

Preparation and thermal properties of graphene nanosheet/Ti composites

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Abstract. Fully dense graphene nanosheet (GNS)/Ti composites with homogeneously distributed GNSs of thicknesses ranging from 5 to 20 nm have been fabricated from ball milled expanded graphite and Ti by hot pressing sintering (HPS). The phase and morphology of as-synthesized GNS–Ti composites are characterized by FESEM and TEM. This new composite outperforms most of carbon nanotube/Ti in thermal conductivity. The authors focused, in this study, on finding the reason of the increasement of thermal conductivity in the as-synthesized GNS–Ti composites. In addition, graphene with titanium substrate has been clearly shown and their growth model from experiment data of thermal conductivity given at the same time.

1. Introduction

Graphene has a high thermal conductivity of $5000\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [1], so it can be used as an ideal thermal performance reinforcement for composite materials. While graphene nanosheets (GNSs) composed of a few graphene layers possess properties similar to that of single-layer graphene but are much easier to produce and handle [2, 3], GNS is a good candidate for the reinforcement of metal matrix to enhance the thermal conductivity [4]. However, pure titanium has poor thermal performance, which greatly limit its applications. In order to enhance the thermal conductivity of pure titanium, we used GNS as a reinforcement to fabricate the GNS/Ti composites. To ensure the as-prepared GNS/Ti composites have a good thermally structure, we employed ball milling technology to disperse the GNS and titanium powders. Then the GNS/Ti powders mixtures have been obtained through the above way. Finally, the dense GNS/Ti bulk composites were prepared by hot pressing sintering (HPS) using the GNS/Ti powders mixtures. In this paper, we got a clear GNS–Ti interface. Relative to pure titanium, the thermal conductivity of the composite are improved obviously. At the same time, thermal conductivity enhancement mechanism has also been a more reasonable explanation.

2. Experimental details

Firstly, GNSs (99% purity) were added to absolute ethyl alcohol and subjected to an ultrasonic dispersion for 40 min until the solution became brown in color, implying that the graphene was exfoliated into several-layered or even single-layered nanosheets. The spherical Ti powders (100 g, 45 μm in diameter, 99% purity) were transformed into 10- μm -thick Ti flakes through ball milling in an attritor at 325 rpm. Then, the refined Ti flakes were added to the solution containing graphene to form a powder slurry. The mixed slurry was mechanically stirred until its color changed from brown to transparent, before being filtered and rinsed with absolute ethyl alcohol to obtain GNSs–Ti composite powders.



Secondly, samples of the GNS/Ti powder were loaded into a 20mm inner diameter and 100mm long graphite die. A sheet of graphite paper was placed between the punch and the powder as well as between the die and the powder for easy removal. The bulk composites were prepared using HPS apparatus. The samples were sintered in a vacuum (residual cell pressure $\leq 3.2 \times 10^{-2}$ Pa). In the sintering process, the heating rate was set up to $10^\circ\text{C}/\text{min}$. An uniaxial pressure of 50MPa was applied from 1000°C upwards and maintained during the dwell at 1300°C for 2 hours. The final product took the form of cylindrical samples with a height of 5mm and diameter of 25mm. Five compositions of powder mixtures were prepared with 0.5%, 1%, 3%, 5%, 10% (vol%) of GNS.

Thirdly, density measurements were conducted using Archimedes's method. Thermal diffusivities of the samples are measured by a light flash apparatus (LFA 447 NanoFlash). The morphology and microstructure of the samples were characterized by field emission scanning electron microscopy (FESEM) (SUPRA40-41-90) and transmission electron microscopy (TEM). And the thin foils, which were further mechanically grinded to below 80 nm in thickness from about 200 nm and ion thinning, were examined in a Tecnai G2 F20 S-TWIN (200 kV) high-resolution transmission electron microscopy (TEM) to observe the boundary between graphene and Ti matrix.

3. Results and discussion

3.1 Microstructure of the as-prepared samples

The image of expanded graphite presents a loose structure containing many flake (figure 1). Magnified image shows the thickness of an individual flake is about 100 nm (figure 1), which indicates expanded graphite is a good start for fabricating GNSs compared with natural flake graphite.

