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Ceramics International 40 (2014) 2535–2538

CERAMICS INTERNATIONAL

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Short communication

Preparation of high performance AlN/Hydantion composite by gelcasting and infiltration processes

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Received 24 June 2013; received in revised form 27 July 2013; accepted 27 July 2013
Available online 2 August 2013

Abstract

A new processing technique was proposed for preparing aluminum nitride (AlN)/Hydantion interpenetrating network composites. The technique comprised gelcasting AlN green bodies, degreasing, and infiltrating Hydantion epoxy resin and hardener into the AlN skeleton under a vacuum condition. The effects of AlN contents on the viscosities of AlN slurries and the flexural strength, thermal conductivity, dielectric constant of the AlN/Hydantion composites were evaluated. The highest thermal conductivity and flexural strength of the AlN/Hydantion composites reached 3.56 W/mK and 101.3 MPa, respectively. The fracture surface of the composite revealed that an interpenetrating polymer network in the AlN ceramic skeleton was formed. The AlN/Hydantion composite exhibited the dielectric constant of 7.3 at 1 MHz.

Keywords: B. Composites; C. Thermal conductivity; D. Aluminum nitride; Gelcasting and infiltrating

1. Introduction

Current requirements on the thermal management of electronic packages have prompted the search of a thermally conductive composite which provides a solution for high-reliability packages with low dielectric constant and low cost [1]. Ceramic powder reinforced polymer materials [2–6] have attracted intensive attention due to their excellent properties to meet the requirement for electronic packaging materials, including light weight, chemical inertness, high fracture strength, low dielectric constant and high thermal conductivity. The properties of light weight, chemical inertness and reliability against fracture are mainly provided by the polymer in the composite. The thermal conductivity of the composite is mainly provided by high thermal conductivity ceramic fillers as the thermal conductivity of the polymer is very low [7]. There is a growing demand for highly conductive composites with the development of electronic chips towards higher density and higher frequency, which requires to remove more waste heat to make the chips stable. The most widely used ceramic fillers such as alumina (Al_2O_3) [8] and silica (SiO_2) [9] become unsuitable due to their low conductivities. AlN is a potential filler owning to its high thermal conductivity (200–320 W/mK), low dielectric constant (8.7) and excellent mechanical properties [10,11]. Epoxy [12] and polyimide [13] are the most widely used polymers as high temperature thermosetting polymer matrix while polystyrene [7] is employed as low temperature thermoplastic polymer matrix. The AlN/polymer composite is usually prepared by polymer molding technique [14,15] with a composition of 30–45 vol% polymer and 55–70 vol% filler.

In this paper, a new processing method for preparing ceramic/polymer composites with high thermal conductivity and improved reliability was reported. AlN powder and Hydantion epoxy resin were used as the row materials. Hydantion epoxy resin was a nontoxic resin with low cost and used in AlN ceramic processing in our previous work [16]. The processing method was based on gelcasting and infiltration techniques [17]. The first step was to gelcast AlN green bodies, and then both Hydantion epoxy resin and hardener were infiltrated into a porous degreased AlN green body under a vacuum condition. After bringing the specimen back to ambient pressure, in situ polymerization occurred in the porous body upon heating up, resulting in the formation of a polymer/ceramic composite which consisted of an interpenetrating polymer

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http://dx.doi.org/10.1016/j.ceramint.2013.07.131

network completely filling in the AlN ceramic skeleton. An important feature of this process was that a continuous polymeric hydantion network can be achieved even at a low volume fraction. Thus, the content of low thermal conductivity polymer can be minimized, achieving polymer fraction consistently lower than that produced by traditional polymer molding processes. It was shown that this special microstructure arrangement of ceramic/polymer interpenetrating network enabled to optimize both thermal conductivity and flexural characteristics.

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. Propanol (Tianjin Kemiou Chemical reagent Co., Ltd., Tianjin, China) was used as the solvent. Slurries with different solid loadings (30–58 vol%) were prepared by ball milling the AlN with the premix solution containing solvent and 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 10000 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 release 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.

Dried green bodies were placed in a muffle furnace in air at 600 °C for 2 h to burn out polymer. And then both Hydantion epoxy resin and hardener were infiltrated into the porous degreased AlN green bodies under a vacuum condition. After bringing the specimens back to ambient pressure, in situ polymerization occurred in the porous body upon heating up. Finally, the Hydantion/AlN composites consisting of an interpenetrating polymer network completely filling in the AlN skeleton were obtained and were named as composite A. As comparison, composite B was the rest green bodies without treatment.

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 composites 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 microstructures of the fractural surfaces of the composites were observed by scanning electron microscopy (JSM-6390, JEOL, Tokyo, Japan).

