Strengthening effect of graphene derivatives in copper matrix composites

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ABSTRACT

Graphene is highly efficient in reinforcing metal matrix composites due to its intrinsic ultrahigh mechanical properties. Several synthesis methods have been developed to produce graphene. Consequently, the selection of graphene materials with various structures, such as layer number, lateral dimension and chemical modification, is a key issue to synthesize graphene-related composites. In the present study, two kinds of graphene derivatives, namely graphene nanoplatelets (GNPs) and reduced graphene oxide (RGO), were adopted to fabricate copper matrix composites through a modified molecular-level mixing process. Microstructure studies showed that GNPs exhibited flake shape, and RGO exhibited irregular strip or sheet shape in the composites powders. Some spherical-shape nanosized GNPs or RGO dispersed within Cu grain interiors were also observed under the transmission electron microscope. Both of the GNPs and RGO were well bonded with the copper matrix after sintering. GNPs showed an obvious aggregative trend when the volume fraction was above 0.5%, but 1.0 vol.% RGO was still uniformly dispersed in the matrix. Tensile tests indicated that GNPs showed good strengthening efficiency at content below 0.5 vol.% while RGO performed better when the content increased from 0.5 to 1.0 vol.%. The difference of relevant strengthening effect and mechanisms involved in the two composites were systematically discussed by combining with theory consideration and experimentation.

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1. Introduction

Graphene has been regarded as a promising nanofiller for its superior mechanical properties of high elastic modulus (1 TPa) and fracture strength (125 GPa) [1,2]. To achieve good adhesion and dispersion, three types of graphene synthesized by different methods have been attempted to incorporate into metal matrices: in-situ synthesized graphene, graphene nanoplatelets (GNPs) and functionalized graphene. In-situ synthesized graphene in the matrices could avoid aggregation and structural integrity of graphene leading to an excellent strengthening efficiency. According to the reports, tensile strength of in-situ graphene/Ni nanolayered composites prepared by chemical vapour deposition reached about 4.0 GPa [3]. In-situ Graphene/Cu composite foil synthesized by a pulse reverse electrodeposition method exhibited a high hardness of about 2.5 GPa [4]. However, those methods were not suitable for preparing bulk composites. GNPs and GO were generally applied to synthesize bulk metal matrix composites as reinforcements. GNPs,

the ultra-thin graphite sheets containing multilayer graphene (thickness was less than 100 nm), showed excellent strengthening efficiency in bulk composites [5–13]. GNPs/Cu composites showed a 114% increase in yield strength compared to unreinforced Cu [10]. Graphene oxide (GO) containing many hydrophilic functional groups can be reduced to graphene layers (RGO) by rapid heating or reducing agent [14–18] and was widely used as graphene precursor for synthesizing bulk graphene/metal composites. After being reduced and decorated with nickel particles, 1.0 vol.% GO highly enhanced mechanical properties of copper matrix with a 94% improvement in yield strength. However, RGO often exhibits significant structural defects [19] which decreased intrinsic strength of graphene layer. By comparison, GNPs exhibit different structure and properties, such as few defects, large thickness and thermal stability. But so far there has been no report on the comparison of the strengthening effects of different graphene materials on the structure and properties of the composites.

Molecular-level mixing method (MLM) involving aqueous solution of GO and Cu acetate was reported to be very promising for synthesis of RGO/Cu composites [14]. Graphene tended to concentrate on the surface of Cu powders during traditional mixing

processes because of large density difference between graphene and Cu. Adsorption of Cu^{2+} ions reduced the density difference and uniformly dispersed GO in as-reduced Cu powders. More importantly, oxygen mediated bonding between GO and Cu^{2+} ions highly improved the interfacial adhesion energy. In a typical MLM process, NaOH solution was used to prevent reducing of GO before forming chemical bonds with Cu^{2+}. But the NaOH might rapidly reduce Cu^{2+} ions and GO upon heating which may create an exactly opposite effect of chemical bonding [20], and was difficult to remove by deionized water.

In the present study, a modified MLM without NaOH was adopted to synthesize GNPs-Cu and RGO-Cu powders. The as-prepared composite powders were sintered by spark plasma sintering process (SPS). The difference of strengthening effect of GNPs and RGO on the Cu matrix composites were systematically investigated. The microstructure of powders characterized by scanning electron microscopy (SEM) showed different morphologies between GNPs and RGO. RGO exhibited fewer graphene layer and smaller size than GNPs in the obtained powders. The mechanism of graphene adsorption on the reduced Cu powders was analyzed based on Raman spectra and Fourier transform infrared spectra (FT-IR). The chemical adsorption was mainly attributed to Cu–O–C bonding in both GNPs/Cu and RGO/Cu composites. Transmission electron microscopy (TEM) further demonstrated the structural difference between GNPs and RGO. Some spherical-shape GNPs and RGO were observed within Cu grain interiors. Although both GNPs and RGO showed excellent strengthening efficiency, tensile properties of the two composites indicated an obvious difference of strengthening effect between them. The main strengthening mechanisms of GNPs/Cu and RGO/Cu composites, including Orowan strengthening, thermal mismatch and load transfer, were prioritized according to structural analysis.

2. Materials and methods

GNPs used in the present study were 98.9% in purity (1.1 wt.% O), 1–5 μm in lateral dimension and 5–10 nm in thickness. GO was ≥99% in purity, 1–5 μm in lateral dimension, 0.8–1.2 nm in thickness and ≥99% in single layer ratio. The main distinctions between the GNPs and GO were the number of graphene layers and chemical groups on their surfaces. Other chemical reagents adopted in this work were analytically pure.

