

Effects of organic additives and glass on the properties of AlN/glass tape-casting slurries and green tapes

XIAO-JUN LUO, BAO-LIN ZHANG, WEN-LAN LI, HAN-RUI ZHUANG

Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China
E-mail: luoxj@mail.sic.ac.cn

Low-temperature co-fired ceramics (LTCC) technology offers significant benefits over both thick film ceramics and HTCC (high temperature co-fired ceramics) due to high-density, high-radio-frequency, fast digital applications requiring hermetically sealed packaging and good thermal management [1]. LTCC tape has been used in the last 20 years for high-reliability, avionics, and automotive applications, as well as in MCMS for communication and computer applications [2]. In recent years, many LTCC systems were made up of Al_2O_3 and glass [3]. However, due to the low thermal conductivity of Al_2O_3 , the LTCC systems of Al_2O_3 and glass have a poor thermal conductivity. AlN, whose thermal conductivity is 10 times greater than that of Al_2O_3 , can be substituted for Al_2O_3 to improve the thermal conductivity of LTCC [4]. As a convenient and low-cost processing, tape casting has been widely used to produce ceramic substrate [5]. However, LTCC is a multicomponent and complicated system. Each component has a substantial effect on the properties of the slurry and green sheet. The present work was conducted on a new type of LTCC AlN/glass to study the effects of organic additives, including dispersant, binder, and plasticizer, on the properties of the slurries. The effects of glass content on the properties of slurry and green sheet was also investigated.

AlN powder and borosilicate glass powder were used as raw materials. The commercial AlN powder (Shenhai Nitride Co. Ltd., China) was synthesized by the self-propagation high-temperature synthesis (SHS) method, with nominal particle size of $0.5 \mu\text{m}$. Borosilicate glass powder was milled to $1.7 \mu\text{m}$. Borosilicate glass used in this study was found to react with water and, therefore, azeotropic mixtures of 66:34 vol% 2-butanone ethanols were used as solvents. Triethyl phosphate (TEP) and polyvinyl butyral (PVB) were introduced as dispersant and binder, respectively. The plasticizer was a 50:50 wt% mixture of polyethylene glycol (PEG) and phthalate (PHT). The mixed powders with dispersant were first ball-milled for 24 hr in solvent with AlN ball. Binder and plasticizers were added to the slurries and milled for another 24 hr. Then the tape was cast on a glass surface through the action of a blade that leveled the slurry. The tapes were dried in a solvent atmosphere.

A rotary viscometer was used (Model NDJ-7, Shanghai Balance Instrument Plant) to measure the apparent viscosity of the suspensions at 350 s^{-1} . Shear-dependent behavior was tested with a rheometer (Model

SR5, Rheometric Scientific, Inc., Piscataway, NJ). The suspensions, containing 16 ml of solvent and 4 g of the AlN/Glass powder, were ultrasonically mixed with different amounts of dispersant for 10 min. Then the suspensions were settled in 25 ml graded tubes. The density and porosity of the green sheets were measured by mercury porosimetry (Model PoreSizer 9320, Micromeritics Instrument Corp., Norcross, GA).

Fig. 1 shows the viscosity of three suspensions (67 wt%) with different dispersants as a function of dispersant content. For the 1.5 wt% dispersant content, the viscosity of the three suspensions simultaneously reached a minimum though the particle sizes were different for AlN and borosilicate glass. This indicates that the adsorption of dispersant onto ceramic particles was not only related to the particle size but also to the chemical nature of the ceramic powder.

Fig. 2 describes the sediment volume of three suspensions versus the concentration of dispersant after resting for 4 weeks. As is shown, the sediment volume decreased as the concentration was increased. After a minimum volume was achieved, further increase in the concentration of dispersants produced a slight increase in sediment volume. For the 1.5 wt% dispersant content, the sedimentation volumes of the three suspensions reached a minimum. This indicates 1.5 wt% dispersant content was optimum for three suspensions. These results agreed well with that of the viscosity tests, though the solid loadings of the suspensions were

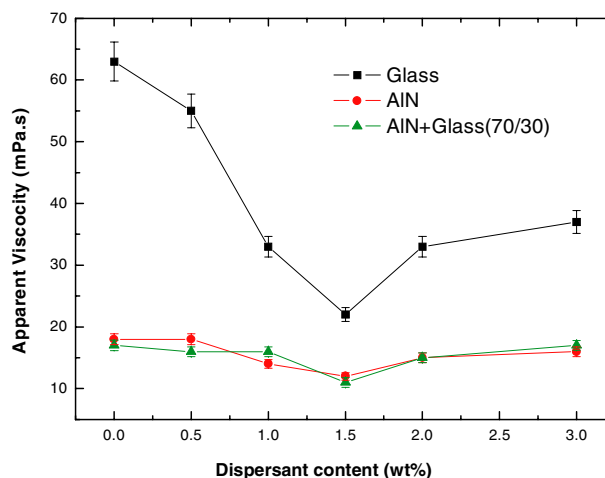


Figure 1 Apparent viscosity of different suspensions at 350 s^{-1} as a function of dispersant content.

