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Thermal properties of graphene/metal composites with aligned graphene

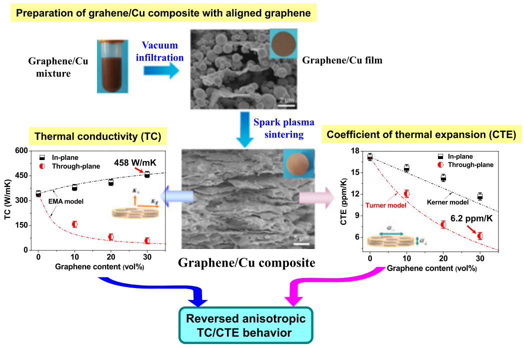
Ke Chu [a],*, Xiao-hu Wang [a], Yu-biao Li [a], Da-jian Huang [a], Zhong-rong Geng [a], Xi-long Zhao [a], Hong Liu [a], Hu Zhang [b]

[a] *School of Mechatronic Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China*
[b] *School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China*

HIGHLIGHTS

- The anisotropic thermal conductivity (TC) and coefficient of thermal expansion (CTE) of graphene/Cu composite is studied.
- The highly aligned graphene was realized in graphene/Cu composite by vacuum filtration and spark plasma sintering.
- The composites showed a reversed anisotropic behavior between TC and CTE as a function of graphene fraction.
- The composite with 30 vol % graphene shows a high in-plane TC of 458 W/mK and a low through-plane CTE of 6.2 ppm/K.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphene holds great potential in metal matrix composites for thermal management due to its excellent thermal properties. However, the graphene/metal composites possessing both high thermal conductivity (TC) and low coefficient of thermal expansion (CTE) have not yet been realized. Herein, we reported an efficient strategy to achieve a high alignment of graphene nanosheets (GNSs) in GNS/Cu composites through a vacuum filtration method followed by spark plasma sintering. Because of the highly aligned GNSs and laminated structure, the GNS/Cu composites exhibited notably anisotropic thermal properties. Intriguingly, the composites showed a reversed anisotropic behavior between TC and CTE as a function of GNS fraction, in which the in-plane TC was substantially higher than through-plane TC, whereas oppositely the through-plane CTE displayed a larger drop than in-plane CTE. Promisingly, the composite with 30 vol% GNSs delivered a high in-plane TC of 458 W/mK and a low through-plane CTE of 6.2 ppm/K, corresponding to a 35% TC enhancement and a 64% CTE reduction compared to pure Cu, respectively. The present GNS/Cu composites with high in-plane TC and low through-plane CTE are promising candidates for specific thermal management applications that require an efficient in-plane heat dissipation but a good through-plane dimensional stability.

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* Corresponding author.
E-mail address: chukelut@163.com (K. Chu).

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1. Introduction

Rapid development of microelectronic industry motivates the continuous miniaturization of electronic devices and increase in on-chip power density, and thus the efficient thermal management has become a critical issue for the normal function and high reliability of electronic components [1,2]. Metal matrix composites (MMCs) with high thermal conductive fillers (SiC, diamond, graphite flakes, carbon nanotubes (CNTs), etc.) are promising candidates for thermal management applications due to their potentially high thermal conductivity (TC), tailorable coefficient of thermal expansion (CTE) and prominent mechanical properties [3–5].

Graphene and its derivatives, such as graphene oxide (GO) and reduced graphene oxides (RGO), have recently attracted tremendous research interest owing to their unique structure and outstanding electronic, mechanical and thermal properties [6]. Study on graphene as a promising filler in MMCs is one of the fast-growing fields in the past five years [7–9]. A large number of experiments have shown that the addition of a small fraction of graphene in the metal matrix can considerably improve the mechanical properties of graphene/metal composites [10–12]. The TC of graphene/metal composites, however, remains far inferior to what can be predicted from the theoretical properties [13–15], attributed presumably to the processing challenges to achieve the uniform graphene distribution, well-bonded interface and good graphene alignment in the composites. In this regard, extensive studies have been undertaken to solve the graphene distribution and interface problems and great progress has been made [9]. Nevertheless, the study of graphene alignment in MMCs is still rare [13].

