Preparation of graphene/Cu layered composites based on the self-assembly of flake powder

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Abstract: Graphene with ultrahigh tensile strength and excellent electrical and thermal conductivity has been regarded as a promising reinforcement of metal matrix composites. The key issues for preparation high performance graphene reinforced metal composites are to disperse graphene uniformly, align graphene in the metal matrix and enhance interfacial bonding strength between graphene and metal. In this work, powder metallurgy method based on the self-assembly of flake powder was adopted to prepare graphene nanoplatelets (GNPs)/Cu layered composites. 10 vol.% GNPs sheets with average thickness of 2 nm and average lateral size of 6 μm were used. The microstructure observation shows that GNPs sheets are uniformly distributed and well aligned in the Cu matrix. No obvious voids and cracks are observed at the interface. The addition of fine GNPs leads to ~31% higher tensile strength and approximately equal electrical conductivity compared to pure Cu.

1. Introduction
Copper matrix composites, combining the electrical and thermal conductivity of the matrix and the mechanical properties of the reinforcements, are widely used in power electronics, automotive, aerospace and other fields. Conventional reinforcements, such as ceramic fiber and particle, can significantly improve the mechanical properties of copper-based composites, but typically reduce electrical and thermal conductivity. As a carbon nanomaterial, graphene[1] not only has ultrahigh mechanical strength and elastic modulus, but also has good electrical and thermal conductivity, and has been shown to improve the strength, toughness, electrical conductivity and thermal conductivity of metal matrix composites[2-4]. Graphene is an ideal reinforcement for copper matrix composites.

Due to its large specific surface area, high surface energy, graphene exhibits a tendency to agglomerate in metal matrix. As reported, methods including powder metallurgy (PM)[5], Flake PM[6], surface chemical modification[7], and molecular-level mixing (MLM)[8] can uniformly disperse graphene in metal matrix and obtain a better strengthening effect. The structure and properties of graphene have obvious anisotropy. The design of layered composites matches the two-dimensional structure and properties of graphene, which is beneficial to the preparation of multifunctional reinforced composites[9]. At present, there are few studies on graphene reinforced metal-based layered composites. In this paper, flake copper powder and graphene nanoplatelets (GNPs) were used as raw materials to prepare GNPs/Cu layered composites directly by hot pressing based on the self-assembly characteristics of flake powder.
2. Experimental

Flake Cu powder and GNPs (purchased from JCNANO Tech Co., Ltd, China) were used as raw materials in this work. 99% purity flake Cu powder was with an average thickness of 100 nm and a lateral size of ~10 μm. 99.7% purity GNPs were with an average thickness of 2 nm and a lateral size of ~6 μm. Firstly, Cu and GNPs were dispersed together in ethanol under ultrasonication for 2 h to form a homogeneous suspension. Then the suspension was filtered and dried. The mixture was mixed thoroughly by ball milling under a rate of 160 rpm for 5 h applying sample/ball weight ratio 1:8. After that, the composite powder was loaded into a graphite mold and vibrated in a loose state to promote self-assembly. Finally, the composite powder was sintered by hot pressing under vacuum at 650 °C for 30 min under a pressure of 35 MPa to prepare GNPs(10vol.%)/Cu composite. For comparison, pure copper was prepared using the same processing parameters as those for the composite.

Scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM) were carried out to observe microstructure of samples. The test directions of conductivity and mechanical properties were consistent with the alignment direction of GNPs. The electrical conductivity was measured and calculated using four point contact method and the measurement for each sample was repeated 9 times. Tensile tests were conducted on a universal testing machine with the crosshead speed of 0.6 mm/min. The test samples with a gauge length of 10 mm and cross-section of 2 mm * 1.5 mm were machined from the sintered billets. Three samples were tested from each sintered billet for tensile tests to minimize the error.

3. Results and discussion

Figures 1(a) and (b) show the SEM micrographs of raw GNPs and Cu powder. Figure 1(a) shows the typical stack-like morphology of GNPs. The flake-like and irregular nature of the copper particles is shown in Figure 1(b). Figure 1(c) shows the SEM micrograph of the GNPs/Cu composite powder fabricated by the ball milling process. No obvious GNPs agglomeration is observed. As shown in Figure 1(d), EDS analysis result from the marked point in Figure 1(c) indicate the presence of C and Cu elements in GNPs/Cu composite powders. The element C is correlated with GNPs. It indicates some Cu particles are covered by GNPs sheets. This coverage can lead to an efficient reinforcing effect of GNPs in the composites.
Figures 2(a) and 2(b) show the SEM micrographs of pure Cu and GNPs/Cu composites. The microstructure of the pure Cu sample prepared from flake Cu powder consists of banding grains and many voids. Nevertheless, a layered microstructure comprised of flattened Cu grains was formed in the GNPs/Cu composite (Figure 2(b)). The GNPs sheets are uniformly distributed and well aligned in the Cu matrix. Fewer voids are observed in GNPs/Cu composites than pure Cu, indicating the addition of GNPs sheets can promote the sintering process.

Figure 2(c) shows the TEM image of interface of GNPs/Cu composite. Well-contacted interface without any voids and gaps is formed between GNPs and the Cu matrix. The good interface bonding is beneficial to improving the strength of GNPs/Cu composites[10]. Figure 2(d) shows the tensile strength and electrical conductivity of pure Cu and GNPs/Cu composites. The GNPs/Cu composite has a tensile strength of 249±9 MPa, ~31% higher than that of the Cu matrix. The enhanced strengths indicate that the aligned GNPs sheets are highly effective reinforcement in the Cu matrix. The electrical conductivity of the as-prepared samples is relatively low due to the existence of voids (see Figure 2(a)). In face of such condition, the GNPs/Cu composite still shows a slight increase of conductivity comparing to pure Cu bulk. Our work suggests that graphene can be aligned conveniently in metal matrix by self-assembly of flake powder for preparing graphene/metal layered composites.

![Figure 2. SEM micrographs of pure Cu (a), GNPs/Cu composite (b), HRTEM image of GNPs/Cu composite interface (c) and properties of as-prepared pure Cu and GNPs/Cu composites.](image)

4. Conclusions
In this study, a method for preparing GNPs/Cu layered composites is proposed based on the self-assembly of flake powder. GNPs sheets are aligned in the Cu matrix and bond well with the matrix. The GNPs/Cu composite shows a ~31% increase of tensile strength compared to the Cu matrix without decrease of electrical conductivity.

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