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Gelcasting of aluminum nitride ceramics using hydantion epoxy resin as gelling agent

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Abstract

A gelling system based on the polymerization of Hydantion epoxy resin and 3,3′-Diaminodipropylamine (DPTA) was developed for gelcasting aluminum nitride (AlN) ceramics. The effect of the dispersant concentration and solid loading on the rheological behavior of the slurries was investigated. The highest solid loading of 58 vol% AlN ceramic slurry and the highest green relative density of 64.5% were obtained with the addition of 15 wt% Hydantion epoxy resin and 0.3 wt% dispersant Polyethyleneimine (PEI). With the addition of 20 wt% Hydantion epoxy resin, the flexural strength of AlN green body reached as high as 34.5 MPa. For sintered AlN ceramics, the relative density, flexural strength and thermal conductivity reached 99.6%, 360 MPa and 185 W/m K, respectively.

Keywords: C.Thermal conductivity; AlN ceramics; Gelcasting; Relative density

1. Introduction

Aluminum nitride is a unique ceramic material with high thermal conductivity as well as electrical insulation [1,2] and has been employed in a range of engineering fields such as ceramic substrates for electronic applications [1,3,4]. Various processing routes were developed for fabricating AlN ceramic to meet different demands, including tape casting [3,4] and gelcasting [5] technique. The Gelcasting is an attractive technique for fabricating complex shaped and high performance ceramic parts [6–8], involving the preparation of concentrated ceramic suspension, casting and in situ polymerization. Acrylamide (AM) [9] monomer is a frequently used gelling agent, but its neurotoxicity limits its wider applications. Recently, Xue [5] prepared aluminum nitride ceramic by gelcasting using ethanol and sorbitol polyglycidyl ether (SPGE) as solvent and gelling agent, respectively. Ethanol as solvent was to avoid the hydrolysis of AlN powder due to its high reactivity with the water, and the polymerization of such a system was a nucleophilic addition reaction instead of a free radical reaction, which made the gelcasting process straightforward [5,10,11]. Our previous work revealed a promising gelling system by using Hydantion epoxy resin as the gelling agent for producing high strength and dense green bodies [12]. Hydantion epoxy resin was non-toxicity and low cost and it's usage in AlN gelcasting process had not been reported.

The aim of this work was to investigate non-aqueous gelcasting of AlN ceramics using Hydantion epoxy resin as the gelling agent. The effects of solid volume fraction the concentrations of dispersant and Hydantion epoxy resin on the rheological behavior of the slurry were investigated [13–16]. The microstructure, mechanical and thermal properties of gelcast AlN green and sintered bodies were presented.

2. Experimental procedure

2.1. Materials and procedures

Commercial AlN powder (Grade H, Tokuyama Soda Co. Ltd., Tokuyama, Japan) with a mean particle size of 1.1 μm was used as raw material. Yttrium oxide (Y_2O_3, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) was added as sintering aid. Propanol (Tianjin Kemiou Chemical reagent Co.

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Ltd., Tianjin, China) was used as the solvent. Slurries with different solid loadings (45–58 vol%) were prepared by ball milling the AlN and 5 wt% Y_2O_3 powder with the premix solution containing solvent and 5–15 wt% Hydantion epoxy resin (Wuxi Meihua Chemical Solvent Co. Ltd., Wuxi, China). Polyethyleneimine (PEI) (Aladdin Chemistry Co. Ltd., Shanghai, China) with average molecular weight of 10,000 was added as the dispersant of AlN slurries. 1 g 3,3′-Diaminodipropylamine (DPTA) (> 98%, Tokyo Chemical Industry Co. Ltd., Tokyo, Japan) based on 10 g Hydantion epoxy resin was added to the slurries as the hardener. The slurries were degassed in a vacuum chamber to reduce gas bubbles before casting to the mold. After consolidation and demolding, the green bodies were gradually dried in an air oven at 100 °C for 24 h. Binder burnout was operated in a muffle furnace in air at 600 °C for 2 h, at a heating rate of 2 °C/min. Sintering was carried out at 1700 °C for 4 h in aluminum oxide tube furnace in nitrogen atmosphere.

