

# Tape casting of aqueous Al<sub>2</sub>O<sub>3</sub> slurries

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## Abstract

The well-dispersed aqueous Al<sub>2</sub>O<sub>3</sub> slurries suitable for tape casting were prepared, the effects of the concentration of dispersant, of the pH value, of solid content etc. on the properties of slurries were investigated, and the results indicated that the rheological of slurries was effected greatly by pH value and organic additives. After cutting, laminating and binder removal, the laminated Al<sub>2</sub>O<sub>3</sub> green bodies were sintered by hot-press in a vacuum furnace. SEM micrographs showed that the microstructure of the aqueous green-body and samples were different from that of non-aqueous, and the mechanical properties of aqueous Al<sub>2</sub>O<sub>3</sub> samples were much high than that of non-aqueous Al<sub>2</sub>O<sub>3</sub>. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Al<sub>2</sub>O<sub>3</sub>; Tape casting; Slurry; Zeta potential; Viscosity

## 1. Introduction

Tape casting is a low cost and an useful process for preparing thin ceramic sheets, It has been widely used to produce ceramic substrate, multilayer structure capacitor, solid electrolytes, solid oxide fuel cell,<sup>1–5</sup> etc. For structure materials, tape casting has already been used to design laminated and multilayered composites to improve the mechanical properties.

The classical tape casting process is made of slurry preparation and tape casting. The stable slurry is composed of ceramic powder dispersed in a solvent which contains dispersant, binder, plasticizer and other surfactant, etc. In generally, tape casting slurry is a typical organic system. Because the volatility and toxicity of organic solvents used in slurries are harmful to the environment and health, and the solvents are difficult to recycle, the development of an aqueous tape casting system is considered to be desirable processing,<sup>6,7</sup> the aqueous slurry system has the advantage of no-flammability, non-toxicity and low cost. In addition, there is widely available knowledge for the aqueous processing system which has

been used for other ceramics technologies. Aside from of aqueous tape casting, there are several other new tape casting methods which have been developed to overcome the problems, such as in situ polymerizable slurries<sup>8,9</sup> in which all solvents and organic additives remain in tape; another way to eliminate the solvent evaporation from slurries is to use UV curable binders.<sup>10</sup> The processing does not need solvents and does not involve solvent evaporation. During drying, the process does not cause high shrinkage and cracking, and it is possible to achieve a high powder loading than that of classical tape casting. The aims of this study were to investigate the rheological behaviors and optimized conditions of aqueous slurries and to compare the difference in the mechanical properties between aqueous samples and non-aqueous samples.

## 2. Experimental procedure

The high purity Al<sub>2</sub>O<sub>3</sub> powder with an average particle size and a specific area 5.7 m<sup>2</sup>/g and 0.48 μm, respectively (Wushen fertile factory) was used in the experiment. NH<sub>4</sub>PAA was used as dispersant, PVA was used as binder, glycerin and PEG were used as plasticizers, NH<sub>4</sub>OH and HCl were used to adjust the pH value of slurries in all processing, and double-distilled water was used as solvent in all formulations.

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First,  $\text{Al}_2\text{O}_3$  powder was mixed with  $\text{NH}_4\text{PAA}$  as dispersant and double-distilled water as solvent in a polyethylene jar and ball-milled with a binder about 24 h with  $\text{Al}_2\text{O}_3$  ball as grinding media. Plasticizers were added to the slurries and ball-milling continued another 16 h. The slurry was degassed in vacuum to remove gas bubbles and then was cast on the glass substrate and dried naturally. The dried tapes were cut into  $40 \times 50$  mm squares, after stacking, pre-pressure, binder-removal, HP-sintering. Finally the sample could be machined into  $2 \times 5 \times 25$  mm rods for testing bending strength and  $5 \times 2 \times 25$  mm rods testing fracture toughness. The processing program is shown in Fig. 1.

