Effect of Ball Milling on the Defeat of Few-Layer Graphene and Properties of Copper Matrix Composites

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Abstract Graphene-reinforced copper composites recently have attracted more attention, since they exhibited excellent mechanical properties and could be used widely in many fields. Few-layer graphene (FLG) and copper powder were mixed by ball milling to produce homogeneous composite powders. Then, FLG-reinforced copper composites (FLG/Cu) were fabricated by spark plasma sintering (SPS) using the composite powders with a FLG volume fraction of 2.4 vol%. The effects of the rotating speed and the time of ball milling were analyzed based on the microstructure evolution and properties of the FLG/Cu composites. Obvious strengthening effect of FLG was found for the composites, and the conductance of the composite reaches 70.4% of IACS. The yield strength of the composite produced by ball milling at a speed of 100 r/min for 4 h is 376 MPa, which is 2.5 times higher than that of copper and higher than that of copper composite enhanced by 5 vol% CNTs (360 MPa). The defects produced in FLG with the increase of rotating speed and time could reduce the mechanical and conductive properties of the composites.

KEY WORDS: Copper; Composites; Ball milling; Mechanical properties; Conductivity

1 Introduction

Graphene, consisting of a single to few layers of covalently bonded sp^2 carbon atoms [1], has extraordinary mechanical properties [2], remarkable electron mobility [3], and super high thermal conductivity [4]. The excellent properties of graphene make it a perfect reinforcement for many kinds of

composites [5, 6]. For graphene-reinforced composites, many researches focused on the effect of graphene on the properties of polymer matrix composites, such as the electrical conductivity, Young's modulus, and tensile strength, which showed that the properties of the polymer matrix were remarkably improved with the introduction of graphene [7, 8].

Recently, Kim and his co-workers produced a nano-layered graphene/Cu composite with ultra-high strength up to 1.5 GPa [9]. These results suggest strongly that graphene is an excellent candidate as reinforcement used in copper matrix composites. However, the technique used in the nanolayered composite is difficult to produce composite in large scale; there are few studies on this field, and more work should be done in order to develop graphene/Cu composite with practical value.

Here, we demonstrated a process to produce few-layer graphene (FLG)-reinforced copper matrix composite (FLG/Cu) with the help of ball milling, since ball mill can easily increase the output of the composite powder. It was found

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that FLG could be distributed in copper powder homogeneously and had a good strengthening effect for the FLG/Cu composites. Furthermore, the effects of the rotating speed and time on structure of FLG and the properties of the composites were studied.

2 Experimental

2.1 Sample Preparation

2.1.1 Fabrication of Composite Powders by Ball Milling Method

Few-layer graphene used in this work was produced in our laboratory by a patent technique [10]. A typical production process of FLG/Cu composite powder by ball milling method is as follows: 0.062 g of FLG, 10 g of copper powder, and 20 g of zirconia balls with a diameter of 5 mm were put into a ceramic ball milling pot with 100 mL of alcohol. Ball milling was performed on a QM-QX planetary ball mill (Nanjing Nan Da instrument plant) at 100, 200, or 300 r/min for 4 or 8 h. Then, the zirconia balls were filtered, and the slurry of FLG and copper was dried at 60 °C in vacuum to produce a composite powder.

2.1.2 Consolidation of FLG/Cu Composite Powders

The FLG/Cu composite powder was sintered by spark plasma sintering (SPS) at 600 °C for 5 min in a vacuum of 0.1 Pa with a pressure of 40 MPa. The final sizes of the FLG/Cu composite were 20 mm in diameter and 4 mm in thickness.

In order to investigate the effects of the ball milling speed and time on the properties of the FLG/Cu composites, the composites were fabricated with the composite powders produced at different ball milling speeds and times. For simplification, the FLG/Cu composites were abbreviated as FLG/Cu-(milling speed, in r/min)-(milling time, in h). For example, FLG/Cu-300-8 means that the composite powder was fabricated at 300 r/min for 8 h by ball milling.

