Nonaqueous Gel Casting of AlN Ceramics using Epoxy

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The AlN ceramics manufactured by a nonaqueous gel casting process were studied. It was shown that trimethylolpropane triglycidyl ether (TMPGE) and tetraethylenepentamine (TEPA) were suitable for the gel casting process through a nucleophilic addition reaction. This system cured at room temperature and avoided oxygen inhibition. The rheological behaviors of the slurries and bending strength of green bodies obtained under different conditions were investigated. Suspensions with a high-solid loading of 59 vol.% and low viscosity (678 mPa·s) were obtained with 1 wt.% dispersant, 20 wt.% TMPGE, and TEPA: TMPGE=1:5. The results showed that the bending strength of the green body is not only associated with the content of TMPGE, TEPA, and solid loading, but also the drying process. The bending strength greatly improved and reached 34.9 MPa after drying at 130 °C, which was strong enough for subsequent processing. With the increase of solid loading, sintered AlN ceramics exhibited higher relative density and thermal conductivity, reaching 99.6% and 152 W/(m·K) at 59 vol.%, while the optimized bending strength of 274 MPa was obtained at 55 vol.%. Meanwhile, complex-shaped ceramics without cracks were prepared.

Keywords: gel casting, aluminum nitride, rheological properties, bending strength.

1. INTRODUCTION

AlN ceramics are widely used in the electronic industry for their high thermal conductivity (319 W·m^{-1}·K^{-1} in theory), good insulation, excellent dielectric properties, and a thermal expansion coefficient matched with Si [1–4]. However, machining AlN ceramic into various shapes is difficult owing to their significant hardness and brittle nature. Gel casting is a valid near-net-shape forming method to fabricate ceramic with complex shapes, initially developed by Omatete and Janney [5]. Compared with traditional gel casting based on free radical reaction, epoxy gel casting is based on a nucleophilic addition reaction between an epoxy and a curing agent. This approach mitigates issues related to oxygen inhibition and the toxic monomer are avoided. Meanwhile, the in-situ polymerization offers the green body a high strength. Consequently, various epoxy prepolymers are explored, such as sorbitol polyglycidyl ether (SPGE) [6], ethylene glycol diglycidyl ether (EGDGE) [7, 8], and glycerol polyglycidyl ether (GPGE) [8], etc.

Various curing agents, such as polyamines, polyacids [9], and anhydrides can react with epoxy resin to form a cross-linking network. Considering that polyamines can react with epoxy resin at room temperature without the need for catalysts, it is economical and benefitial to avoid the temperature difference in the samples. Accordingly, polyamines are widely used as efficient hardeners for epoxy gel casting, such as dipropylenetriamine (DPTA) and bis (3-aminopropyl) amine (BAPA). X. Mao [10] prepared translucent alumina ceramics by SPGE-DPTA gel casting. M. Dong prepared AlN ceramics by SPGE-TEPA [11]. S. M. Olhero [12] fabricated ceramic microneedles using using EGDGE-BAPA system. Compare the resorcinol diglycidyl ether (RDGE) with aromatic structure, Cyril et al. [13] found 1,4-Butanediol diglycidyl ether (BDGE) with a flexible skeleton is more suitable for the gel casting process, which could decrease the formation of internal stressed created during the cross-linking with the same curing agent. As mentioned above, aliphatic glycidyl ether and polyamines are preferred in epoxy gel casting. Like other colloidal shaping techniques, a stable suspension with high solid loading and low viscosity are the key factor to obtain homogeneous and dense bodies, which are influenced by the proportion of ceramic powders, dispersants, epoxy resin, and curing agents [12, 14, 15]. The epoxy resin with good solubility and low viscosity is suitable for casting [8].

Trimethylolpropane triglycidyl ether (TMPGE) with a flexible skeleton contains three epoxy groups that can participate in the curing reaction, thereby enhancing the cross-linking density. Additionally, the viscosity of TMPGE is 135 mPa·s, which is lower than that of SPGE (~ 5000 mPa·s). This low viscosity facilitated achieving high solid loading. Consequently, TMPGE was selected as a prepolymer in the epoxy gel casting system to prepare AlN ceramics. Compared with DPTA which has five active hydrogen atoms, tetraethylenepentamine (TEPA) contains seven active hydrogen atoms of amine. Therefore, TEPA served as the curing agent due to its effectiveness as a hardener for epoxy at room temperature. To avoid the hydrolysis of AlN powder, ethanol was used as the solvent. Based on this consideration, the aim of this study is to evaluate the TMPGE-TEPA gel casting system for AlN forming. The effects of epoxy resin, curing agent, dispersant, and solid loading on the rheological behaviour and green body's performance were investigated. The

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microstructures, bending strength, and thermal conductivity of sintered AlN ceramics were also presented.