### 3. Results and discussion

#### 3.1. Zeta potential of $\text{Al}_2\text{O}_3$

The high performance aqueous ceramic slurry can be acquired through adjusting the pH value and selecting the exact dispersant. According to the DLVO theory,<sup>11</sup> the Van Der Waals forces and the repulsive forces originated in the electrical double layers surrounding the

particles because the counterions have a strong influence on the diffuse electrical double layer. Moreover, the surface charge of the particles has a tight relationship with the pH value and the concentration of other specifically adsorbed ions and the ionic strength of the slurry. This means that the zeta potential has a direct relationship with the pH value and the ionic strength of the slurry; therefore, the adjustment of the pH value and the ionic strength can produce a high surface-charged density on the particle surface which makes a strong double-layer repulsion and particles far from the point of zero charge of powder acquire the well-dispersed ceramic slurries. Sometimes, in order to acquire the large particle repulsive interaction, very low and very high pH values, which may make powder change, should be used.

Zeta potential is a very important physical parameter which can decide the stability of aqueous ceramic slurry; the bigger the zeta potential, the bigger the repulsive energy and the more stable the slurries. Fig. 2 shows the relationship between the pH value and the zeta potential. Curve A is the zeta potential of  $\text{Al}_2\text{O}_3$  without any additive at different pH values; the isoelectric at which the zeta potential is zero was about 8.5. In this experiment,  $\text{Mg}(\text{NO}_3)_2$  was added to the slurry to restrain

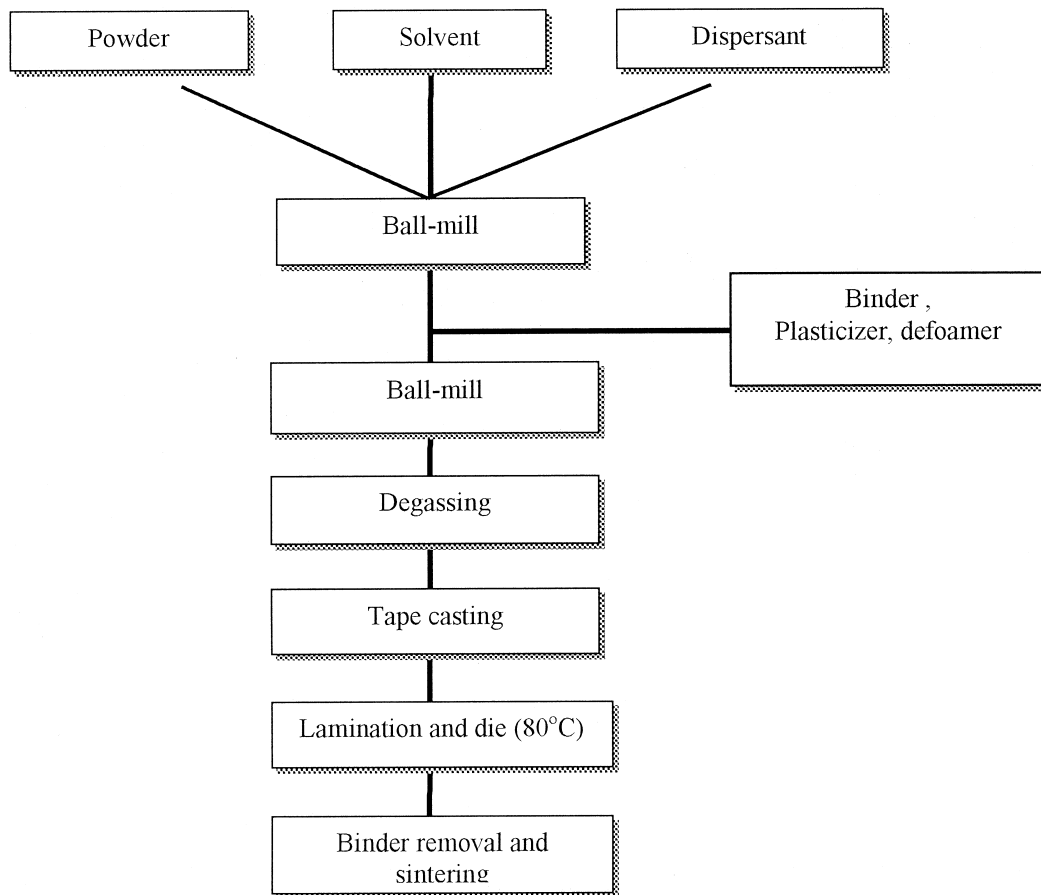


Fig. 1. The processing program of tape casting.

