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Synthesis of AlN whiskers using cobalt oxide catalyst and their alignments for the improvement of thermal conductivity

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HIGHLIGHTS

- AlN whiskers with high aspect ratio were synthesized from Al_2O_3.
- Co_3O_4 droplets on the surface of Al_2O_3 acts as a catalyst for the whisker growth.
- AlN whiskers are aligned within PVA in perpendicular and parallel with heat flow.
- AlN whisker/PVA composite in perpendicular alignment shows a excellent heat conductivity.

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ABSTRACT

We synthesized one dimensional (1-D) AlN whiskers by using the cobalt oxide catalyst-assisted carbothermal reduction method. The formation of AlN whiskers is investigated by the thermo-gravimetric and differential thermal analysis, Fourier-transformed infrared spectra, X-ray diffraction patterns, scanning electron microscopy and transmission electron microscopy observations. It was found that Co_3O_4 droplets on the surfaces of Al_2O_3 acted as a catalyst for the growth of AlN whiskers by vapor-liquid-solid (VLS) mechanism. In addition, AlN whiskers/PVA composites aligned in parallel with the heat flow direction showed an excellent thermal conductivity about three times higher than those of the perpendicularly aligned whisker composites.

1. Introduction

In order to enhance the heat dissipation in the electronics, significant attentions have been focused on the investigation and development of thermal interface material in recent years [1–4]. Polymers can be endowed with an improved thermal conducting property by introducing the heat conductive fillers with the high thermal conductivity [5–12]. In recent years, many efforts have been made on the dispersion of one dimensional (1-D) ceramic fillers such as nanowhiskers, nanowires and nanotubes into polymer to enhance the thermal conductivity of composites by effectively reducing the interface areas between the fillers and the matrices and increasing the mean free path of thermal transport along the longitudinal direction of 1-D ceramic fillers in composites [13–15].

Various synthesis routes have been developed to fabricate AlN whiskers including the direct nitridation of metallic aluminum [16], the combustion synthesis of aluminum and AlN [17], the carbothermal reduction and nitridation (CRN) method calcining a mixture of alumina and carbon at 1800 °C [18,19]. Jung *et al.* [20] reported the synthesis of AlN whiskers by the modified CRN method in which they used the Al (III) complexes and Fe ions as the precursor of Al and the catalyst, respectively. The growth of AlN whiskers has been mainly explained by the vapor-solid (VS) [21] or the vapor-liquid-solid (VLS) mechanism [22]. It is known that the metallic catalysts like Cu, Ni, and Fe [17], the salt catalysts like $MgCl_2$ [23] and NH_4Cl [24], and the metallic oxide of MgO [25] play a role of catalyst to supply the sites of vaporization-liquefaction-

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solidification; the growth of various whiskers. Wu *et al.* [26,27] reported that cobalt sulfate was used as the starting catalyst for synthesis of AlN nanobelts or nanotubes by evaporating metallic aluminum. In these papers, they did not explain the mechanism of the formation of AlN nanotubes or nanobelts.

In this study, we also used cobalt sulfate as the starting catalyst for synthesis of AlN whisker by using carbothermal reduction and nitridation method. We would like to suggest a new method for the synthesis of 1-D AlN whiskers from Al_2O_3 powders by adopting Co_3O_4 as a catalyst. The role of Co_3O_4 for the formation and growth of AlN whiskers was investigated. Moreover, the effect of 1-D AlN whisker alignment within polymer matrix to the improvement of thermal conductivities of polymer composite was also studied.

2. Experiment

2.1. Raw materials

For the synthesis of AlN powders, starting materials were alumina (Al_2O_3, average particle size of 8 μm, Denka Co., Ltd, Japan), carbon black (C, Alfa Aesa Co., Ltd., USA) and cobalt sulfate heptahydrate as a catalyst ($CoSO_4{\cdot}7H_2O$, Sigma Aldrich Co., Ltd, USA). For the preparation of composites, polyvinyl alcohol (PVA, Kuraray Poval, Kuraray Co., Ltd, Japan) was used as a polymer matrix.

2.2. Synthesis of AlN spheres and AlN whiskers

Al_2O_3 powder, carbon black and distilled water without/with the catalyst of cobalt sulfate heptahydrate ($CoSO_4{\cdot}7H_2O$) were mixed by using a high speed mixer. The molar ratio of Al_2O_3: C: $CoSO_4{\cdot}7H_2O$ was 1: 5: 0.0726. The starting materials including 51 g of Al_2O_3, 30 g of carbon black and 10.2 g of $CoSO_4{\cdot}7H_2O$ (the total weight is 91 g) were placed in three graphite crucibles and heat-treated in a graphite furnace at the different synthesis temperatures between 1200 and 1800 °C for 2 h under nitrogen flowing 2 L/min. Excess carbon was removed by burning out at 600 °C for 3 h. Finally, we obtained 42.9 g of AlN product. The yield of our product against the starting material of Al_2O_3 was 82.4%. For the case with the catalyst, AlN whisker powders were formed, while AlN spherical powders were synthesized for the case without the catalyst.