The diffusivity and specific heat capacity of the composites (3 mm thick) were measured by a laser flash technique using a thermal constant analyzer (LFA427, Netzsch, Selb, Germany). The bulk densities of the composites were measured by the Archimedes' method. Thermal conductivity k was calculated by Eq. (1) from the measured diffusivity α, bulk density ρ, and specific heat capacity c as follows:

$$K = \alpha\rho\, c \qquad (1)$$

The dielectric capacitance of the composites material was measured by using a disc-shaped specimen (ϕ10 × 2 mm) with a Impedance Analyzer (Agilent 4294A) at 1 MHz at room temperature. The sample was coated on both sides of the cross-sectional surfaces with a silver paste. The dielectric constant can be calculated by Eq. (2) by measuring the capacitance c:

$$\xi r = cd/A \qquad (2)$$

where ξr is the dielectric constant of the specimen, c is the capacitance of the specimen, A is the area of cross-sectional surface, d is the thickness of the specimens.

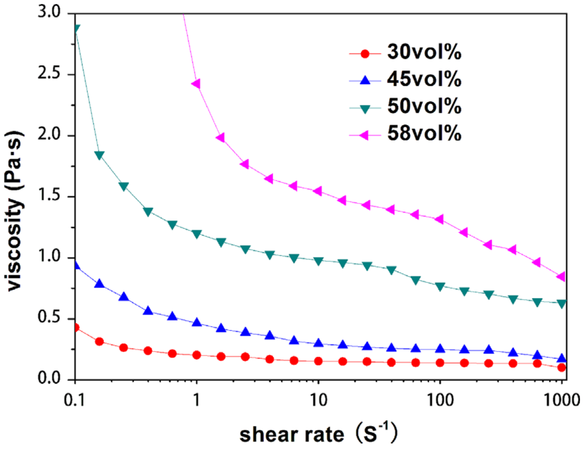

Fig. 1. Viscosities of AlN slurry with different solid loading as a function of the shear rate (PEI: 0.3 wt%).

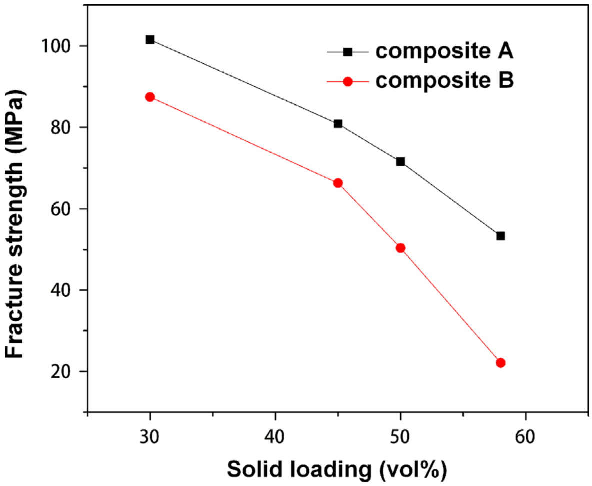

Fig. 2. The effect of AlN contents on flexural strength of composite A and composite B.

3. Results and discussion

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

$$\Phi=\frac{m/\rho}{m/\rho+V} \tag{3}$$

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. 1 shows the rheological curves of slurries with different solid loadings. All these slurries were prepared by adding 0.3 wt% PEI as dispersant. All slurries showed shear thinning behavior, and the viscosity increased with the increase of the 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 milling for 72 h, which was still suitable for casting and preparing a high density green body [18].

Fig. 2 shows the effect of AlN contents on flexural strength of composite A and composite B. The flexural strengthes of two composites decreased obviously when the AlN slurry concentration increased from 30 vol% to 58 vol%. For composite A, the strength reached as high as 101.3 MPa when the slurry's solid loading was down to 30 vol%. The strength of composite A was obviously higher than that of composite B. The AlN skeleton of composite A was infiltrated by Hydantion epoxy resin which would form the epoxy resin network. These polymer ligaments form plastic bridging sites whose stretching may adsorb a large amount of energy during fracture propagation in the ceramic skeleton, thus explaining the relatively high fracture value measured in this composite.

Fig. 3 shows the effect of AlN contents on thermal conductivities of composite A and composite B. The thermal conductivities of two composites increased obviously when the AlN slurry concentration increased from 30 vol% to 58 vol%. The thermal conductivities of composite A was higher than that of composite B. The highest thermal conductivity value, 3.56 W/mk was achieved by composite A when the AlN slurry content was 58 vol%. The phenomenon could be explained by the formation of an interpenetrating polymer network completely filling in the AlN ceramic skeleton in the composite A. The AlN skeleton offered excellent thermal conductivity passage which would endow the composite with high thermal conductivity.

