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Preparation and properties of AlN ceramic suspension for non-aqueous gel casting

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ABSTRACT

A non-aqueous gel casting process based on the mixed solvent (ethanol and polyethylene glycol) and low-toxicity N,N-dimethylacrylamide (DMAA) was developed for an aluminum nitride (AlN) ceramic. In the present work, rheological properties of non-aqueous concentrated AlN suspensions were investigated in the presence of mixed solvent, dispersant, milling time, monomer and solid loading, in order to screen for the most suitable experimental conditions to obtain a good rheological behavior for gel casting. The results showed that the 50 vol% slurry with 0.2 wt% dispersant concentration, 2 h milling time, 6 wt% -monomer content, and a solvent ratio of 3:1, can meet the requirements for the casting process of AlN ceramic slurries. After being dried at 100 °C for 1 h, the optimum bulk density and maximum flexural strength of the AlN green bodies were as high as 1.97 g/cm^3 and 18.68 MPa, respectively. SEM photographs revealed that the green body had a relative uniform microstructure when the solid loading was 50 vol%. The shrinkage and deformation of shaped sintered bodies prepared through gel casting were small after sintering. The sintering shrinkage, apparent porosity, bulk density and flexural strength were 14.8%, 0.22%, 3.21 g/cm^3 and 310 MPa, respectively.

1. Introduction

According to Spina et al. aluminum nitride ceramic is one of the most promising novel ceramics, with a series of excellent properties such as high thermal conductivity (theoretical value of 320 W m^{-1} K^{-1}), low dielectric constant (9 at 1 MHz), low dielectric loss (4×10^{-4} at 1 MHz), high electrical resistance and a thermal expansion coefficient matched with silicon [1–3]. Aluminum nitride has been employed in a range of engineering fields, such as ceramic substrates for electronic applications [4,5]. The gel casting is an attractive wet forming technique which combines organic chemistry and traditional process for fabricating complexly shaped and high performance ceramic. Firstly, an organic monomer was introduced into a ceramic slurry with low viscosity and high solid content. Then, in the presence of an initiator and a catalyst, crosslinking polymerization of organic monomers occurred, forming a three dimensional network structure. Thus, ceramic particles were in situ solidified and a green body with high homogeneity and moderate mechanical strength was produced. In the past decades, gel casting, including aqueous systems and non-aqueous systems, has been applied to various ceramic materials, such as Al_2O_3 [6–9], SiC [10], SiO_2 [11], ZTA [12], YAG [13], Si_3N_4 [14], ZrO_2 [15], etc. However, preparation of AlN ceramic by gel casting has been rarely reported. The main reason is that AlN undergoes a significant hydrolysis phenomenon during the preparation of aqueous gel casting slurries, which can be described by the following equations according to Bowen et al. [16]:

$$AlN + 2H_2O \rightarrow AlOOH_{(amorph)} + NH_3 \quad (1)$$

$$AlOOH_{(amorph)} + H_2O \rightarrow Al(OH)_3 \quad (2)$$

$$NH_3 + H_2O \rightarrow NH_4{}^{+} + OH^{-} \quad (3)$$

Recently, Kumar et al. [17] studied the addition of alumina to phosphoric acid-treated aluminum nitride powders. It was discovered that this resulted in the rupture of the passivating shield around AlN resulting in hydrolysis reactions leading to the formation of hydroxides. Guo et al. [18] prepared AlN aqueous gel casting slurries using hydrolysis resistant AlN powder modified with aluminum dihydrogen phosphate and phosphoric acid. Ganesh et al. [19] also treated AlN powder in an ethanol solution of aluminum dihydrogen phosphate and phosphoric acid. The Al$(H_2PO_4)_3$ layer was coated onto the surface of the AlN powder, which prevented its further hydrolysis process. The detailed reactions for the treatment process, reported by Ganesh et al. are as follows:

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$$AlN + H_2O \rightarrow Al(OH)_3 \quad (4)$$

$$Al(OH)_3 + H_3PO_4 + n[Al(H_2PO_4)_3] \rightarrow (n+1)Al(H_2PO_4)_3 + 3H_2O \quad (5)$$

Li et al. [20] prepared high-performance modified AlN powder, using $Y(NO_3)_3 \cdot 6H_2O$ as the modifying agent. A Y_2O_3 coating was formed on the AlN surface, preventing its further hydrolysis (Eqs. (1)-(3)) and maintaining the pH value of the modified AlN powder suspension at 7.75 during the slurry preparation. Therefore, surface modification with rare earths can effectively inhibit the hydrolysis of the AlN powder. Nevertheless, as indicated by reaction (4), the hydrolysis of AlN, to some extent, still exists during the treatment process. In the present work, in order to avoid the hydrolysis of AlN powder during the treatment process, non-aqueous gel casting was applied for synthesis of AlN ceramics. Shen et al. [21] have prepared AlN ceramics using 1-methyl-2-pyrrolidinone as solvent and Solsperse-24,000 as dispersant. Xue et al. [22] have also prepared AlN ceramics using ethanol as solvent, polyethyleneimine as dispersant, sorbitol polyglycidyl ether as gelling agent and tetraethylenepentamine as hardening agent, respectively. In order to obtain concentrated slurries with low viscosity and good liquidity, the effects of solvent ratio, dispersant concentration, milling time, monomer content and solid loading on the rheological properties of the AlN slurries were investigated by viscosity measurements. Properties of the AlN green and sintered bodies were also studied.

