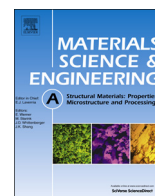Contents lists available at ScienceDirect

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# Enhancement of the mechanical properties of graphene–copper composites with graphene–nickel hybrids

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## ARTICLE INFO

## ABSTRACT

The present work reports the mechanical improvement in Cu matrix composites reinforced with graphene nanosheets decorated with Ni nanoparticles (GNS–Ni) hybrids. The GNS–Ni hybrids were firstly synthesized by an *in situ* chemical reduction method and then incorporated into the Cu matrix to fabricate bulk GNS–Ni/Cu composites by spark plasma sintering. Benefiting from the unique characteristic of GNS–Ni hybrids, the GNS–Ni/Cu composites exhibited homogeneously dispersed GNSs and a strong GNS–Cu interface interaction, therefore leading to a 61% increase in Young's modulus (132 GPa) and a 94% improvement in yield strength (268 MPa) by addition of only 1.0 vol% GNSs. The GNS–Ni/Cu composites exhibited a load transfer mechanism as verified by a modified shear-lag model. Our study thus shows the potential for GNS–Ni hybrids to be successfully used as a reinforcing phase in metal matrix composites.

## 1. Introduction

Metal matrix composites have been widely recognized to have a higher specific modulus, higher specific strength, lower coefficients of thermal expansion and better wear resistance, as compared to the unreinforced metal [1]. Because of these attributes metal matrix composites are under consideration for a wide range of applications. Carbon nanotubes (CNTs) are one of the most exciting nanostructural materials of the 20th century due to their excellent mechanical–physical properties [2,3]. Although extensive studies have been carried out on the CNT-reinforced metal matrix composites [4], there are still unresolved issues such as the tendency of nanotubes to agglomerate during processing, the limited availability of high-quality nanotubes in large quantities and the high cost of their production [5].

Graphene, a single layer of sp$^2$-hybridized carbon atoms arranged in a two-dimensional (2D) lattice, has attracted tremendous attention in recent years owing to its exceptional thermal, electrical and mechanical properties [6–8]. Mechanical measurements show that a perfect single-layer graphene exhibits a Young's modulus of 1.0 TPa and a fracture strength of 130 GPa [9]. In contrast to monolayer graphene, graphene nanosheets (GNSs) or graphene nanoplatelets

formed by several layers of graphene have been also found to possess outstanding mechanical properties [10–12], which make them excellent potential reinforcements in metal matrix composites. To date, a number of studies on GNS composites have been focused on polymer matrix composites [13,14]. It has been reported that the improvement in the mechanical properties of GNS–polymer composites is much better in comparison to that of other carbon filler-based polymer composites [15]. However, only a few reports have so far been published on the use of GNSs to improve the mechanical properties of metal matrix composites [16–21]. The main problem lying in the preparation of GNS/metal composites is to disperse GNSs homogeneously throughout the metal matrix, since the poor dispersion and exfoliation of GNSs not only significantly lower their efficiency as reinforcement but also would cause stacking GNSs to slip by each other when forces are applied to the composites. In addition, the weak interface originating from the poor wettability of GNS–metal might significantly deteriorate the mechanical performance of such GNS/metal composites. Therefore, the uniform dispersion of GNSs and good interfacial adhesion of GNS–metal are the two main obstacles for preparing GNS/metal composites with desired mechanical properties. To solve this problem, some efforts have been made but challenges still remain. For example, Bartolucci et al. [19] fabricated GNS/Al composites by a traditional powder metallurgy route, the resulting composites, however, even showed much lower mechanical properties than Al matrix. Nevertheless, by applying the novel processing such as flake powder metallurgy [16] and molecular-level mixing [17],

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other studies [16–18] reported that the incorporation of GNSs can dramatically improve the matrix mechanical properties, showing great advantages of graphene in strengthening the metal matrix composites.

Most recently, GNS–metal nanoparticles (GNS–MNPs) hybrids, namely GNSs decorated with MNPs such as Pd, Pt, Au, Ag and Ni have been extensively investigated and hold the key for rendering new functionalities while preserving some of the unique properties of the graphene [22,23]. We propose that the incorporation of GNS–MNPs into metal matrix is expected to solve the above-mentioned dispersion and interface problems of GNS/metal composites for the following two reasons. The MNPs anchored on the separated GNS surface can serve as spacer to prevent the GNSs from aggregating and restacking during the processing, which would lead to a homogeneous distribution of GNSs in the final composites. In addition, MNPs facilitate the formation of the solid solution or intermediate compound with metal matrix at GNS–metal interface, which can effectively reduce the interface energy and improve the interfacial bonding between the GNSs and metal matrix. It has been demonstrated that the interfacial bonding between CNTs and Cu matrix can be significantly improved by pre-coating CNTs with Ni [24]. To the best of our knowledge, there are no reports focusing on mechanical improvement in GNS/metal composites from the use of GNS–MNPs hybrids.