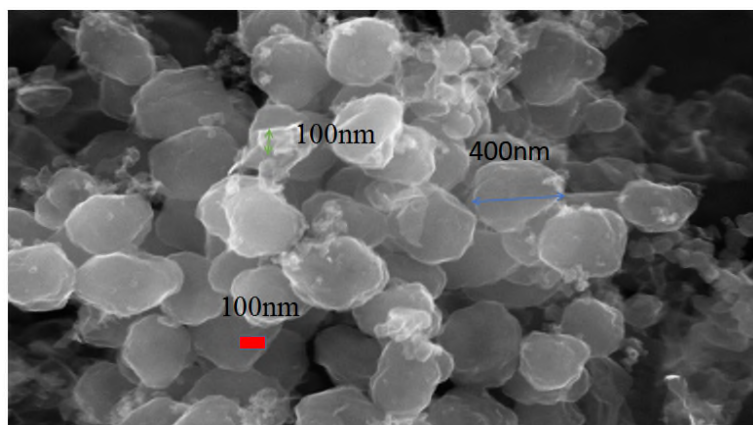


Figure 1. Images of original material.

The SEM observations of the composites reveal no obvious defects in the specimens and the micrographs were featureless, as shown in figure 2, confirming their fully dense structure. To evaluate the distribution of GNSs in the Ti matrix, fracture surface of the composite containing 3 vol.% GNSs was investigated (figure 2b). By comparing with the pure Ti (figure 2a), the growth of the grain are found to be restrained remarkably with the presence of GNSs. Moreover, it is shown that the grain sizes of Ti are homogeneous, which verify the good dispersion of GNSs in the matrix (figure 2c). Compared with the pure Ti, in GNS/Ti composite the phenomena of transgranular fractures increase, suggesting the high strength of GNSs. The SEM images show no thin GNSs (below 20nm) but a few pulled-out sheets dispersed in the matrix (marked by yellow rings in figure 2b), but most of these pulled-out sheets are as thick as 50nm (figure 2d). This phenomenon can be explained as follows: when the sheets are thin (less than 20nm) and vertical to the fracture surface, they are easy to rupture under the shearing stress. Besides, when the thin sheets are located on the fracture surface, they cannot be identified in a SEM image due to the small thickness of GNSs. On the contrary, when we get thick GNSs in the grain boundary, they are strong enough to bear the shearing stress and expose themselves when fractures occur.

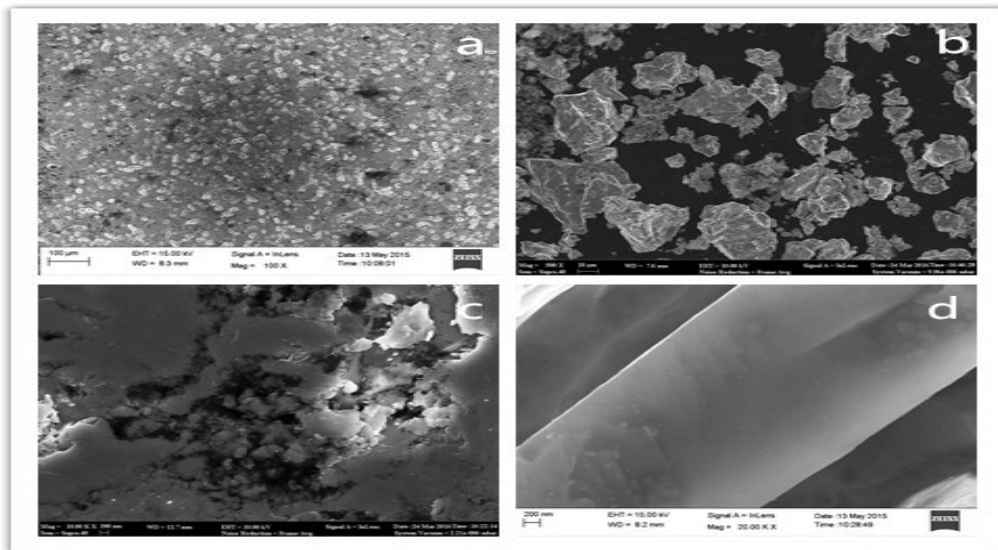


Figure 2. SEM images of fractured surfaces of (a) pure Ti and (b-d)GNS/Ti composite containing 1vol% GNSs;(c) and (d) are magnified parts of (b).

To investigate the morphology of as-prepared composites, FESEM and TEM measurements were carried out. Figure 3 shows the FESEM, TEM, HRTEM images and the SAED pattern of GNS/Ti composite. As shown in figure 3(a), it can be seen that a large amount of Ti nanoparticles are loaded on the surface of GNS with a crumpled and rippled structure of GNS-Ti composite. The spherical Ti nanoparticles are attached on GNSs and are wrapped by GNSs, which could be beneficial to prevent Ti from agglomerating and enables a good dispersion over the graphene sheets, as shown in figure 3(b). Further characterization of the microstructure of the composites was carried out by TEM. Figure 3 are representative TEM and HRTEM images of a composite containing 5 vol.% GNSs. The image reveals that the GNSs semi-wrap around the Ti grains and connect with each other to form a network structure (figure 3a). It is observed that more than half of the GNSs are below 10nm in thickness and sheets with the thickness of more than 20 nm have rarely been observed. Some of the GNSs are as thin as 5 nm, which means it comprises of only seven layers of graphene, as shown in figure 3c. It can also be seen that only very small fraction of overlap exist in the Ti grain boundary (figure 3b), indicating the effectiveness and success of our strategy in preparing and dispersing of GNSs.