$\text{Al}_2\text{O}_3$  grain growth, so it was necessary to know the  $\text{Mg}^{2+}$  influence on the zeta potential of  $\text{Al}_2\text{O}_3$ . Curve B is the zeta potential of  $\text{Al}_2\text{O}_3$  with 0.001 M  $\text{Mg}^{2+}$  at different pH values. The shape of curve A was different from curve B because  $\text{Mg}^{2+}$  in slurry B had a strong influence on the diffuse double layer. The high concentration of counterions can compress the thickness of the double layer and reduce the zeta potential. It was clear that the zeta potential of  $\text{Al}_2\text{O}_3$  with 0.001 M  $\text{Mg}^{2+}$  was smaller than that of pure  $\text{Al}_2\text{O}_3$  and the value of the isoelectric point changed from 8.5 to 7.6. When the pH value was about 11, the potential suddenly decreased; the change may be caused by  $\text{Mg}^{2+}$ , which transformed into  $\text{Mg}(\text{OH})_2$  and absorbed on the surface of  $\text{Al}_2\text{O}_3$  particles at high pH value.  $\text{Mg}(\text{OH})_2$  can affect the structure of the double-electrical layer and the zeta potential.

The mechanism of particle dispersion by polyelectrolyte is based on both electrostatic repulsion and steric stabilization. Anionic polyelectrolyte can absorb on the surface and acquire a high stabilization energy. In the meantime, the polyelectrolyte can dissociate and cause the electrostatic repulsion among particles. Therefore, the electrostatic repulsion energy has a tight relationship with the ionization degree of polyelectrolyte used as dispersant, but the ionization of polyelectrolyte was strongly affected by the pH value. It was reported<sup>12</sup> that a similar polyelectrolyte (PMAA-Na) cannot dissociate at pH below 3.5, but can completely dissociate at pH over 8.0. The result showed that the pH value will greatly affect the zeta potential. Fig. 2 curve C is the zeta potential of  $\text{Al}_2\text{O}_3$  with addition of 0.2 wt%  $\text{NH}_4\text{PAA}$ . The curve is obviously different from A and B due to the polyelectrolyte dispersant absorb on the surface (compare with curves A and B). The IEP of  $\text{Al}_2\text{O}_3$  with  $\text{NH}_4\text{PAA}$  was about 4.6 which was smaller than that of A and B.

For the polymeric stabilization mechanism,<sup>13</sup> some polyelectrolytes which can avoid the problems with

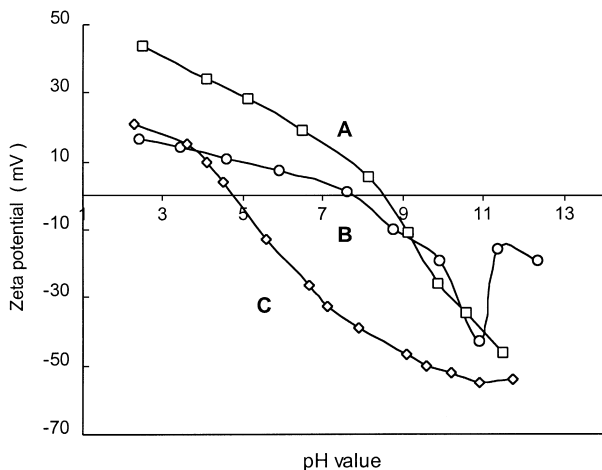


Fig. 2. The relationship between the pH value and the zeta potential.