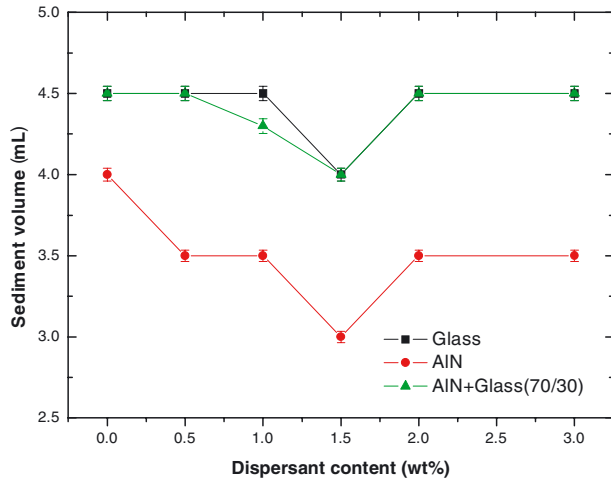


Figure 2 Sedimentation volume of the three powders versus the content of dispersant.

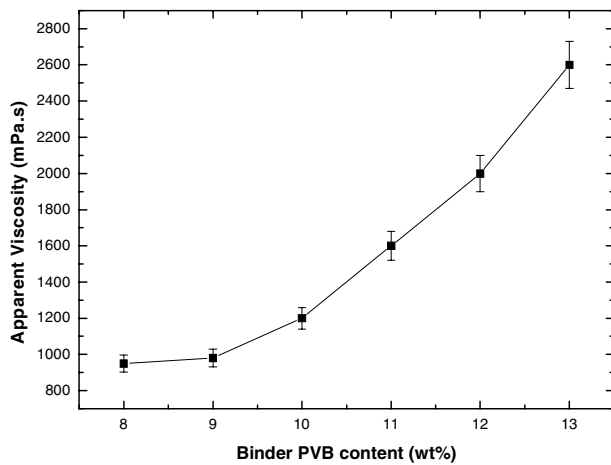


Figure 3 Apparent viscosity of the AlN/glass (70/30) slurries at 350 s^{-1} as a function of PVB binder content (with 1.5 wt% TEP).

different in the sedimentation and apparent viscosity experiments.

Fig. 3 shows apparent viscosity of AlN/glass slurries as a function of the binder PVB content. It can be seen that the viscosities increase with increase in PVB content. This is understandable, since the binder has a high molecular weight and can form organic bridges between the particles. In this study, 12 wt% PVB was the lowest content to guarantee sufficient strength of the green tape. In most cases, it was necessary to add a plasticizer to soften the PVA and thus improve the flexibility of the tape. The relation between viscosity and plasticizer/binder weight ratio is shown in Fig. 4. It can be seen that the plasticizers tend to reduce the viscosity of AlN/glass slurries.

The viscosities for samples with all-organic additives were measured at a continual shear rate. As Fig. 5 shows, the viscosity was found to decrease with 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 a two-dimensional structure rather than a three-dimensional

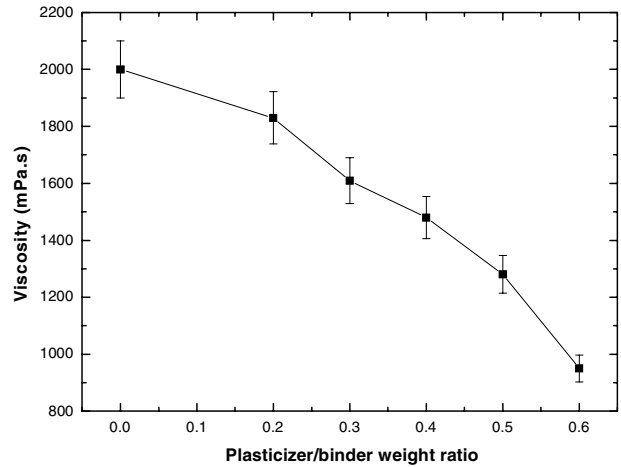


Figure 4 Apparent viscosity of the AlN/glass (70/30) slurries at 350 s^{-1} versus plasticizer/binder ratio (with 1.5 wt% TEP, 12 wt% PVB binder).

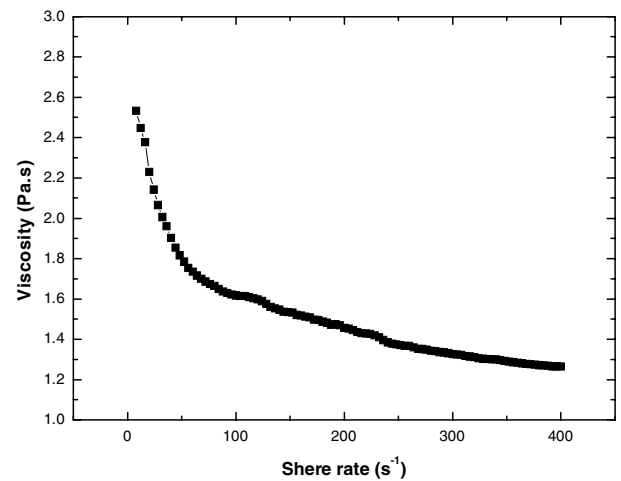


Figure 5 Viscosity of the AlN/glass (70/30) slurries with all organic additives as a function of shear rate (with 1.5 wt% TEP, 12 wt% PVB, plasticizer/binder = 0.5).

one was one such favorable rearrangement. Therefore, it was understandable that the viscosity decreased with increase in shear rate.