2.2. Characterization

The viscosities of AlN slurries were characterized using a rotational rheometer (AR2000EX, TA Instruments, USA) with a diameter of 40 mm parallel plate. Slurries were all pre-sheared at a shear rate of 100 s^{-1} for 10 s. The measurements were performed within the shear rate range of 0.1–1000 s^{-1} at 25 °C. The flexural strengths of the green and sintered bodies were determined by three-point bending tests using an electronic universal testing machine (KD11-2, KEJALI Technology Co. Ltd., China) with a crosshead speed of 0.5 mm/min. The relative densities of green and sintered bodies were measured by the Archimedes' method. The microstructures of the fractural surfaces of green and sintered bodies were observed by scanning electron microscopy (JSM-6390, JEOL, Tokyo, Japan). The thermal conductivity of sintered ceramics (3 mm thick) was measured by a laser flash technique using a thermal constant analyzer (LFA427, Netzsch, Selb, Germany).

3. Results and discussion

Fig. 1 shows the effects of PEI concentration on the viscosity of AlN slurry with 50 vol% solid loading. With the addition of PEI, the viscosity of the slurry decreased quickly which reached the lowest point, 0.1761 Pa s when the PEI content was 0.3 wt%, indicating that PEI was a very effective dispersant for AlN particle. Then the viscosity increased smoothly When the concentration of the dispersant increased from 0.3 wt% to 0.5 wt%. Continue to increase the PEI concentration, the viscosity would increase obviously. Molecules of the dispersant are absorbed onto the surface of the ceramic powders which changes the charge distribution on the particle surface. The electrical double layer interaction between two similarly charged surfaces will repel each other to disperse the slurry. However, at high surface charge densities, the so called double layer will be compressed which will break the electric double layer and Destabilize the slurry [16].

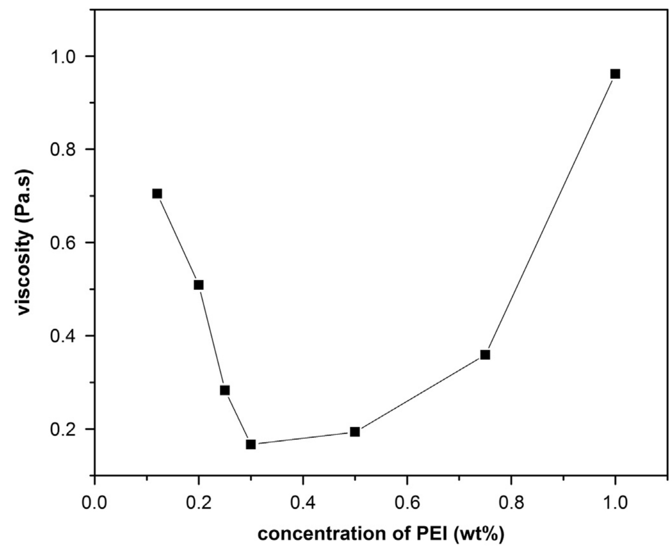

Fig. 1. The effects of dispersant concentration on the viscosity of 50 vol% AlN slurry (shear rate: 100 s^{-1}).

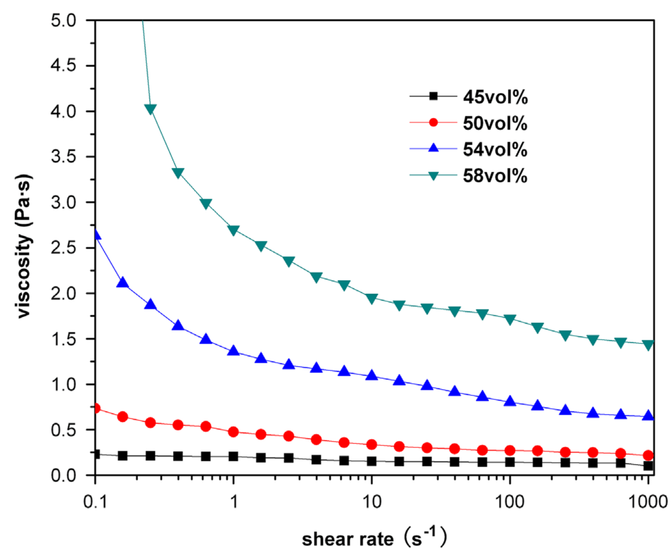

Fig. 2. Viscosity of AlN slurry with different solid loading as a function of the shear rate (PEI: 0.3 wt%).