2. Experimental procedure

2.1. Raw materials

A commercial AlN power (Nitrogen content: 33.8%; purity: 99.9%; Advanced Technology & Materials Co. Ltd., Beijing, China) with a particle size of 3–5 μm was used as the raw material. Y_2O_3 (purity: 99.9%) was used as the sintering additive. The morphology of the AlN powders was shown in Fig. 1. Ethanol and Polyethylene glycol of suitable proportion were used as the mixed solvent. Benzoyl peroxide (1 g BPO dissolved in 5 ml N,N–dimethylacetamide) was used as the initiator. Other raw materials for the experiment are listed in Table 1.

2.2. Experimental procedure

The gel casting process is described in the following. AlN powder was added into a premix solution, which was prepared by dissolving 0.2 wt% PEI with respect to the AlN powder in the mixed solvent, followed by the addition of 6 wt% DMAA and MBAM in an 8:1 ratio. After 2 h milling, the well dispersed slurries were degassed in order to eliminate the air bubbles. Afterward, the necessary amount of initiator and catalyst were added into the AlN ceramic slurries in turn. Then the slurries were cast in a stainless steel mold and soaked at a specific temperature for 2 h for solidification. After being dried in an air oven at 100 °C for 1 h, green bodies were obtained. Finally, sintering was carried out at 1850 °C for 2 h in N_2 atmosphere.

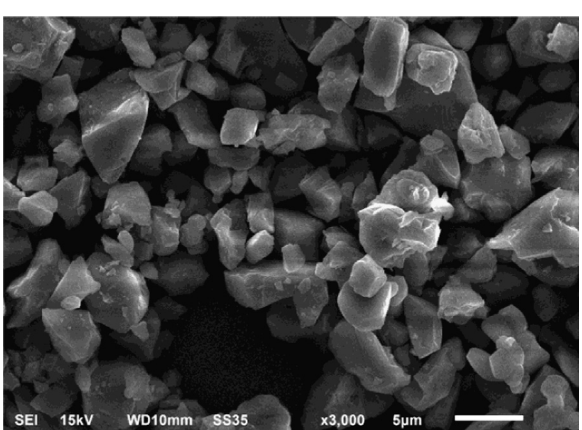

Fig. 1. Scanning electron microscopy photograph of AlN powder.

2.3. Characterization and test

The viscosities of AlN slurries were characterized using a rotational rheometer (R/S CC25, Brookfield Corporation, USA). A scanning electron microscope (SEM, Model JSM-5900, Japan) was used to observe the microstructure of AlN powder and the fracture surface of the green bodies. The green body was characterized by fourier transform infrared spectrometer (IR, Nexus670, Nicolet). Flexural strength of the green bodies was examined using an universal testing machine (CM-62303, MTS System Corporation, China) by the three-point flexural method with a sample dimension of 3 mm × 4 mm × 40 mm, and with a crosshead speed of 0.5 mm/min. The pore size distribution of the green bodies was measured by the mercury porosimeter (Quantachrome Company Poremaster). Archimedes method was employed to determine the bulk density and porosity of the green and sintered bodies.

3. Results and discussion

3.1. Effect of solvent ratio on viscosity of slurries

Ethanol and polyethylene glycol were used as the mixed solvent. Fig. 2 shows the effect of solvent ratio on the viscosity of AlN slurries with 50 vol% solid loading. All slurries showed shear thickening behavior and the viscosity increased corresponding to the content of PEG. Owing to the difference in surface tension, PEG and ethanol have different wettability for AlN powder. The higher the ethanol content, the greater the surface tension of the mixed solvent, the better the wettability of the mixed solvents for AlN powder. By adjusting the solvent ratio, a slurry with good rheological properties can be obtained. A slurry with solvent ratio of about 3:1 and a viscosity lower than 1 Pa s was obtained, which was suitable for the gel casting process.

3.2. Effect of dispersant content on viscosity of slurries

Dispersants play an important role on improving the dispersion stability of powders and the rheological properties of slurries, which are very sensitive to its dosage. Fig. 3 shows the effect of PEI content with respect to the AlN powder on the viscosity of AlN slurries with 50% solid loading. With the addition of PEI, the viscosity of the slurry decreased rapidly. The added dispersant was absorbed and covered on the surface of the AlN powder, and improved the rheological properties by proving to be a steric effect. 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 [23]. As can be seen in Fig. 3, the optimum dosage of PEI is 0.15–0.25 wt%. However, excessive dosage of PEI led to an increase in viscosity. When excessive PEI molecules were absorbed onto the surface of AlN powders, the electrical double layer was compressed, which significantly weakened the repulsion effect and increased the viscosity of slurries.