2. EXPERIMENTAL PROCEDURE

Commercial AlN powder (Toyo Aluminum, Japan) was firstly mixed with 2 wt.% Y_2O_3 (99.99 %, Aladdin, China) and 1 wt.% YF_3 (99.9 %, Aladdin, China) as sintering additives through ball-milling, followed by drying and sieving to serve as the solid loading phase of the slurry. TMPGE (Adamas, China) and TEPA (Aladdin, China) were applied as epoxy resin and curing agent respectively. Triethanolamine (TEA) was selected as the dispersant. $10-25$ wt.% TMPGE premixed solution was prepared by dissolving the epoxy resin into ethanol. The solid loading phase ($48-62$ vol.%), and dispersant ($0.8-3$ wt.%, based on the mass of solid powder) were added into the premixed solution and mixed. After homogenization, curing agent TEPA ($10-25$ wt.%, relative to the mass of resin) was added to the suspension and mixed at 1000 rpm for 5 min. The obtained slurries were degassed in a vacuum chamber and subsequently poured into the molds. After gelling and drying at room temperature for 24 h, the green bodies were demolded and further dried at varying temperatures for 3 h. Binder burnout was carried out in air at 550 °C for 1h with a heating rate of 0.5 °C/min. Subsequently, sintering was conducted at 1700 °C for 3 h under a nitrogen flow in a graphite furnace.

The rheological behaviours of the AlN suspensions were measured with a viscometer (DV2T, Brookfield, USA). The sediment distance, which represented the volume of the supermatant liquid, was recorded at various times in a sealed tube containing 15 ml AlN suspension. The microstructure of the fractured surface of the sintered ceramics was examined using scanning electron microscopy (SEM, EM-30 Plus, Coxem, Korea). The bending strength of rectangular AlN green bodies and ceramics was measured with a universal tester (Z020, Zwick Roell, Germany) with a span of 30 mm. The thermal conductivity of the AlN ceramics was determined using the laser thermal conductivity apparatus (LFA 467, Netzsch, Germany).

3. RESULTS AND DISCUSSION

3.1. Rheological behavior of the slurry

In gel casting, a homogenous and stable slurry with high solid loading and low viscosity is a critical step to obtain a dense and uniform green body. The rheological behavior of the slurry is affected by the composition of the slurry, such as dispersant, solid loading, epoxy prepolymer, and curing agent.

TEA is an effective dispersant to increase the stability in non-aqueous suspensions [16–18]. Fig. 1 shows the influence of TEA content on the viscosity of 55 vol.% AlN slurry. The viscosity of the AlN slurry decreases with the increasing shear rate, indicating a typical shear-thinning behavior [15]. The viscosity at 100 rpm decreases from 423 to 262 mPa·s with TEA content increases from 0.8 to 1 wt.%, and then increases to 469 mPa·s. It demonstrated that TEA can effectively improve the dispersibility of AlN particles. The sedimentation distance of 15 vol.% AlN suspensions containing 1.0 wt.% TEA is illustrated in

Fig. 2. In comparison to the suspension without epoxy prepolymer, the sedimentation distance is reduced, indicating that TMPGE also functions as a dispersing. Consequently, both epoxy resin and dispersant TEA will coat the surface of the surface of AlN particles in the slurry, forming a polymer layer and a double electric layer, which enhances steric resistance and electrostatic repulsion between AlN particles. Therefore, the addition of the TEA is advantageous for reducing slurry viscosity and enhancing slurry stability. As the TEA content continues to increase, the cross-linking of long chains of organic may lead to polymer agglomeration once the surfaces of AlN particles are fully covered. Consequently, 1.0 wt.% TEA demonstrated excellent dispersibility in AlN slurries with high solid loading.
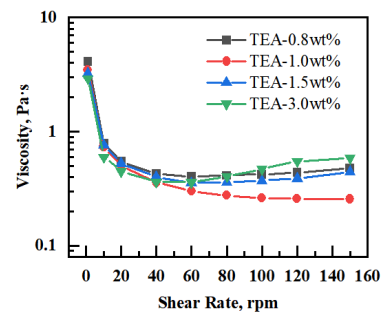