Solid loading Φ of AlN in the slurry was calculated according to the following formula:

$$\Phi = \frac{m/\rho}{(m/\rho) + V} \quad (1)$$

where m is the mass of aluminum nitride powder (g), ρ is the theoretical density of aluminum nitride (g/cm^3), and V is the volume (ml) of the premix solution in the suspensions.

Fig. 2 shows the rheological curve of slurries with different solid loadings. All these slurries were prepared by adding 0.3 wt % PEI as dispersant. It can be seen from the curves that all slurries show shear thinning behavior, and the viscosity increased with the increase of solid loading. For the slurry with a solid loading up to 58 vol%, the viscosity at 100 s^{-1} was about 1.5 Pa s after being milled for 72 h, which was still suitable for casting and preparing a high density green body [17].

Fig. 3 shows the viscosity of 50 vol% AlN slurry with different Hydantion epoxy resin concentration. The AlN slurries all exhibited typical shear thinning behaviors. The viscosities of the slurries increased when the Hydantion epoxy resin was added to the slurry. However, even the Hydantion epoxy resin concentration reached as high as 15 wt%, the viscosity of the slurry at the shear rate of 100 s^{-1} was still less than 1.0 Pa s, which was suitable for the gelcasting process [17].

Fig. 4 shows that the relative density of the dried green bodies and the sintered AlN ceramics with different solid loading using 15 wt% Hydantion epoxy resin. As the solid loading increased from 45 vol% to 58 vol%, the relative density of AlN green bodies and sintered ceramics increased from 53.3% to 64.5% and from 98.3% to 99.6%, respectively. Higher solid loading could lead to higher green density, as well as denser sintered ceramics, which was mainly due to the packing behavior in the slurries and the gelcasting procedure.

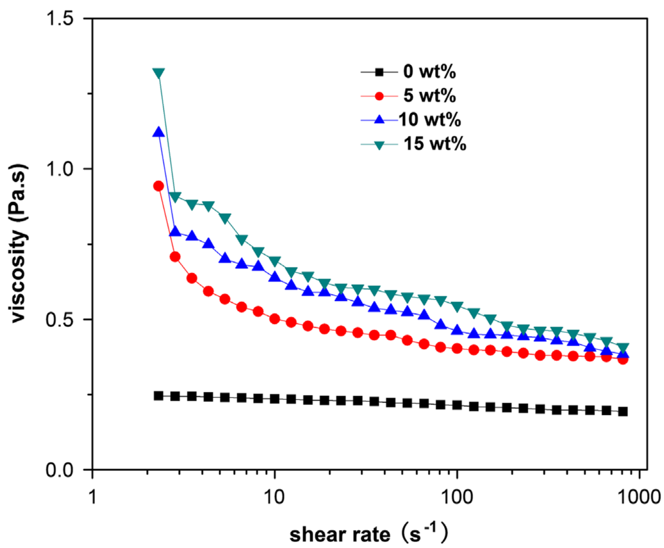

Fig. 3. Viscosity of 50 vol% AlN slurries with different concentration of Hydantion epoxy resin as a function of the shear rate.

Fig. 5 shows the effect of Hydantion epoxy resin content on relative density and flexural strengths of green bodies and sintered ceramics. The relative densities of the green and sintered bodies changed little when the Hydantion epoxy resin concentration was less than 20 wt%, and the highest densities of green and sintered AlN ceramic were obtained by adding 15 wt % Hydantion epoxy resin. A moderate amount of Hydantion epoxy resin formed integral spatial network which benefited the formation of the densified green bodies. However, excessive Hydantion epoxy resin would lead to reduced densities of the green bodies. When the Hydantion epoxy resin concentrations increased from 5 wt% to 20 wt%, the flexural strength of the green bodies increased from 6.6 MPa to 34.5 MPa, which was much higher than those of the EGDGE (Ethylene glycol diglycidyl ether) system [12,17].

