Materials Chemistry and Physics 147 (2014) 11–16

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Materials science communication

Fabrication and characterization of silicon-based ceramic/aluminum nitride as thermally conductive hybrid filler in silicone rubber composite

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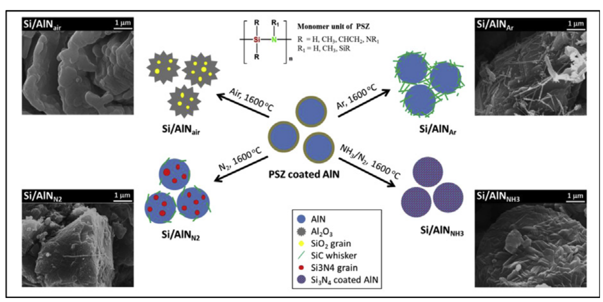
HIGHLIGHTS

- Si/AlN fillers were fabricated by pyrolysis of PSZ/AlN at 1600 °C in air, Ar, N_2 and NH_3.
- Pyrolysis in various atmospheres resulted in different morphology of Si/AlN fillers.
- Si/AlN which was pyrolysis in Ar or NH_3 can be used as thermally conductive fillers.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 December 2013
Received in revised form
9 April 2014
Accepted 5 May 2014

Keywords:
Composite materials
Ceramics
Thermal conductivity
Heat treatment

ABSTRACT

Silicon-based ceramics and aluminum nitride (Si/AlN) were fabricated by pyrolysis of polysilazane (PSZ) coated AlN at 1600 °C in air, Ar, N_2 and NH_3 atmospheres. The results from XRD, XPS and SEM/EDS revealed the existence of crystalline phase of Si-based ceramics on AlN particles including SiO_2 in Si/AlN$_{air}$, SiC whisker in Si/AlN$_{Ar}$, SiC whisker/Si_3N_4 grain in Si/AlN$_{N2}$, and Si_3N_4 ceramics in Si/AlN$_{NH3}$. It was found that the thermal conductivity of silicone rubber filled with Si/AlN hybrid fillers which were fabricated in Ar and NH_3, was improved. This might be due to the existence of nanoscale SiC whiskers and a thermal conductive layer of Si_3N_4 on Si/AlN$_{Ar}$ and Si/AlN$_{NH3}$ surface, respectively. Thus, it can be suggested that Si/AlN hybrid fillers, especially for the case of Si/AlN$_{(Ar\ and\ NH3)}$, can be applicable to use as thermally conductive fillers. This work may have found to be an alternative way to improve thermal conductivity, but more work needs to be done to really achieve significant improvement.

1. Introduction

Thermally conductive and electrically insulating polymer composites have received extensive attention in electronic devices because these composites can dissipate heat and prevent overheating in electronic devices during operation. Nowadays, these composites have been used in many applications including (1) thermal interface materials between heat dissipating system and

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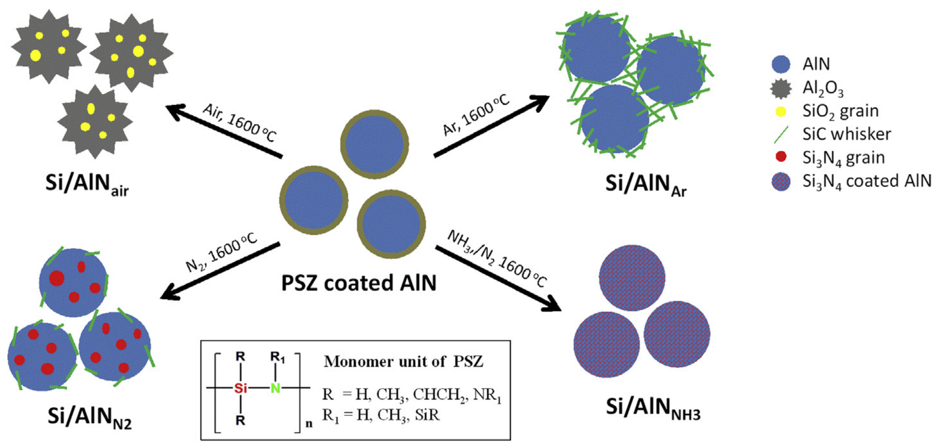
http://dx.doi.org/10.1016/j.matchemphys.2014.05.004
0254-0584/



Scheme 1. A route for a fabrication of Si/AlN hybrid fillers *via* pyrolysis of PSZ coated AlN at 1600 °C in various atmospheres.

chips in microelectronic devices [1], (2) encapsulating materials in silicon integrated circuits [2] and solar photovoltaic cells [3], (3) plastic heat sink in LED light bulbs [4] and (4) mobiles phone shell [5] and so on. Typically, thermally conductive composites are made of polymer matrix filled with thermally conductive fillers. It is acknowledged that polymers such as polycarbonate and epoxy resin possess low dielectric constant, low weight, high strength, high rigidity and high impact resistance [2,5,6]. In addition, silicone rubber and ethylene vinyl acetate possess high electrical resistivity, excellent flexibility, high damping capacity and high resistance to permanent deformation [1,3]. It is well known that polymer composites can be designed to have desirable properties by addition of specific hybrid fillers into the polymer composites [7,8]. Generally, the thermal conductivity of polymers is very low; therefore, the use of high intrinsically thermally conductive and electrically insulating ceramic, for example; AlN, silicon nitride (Si_3N_4) and silicon carbide (SiC) as fillers, can obviously enhance the thermal conductivity of the thermally conductive polymer composites.

