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Enhancement of cross-plane thermal conductivity and mechanical strength via vertical aligned carbon nanotube@graphite architecture

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ABSTRACT

A three-dimensional (3D) carbon nanotube/exfoliated graphite block (CNT/EGB) was prepared by growing vertical aligned carbon nanotube (VACNT) at the surface of SiO_2-coated exfoliated graphite plate (EGP) through chemical vapor deposition followed by hot-pressing. In such 3D CNT/EGB, EGPs were bridged by the VACNTs in the cross-plane direction, and the interface between EGPs and VACNTs was covalently bonded by SiC which formed by reaction of SiO_2 and the adjacent carbon of EGPs and VACNTs. The length and growth density of VACNTs were adjusted by the growth time and concentration of catalysts. Thermal conductivity and mechanical strength of CNT/EGB were controlled by the growth states of VACNTs and hot-pressing. CNT/EGB showed a maximum cross-plane thermal conductivity ($k_\perp$) of 38 W/mK, which is more than twice as much as that of EGB (14 W/mK). A remarkable increase in $k_\perp$ was attributed to the efficient heat flow of VACNTs bridging EGPs in the cross-plane direction and the thermal conductive SiC interface between VACNTs and EGPs. Additionally, the increased bending (76 MPa) and compressive strength (59 MPa) of CNT/EGB was due to the combination of strong pull-out effect of high-density nanotubes and the strong covalent interconnections between VACNTs and EGPs.

1. Introduction

In the thermal management system (TMS), heat dissipation is essentially important for controlling the temperature of thermo-sensitive components or poor heat-resistant sophisticated appliances during a long-term operation. And the high thermal conductive heat dissipation material (HDM) is increasingly important for the design of TMS [1–4]. Among several potential HDMs, carbon-based HDMs, such as the graphite block, graphite paper and carbon foam, have been widely used in sealing elements, rocket nozzles and friction materials owing to their excellent heat conductance, light weight, resistance to corrosive environment as well as high mechanical properties [5–7]. The graphite block (GB) prepared from the nature graphite plate (GP) or exfoliated graphite plate (EGP) has been substantially studied as one of important carbon-based HDMs because of its high in-plane thermal conductivity ($k_\parallel$) and good mechanical strength [8–11].

Critoph et al. [8] prepared GB by compressing EGPs with a high $k_\parallel$ of 337 W/mK at a density of 0.831 g/cm^3. However, the maximum value of cross-plane thermal conductivity ($k_\perp$) was only 8.9 W/mK. Kang et al. [10] presented highly thermal conductive GB by hot-pressing the mixture of GPs and mesophase pitch at 500 °C followed by high temperature graphitization. The graphitization progress not only resulted in a high $k_\parallel$ (522 W/mK) and $k_\perp$ (25 W/mK), but also caused the poor cross-plane bending strength of 7.7 MPa. Due to the two-dimensional (2D) layered structure of graphite with large anisotropy, the GB prepared from pure GP or EGP usually shows low mechanical strength because of the interface slippage, and low $k_\perp$ (usually less than 10 W/mK) because of low connectivity between adjacent layers and the presence of pore space [9,11]. However, in many cases, such as the gasket of aircrafts in aerospace industries, the heat should be transferred through the cross-plane direction [12,13]. Therefore, the GB containing high $k_\perp$ and mechanical strength as well as light weight is essentially important for the future TMS [14,15].

Recently, a 3D graphite-based nanostructure prepared by intercalating 1D thermal conductive carbon nanotube (CNT)

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(theoretical expectations in the range of 3000–6000 W/mK) into the graphite structure shows a great potential in enhancing phonon mobility in the cross-plane direction and mechanical reinforcement [2,16–22]. Ko et al. [16] grew CNTs on EGPs and the resulted GB got a 10.3% increase of $k_{\perp}$ (8.6 W/mK), compared with the pure GB without CNTs. Liu et al. [17] found that the GB prepared from the GPs with CNTs growing on the surface resulted in an increase (52.2%) in the bending strength. The effect of the microstructure of CNT on the thermal and mechanical properties of GB was systematically studied in the former work, and a significant improvement of $k_{\perp}$ (24.3 W/mK) and bending strength (46 MPa) were obtained, mainly due to the improved phonon mobility in the cross-plane direction offered by CNT at the interlayer of GB and the pull-out effect of CNT [18].

Thus, 3D CNT-intercalated graphite composite becomes an ideal nanostructure for efficient heat dissipation. In spite of great potential in high $k_{\perp}$ and mechanical strength, the 3D CNT-intercalated graphite composite still suffer from several bottlenecks. One is the CNT grown on the graphite usually shows a low density with curved structure, which reduces the intrinsic thermal conductivity of CNT and causes many gaps in the consolidated block [12,13,18]. The other is the weak bonding between graphite and CNT results in a large interfacial thermal resistance, which restricts the phonon to vibrate across the interface of graphite and CNT [23,24]. Therefore, a new comprehensive approach aimed at increasing the density of CNTs and strengthening the interfacial bonding between CNT and graphite is needed, and thus the vertical aligned carbon nanotube (VACNT) grown at the surface of graphite structure could be a promising candidate material to prepare the GB with high $k_{\perp}$ and mechanical strength [25,26]. Due to the difficulty in controlling the microstructure of VACNTs at the surface of graphite and CNT-graphite interface structure after hot-pressing [27,28], the thermal conductive property of the GB based on this architecture has seldom been reported, though it shows excellent properties in energy storage, photovoltaic, and nanoelectronic [29–33].