2.2 Characterization

X-ray diffraction (XRD) analyses were performed on a Philips X'Pert X-ray diffractometer with CuK_α radiation. Raman spectra were obtained from 500 to 3000 cm^{-1} on a B&W Tek Confocal Micro-Raman spectrometer using a 532-nm laser. Microstructural analyses were carried out on an OLYMPAS PMG3 type optical microscope (OM) and a Quanta 200F scanning electron microscope (SEM), respectively. X-ray photoelectron spectroscopy (XPS) was

performed on a PHI 5700 ESCA System. Compressive tests were performed using an Instron 5500R All-purpose Electronic Tester with a crosshead speed of 0.5 mm/min. The loading direction is parallel to the pressing direction of SPS. The samples had a cylindrical disk shape of 3 mm height and 3 mm diameter. Samples with a rectangle shape (10 mm $\times$ 4 mm $\times$ 1 mm) were cut by wire-electrode cutting and broken with a tensile force along the length direction, and then the fracture surfaces were used for fractographic analysis. The conductance of the composites was tested by four probe method with a 2512B Low DC Resistance Tester (Suzhou Changsheng Electronic Technology Co., Ltd.). The samples for conductivity tests were cut into sheets with a length of 14 mm, width of 4 mm, and thickness of 0.2 mm.

3 Results and Discussion

The FLG powder used in this work was produced in our laboratory by a patent technique named as self-propagating high-temperature synthesis (SHS) by igniting the mixture of Mg powder and CaCO_3 powder in a container filled with CO_2 gas at room temperature [10]. The SEM image of the FLG powder is shown in Fig. 1a. It can be found that the FLG is composed of many thin and crumpled sheets with a three-dimensional structure.

Raman spectroscopy is an effective technique to characterize the structural and electronic properties of graphene [11, 12]. The Raman spectrum of the FLG is shown in Fig. 1b, and there are three peaks: a D band at $\sim 1347 \text{ cm}^{-1}$, a G band at $\sim 1578 \text{ cm}^{-1}$, and a second-order D (2D) band at $\sim 2687 \text{ cm}^{-1}$. The existence of G peak and the position of 2D peak at $\sim 2687 \text{ cm}^{-1}$ are important criteria, which suggest that the synthesized powder in Fig. 1a is FLG. The synthesis method of FLG will be introduced and discussed in other articles.

The XRD patterns of FLG/Cu composite powders produced by ball milling are shown in Fig. 2. It can be found that the powders at different ball milling speeds and times have similar XRD patterns. All the peaks in Fig. 2 (2θ of 43.3°, 50.4°, and 74.1°) belong to Cu (PDF No. 851326). No peaks corresponding to graphite or copper oxides can be found, suggesting that graphite and copper oxide were not produced during the process of ball milling and drying.

Figure 3a shows a Raman spectrum of FLG/Cu-300-4 composite powder. The peaks correspond to FLG as mentioned above, while the high intensity of the background is due to the fluorescence of copper. The ratio of the D peak to G peak (I_D/I_G) in Raman reflects the defect concentration of carbonaceous materials; the lower the ratio, the less the defect concentration is [13]. Meanwhile, the position of the 2D peak and the ratio of the peak

Fig. 1 SEM image **a** and Raman spectrum **b** of the filler

Fig. 2 XRD patterns of the FLG/Cu composite powders with different ball milling speeds and time

intensity of G and 2D (I_{2D}/I_G) can be used for the identification of the number of graphene layers [14].

In order to evaluate the defect concentration and thickness of FLG in different samples, we randomly selected ten test points for each sample. The ratios of I_D/I_G and I_{2D}/I_G

for different samples are shown in Fig. 3b. The average values of I_D/I_G corresponding to FLG, FLG/Cu-100-4 composite powder, and FLG/Cu-300-4 composite powder are 0.25, 0.39, and 0.49. The increase of the I_D/I_G ratios with the increase of milling speed indicates that the structure of FLG is destroyed gradually during the process of ball milling; the higher the speed of ball milling, the higher the defect concentration in FLG is. In addition, the ratio of I_D/I_G increases with the increase of milling time from 4 to 8 h at 300 r/min, suggesting that long milling time at 300 r/min also produces more defects in FLG.

