Anisotropic thermal expansion coefficient of multilayer graphene reinforced copper matrix composites

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ABSTRACT

Multilayer graphene reinforced copper matrix (Cu-MLG) composites were fabricated via molecular-level mixing combined with vacuum hot-pressing (VHP). The MLG displayed a preferred orientation in the copper matrix, with the in-plane surface perpendicular to the hot-pressing direction, resulting in significant anisotropy in the thermal properties of Cu-MLG composites. Theoretical predictions were made using four models (Schapery, Kerner, Turner and mixture rule) to investigate the effect of the preferential orientation of MLG on the CTE anisotropy of Cu-MLG composites. The CTE anisotropy was further analyzed by carrying out molecular dynamics (MD) simulations to determine the variation in bond lengths for copper and MLG in different directions in the interface regions. The MLG bond length increased gradually with increasing temperatures in the in-plane direction, while in the out-plane directions, it increased significantly at first and then decreased at higher temperatures. The variations of bond lengths for MLG are consistent with the CTE anisotropy of the Cu-MLG composites in the same direction.

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1. Introduction

The most challenging objective in the electronic industries is to develop materials that demonstrate a tunable thermal property with today's microelectronic devices. The development of composite material with balanced thermal properties is highly appreciated and currently competing the traditional monolithic conductive material. Carbon materials, such as graphite flakes and carbon nanotubes, were utilized to improve the coefficient of thermal expansion (CTE) and thermal conductivity of metal matrix composites [1—5]. As a newly emerged member of carbon material, graphene has attracted both academic and industrial interests due to its excellent mechanical and thermal properties, and has been studied and applied in a broad range of fields [6—10]. Notably, the linear CTE of the monolayer graphene was proved to be negative in the in-plane direction [11—13], which makes graphene a competitive material for enhancing the thermal properties of many kinds of composites. Reports show that the CTE of graphene/epoxy composite was lowered by 31.7% with a 30 vol% addition of graphene [14]. Nevertheless, while these works illustrate the enhancements graphene can have on polymer matrix composites, few reports of graphene on the CTE behavior of metal matrix composites exist [5,15].

The reason for the limited studies on the CTE of graphene/metal composites is the difficulty in fabricating composites with graphene uniformly dispersed in the metal matrix. It is widely accepted that graphene agglomerates are prone to form during mixing, which results in a severe deterioration of the composite properties [15—17]. The agglomeration of graphene in metal matrix is attributed to a number of reasons. The primary reason is due to the van der Waals forces between the interlayers of graphene [18,19]. Graphene sheets reduced from graphene oxide (GO) become hydrophobic and tend to irreversibly aggregate, due to the

relatively strong π-π interaction induced when the oxygen-containing functional groups are removed during the reduction process. Recently, a molecular-level mixing method was developed for fabricating graphene reinforced copper matrix composites, by which the dispersion uniformity of graphene was well improved [17]. Nevertheless the fabrication process is currently too complicated for industrial mass production. Another reason, particularly for metals with high atomic number, is the significant difference in specific gravity between graphene and the metal matrix (graphene, $1.06 \, g \, cm^{-3}$ [20], less than 1/8 of copper). Methods such as ball milling [21], electrodeposition [22], and electrochemical deposition [23] were employed to improve the dispersion uniformity of graphene in the metal matrix, resulting in enhanced properties. However, the agglomeration associated with the processing of graphene composites is still problematic.

While some success has been achieved in fabricating composites with graphene uniformly distributed in metal matrix, there is very little studies on exactly how graphene affects the thermal properties of the metal matrix. In most of these composites, the graphene sheets are found to preferentially locate at the grain boundary of matrix [17,24], but how they interact with the interfacial metal atoms and affect the thermal performance of composites remains elusive. In order to enhance the application of the superior thermal properties of graphene, it is necessary to understand the nature of the graphene/metal interface and how the interface atom behavior influences the thermal mechanisms.

In this paper, a simplified molecular-level mixing/vacuum hot-pressing (VHP) process was employed to fabricate copper-multilayer graphene (Cu-MLG) composites with MLG well dispersed in copper matrix. The effect of the preferential orientation distribution of MLG on the thermal expansion behavior of Cu-MLG composites was investigated and further compared with the theoretical predictions. In addition, the molecular dynamics simulations were employed to interpret the CTE anisotropy of the Cu-MLG composites.