Fig. 1. Rheological behavior of the 55 vol.% AlN slurries with different amounts of TEA
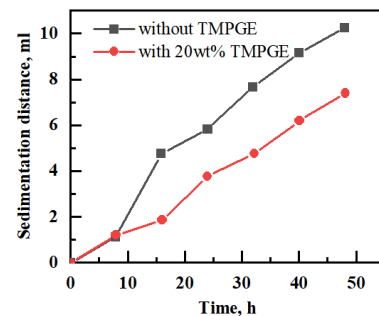

Fig. 2. The effect of TMPGE on the sedimentation distance of 15 vol.% AlN suspensions with 1 wt.% TEA

The influence of TMPGE on the rheological properties of the 55 vol.% AlN suspensions without curing agent is illustrated in Fig. 3 a. All slurries exhibit a shear thinning behavior, attributed to perturbations under shear stress. As the epoxy resin content increases, viscosity initially decreases slightly before rising, as illustrated in the insert figure in Fig. 3 a. However, the viscosity of 55 vol.% AlN is only $252-402$ mPa·s at 100 rpm for all samples, which is suitable for casting.

Because the 62 vol.% AlN slurry was difficult to pour out for its high viscosity, slurries with solid loading ranging from 48 to 59 vol.% were utilized to investigate their rheological behaviors (Fig. 3 b). The viscosity exhibits a slight increase as the solid loading rises from 48 vol.% to 55 vol.%, followed by a rapid increase when the solid loading reaches 59 vol.%. With the increasing solid loading, the distance between AlN particles reduces and the particle interactions intensify, leading to flocculation and elevated viscosity.
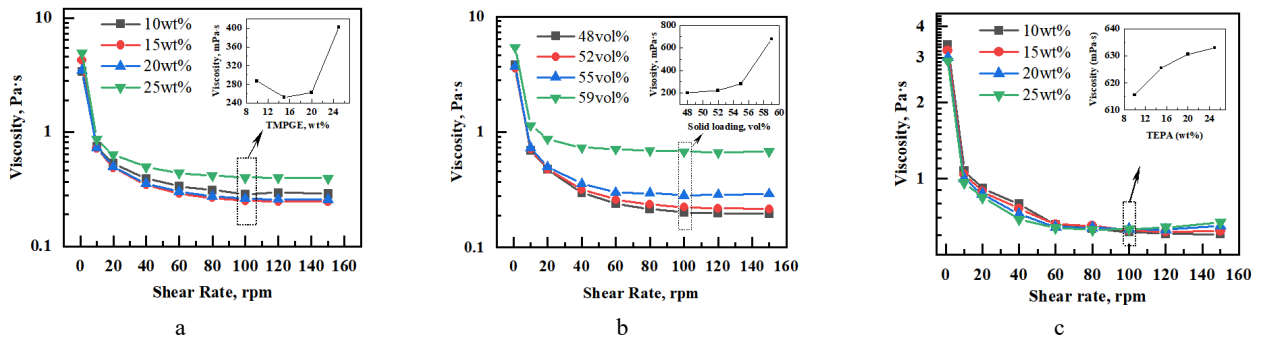
Fig. 3. The effects of: a – TMPGE; b – solid loading; c – TEPA on the viscosity of AlN slurry

However, when the solid loading is up to 59 vol.%, the viscosity at 100 rpm is 678 mPa·s, which is still suitable for casting. Fig. 3 c illustrates the effects of curing agent concentration on the viscosity of 55 vol.% AlN slurries. The viscosity increases only slightly from 615 mPa·s to 633 mPa·s as the TEPA content varies from 10 wt.% to 25 wt.%. It indicates that the amount of TEPA has a negligible impact on slurry viscosity. However, compared with the 55 vol.% AlN slurry without curing agent as shown in Fig. 3 a, the viscosity increases from 262 mPa·s to 631 mPa·s for the slurry with 20 wt.% TMPGE. The results suggest that there are interactions between TMPGE and TEPA at room temperature.