It is obvious that the ratio of I_{2D}/I_G for FLG is similar to that of FLG/Cu-100-4 composite in Fig. 3b, indicating that the milling speed of 100 r/min has little effect on the structure of FLG. However, the ratio of I_{2D}/I_G for FLG/Cu-300-4 is higher than that of the FLG/Cu-100-4, suggesting that FLG could be exfoliated further at higher milling speed.

Scanning electron microscope images of the composite powders with different milling speeds are shown in Fig. 4. In Fig. 4a, a FLG sheet embeds in the copper powder,

Fig. 3 Raman spectrum of composite powder of FLG/Cu-300-4 **a** and the ratios of I_D/I_G and I_{2D}/I_G for different samples **b**

Fig. 4 SEM images of different composite powders: **a** FLG/Cu-100-4; **b** FLG/Cu-200-4; **c** FLG/Cu-300-4; **d** FLG/Cu-300-8

while the surface of copper particles is relatively clean compared with the copper particles in other composite powders. With the increase of rotating speed, more crumpled and thinner FLG can be found everywhere including on the surface of copper particles, as shown in Fig. 4b, c, and d. This means that the FLG sheets have been separated and become smaller sheets with the increase of rotating speed and milling time. According to the SEM images of the composite powders, two types of FLG can be found, one is thin and covered on the surface of copper powder, and another is graphene sheets with a diameter of several micros with a 3D structure distributed between copper particles.

The OM photograph of the microstructure of the composite is shown as the inset of Fig. 5a. It can be found that

most part of the composite is bright, while some black dots with different shapes can be found to be distributed randomly with a diameter of several micros. According to the SEM result of the composite powders which are shown in Fig. 4, two types of FLG existed in the composites, so the black dots should be the FLG sheets with a diameter of several micros between copper particles. The black dots can act as a sign of the effect of the distribution of graphene, since they were distributed randomly.

Scanning electron microscope images of the FLG/Cu composites with different ball milling speeds eroded in FeCl_3 solution (10 g FeCl_3 , 2 mL concentrated HCl, and 100 mL water) for 60 s are shown in Fig. 5a and b. It is obvious that many wrinkled sheets are distributed everywhere on the eroded surface of the composites, and that

Fig. 5 SEM images showing the structures and fracture surfaces of composites FLG/Cu-100-4 and FLG/Cu-300-4: **a** structure of FLG/Cu-100-4 (the inset is the OM image of the composite); **b** structure of FLG/Cu-300-4; **c** fractograph of FLG/Cu-100-4; **d** fractograph of FLG/Cu-300-4

almost all of the particles are covered by thin sheets. Since two kinds of FLG sheets existed in the composites, as shown in Fig. 4, and one has been found in the OM image as black dots in the inset of Fig. 5a, the thin sheets covering the particles must belong to another kind of FLG sheets, which cover the copper particles. The results suggest that FLG sheets have been distributed homogeneously in the composites and that copper particles could be covered by FLG sheets during the milling process, which may protect the copper particles from eroding. As a result, ball milling is an effective method to produce the FLG/Cu composites by mixing FLG and copper particles homogeneously.

The tensile fractographs of the composites are shown in Fig. 5c and d. Many dimples can be found in the fractographs, which result from the toughening fracture of the

matrix. The dimples of FLG/Cu-100-4 are larger in quantity and smaller in size compared with those of FLG/Cu-300-4, indicating that the former material has better mechanical properties. Both of the fractographs show a characteristic of intergranular fracture. Some small holes can be found in the fractographs, indicating the existence of some kinds of defects in the composites.