2.3. Preparation of AlN/polymer composites

There are two types of fillers such as AlN spherical and whisker powders. To produce the AlN/PVA composites, the AlN powders with the desired volume fraction (V_f) of 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 were dispersed in a 10% PVA aqueous solution, and then the mixture was stirred by using a magnetic bar at 80 °C for 3 h. The mixed AlN/PVA slurries were de-aired in a vacuum chamber. The de-aired slurry was poured into a doctor blade machine to make the AlN/PVA film with the thickness of 0.20 mm and then dried at 80 °C, as shown in Fig. 1. 1-D AlN whiskers tend to be aligned in parallel with the AlN/PVA composite film plane. We prepared the composite samples with two types of alignment direction; (1) the perpendicular alignment against the heat flow (parallel alignment direction to the film surface) and (2) the parallel alignment against the heat energy flow (normal alignment direction to the film surface). For the sample with the perpendicular alignment, 10 layers of the composite films with size of 11 × 11 × 0.2 mm^3 were laminated by using a hot press at 90 °C under 10 MPa to form the bulk composite samples with the dimension of 11 × 11 × 2 mm^3 (Fig. 1(a)). For the parallel alignment of AlN whiskers against the heat flow, 55 layers of the composite films were laminated by using the hot press at 90 °C under 10 MPa to form the bulk composite samples with the dimension of 11 × 11 × 11 mm^3, and then cut in normal direction to the film surface (Fig. 1(b)).

2.4. Measurements

The pyrolysis of the catalyst and the precursor was investigated via the thermo-gravimetric and differential thermal analysis (TGA-DTA, DTG-60H and TA-60WS, Shimadzu) in a nitrogen atmosphere with a linear temperature ramp of 5 °C/min in the range of room temperature to 1500 °C. Fourier-transformed infrared (FT-IR) spectra were recorded on a JASCO FT-IR system (FT/IR4100), which operates from 4000 to 400 cm^{-1}. The FT-IR transmission spectra were obtained from the specimens embedded in a KBr matrix. The crystal phases of the AlN products were studied via X-ray diffraction (XRD, 40 kV, 200 mA, Rigaku, Japan), using Cu Kα radiation (λ = 1.5418 Å). The morphology of AlN product was examined via the field emission scanning electron microscopy (FE-SEM, JEOL JSM-7600F) and the transmission electron microcopy (TEM, JEM-3000F, JEOL, Ltd). The growth direction of AlN whiskers was studied by the high resolution TEM (HR-TEM) and the selected area diffraction (SAED). The microchemical analysis was performed by using the energy dispersive X-ray (EDX) analysis attached to the TEM. The specimen for the TEM observation was cut by the focused ion beam (FIB, HELIOS 600, FEI Co., USA). The thermal diffusivity (α) and the specific heat capacities (C_p) of the composites were measured by using the laser flash method (LFA-427 Nanoflash apparatus, NETSZCH, Germany). The density (ρ) of samples was measured by Archimedes method. The thermal conductivity (k) of the composite samples was calculated with the equation of $k = \alpha \times \rho \times C_p$.

3. Results

3.1. Synthesis of AlN whiskers

We analyzed the TGA-DTA of $CoSO_4{\cdot}7H_2O$ to figure out a stable chemical state with increasing the temperature (Fig. 2(a)). It shows that there are four stages of pyrolysis of $CoSO_4{\cdot}7H_2O$; (1) the formation of one and half hydrate cobalt sulfate ($CoSO_4{\cdot}1.5H_2O$) with the weight loss of 35.31% in the range of room temperature to 160 °C. (2) anhydrous cobalt sulfate formation ($CoSO_4$) with weight loss of 9.39% in the range of 240–350 °C, (3) Co_3O_4 formation with weight loss of 26.72% (26.58%, theoretically) in the range of 700–835 °C, and (4) the decomposition of Co_3O_4 to CoO with weight loss of 2.34% in the range of 835–986 °C (1.90%, theoretically). CoO is thermodynamically stable over 986 °C.

Fig. 2(b) and (c) show TGA and DTA curves of carbon black, the mixtures of Al_2O_3 and carbon without and with the catalyst of $CoSO_4{\cdot}7H_2O$ under nitrogen atmosphere, respectively. TGA curves of carbon black slightly decreased from 420 to 700 °C and significantly decreased over 700 °C due to the combustion of carbon. For the mixture of Al_2O_3 and carbon without the catalyst, there was no change in TGA curve from room temperature to 420 °C. Over 420 °C, the TGA curve of the mixture started to decrease due to the combustion of carbon. However, there was a difference between the TGA curves of the mixture without and with the catalyst. The mixture with the catalyst of $CoSO_4{\cdot}7H_2O$, in the first range of room temperature to 160 °C, showed the weight loss of 4.01% (3.94%, theoretically) due to the dehydration of $CoSO_4{\cdot}7H_2O$ to $CoSO_4{\cdot}1.5H_2O$. In the second range of 240–420 °C, there was the weight loss of 0.99% (1.08%, theoretically) due to the dehydration of $CoSO_4{\cdot}1.5H_2O$ to $CoSO_4$. In the third range of 420–600 °C, small amount of weight loss was 0.57%, relating to the combustion of carbon. The weight loss in the range of 600–690 °C was about 3.89%, contributing to the decomposition of $CoSO_4$ to cobalt oxide