In this paper, a 3D hierarchical carbon nanotube/exfoliated graphite block (CNT/EGB) was prepared by the growth of VACNT at the surface of EGP (VACNT@EGP) followed by hot-pressing (Fig. 1). Skillfully, the SiO_2 coating on the EGPs was used to facilitate the growth of dense and aligned CNTs at former stage, and then it was transformed into the thermal conductive SiC interface bonding the VACNTs and EGPs at later stage. The length and growth density of VACNTs were adjusted by the concentration of catalyst and the reaction time of chemical vapor deposition (CVD). The interfacial bonding structure between VACNTs and EGPs was controlled by the hot-pressing temperature and pressure. The microstructures of VACNTs at the surface of EGPs were observed by scanning electron microscope (SEM) and transmission electron microscopy (TEM). The changes in interfacial chemical and crystalline structures of the composite during the process were studied by spectroscopic techniques. Thermal conductivity, mechanical strength, and the density of CNT/EGB (EGB) were controlled by the growth of VACNTs and the following hot-pressing. For this 3D CNT/EGB, its $k_{\perp}$ could be enhanced by efficient heat flow of intercalated VACNTs bridging adjacent EGPs with strong covalently bonded contact between nanotubes and graphite layers, and a significant increase of its mechanical strength could be expected because of strong pull-out effect of the intercalation of high density nanotubes as well as the strong interface between nanotubes and graphite layers which strengthen the binding between the EGPs.

2. Experiments

2.1. Materials

Graphite intercalation compound (GIC) was purchased from Qingdao Huatai Graphite Co., Ltd. Mesophase pitch was obtained from Changzhou Herman Carbon Co., Ltd. All chemical reagents from Tianjin Jiangtian Chemical Co., Ltd were used without further treatment.

2.2. Thermal expansion and exfoliation of graphite

GIC was put in a tube furnace to be heated up to 1100 °C for 30 min in an atmosphere of argon (500 sccm), and expanded graphite (EG) with an expansion rate of 300% was prepared. The EG was immersed into acetone and mixed by shear mixer (10000 r/min, 10 min). The EGP was obtained after the water washing followed by drying.

2.3. The SiO_2 coating of EGP

The EGP was soaked in a solution of tetraethoxysilane (TEOS) with an EGP/TEOS mass ratio of 1:10 for 1 h. After filtration,

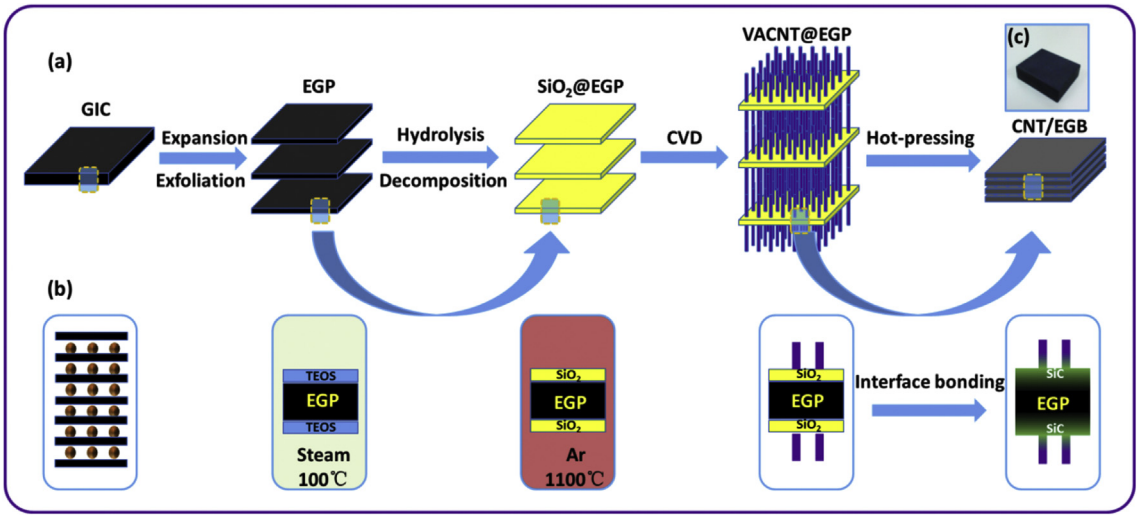

Fig. 1. (a) Schematic representation of the procedure for the preparation of the VACNT@EGP architecture and CNT/EGB. (b) The drawing of enlargement of the area circled in Fig. 1(a), and (c) the photograph of the as-prepared CNT/EGB. (A colour version of this figure can be viewed online.)