The mechanical properties of the FLG/Cu composites are characterized using compressive tests. The stress–strain curves of the composites are shown in Fig. 6a with the specimens after compression being shown as the inset of Fig. 6a. The yield strengths and the maximum compressive strengths of the composites are shown in Fig. 6b. The yield compressive strength of the FLG/Cu-100-4 composite is 376 MPa, which is 2.5 times higher than that of copper

Fig. 6 **a** Stress–strain curves of FLG/Cu composites (the inset showing the specimens after compressed); **b** Comparison of the yield strength and the maximum compressive stress of FLG/Cu composites

Table 1 The conductivities and densities of composites

Sample	Conductivity (% IACS)	Relative density (%)
FLG/Cu-100-4	70.4	94.7
FLG/Cu-200-4	62.8	93.3
FLG/Cu-300-4	61.4	91.7
FLG/Cu-300-8	58.1	91.1

produced by the same SPS method (150 MPa) and also higher than that of copper composites enhanced by 5 vol% CNTs (360 MPa) [15]. It is obvious that the mechanical properties of the composites are greatly improved by the introduction of FLG. The maximum strength of FLG/Cu-300-8 is a little lower than that of FLG/Cu-300-4. The yield strengths of the FLG/Cu composites decrease from 376 to 337 MPa as the rotating speed increases from 100 to 300 r/min.

The relative densities of FLG/Cu composites are shown in Table 1. It is obvious that the relative densities decrease slightly from 94.7% to 91.1% with the increase of ball milling speed and milling time. Our experience in SPS copper materials suggests that the relative density of pure copper by SPS method should be higher than at least 98%; the decreased density may result from the increased porosity caused by the wrinkled graphene sheets stacked between the copper grains and the impurity introduced in the composites with the increase of ball milling speed and milling time.

The defects in FLG and the densities of the composites could play important roles on the mechanical properties. Based on the Raman results, the defect concentration in FLG increases with the increase of milling speed and time. It is reasonable to conclude that larger defect concentration may lead to the decrease of the strength of FLG, because the Young's modulus of graphene oxide with high

concentration of defects is only ~ 200 GPa [16], while the Young's modulus of graphene is ~ 1 TPa [2]. The load bearing capacity of FLG with more defects is lower than that of FLG with fewer defects. In addition, the decreased density of the composites means the increased porosity and impurity in the composites with the increase of ball milling speed and milling time. So the composites milled at high speed have lower mechanical properties compared with those milled at low speed. Ball milling with a speed of 100 r/min for 4 h is appropriate for the FLG/Cu composites.

The conductivities of FLG/Cu composites were also measured, which are listed in Table 1. Here, IACS means International Annealed Copper Standard, a unit of electrical conductivity for metals and alloys relative to a standard annealed copper conductor; an IACS value of 100% refers to a conductivity of 58.0 MS/m at 20 °C. It is obvious that the values of the conductivity decrease from 70.4% IACS for FLG/Cu-100-4 to 58.1% IACS for FLG/Cu-300-8 with the increasing of rotating speeds and times. The increase of the conductivity of the composite at high mill speed and long mill time can be attributed to the decreased density of the composite and the impurities introduced during the milling process. Consequently, the FLG/Cu composites, as a new kind of copper composites, exhibit good mechanical properties and electrical conductivity and can be expected to obtain better properties by increasing the relative density of the composites, improving the quality of graphene, and enhancing the strength of the interface in the future.

4 Conclusions

FLG/Cu composite powders were produced by mixing FLG with copper powder using ball milling. 2.4 vol% FLG/Cu composites were successfully fabricated by SPS

method. Ball milling with a speed of 100 r/min for 4 h is appropriate for the FLG/Cu composites. Few-layer graphene has good strengthening effect on the FLG/Cu composites. The yield strength of the FLG/Cu-100-4 composite is 378 MPa, which is 2.5 times higher than that of copper and higher than that of copper composite reinforced by 5 vol% CNTs (360 MPa). The conductivity of the FLG/Cu-100-4 composite reaches 70.4% IACS.

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