Fig. 6 shows the SEM micrographs of the fracture surface of the AlN green bodies and sintered ceramics. It can be seen from Fig. 6(a) and (b) that the AlN particles were packed uniformly without any large defect and the particles were connected by the slender polymer chains, which led to the high strength of the green bodies. The green body obtained from 58 vol% AlN slurry was obviously more compact than that from 45 vol% slurry. It can be seen from Fig. 6(d) that the AlN ceramics obtained from 58 vol% AlN slurry exhibited a homogenous and dense microstructure. However, some obvious defects and pores were observed in the AlN ceramic obtained from 45 vol% AlN slurry, as shown in Fig. 6(c), which means that the solid loading of the slurry and the density of green body are very important factors for achieving AlN ceramic with good microstructure and performance. The flexural strength and thermal conductivity of the AlN ceramic obtained from 58 vol% slurry were 360 MPa and 185 W $(m\,K)^{-1}$, respectively.

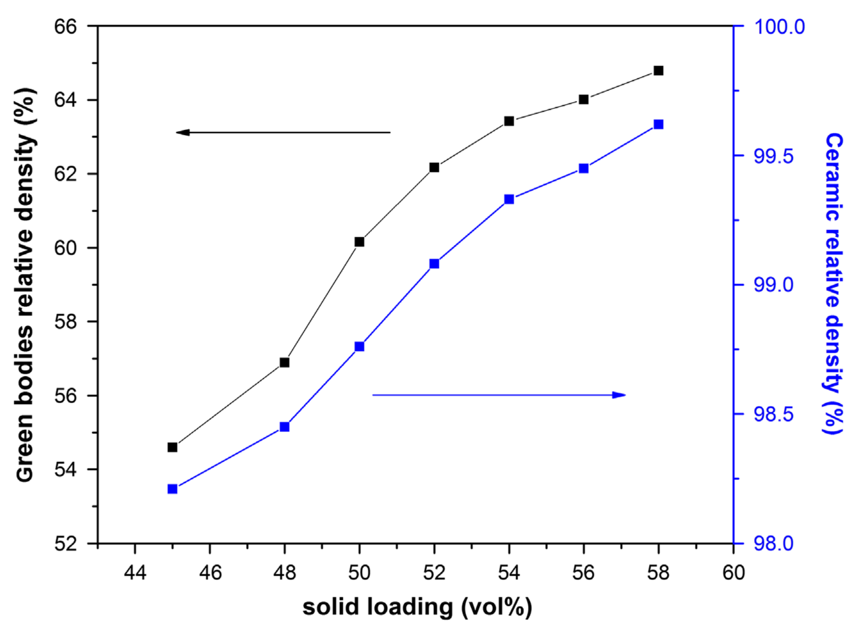

Fig. 4. The relative densities of green bodies and sintered ceramics as a function of solid loading.