Steps involved in the modified MLM were as follows: (1) GNPs were successively sensitized and activated by hydrochloric acid solution of 10 g/L $SnCl_2$ and 0.25 g/L $PdCl_2$. (2) The activated GNPs were dispersed in 100 ml deionized water by sonicating (100 W) for 2 h. 1000 ml aqueous solution of Cu acetate (50 mg/ml) was slowly poured into the GNPs suspension. The mixed solution was sonicated for another 2 h to facilitate the adsorption of Cu^{2+} ions. The solution was subsequently vaporized under magnetic stirring at 363 K, and the mixture was further dried at 373 K in an electro-thermal constant-temperature dry box. (3) The dried powders were holding at 523 K to decompose Cu acetate followed by reduction at 673 K for 5 h by hydrogen in a tube furnace. (4) The as-reduced powders were consolidated by SPS at 600 °C (50 °C/min) for 5 min under a uniaxial pressure of 45 MPa. The RGO/Cu composites were prepared by the same procedure except activating. For comparison, bulk Cu was also prepared under the same conditions. Cu composites with GNPs and RGO in range of 0.05 vol.% to 1 vol.% were manufactured to study the effects of GNPs or RGO level on mechanical properties of composites.

The morphology and microstructure of the composite powders were characterized by SEM equipped with an energy dispersive X-ray spectrometer (EDS). Raman spectra preformed from 500 to 3000 cm^{-1} with a 532 nm laser and FT-IR recorded in the range of 500–4000 cm^{-1} were used to analyze the structural integrity, reduction and adsorption mechanism of graphene derivatives. Metallurgical microscopy was used to observe the distribution of graphene. TEM equipped with an EDS was used to study the nanostructure of GNPs and RGO, and to investigate interface structure of the two composites. Tensile tests were conducted at ambient temperature (25 °C) on a universal testing machine with the crosshead speed of 0.6 mm/min. The test samples were designed to be with a gauge length of 10 mm and section of 2 mm × 1.5 mm. The fracture surface of the typical samples was characterized by the SEM-EDS analysis system.

3. Results and discussion

Fig. 1 showed the distribution of GNPs (a–d) and RGO (e–h) in Cu matrix composite powders at four stages during preparation process. Fig. 1(a) showed that the activated GNPs exhibited a stacking flake structure. Sonication made the dispersion of the GNPs uniform in Cu acetate (Fig. 1(b)). Fig. 1(c) presented the GNPs/
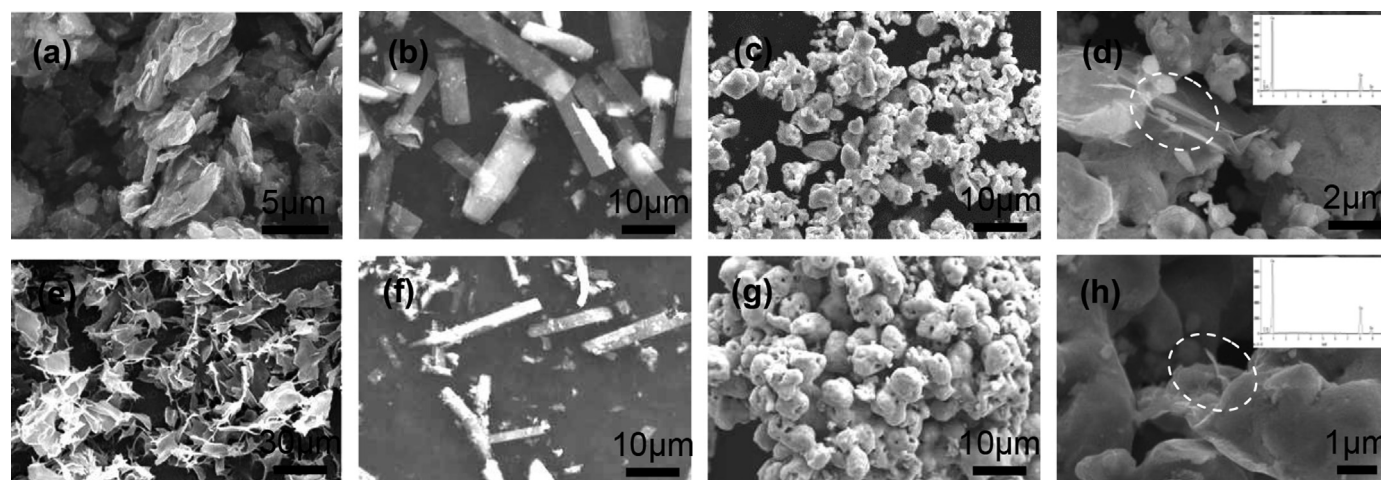

Fig. 1. (a) SEM image of the activated GNPs; (b) SEM image of the GNPs/(Cu acetate); (c) SEM image of the GNPs/Cu powders; (d) High magnification SEM image of the GNPs/Cu powders; the inset shows the EDS of the selected area; (e) SEM image of the GO powders from JCNANO; (f) SEM image of the GO/(Cu acetate); (g) SEM image of the RGO/Cu powders; (h) High magnification SEM image of the RGO/Cu powders; the inset shows the EDS of the selected area.