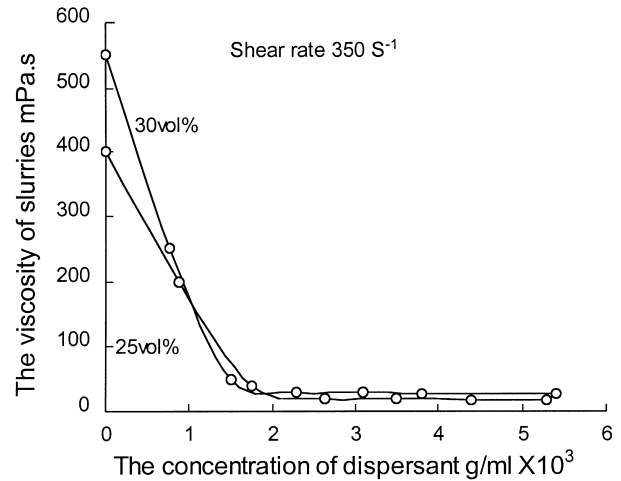


Fig. 3. The relationship between the concentration of dispersant and the apparent viscosity of slurry.

working at very high and very low pH values are used as dispersant to acquire the stable slurry. The polyelectrolytes can absorb or graft on the particle surface and acquire a low viscosity and a good colloidal stability. In this experiment, polyelectrolyte  $\text{NH}_4\text{PAA}$  which has good dispersing effectiveness for  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ <sup>14,15</sup> slurries were used as the dispersant for preparing aqueous slurry.

### 3.2. The properties of slurries with various additives

In order to prepare the optimal aqueous slurries for tape casting, many factors which can affect the properties of slurries should be investigated, such as: pH value, the concentration of dispersant, organic additives, etc.

Fig. 3 shows the relation between the concentration of dispersant and the apparent viscosity of slurries at shear rate of  $350 \text{ S}^{-1}$ . For two kinds of  $\text{Al}_2\text{O}_3$  slurries with 25 and 30 vol% solid content, respectively, the viscosity of slurries were decreased due to the increase of the concentration of dispersant. When the concentration of  $\text{NH}_4\text{PAA}$  was about 0.0015 g/ml, the viscosity of  $\text{Al}_2\text{O}_3$  slurry changed to 50 mPa.s, which was near a constant. With the concentration of dispersant increased in advance, the viscosity of slurries did not change very much. 25 and 30 vol%  $\text{Al}_2\text{O}_3$  slurries had the consistent results. The results indicated that  $\text{NH}_4\text{PAA}$  has great efficiency in dispersing  $\text{Al}_2\text{O}_3$  slurry.

Although the viscosity of aqueous slurries was mainly determined by zeta potential, the pH value and ion strength can strongly influence the electronic properties of the particle surface and also the zeta potential. In order to clarify the rheological behaviors of slurries with and without polyelectrolyte dispersant at different pH values, HCl and NaOH were used to adjust the pH value of slurries and the viscosity were measured. Fig. 4 shows the relationship between pH value and the viscosity of slurries without any additives. The results

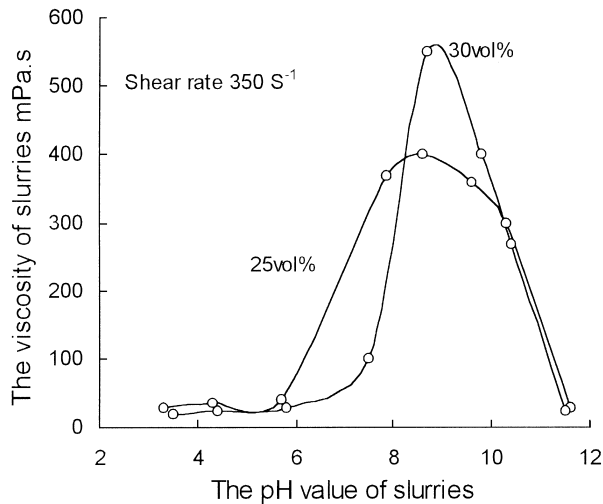


Fig. 4. The relationship between pH value and viscosity of slurries (without dispersant).

showed that the pH value had a great effect on the viscosity of slurries. With the pH value increased, the viscosity of 25 vol%  $\text{Al}_2\text{O}_3$  slurry increased and reached its maximum value at pH 8.5. Then the viscosity decreased due to the pH value increased in advance. The results in Fig. 4 are in accordance with Fig. 2 curve A. The zeta potential at the isoelectric point was so small that produced the maximum viscosity of the slurry that 30 vol%  $\text{Al}_2\text{O}_3$  slurry had the same result.