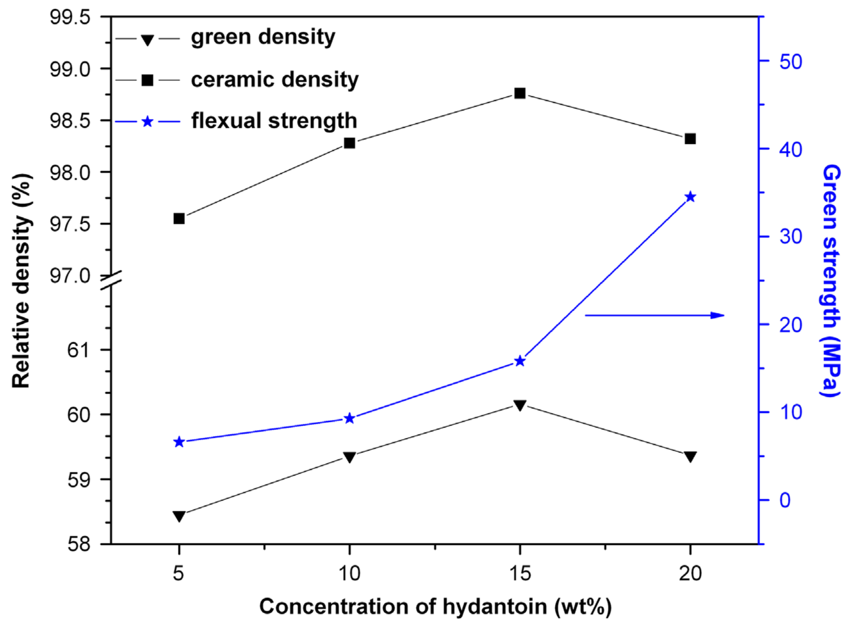

Fig. 5. The effect of Hydantion content on relative density and flexural strength of green bodies and sintered ceramics.

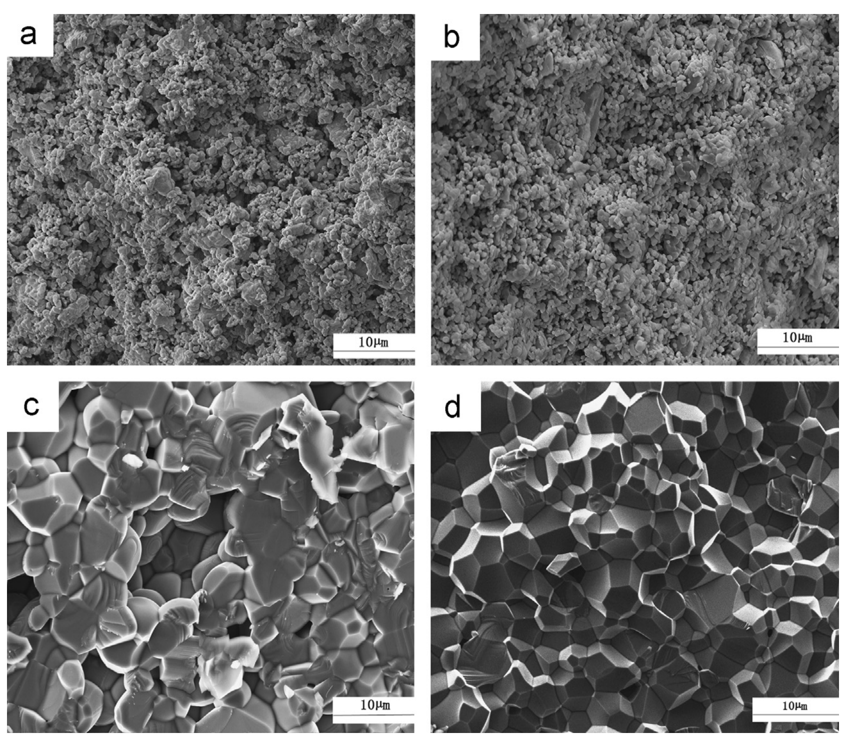

Fig. 6. SEM micrographs of the fracture surface of the AlN green bodies (a, b) and sintered ceramics (c, d): (a) 45 vol%, 15 wt% Hydantion; (b) 58 vol%, 15 wt% Hydantion; (c) 45 vol%, sintered at 1700 °C; (d) 58 vol%, sintered at 1700 °C.

4. Conclusions

Non-aqueous gelcasting was used to prepare AlN ceramics using Hydantion epoxy resin as the gelling agent and DPTA as the hardener. By adding 0.3 wt% PEI as the dispersant, the AlN slurry with a solid loading of 58 vol% and viscosity of about 1.5 Pa s was obtained. The viscosity of the AlN slurry increased with the increase of the concentration of Hydantion epoxy resin when it ranges from 0 to 15 wt%. The relative density of AlN green body reached 64.5% when the solid volume fraction of AlN slurry reached 58%. The relative density, flexural strength and thermal conductivity of the AlN ceramics reached 99.6%, 360 MPa and 185 W (m K)$^{-1}$, respectively.

Acknowledgments

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