be easy to release from the glass plate and its surface was smooth. The final thickness of green sheet was 0.3 mm and no crack was observed.

3.4. Characteristics of green sheet

For aqueous system, green sheet density has been found to be affected by many factors such as viscosity of slurry, the nature and content of all kind of raw materials [23,24] and even PH variation [4,25]. Measured values of theoretical densities for aqueous-based tapes were between 42 and 63% for alumina, and from about 45 to 50% for mullite [17]. In this work, the viscosity of aqueous AlN slurry was controlled in the 500–700 mPa·s around at 350 s^{-1}. The relative density of green sheet was measured by mercury porosimetry and its average value was 52.6% for a green tape with 0.3 mm thickness after 1 week storage. A plot of the cumulative pore volume versus pore diameter is given in Fig. 7. It can be seen that the green sheet had very narrow pore size distribution. The median pore diameter was 0.9985 μm. Fig. 8 was the X-ray pattern of aqueous AlN green tape. No other crystalline phase was found except AlN and sintering aid yttria.

4. Conclusions

The treated AlN had a good stabilization in aqueous ball-milling media. The oxygen content picked up with the increase of ball-milling time. After 72 h aqueous ball-milling, the oxygen content was 1.84 wt.% for AlN powder with DP270 and 2.08 wt.% for AlN without DP270. DP270 played a dual role in this experiment. It not only efficiently dispersed AlN powder in water to form a stable suspension, but also formed a coat onto AlN surface to limit hydrolysis of the AlN powder. It was found that the viscosity and sedimentation volume of AlN slurry reached minimum at 0.4 wt.% content of the dispersant DP270, which is believed to be a well-dispersed state of particles. The isoelectric points were, respectively, at pH 3.35 and pH 3.90 for the treated AlN with and without DP270. The final tape casting AlN slurry showed a shear-thinning behavior, which was suitable to tape casting processing. Aqueous AlN green tape attained had a smooth surface and a narrow pore size distribution. Its relative density was 52.6%. No other crystalline phase was detected by XRD except for AlN and sintering aid yttria in AlN green sheet.

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