3.2. Bending strength of the green bodies

In the epoxy gel casting system, an organic three-dimensional network is formed through a nucleophilic addition reaction between the epoxy prepolymer and the curing agent. The content of TMPGE and TEPA influences the mechanical characteristics of the green body. Bending strength was measured for green bodies that were gelled and dried at room temperature. As shown in Fig. 4 a, bending strength first increases from 1.97 MPa to 3.19 MPa as TMPGE content varies from 10 wt.% to 20 wt.%, and then decreases with further additions of TMPGE. As depicted in Fig. 3 a, the viscosity of AlN slurry increased obviously with 25 wt.% TMPGE, which can lead to inhomogeneity and defects during the pouring process, ultimately deteriorating the mechanical strength of the green body [19]. With increasing content of TEPA, as shown in Fig. 4 b, bending strength experienced a rapid enhancement, followed by a gradual increase once the TEPA content exceeded 20 wt.%. The mechanical strength of the green body primarily arises from in-situ polymerization between epoxy and curing agent. With the increase of TMPGE and TEPA, more compact crosslinking networks are formed,

resulting in the improvement of the bending strength.

Fig. 4 c illustrates the influence of solid loading on the bending strength and density of AlN green bodies obtained from slurries containing 20 wt.% TMPGE, 20 wt.% TEPA, and 1 wt.% dispersant. As expected, the density increases with solid loading. The bending strength reaches the maximum value at 55 vol.%.

Although optimizing the content of compositions in the slurry can enhance the bending strength of AlN green bodies, it remains relatively low. To further improve mechanical strength, the solidified green body is dried at various temperatures for 3 h after being cured at room temperature. As shown in Fig. 5, the bending strength of the green body gradually increases with the temperature. When heated from room temperature to 130 °C, the bending strength rises to reach 34.9 MPa, which is high enough for machining. It is evident that elevated temperatures accelerate the curing reaction, facilitating the complete curing of the epoxy resin and enhancing the strength of the three-dimensional organic network. However, as the temperature continues to rise, the bending strength of the green body decreases.
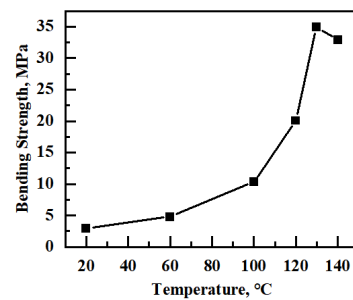

Fig. 5. Influence of drying temperature on the bending strength of AlN green bodies obtained form 55 vol.% slurry
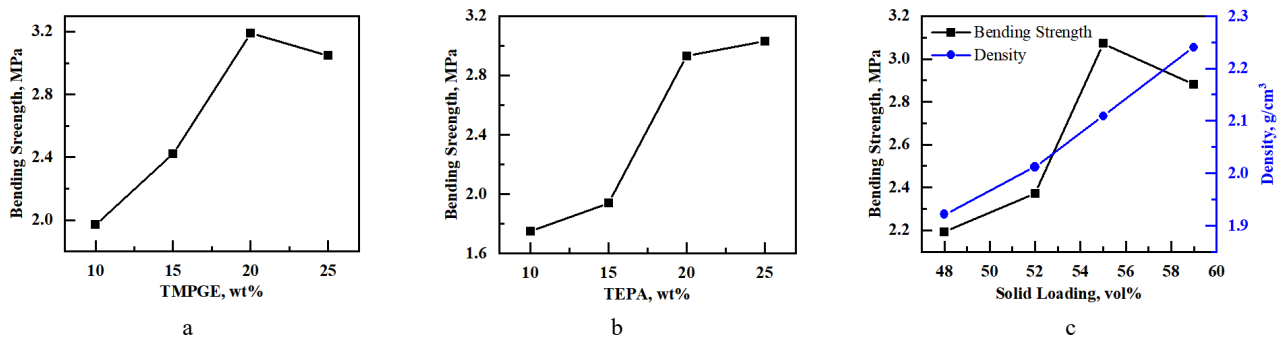

Fig. 4. Effect of: a – TMPGE; b – TEPA; c – solid loading on the bending strength of AlN green bodies

3.3. Characterization of the sintered bodies

Fig. 6 shows the effect of solid loading on the performance of sintered ceramics. As solid loading increases, the shrinkage decreases, and density increases as anticipated. Therefore, the thermal conductivity of AlN ceramic is improved with high densification [20]. The maximum bending strength of 274 MPa was attained at a solid loading of 55 vol.%, which is consistent with the results presented in Fig. 4 c. Despite exhibiting a higher density at 59 vol.% solid loadings compared to that at 55 vol.%, diminished fluidity in the slurry resulted in reduced bending strength. This indicates that both high solid loading and low viscosity of the slurry are critical for achieving high bending strength in AlN ceramics.
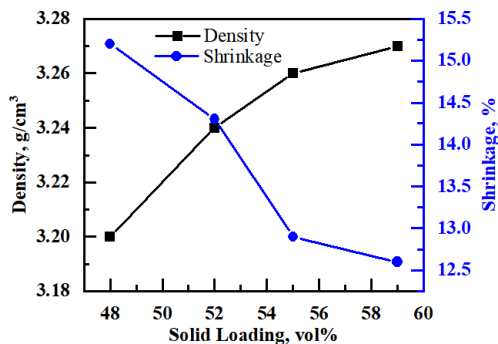