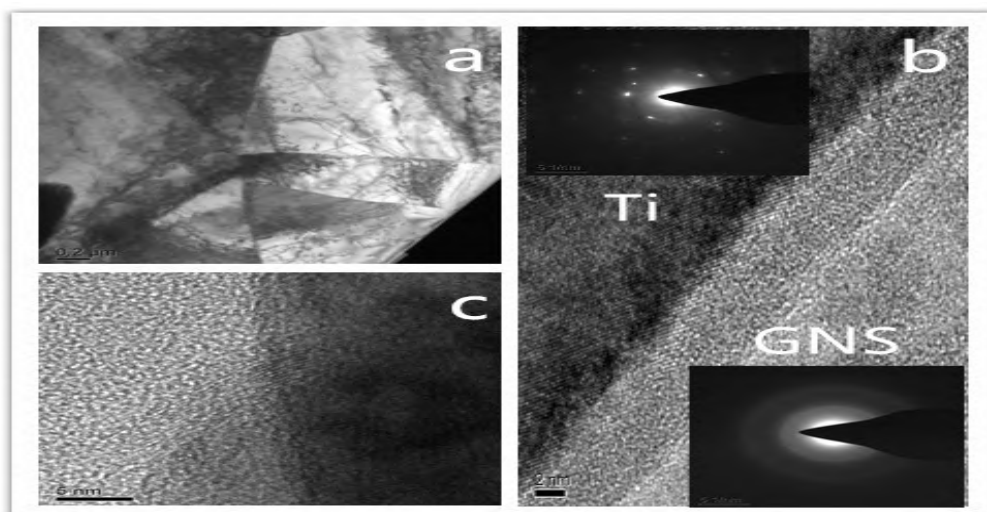


Figure. 3 TEM and HRTEM images of a GNS/Ti composite containing 5 vol.% GNSs: (a) GNSs surrounding Ti nanoparticles; (b) the interface of GNSs between Ti nanoparticles and the SAED pattern of GNS/Ti composite.(c) GNSs with a thickness of 5 nm.

There are two key factors of preparing and dispersing GNSs well in our method. The first one is the usage of planetary ball mill. The possibility of preparing tailored carbon nanomaterials by mechanical deformation has been widely investigated before [5], and the mostly used experimental method is mechanical milling in a ball milling device. The two most common types of ball milling equipments, planetary and vibratory mills, have been both experimentally tested. In this study we exploit planetary ball mill as the main implement to exfoliate graphite into GNSs because the planetary mill favors the cleavage of the particles [5]. One of the effective methods for preparing graphene is called laborious drawing or micromechanical exfoliation [6].

The other important factor is the selection of dispersal media. It is well-known that the presence of a liquid in the milling process leads to lubrication, moderates the violent shocks and avoids large agglomerates of the particles. For instance, Inam et al. have reported dimethylformamide as an effective dispersant for making CNT/ceramic composites. Furthermore, it has been reported recently that graphite [7] could be exfoliated in certain solvents to achieve defect-free monolayer.

In order to obtain fully dense composites and retain nano-crystalline Ti grain size without damaging the GNSs during sintering, HPS was employed. The relative density of HPSed samples is all above 94%.

3.2. Thermal properties of the as-prepared samples

3.2.1 Model. Thermal diffusivities of the samples are measured by a light flash apparatus (LFA 447 NanoFlash). The details of the laser flash measurement procedures have been reported elsewhere [8]. The thermal conductivity (λ) was calculated from the thermal diffusivity (α) using the equation (1).

$$\lambda = \rho \alpha C_p \quad (1)$$

where ρ and C_p are the density and specific heat of the composites, respectively. Density was calculated from sample weight and dimensions. Heat capacity was tested by a differential scanning calorimeter (TA Instruments, 2920) with a temperature increase rate of 10 °C/min from room temperature to 250 °C.