Graphene is naturally highly anisotropic due to its two-dimensional (2D) sp^2-hybridized carbon network along the basin plane [6]. Actual measurements show that the in-plane TC of graphene (1000–5300 W/mK) is extremely higher than through-plane TC (5–20 W/mK) by two to four orders of magnitude [16]. Thus, the achievement of highly aligned graphene in the metal matrix may be the dominant factor to realize the remarkable TC enhancement in graphene/metal composites. Boden et al. [13] adopted the combined ball-milling and spark plasma sintering (SPS) to prepare the graphene/Cu composites that displayed an intriguing self-alignment of graphene and the anisotropic thermal properties with in-plane TC being larger than through-plane TC by almost a factor of 3. Unfortunately, their best sample presented a disappointing in-plane TC of 292 W/mK, even inferior to that of pure Cu (340 W/mK). Such pressure-assisted self-alignment of graphene was also observed in the similar graphene/Cu composites reported by other research groups [14,15], but the frustrating TC remained. For instance, compared to the thermal properties of Cu matrix, the 4 vol% graphene/Cu composites prepared by the molecular-level mixing + SPS showed a ~35% reduction in in-plane thermal diffusivity [14], and a ~43% TC decrease could be found in 10 vol% graphene/Cu composites fabricated by the ball-milling + SPS [15]. These results elucidate that the pressure-assisted self-alignment may have a relatively low alignment degree that is not favorable for the TC improvement of graphene/metal composites. Cao et al. [17] recently developed a bioinspired strategy to well align the graphene in Cu matrix. The 2.5 vol% graphene/Cu composite with a nanolaminated structure delivered ~177% and ~25% improvements of yield strength and elastic modulus relative to pure Cu, respectively, while retaining the good ductility (32.3% elongation) and electrical conductivity (93.8% IACS) of Cu matrix. However, the thermal properties of their composites were not demonstrated.

On the other hand, the graphene/Cu composite films have also been investigated, such as RGO-graphene film [18], graphene-Cu-graphene heterogeneous film [19] and nitrogen-doped graphene-Cu film [20], which exhibited a high in-plane TC (376–543 W/mK) superior to that of a majority of graphene/Cu bulk composites [13,15,21]. Nonetheless, a clear drawback of these composite films is their dimensional limit and they can hardly be machined to the required parts with complex 3D shapes, thus seriously restricting their practical applications. Another important thermal property of graphene is its negative CTE (−1.28–−8 ppm/K [22,23]). The graphene incorporation might theoretically lower the CTE of MMCs to a large extent. Unexpectedly, until now, the CTE behavior of graphene/metal composites has not been reported yet.

In this study, we reported an efficient strategy to achieve a high alignment of graphene nanosheets (GNSs) in GNS/Cu composites through a two-step procedure involving a vacuum filtration process and followed SPS. As illustrated in Fig. 1a, the GNS/Cu film with homogeneously distributed and well pre-aligned GNSs were first prepared by vacuum filtration. Then, the film was broken into the flakes that were consolidated into the bulk composites by SPS resulting in the alignment of GNSs perpendicular to the pressure axis. It was demonstrated that the composites presented the highly aligned GNSs and well-packed laminated structure, leading to an extraordinary in-plane TC of 458 W/mK along with a drastically low through-plane CTE of 6.2 ppm/K at the GNS content of 30 vol%. The facile fabrication approach and the excellent and special thermal properties of GNS/Cu composites may open up new possibilities for the development of advanced graphene/metal composites for thermal management applications.

2. Experimental procedure

2.1. Materials

Atomized Cu powder (99.9% in purity, 0.5–2 μm in particle size) was purchased from Xingye Metal Materials, Co. Ltd. The Tanfeng Tech Co. Ltd. provided GNSs (5–30 μm in lateral size and 5–10 nm in thickness) that were further thermally annealed at 2000 °C in an argon atmosphere. All the chemicals were used as received without further purification.

2.2. Fabrication of GNS/Cu composites

The GNS/Cu composites were fabricated by the combined vacuum filtration and SPS. The detailed optimization of process parameters is given in the Supporting Information (Fig. S1–S4 and related notes). The GNSs (30 mg) were dispersed in 30 ml of ethanol under sonication for 1 h to generate a uniform suspension [24,25]. Then a certain amount of Cu powders were added to the GNS suspension and vortex-mixed for 30 min. The obtained GNS/Cu mixture was vacuum-filtered on a Teflon filter membrane (50 mm in diameter, 0.45 mm in pore size) to form a brown GNS/Cu film on the membrane surface. The vacuum filtration was repeated to prepare a batch of GNS/Cu films with the mass of each film controlled to be ~3 g. After naturally drying for 24 h, these films were peeled off from the membrane and further broken into the small flakes with a lateral size of 3–5 mm. Subsequently, the GNS/Cu flakes were consolidated into the bulk composites on a SPS furnace (mod.1050, Sumitomo Coal Mining Co. Ltd., Japan) at 760 °C for 5 min under a pressure of 50 MPa. The GNS/Cu composites with different GNS contents of 0, 10, 20 and 30 vol% were fabricated. Note that the composites with GNS contents higher than 30 vol% were hard to be fully densified (>3% porosity) [26,27], so the dense composites with 10–30 vol% GNSs (<1% porosity) were investigated in this work to exclude the effect of porosity.

2.3. Characterization

The TC of the samples was determined by a laser flash method [28]. The thermal diffusion coefficient (D) of the samples was tested on a Netzsch LFA 427 Nanoflash at room temperature. The specially designed sample holders were used to measure D at both in-plane and through-plane directions, as illustrated in Fig. 1b. The sample dimensions were Ø 25.4 mm × 0.2 mm and Ø 12.7 mm × 3 mm for in-plane D and through-plane D measurements, respectively. The specific heat (C_p) of the samples was measured by a differential scanning calorimetry (DSC) on a Netzsch 204 F1 DSC calorimeter. The bulk density (ρ) of