PSZ is a preceramic polymer consisting of silicon, nitrogen, oxygen and, in certain case, carbon [9]. More interestingly, PSZ is a versatile material as it is compatible and can be applied with inorganic materials both in metals and ceramics. In addition, PSZ has been extensively used in coating, blending even in dip-coating applications [9,10]. It is interesting to note that pyrolysis of PSZ at the temperature higher than 700 °C in various atmospheres could convert polymeric structure of PSZ into amorphous phase of Si–O–N–C ceramics [10,11], and form binary phase of crystalline silicon oxide (SiO_2), Si_3N_4, SiC ceramics at the temperature around 1400–1600 °C [9–12].

In the present work, the pyrolysis of PSZ coated AlN at the temperature of 1600 °C in air, Ar, N_2 and NH_3 atmospheres were accomplished in order to fabricate hybrid fillers of AlN and Si-based ceramics, which are abbreviated hereafter as Si/AlN_{air}, Si/AlN_{Ar}, Si/AlN_{N2} and Si/AlN_{NH3}, respectively. Then, characterizations of Si/AlN hybrid fillers were investigated to identify and evaluate the effect of pyrolysis at different atmospheres on hybrid fillers. After that, the thermal conductivity of silicone rubber filled Si/AlN hybrid fillers was observed.

2. Experimental

A route for the fabrication of $Si/AlN_{(air,\ Ar,\ N2\ and\ NH3)}$ hybrid fillers was shown in Scheme 1. First, AlN with a particle size of 5 μm was dipped and stirred in PSZ solution (AlN:PSZ = 2:1 w/w) at room temperature for 1 h, then filtered and heated at 180 °C for 24 h to allow crosslinking of PSZ film on AlN surface. The pyrolysis of PSZ coated AlN in air, Ar, N_2 and NH_3 atmospheres was carried out by using tube furnace with the heating rate of 3 °C min^{-1} to the temperature of 1600 °C then dwell of about 2 h, finally cooling with the rate of 10 °C min^{-1} to room temperature (except Si/AlN_{NH3}, which was heated under NH_3 up to 800 °C and change to N_2 with dwell time 1 h, then the rest was the same as pyrolysis in N_2). After that, silicone rubber was compounded with hybrid fillers at the filler content of 56 wt% in two roll mixing mill and compression molded at 160 °C with a pressure of 10 MPa for 20 min in an automatic hot press machine. Crystallinity of Si/AlN hybrid fillers was performed on X-ray diffractometer (XRD) (D2 phaser) using a monochromatic Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) (ESCALAB 250) was used to analyze elemental composition and chemical state of the elements. Energy-dispersive X-ray spectroscopy (EDS) and Field emission-scanning electron microscopic (FE-SEM) observation of hybrid fillers were performed on a JEOL JSM-6500F operated at a voltage of 20 kV. Thermal conductivity of the composites was measured triplicate in each sample using a Hot Disk Thermal Analyzer (Hot Disk AB).

3. Results and discussion

Surface morphology of untreated AlN and Si/AlN hybrid fillers was observed by FE-SEM as shown in Fig. 1 and Fig. S1. EDS analysis was also performed to determine the distribution of Si-based ceramics on hybrid fillers as shown in Support Information Fig. S2 and Table S1. Untreated AlN revealed a clean and smooth surface, while Si/AlN_{air} exhibited a fracture on AlN particle with a smooth grain-like surface. In addition, it has been reported that Si/AlN_{air} particle was expanded due to a lot of nitrogen gas was evolved from inside AlN during the oxidation reaction and results in the increase in gas pressure around the AlN grains, then cause the formation of expansive cracks throughout AlN particle [13]. Moreover, EDS results revealed that SiO_2 was partly distributed on AlN surface. However, for the case of Si/AlN_{Ar}, a well-distributed whiskers with a diameter around 50–100 nm was observed on the surface of Si/AlN_{Ar}. Meanwhile, Si/AlN_{N2} exhibited the appearance of whiskers and grains on the surface of hybrid filler. It has been reported that pyrolysis of PSZ under Ar can convert PSZ into SiC whisker [14], whereas pyrolysis under N_2 would convert PSZ into both SiC whisker and irregular shape of Si_3N_4 [15]. Besides, it was found that the surface morphology of Si/AlN_{NH3} showed a sharp polygon surface. These observations suggested that pyrolysis in various atmospheres resulted in different morphology of Si/AlN hybrid fillers.