Fig. 5 shows the relationship of the pH value and the viscosity of slurries with dispersant. The results indicated that the change in the viscosity is very different from that of the slurries without dispersant. When a polyelectrolyte was used as dispersant in the slurries, it can provide so-called electrosteric stabilization energy to particles. The total stabilization energy consists of two parts: one is the steric stabilization energy which has a tight relationship with the polyelectrolyte molecule

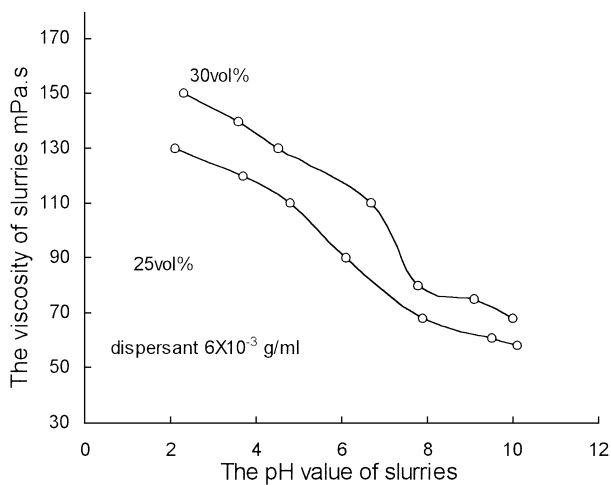


Fig. 5. The relationship between pH value and viscosity of slurries (with dispersant).

structure. The reason is that  $\text{NH}_4\text{PAA}$  is a long link molecule, which can absorb on the surface of particles to prevent particles from contacting each other and giving the slurries stability. At this point, the main factors which influence the stability of slurries are the length of dispersant molecules, the functional group as well as the activity points of the particle and dispersant. The contribution of steric stabilization energy to the slurry is not strongly affected by pH value. Another principal factor is electrostatic repulsion stabilization energy which has a relationship with the ionic strength and the structure of the double-electrical layer, because the change of pH value can greatly affect the degree of ionization of  $\text{NH}_4\text{PAA}$  which is absorbed on the surface of particles. The result will affect the electrostatic repulsion among particles and the value of the zeta potential; with the increase of electrostatic repulsion, it will have much more contribution to the stability of slurry. Fig. 5 shows that the viscosity of  $\text{Al}_2\text{O}_3$  slurry with dispersant decreased with the increase of pH value, although the steric stabilization energy was the main factor which controlled the properties of the slurry. The electrostatic repulsion (zeta potential) still has influence on the viscosity of  $\text{Al}_2\text{O}_3$  slurry with dispersant.

The effect of pH value on the viscosity of slurries with binder and dispersant is shown in Fig. 6. The viscosity did not greatly change through adjusting the pH value, because binder PVA is a long-link molecule, which absorbed on the surface of the particles and reduced the effectiveness of dispersant and pH value on the viscosity. The solid concentration of the slurry used for tape was much higher and contained a large amount of organic additives. The viscosity of slurry was hardly changed with the variation of the pH value. Normally, there is about 5–10 wt% or more organic additives in tape casting slurry, including: dispersant, binder, plasticizers, etc. The slurry is a very complex system. It is

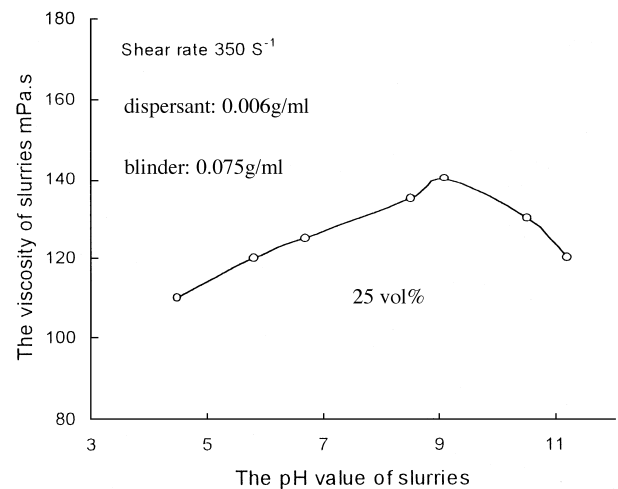


Fig. 6. The effects of pH value on the viscosity of slurries (with binder and dispersant).

hard to distinguish which one is the main factor that effect on the properties of slurry. The rheological properties of slurries are mainly controlled by the amount of organic additives.