Through the calculation of formula (1), the data of GNS/Ti's thermal conductivity are shown in figure 4. At the same time, we obtain that thermal conductivities of the composite matrix and GNS are 14.82 and 2985.42 Wm⁻¹K⁻¹ respectively. This behavior can be described an effective medium theory [9] reported by Nan et al. The effective thermal conductive of the composite (λ_e) is given by the equation (2).

$$\frac{\lambda_e}{\lambda_m} = 1 + \frac{(V_f a)}{3} \frac{\lambda_f / \lambda_m}{a + \left(\frac{2R_k \lambda_f}{d} \right)} \quad (2)$$

where λ_m and λ_f are thermal conductivities of the composite matrix and GNS, respectively; V_f , d and a are the volume fraction, diameter and aspect ratio of GNS, respectively; and R_k is the thermal interface resistance. For a perfect interface without any thermal resistance ($R_k = 0$) and $a > 1$, the thermal conductivity enhancement is further simplified as:

$$\frac{\lambda_e}{\lambda_m} = 1 + \frac{V_f \lambda_f}{3 \lambda_m} \quad (3)$$

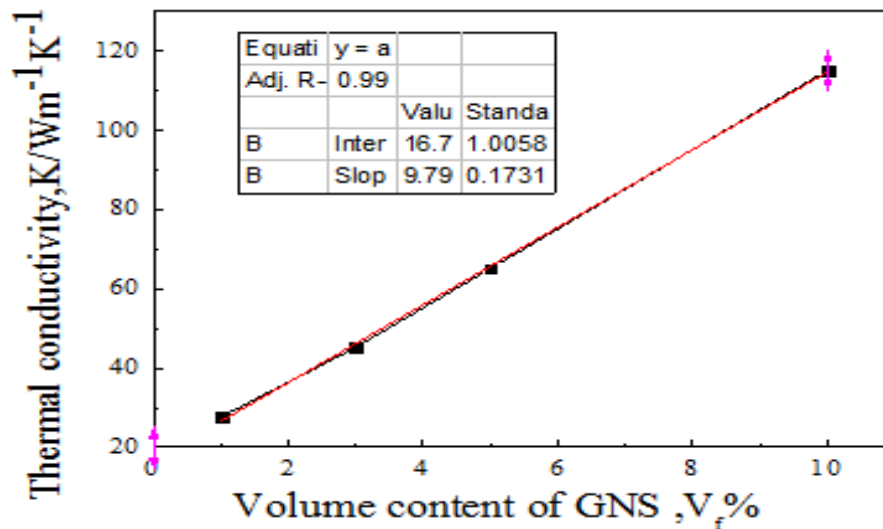


Figure 4. Thermal conductivity vs GNS content for GNS/Ti composites.

Figure 4 shows the plots of thermal conductivity vs GNS content for GNS/Ti composites. This result shows that the incorporation of graphene sheet into metals can significantly improve their thermal conductivity. Two beneficial factors for the effective thermal conductivity improvement achieved are the homogeneous dispersion of GNSs in the GNSs/Ti matrix and the low thermal boundary resistance (TBR) at GNS-Ti interface. The GNS clusters or stacks cause the phenomenon of reciprocal phonon vector, which acts like a heat reservoir and restrict the heat flow diffusion [10, 11], while a homogeneous GNS dispersion effectively increases the heat flow region and enhances the diffusion of phonon in the composites.

Through mathematical calculation, we can draw that the rule of thermal conductivity in the prepared-samples can accord with the law of the third formula. At the same time, we can roll out the thermal interface resistance may be attributed to the zero. As shown in the figure 4(b) this conclusion proves that the composite interface bonding is good.

3.2.2 Theory. GNS in composite structures were placed at grain boundaries in agreement with their positions in the sintered mixtures of titanium and GNS powders. According to the rule of mixture, thermal expansion of composites constitutes of proportional contributions from both titanium and graphene according to their volume percentages. Therefore, the good approximations of experimental values and rule of mixture predictions are representative of good interface bonding between the two phases. Because titanium and graphene flakes are both soft in nature, the two phases can expand freely along the directions parallel to the basal planes. Since the expansion of titanium and graphene is additive by proportion, the shear stress at the titanium-GNS interfaces must also be minimal without restraining either phase to expand.

4. Conclusions

GNSs/Ti composites were successfully fabricated by HPS. In the fabrication process the graphene reinforcement was applied in the form of graphene /alcoholcolloid for a safer and simpler manufacturing process. The GNSs after ball milling are 5-20 nm in thickness and its composite interface bonding integrates well with Ti matrix. This simple and effective process suggested that preparation of GNSs /Ti MMCs with enhanced thermal conductivity may provide benefits in the development of compact and light-weight heat exchangers. The suggested process may be applied to the sheet material, which will be formed into a plate or cylindrical shape heat exchanging unit.

5. Reference

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