2. Experimental

2.1. Preparation of Cu-MLG composite powders

Graphene oxide (GO) (purity 98.5%, lateral size < 2 μm), purchased from Carmery Graphene Co., Ltd, was used as raw material. The other chemical reagents used in this study were analytical grade, and purchased from Tianli Chemical Reagent Co., Ltd. The Cu-MLG composite powders were prepared by a simplified molecular-level mixing process which involves: a) mixing GO and Cu^{2+} ion ($Cu(NO_3)_2 \cdot 3H_2O$) in the ethylene glycol (EG) solution. Dispersing 0.75 g of GO in 500 ml of ethylene glycol (EG) and ultrasonicating to form a uniform GO dispersion, gradually adding 0.1 mol of $Cu(NO_3)_2 \cdot 3H_2O$ dispersed in 100 ml of EG to the GO dispersion, mixing the combined dispersion by magnetically stirring at room temperature for 1 h; b) co-reduction of GO and Cu ion to form Cu-MLG composite powders. Heating the mixture at 90 °C in a water bath and slowly adding 50 ml of 80% N_2H_4 dissolved with 3 g of NaOH, reacting at 90 °C for 12 h to precipitate the Cu-MLG composite powders; c) washing the Cu-MLG composite powders with ethanol then distilled water, and freeze drying in a lyophilizer. In this process, the Cu nucleates on the remanent OH sites on the reduced graphene, resulting in the formation of nanoscale distributed Cu-MLG composite powder as illustrated in Fig. 1(a). For comparison, additional powders were also synthesized under identical conditions, but with different initial concentrations of GO (18, 30 and 48 vol%).

2.2. Fabrication of the bulk Cu-MLG composites

The as-prepared Cu-MLG composite powders with various graphene content were cold pressed into 25 mm diameter discs using a uniaxial pressure of 150 MPa, and then vacuum hot-pressed (VHP) at 923 K under 150 MPa (as illustrated in Fig. 1(b)). Based on the mixing ratios, the corresponding bulk Cu-MLG composites had compositions of Cu-18 vol % MLG, Cu-30 vol% MLG and Cu-48 vol% MLG.

2.3. Microstructure and thermal properties of the Cu-MLG composites

The morphology of the Cu-MLG composite powders and bulk composites were investigated using field-emission scanning electron microscopy (SEM, JEOL JSM-7000 F). More detailed microstructure analysis was carried out using transmission electron microscopy (TEM, JEOL JEM-2100). The Raman spectra of graphene both in the powders and bulk samples were investigated by Raman spectroscopy (HORIBA, hr800) using 633 nm excitation. The texture of the composites were examined by electron back scattered diffraction (EBSD) using a Tescan Mira-3 field-emission scanning electron microscope equipped with an EDAX-TSL orientation imaging system.

The CTE was evaluated using a TA Instruments-Dolatometer (DIL802) at temperatures ranging from 373 K to 573 K with a heating rate of 2 K/min. The average CTE values over this temperature range are reported. The TD was measured using a NETZSCH Nanoflash (LFA447) at 298 K. To determine the thermal anisotropy of the composites, the CTE and TD were measured in both the longitudinal and transverse directions (with respect to the VHP direction, as shown in Fig. 1(b)). Samples for these tests were sectioned, as illustrated in Fig. 1(c), by electro discharge machining.

2.4. Theoretical predictions of the CTEs

To investigate the effect of graphene content on the CTEs of the Cu-MLG composites, different models were employed to predict the CTE variation with increasing MLG content. There are several basic assumptions that are common to all the theoretical calculations to be presented as follows,

1) The MLGs are of regular planar shape and homogenously dispersed in the matrix,
2) The interface between the MLG and matrix is perfect, without defects,
3) The temperature distribution is uniform in the composite and the matrix properties are isotropic, while the MLG is ortho-tropic, and the properties do not vary with temperature.

Several theoretical analyses have been presented in the literature for determining the CTE of metal matrix composites. Of these, the simplest and most used are those of Schapery [25,26], Kerner [27], Turner [28], and the modified rule of mixtures [29].

The Schapery model, based on extremum principles of thermoelasticity, is derived for a composite with an isotropic reinforcement distributed in an isotropic matrix, is presented as below,

$$\alpha_c = \alpha_2 + (\alpha_1 - \alpha_2)(1/K_c - 1/K_2)/(1/K_1 - 1/K_2) \tag{1}$$

$$K_c = K_1 + V_2/[1/(K_2 - K_1) + 3V_1/(3K_1 + 4G_1)] \tag{2}$$

where V, α and K refer to the volume fraction, coefficient of linear thermal expansion and bulk modulus, respectively. C, 1 and 2 refer to the composites, copper and graphene, respectively. The symbols