After adjustments of the pH value, the concentration of dispersant, the amount of organic additives and the optimal slurry for tape casting was required. The slurry formulation is in Table 1. The pH value for tape casting slurry was about 10.5. The slurry was cast in tape at a blade speed of 12 mm/s and a blade height of 0.6 mm. Very good, flexible tapes with no cracks were produced.

### 3.3. The analysis of TGA

Fig. 7 shows the TGA curves of  $\text{Al}_2\text{O}_3$  green tape in different atmospheres; curve A was in an air atmosphere, curve B was in an argon atmosphere. The weight loss occurred at about 75°C, which was due to water evaporation in tape, because the organic additives, such as PEG and PVA, began to decompose. The obvious weight loss happened about 175°C and all organic additives decomposed about 500°C. The results showed that the shape of curves had a little divergence in different

atmospheres; the amount of weight loss in air was about 11%, and 13% in argon. In air, the organic additives can be degraded and oxidized into carbon oxides, water as well as other small organic molecules. After binder removal finished, there were not any organic remains in the green tape. But in the argon atmosphere, organic additives can only be degraded into small organic molecules step by step. After degrading completely, a small amount of carbon was kept in the green body. TGA showed that the weight loss in air was about 1–2% more than that in argon. Part of the weight was carbon, which is harmful to improving the mechanical properties of the material.

### 3.4. The microstructure of green body

Fig. 8 shows the SEM micrographs of  $\text{Al}_2\text{O}_3$  tape after binder removal; Fig. 8A is the upper surface, B the lower surface. It was clear that the particle distribution was not so good in A. Normally the particles distribution in slurry was very uniform, with the evaporation of solvent in tape, the slurry contracted slowly and organic additives, such as binder and plasticizers, linked to a net and formed an organic membrane. The drying process can be divided two steps: (1) the drying force is mainly capillary action under the surface of green body; (2) if the liquid in tape has disappeared, the drying force is evaporation. This process is not so quick that the upper layer and lower layer cannot be dried in the same time. This process can lead to many small holes, which may be caused by water evaporation during slurry drying. The other reason is that the drying process takes too much time so makes the organic additive overflow from the slurry and form many small holes after binder removal. In Fig. 8B, the distribution of particles shows uniformity, but there were still many small holes, which were caused by binder removal. The strength and appearance of aqueous tape did not differ much from that of the non-aqueous  $\text{Al}_2\text{O}_3$  tape.

### 3.5. The mechanical properties of $\text{Al}_2\text{O}_3$

In order to compare the mechanical properties of  $\text{Al}_2\text{O}_3$  prepared by aqueous with non-aqueous  $\text{Al}_2\text{O}_3$ , the organic solvents and organic additives were selected to produce non-aqueous  $\text{Al}_2\text{O}_3$  tape. The process was just the same as for aqueous  $\text{Al}_2\text{O}_3$ .<sup>16</sup> Table 2 shows the mechanical properties of aqueous  $\text{Al}_2\text{O}_3$  and non-aqueous  $\text{Al}_2\text{O}_3$  respectively. The samples prepared in aqueous  $\text{Al}_2\text{O}_3$  produced higher results than those in non-aqueous.  $\text{Al}_2\text{O}_3$  for aqueous  $\text{Al}_2\text{O}_3$ , the bending strength and fracture toughness were 477 MPa and 5.75 MPam<sup>1/2</sup>, respectively, at 1650°C, but for non-aqueous  $\text{Al}_2\text{O}_3$  were 366 MPa and 3.78 MPam<sup>1/2</sup>, respectively, at 1650°C.