In this work, taking the advantage of the unique structure of GNS–MNPs hybrids, we report the mechanical improvement in Cu matrix composites with Ni nanoparticles decorated GNSs (GNS–Ni). The GNS–Ni hybrids were firstly synthesized by in situ chemical reduction method (reducing a mixture containing graphene oxide (GO) nanosheets and nickel ions) and then incorporated into the Cu matrix to fabricate bulk GNS–Ni/Cu composites by spark plasma sintering (SPS). The particular structure of GO, which contains several functional groups and domains (e.g., uncharged polar hydroxy and epoxide groups, charged hydrophilic carboxylate groups located at edges, and $\pi$-bonds, including $sp^2$ electrons and hydrophobic graphenic domains) [25], makes GO an ideal platform for synthesizing GNS–MNPs hybrids. The selection of Ni nanoparticles is due to the fact that Cu and Ni are soluble to each other and, at any composition and temperature, the phases are homogeneous [26]. Thus, the Cu–Ni dissolution bonding is thus expected to achieve the improved GNS–Cu interfacial bonding. The GNS–Ni hybrids were characterized by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectra. The GNS–Ni/Cu composites showed homogeneously dispersed GNSs in the matrix with a strong GNS–Cu interface interaction, which resulted in highly enhanced mechanical properties, with a 61% increase in Young's modulus and a 94% improvement in yield strength by addition of only 1.0 vol% GNSs. The yield strength of the composites was further analyzed by a modified shear-lag model. The strengthening efficiency of the GNS–Ni hybrids was also evaluated by comparison with reported values from other reinforcements including CNTs and bare GNSs.

## 2. Experimental

### 2.1. Preparation of GO

GO was prepared by a modified Hummers' method [27]. All the chemical reagents (purity 99%) were of analytical grade. Briefly, 3 g of flake graphite powder and 2.5 g of $NaNO_3$ was refluxed in concentrated $H_2SO_4$ (98 wt%) and continuously stirred in an ice bath, followed by gradually adding 5 g of $KMnO_4$ under slow stirring. The mixture was stirred for 2 h and then removed from the ice bath. After increasing the temperature to 40 °C, 30 ml of deionized (DI) water was slowly added to the mixture under stirring for 30 min and

the temperature was then increased to 85 °C for 20 min. Then, 10 mL of 30 wt% $H_2O_2$ solution was added to the suspension and stirred for 2 h until the suspension turned into a bright yellow color. Then, the mixture was filtered and washed thoroughly with dilute HCl solution and DI water, respectively, to remove metal ions and the acid. Exfoliation was performed by sonicating graphite oxide suspension for 2 h, and GO powder was finally obtained after centrifugation and vacuum drying.

### 2.2. Preparation of GNS–Ni hybrids

Fig. 1 shows the typical synthesis procedure of GNS–Ni hybrids and GNS–Ni/Cu composites. The in situ chemical reduction method was employed to synthesize the GNS–Ni hybrids. The mechanism for the in situ chemical reduction is as follows. GO is negatively charged due to the abundant functional hydroxyl and carboxyl groups (Fig. 1b). When the Ni salts ($NiSO_4 \cdot 6H_2O$) were added into the GO suspension, Ni ions prefer to aggregate and nucleate at the functional groups sites of GO because of the low nucleation energy at these functional groups sites (Fig. 1c). After introduction of the reducing agent ($N_2H_4 \cdot H_2O$), the nickel ions were in situ reduced to Ni nanoparticles, while GO nanosheets were simultaneously reduced to GNSs (Fig. 1d).

In the typical synthesis procedure, 50 mg of GO was put into a solution of 100 mL of DI water under sonication for 1 h to re-exfoliate the GO thoroughly. Then 10 mL of $NiSO_4 \cdot 6H_2O$ (2.5 g, 10 mmol) was also added into the GO aqueous solution, and the mixture was stirred vigorously for 60 min. After that, 10 mL of $N_2H_4 \cdot H_2O$ (85 wt%) was added into the mixed solution by adjusting the pH value to 10.5 with 0.2 M NaOH solution. After 30 min reaction, the resulting GNS–Ni products were separated by centrifugation, washed several times using pure ethanol, and dried in a vacuum oven at room temperature. The GNS content (20 wt%/53vol%) in the GNS–Ni hybrids was determined based on the initial dry weight of GNSs and the final dry weight of GNS–Ni hybrids.

### 2.3. Preparation of GNS–Ni /Cu composites

For GNS–Ni/Cu composites fabrication, 0.5 and 1.0 vol% GNSs (0.94 and 1.88 vol% GNS–Ni) were wet-mixed with electrolytic Cu powder ($\sim 5$ μm, 99.9% pure) in ethanol solution for 3 h under sonicating (Fig. 1f). The mixtures were vacuum dried at 60 °C for 24 h. Consolidation was performed by SPS system (mod. 1050, Sumitomo Coal Mining Co. Ltd., Japan) (Fig. 1g) [28]. The mixed powders were loaded into a graphite die with 30 mm in inner diameter. A sheet of graphitic paper was placed between the punch and the powders as well as between the die and the powders for easy removal. The compact powders were sintered at 580 °C for 2 min under a uniaxial pressure of 50 MPa. After sintering, the surfaces of samples were ground to remove the graphite layer. For comparison, a sintered pure copper specimen was also fabricated under the same SPS processing.

### 2.4. Characterization

The morphology and microstructure of samples were characterized by field emission SEM (JEOL JSM-6700F), and TEM/HRTEM (JEOL 200CX). The consolidated samples for the surface morphology observation were etched with a $FeCl_3$:HCl:$H_2O$ (1:1:2) solution for 10 s, and then polished using a silicon carbide grid. The powder XRD patterns were recorded with a Shimadzu XRD-6000 diffractometer operated with Cu Kα radiation. XPS measurements were performed using a PHI 5000C ESCA spectroscopy. Raman spectra were collected on a thermal dispersive spectrometer using a laser with an excitation wavelength of 532 nm at a laser power of 10 mW. Density was measured by Archimedes' method giving values above 99% of the theoretical composite densities calculated by the rule of mixtures. Tensile tests were performed using a INSTRON 5566 apparatus