Fig. 6 shows viscosity as a function of glass content when dispersant, binder, and plasticizer/binder weight ratio were respectively 1.5 wt%, 12 wt%, and 0.5.

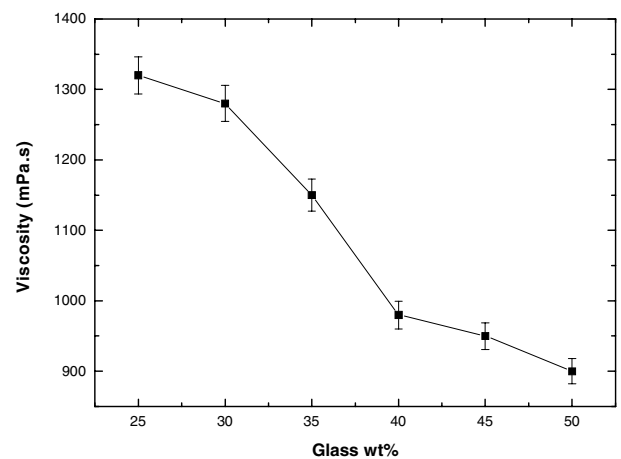


Figure 6 Apparent viscosity of the AlN/glass slurries at 350 s^{-1} versus glass content (with 1.5 wt% TEP, 12 wt% PVB, plasticizer/binder = 0.5).

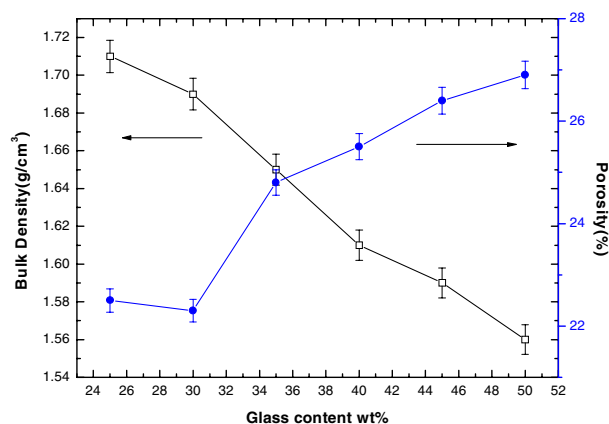


Figure 7 Bulk density and porosity of AlN/glass green tape as a function of glass content (with 1.5 wt% TEP, 12 wt% PVB, plasticizer/binder = 0.5).

Viscosity decreased with increase of glass content. However, the viscosity of glass without PVB was higher than that of AlN (see Fig. 1) when both solid loadings were the same. These results were possibly related to PVB. PVB had a greater chemical affinity for oxides than for non-oxides. At the same PVB content, the viscosity of oxide slurry is lower than that of non-oxide slurry. This indicates that glass content (oxides) in the AlN/glass system can produce an important influence on the rheology properties of the AlN/glass slurries. Bulk density and porosity of the green tape with different glass content are shown in Fig. 7. It can be seen that

the porosity of green tapes increased with the increase in glass content, while the bulk density of green tape decreased.

In conclusion, both organic additives and glass content could produce important effects on the properties of AlN/glass slurries. 1.5 wt% dispersant TEP was the optimum content to make AlN/glass stable, and it made the viscosity of the slurry and the sedimentation volume a minimum. Shear-thinning behavior was observed for AlN, glass, and AlN/glass with 1.5 wt% dispersant. Binder PVB increased the viscosity of slurry, but plasticizers decreased the viscosity of the slurry. The increase in glass content made the viscosity of slurry and bulk density of the green tape decrease, while the porosity of the green tape increased.

References

1. C. Q. SCRANTOM and J. C. LAWSON, in IEEE Symposium on Technology for Wireless Applications (IEEE, New York, 1993) p. 193.
2. M. R. GONGORA-RUBIO, P. ESPINOZA-VALLEJOS, L. SOLA-LAGUNA and J. J. SANTIAGO-AVILES, *Sensors and Actuators A* **89** (2001) 222.
3. RAO R. TUMMALA, *J. Amer. Ceram. Soc.* **74** (1991) 895.
4. QINGXUE ZHANG, WENLAN LI and HANRUI ZHUANG, *Chinese J. Mater. Res.* **17** (2003) 79.
5. RICHARD E. MISTLER, *Amer. Ceram. Soc. Bull.* **77** (1998) 82.

Received 13 August
and accepted 30 December 2003