Fig. 9 shows SEM micrographs of  $\text{Al}_2\text{O}_3$  at 1650°C; Fig. 9A was prepared in aqueous and Fig. 9B in

Table 1  
Formulation of water-based  $\text{Al}_2\text{O}_3$  slurry

Materials	Wt%	Function
$\text{Al}_2\text{O}_3$	54–61	Powder
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.6–2	Grain growth inhibitor
$\text{NH}_4\text{PAA}$	1.1–2.4	Dispersant
Water	33.8–37.5	Solvent
PVA	3.70–4.5	Binder
Glycerin	2.6–4.6	Plasticizer
PEG	1.4–3.2	Plasticizer

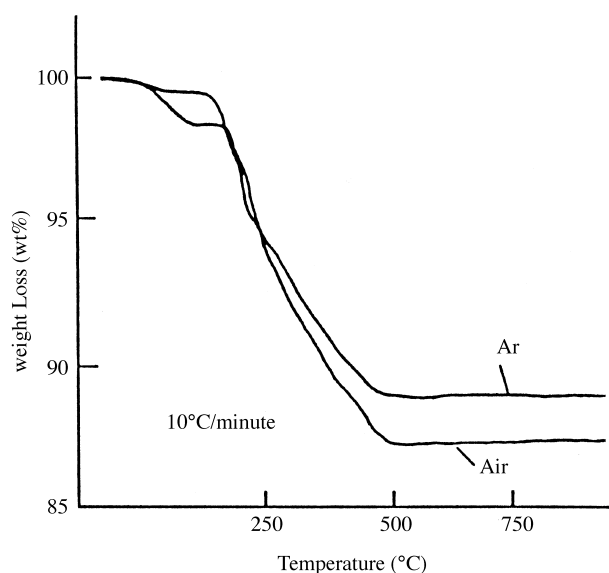


Fig. 7. TGA curves of  $\text{Al}_2\text{O}_3$  green tapes in different atmospheres.

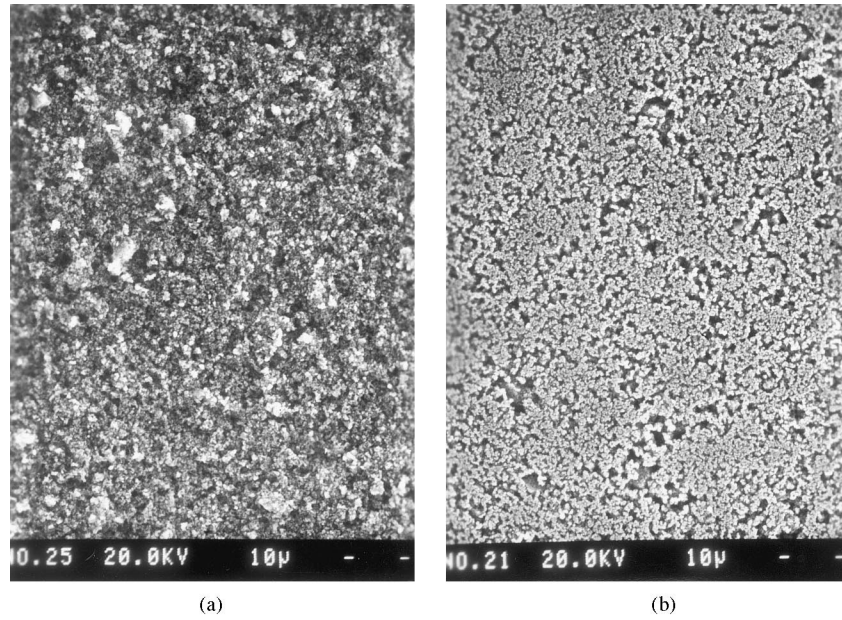


Fig. 8. SEM micrographs of Al<sub>2</sub>O<sub>3</sub> tapes after binder removal: (A) upper surface; (B) lower surface.