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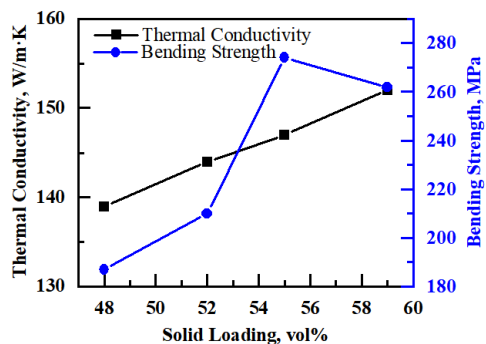
b

Fig. 6. Effect of solid loading on the properties of AlN green bodies: a – density and shrinkage; b – thermal conductivity and bending strength

The XRD and SEM of the sintered AlN ceramics derived from 55 vol.% slurry are illustrated in Fig. 7. The primary phase is AlN and the secondary phase is $Y_3Al_5O_{12}$. This indicates that all the sintering aids reacted with the oxide layer covered on the surface of the AlN particle, forming a liquid phase that promotes densification during sintering [21, 22]. The microstructure exhibits homogeneity and is dense. Meanwhile, the secondary phase $Y_3Al_5O_{12}$ is mainly distributed at the triple grain boundary junction. The isolated distribution of this secondary phase facilitates heat transmission by increasing the contact area and introducing compressive stresses among AlN grains [23 – 25]. Fig. 8 presents the sintered AlN with a complex shape from 55 vol.% AlN slurry; no evident cracks or warping were observed, demonstrating the effectiveness of TMPGE-

TEPA in gel casting of AlN ceramics.
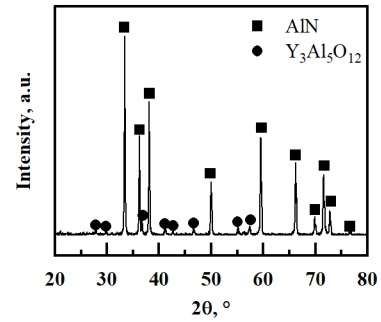
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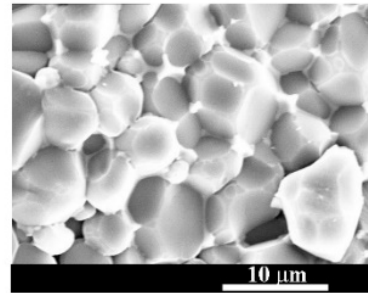
b

Fig. 7. a – XRD pattern; b – SEM image of the sintered AlN ceramics

Fig. 8. Photograph of AlN ceramic with complex-form

4. CONCLUSIONS

In this study, a nonaqueous epoxy gel casting system TMPGE-TEPA was employed for the fabrication of AlN ceramics. The optimum dispersant concentration was 1.0 wt.% and the viscosities of the slurries were slightly influenced by TEPA content. A high solid loading (59 vol.%) and low viscosity (678 mPa·s at 100 rpm) AlN slurries were achieved with the addition of 1.0 wt.% TEA, 20 wt.% TMPGE, and 20 wt.% TEPA (related to the resin). The bending strength of the green bodies was associated with the content of TMPGE, TEPA, and solid loading, while also being significantly affected by drying temperature. When the temperature during the second drying stage increased to 130 °C, bending strength of the green bodies improved to 34.9 MPa. For sintered AlN ceramics, both density and thermal conductivity enhanced with increasing solid loading; however, bending strength reached its

maximum at 55 vol.%. AlN samples derived from 55 vol.% slurries exhibited a homogeneous microstructure along with a high relative density of 99.3 %, thermal conductivity of 147 W/(m·K), and a bending strength of 274 MPa. Additionally, complex-shaped ceramics featuring smooth surface without cracks were successfully prepared. This demonstrated that the TMPGE-TEPA gelling system is applicable for fabricating complex-shaped AlN ceramics.

Acknowledgments

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