Fig. 4 shows the effect of AlN contents on dielectric constants of composite A. The dielectric constant of the composite A increased slightly with the increase of AlN content. The highest

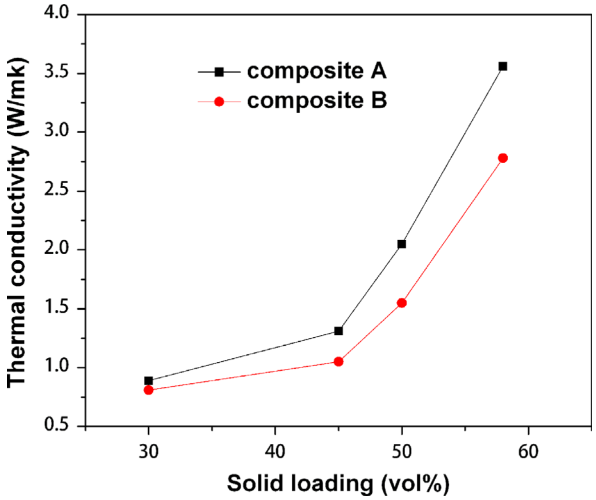

Fig. 3. The effect of AlN contents on thermal conductivities of composite A and composite B.

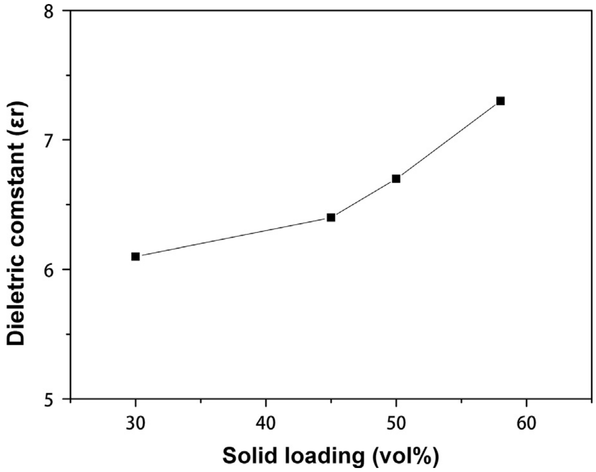

Fig. 4. The effect of AlN contents on dielectric constant of composite A.

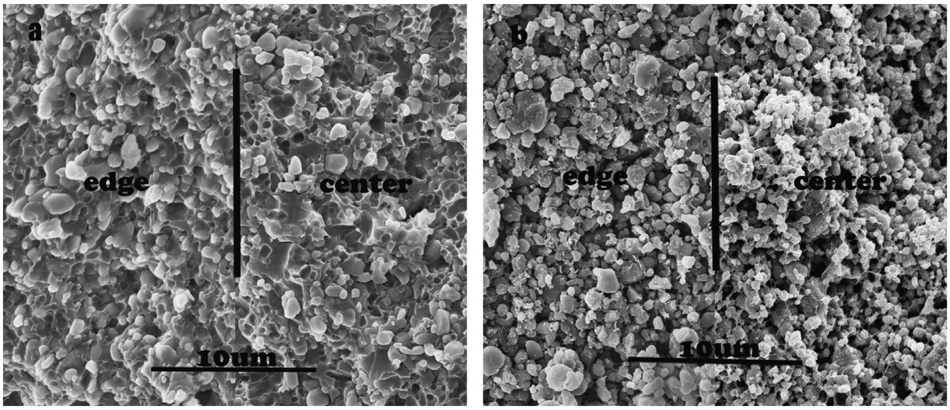

Fig. 5. SEM micrographs of the fracture surface of composite A (a) and composite B (b): (a) 58 vol%, degreased AlN green body, infiltrated by Hydantion epoxy resin; (b) 58 vol%, non-degreased AlN green body, no infiltration.

dielectric constant of composite A was 7.3, which was low enough to meet the electrical packages demand [19].

Fig. 5a shows the SEM micrographs of the fracture surface of the composite A near the edge and in the central part, respectively. It was noticed that the Hydantion polymeric network formed within the narrow ceramic porosity of dense AlN green bodies in the whole body of composite A. And the polymer network appeared to be fully percolated with no visible porosity. These polymer ligaments formed plastic bridging sites in the AlN skeleton. This microstructure features can be used to explain the results in the Figs. 2 and 3.

Fig. 5b shows the SEM micrograph of the fracture surface of the composite B near the edge and in the central part, respectively. Composite B was the AlN/Hydantion green body which was not infiltrated by Hydantion epoxy resin. Composite B was used for comparison.

4. Conclusions

Aluminum nitride (AlN)/Hydantion interpenetrating network composites were prepared by the technique which was based on gelcasting the AlN Green bodies, followed by infiltrating the Hydantion epoxy resin into the AlN skeleton under a vacuum condition. The thermal conductivity, dielectric constant and flexural strength of the composites were measured. The highest thermal conductivity and flexural strength of the AlN/Hydantion composites obtained by the gelcasting and infiltration methods reached 3.56 W/mK and 101.3 MPa, respectively. The microstructure of the composite fracture surface revealed that an interpenetrating polymer network which filled in an A1N ceramic skeleton was formed. The dielectric constant was low for the AlN/Hydantion composite which was suitable to be used as electronic packaging materials.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Grant nos. 51021063, 51072235) and Hunan Provincial Natural Science Foundation of China (No. 11JJ1008).

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