Table 2  
Mechanical properties of Al<sub>2</sub>O<sub>3</sub> in different temperatures

Temperature (°C)	Bending strength (MPa)		Fracture toughness (MPa.m <sup>1/2</sup> )		Relative density (%)	
	Non-aqueous	Aqueous	Non-aqueous	Aqueous	Non-aqueous	Aqueous
1600	345	459	3.71	5.14	96.1	97.8
1650	366	477	3.87	5.75	96.7	98.8
1700	394	435	3.94	4.87	97.2	99.6
1750	407		4.59		98.7	

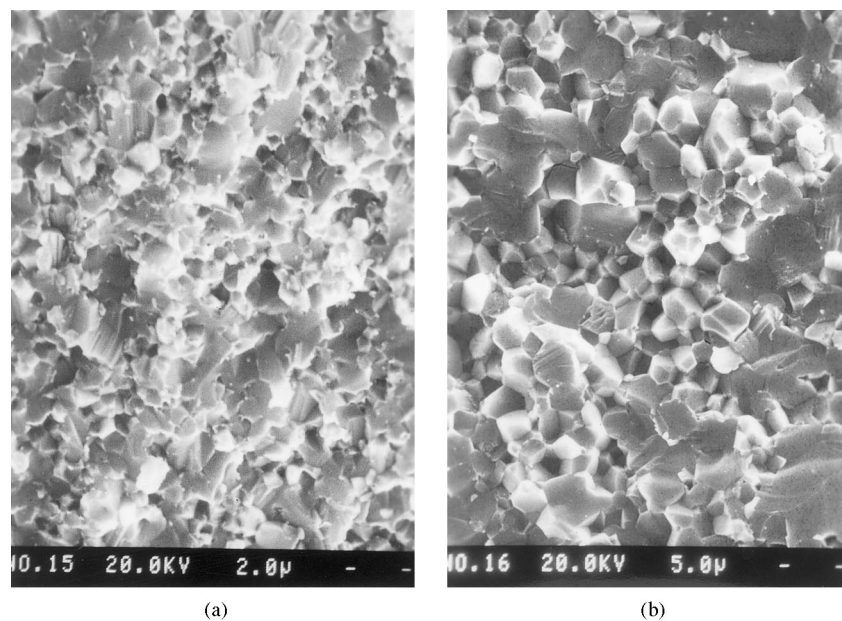
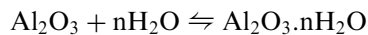


Fig. 9. SEM micrographs of Al<sub>2</sub>O<sub>3</sub> at 1650°C: (A) aqueous; (B) non-aqueous.

non-aqueous  $\text{Al}_2\text{O}_3$ . The fracture surface showed that the sample was mainly intragranular fracture in Fig. 9A. It was clear that there were some big abnormal grains in Fig. 9A, because  $\text{Al}_2\text{O}_3$  powder must be ball-milled for a long time in water before tape casting.  $\text{Al}_2\text{O}_3$  powder can form  $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ; the equation is:



During sintering,  $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  lost the combining water and changed into  $\text{Al}_2\text{O}_3$ , which has high activity surfaces and low sintering temperature. The high activity  $\text{Al}_2\text{O}_3$  can decrease the sintering temperature and make the interface of lamination disappear at low temperature. In fact, the non-aqueous  $\text{Al}_2\text{O}_3$  sample exhibited obvious interface between layers at  $1650^\circ\text{C}$ , but the interfaces of the aqueous sample disappeared at  $1600^\circ\text{C}$ .

#### 4. Conclusion

$\text{NH}_4\text{PAA}$  was selected as dispersant, PVA as binder, glycerin and PEG were used as plasticizer. The high quality aqueous  $\text{Al}_2\text{O}_3$  tapes were produced through the tape casting process. For aqueous  $\text{Al}_2\text{O}_3$  slurries, there were many factors which can affect the rheological of slurries, especially the pH value and ionic strength, but the pH value does not greatly affect the viscosity of slurry stabilized by a polymeric mechanism. For the high concentration of organic additives slurry, the rheological of slurries was mainly controlled by the properties of the organic additives. The microstructure and mechanic properties of  $\text{Al}_2\text{O}_3$  tape acquired in aqueous slurries were different from that of in non-aqueous slurries.

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