Characterization and Tribological Properties of Graphene/Copper Composites Fabricated by Electroless Plating and Powder Metallurgy

Zhigang Zhang^{1,2} · Xiaotong Lu^{1,2} · Jianrong Xu^{1,2} · Hongjie Luo^{1,2}

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Abstract

Self-lubricating copper matrix composites reinforced with graphene were prepared by electroless plating and powder metallurgy. The morphology and structure of graphene, Cu@graphene powder, and Cu@graphene/Cu composites were characterized and the tribological properties of Cu@graphene/Cu composites were investigated. The X-ray diffraction pattern of Cu@graphene confirms the coexistence of characteristic peaks of both copper and graphene, with a weakened characteristic peak of carbon impurity. The obtained morphology of Cu@graphene reveals that the surface of the graphene is completely covered with a uniform and compact copper layer with lots of copper nanoparticles. Raman and Fourier transform infrared spectroscopy analyses show that the oxygen functional groups and defects on the surface of the redox graphene can be reduced through the electroless plating process. The tribological results indicate that the coefficient of friction of Cu@graphene/Cu composites initially decreases and then increases with an increase in Cu@graphene content. The lowest coefficient of friction, which is about 29.47% lower than that of pure Cu, is achieved in the Cu@graphene/Cu composites with 3.0 wt% Cu@graphene. The chemical composition and topography of the wear tracks for Cu@graphene/Cu composites infer that the formation of a well-consolidated graphene-rich lubricious tribolayer at the contact surface and a higher microhardness work together to enhance the tribological performance of Cu@graphene/Cu composites.

Keywords Graphene · Copper matrix composite · Electroless plating · Tribological property · Microstructure

1 Introduction

Self-lubricating copper matrix composites (CMCs) are well known as one of the advanced materials widely used as brushes, contact strips, and bearing materials, owing to their high ductility, as well as the excellent electrical and thermal conductivity of the copper matrix, coupled with a remarkable self-lubricating property of reinforcement [1, 2]. The widely used solid lubricants, such as graphite [2, 3], MoS₂ [4, 5], WS₂ [6, 7], carbon nanotubes [8], and graphene [8, 9], can promote the formation of a well-covered lubricating

film and transfer film on the sliding surfaces [2], owing to their lamellar crystal structure with stacked layers weakly bonded with each other, while the bonding within the layers is quite strong [10].

As a novel solid lubricant, graphene, a two-dimensional honeycomb lattice structure of *sp*²-hybrid carbon, possesses not only extraordinary self-lubricant properties but also enhanced mechanical properties, excellent electrical and thermal conductivity, and low coefficient of thermal expansion [11, 12]. These outstanding properties make graphene widely reckoned as an ideal reinforcement for producing high-performance CMCs [13]. However, two key challenges in the synthesis of graphene-reinforced CMCs lie in the difficulty of achieving a homogeneous distribution of graphene in the copper matrix, as well as intimate and strong interfacial bonding between the graphene and copper matrix, resulting in a substantial compromise of the reinforcing efficiency of graphene. To address these problems, novel or modified fabrication methods have been employed to fabricate graphene/copper composites. Xiong et al. [14] prepared nacre-like reduced graphene oxide-reinforced Cu

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✉ Zhigang Zhang
zhangzg@smm.neu.edu.cn

¹ Key Laboratory for Ecological Metallurgy of Multimetallurgical Mineral (Ministry of Education), Northeastern University, Shenyang 110819, China

² School of Metallurgy, Northeastern University, Shenyang 110819, China

matrix composites, based on a preform impregnation process, which exhibited a simultaneous enhancement of the strength and ductility. Hwang et al. [15] proposed molecular-level mixing and spark plasma sintering (SPS) process to fabricate graphene/Cu nanocomposites with ultrahigh tensile properties, due to the close combination between graphene and Cu matrix. Chen et al. [16] prepared aligned graphene/Cu composites with a dramatically improved tribological performance via molecular-level mixing and spark plasma sintering. As the graphene content in the graphene/Cu composites reached to a certain amount, an integrated graphene-rich film with lower shear strength was formed on wear track, which could reduce wear and friction effectively. Gao et al. [17, 18] fabricated graphene-reinforced copper matrix composites by electrostatic self-assembly and powder metallurgy under a pressure of 25 MPa. The composite with 0.3 wt% graphene exhibited the highest ultimate tensile strength, Vickers hardness, and thermal conductivity, as well as the lowest friction coefficient. Graphene-reinforced copper matrix composites were prepared by ball-milling and hot-pressing (HP) sintering [19] or SPS [20]. The ball-milling can disperse uniformly the graphene in the copper matrix under proper graphene content and ball-milling parameters. Mai et al. [21] reported that a self-lubricating copper matrix composite was hot-pressed and reinforced by graphene nanosheets anchored with nickel nanoparticles (Ni@GNS), and the incorporation of Ni@GNS with up to 2 wt% significantly reduced the friction and improved the wear resistance of the copper matrix.

Electroless plating is an autocatalytic plating process in which the metal ions in an aqueous solution are reduced to metal by a suitable reducing agent without external electrical assistance and then deposited on the substrate surface, with abundant catalytic active sites to form a compact metal coating [22]. It is a promising way to produce uniform and dense metal coatings due to its advantages, including low cost, fine coverage, and environmental friendliness. Due to the surface metallization done by electroless plating, the interfacial wettability and bonding strength of graphene and Cu can be notably enhanced. For instance, Li et al. [22] applied an electroless plating method to prepare Cu-graphene coatings by reducing graphene oxide (GO) into graphene during the Cu-GO co-deposition of electroless plating. A coating with enhanced mechanical properties and corrosion resistance, compared to that produced by regular pure Cu plating, was obtained under the GO concentration of 60 mg/L. Jiang et al. [23] adopted electroless plating to coat a uniform layer of nickel nanoparticles on the surface of graphene through three steps, i.e., sensitization, activation, and plating. The spark plasma-sintered copper composites enhanced with electroless-plated graphene showed an increase in mechanical tensile strength, as well as superior ductility, elongation, and electrical conductivity. Zhang et al. [24] proposed

a new method of combining electrostatic self-assembly and electroless plating to fabricate graphene nanoplatelets (GNPs)/Cu composites. The sensitized and activated GO and positive flake Cu powders with cetyltrimethyl ammonium bromide (CTAB) were electroless plated in a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ plating solution and then heated in an H_2 -Ar atmosphere to obtain the Cu/GNPs/Cu composite powders. The interfacial wettability of GNPs with Cu powders and their interface bonding strength were both enhanced by the formation of oxygen-mediated groups.

As described above, electroless plating is the most effective and widely used way to coat a metal layer on a graphene surface. However, most investigations have focused on the fabrication process and improving the mechanical and/or electrical properties of the graphene/copper composites. In addition, pressure-assisted methods, such as SPS and HP, have been adopted for the consolidation of green compacts in the sintering process. However, limitations such as high production cost and sophisticated equipment make these techniques hardly accessible and scarcely useful for practical applications. There are few studies focused on investigating the tribological behavior of self-lubricating graphene/copper composites prepared by an electroless plating process and a pressureless sintering technique.

In this study, the self-lubricating copper matrix composites reinforced with graphene were fabricated by an electroless plating process, followed by powder metallurgy. A simple electroless plating route was adopted to prepare a copper coating on the graphene surface, with copper sulfate (CuSO_4) as the main salt and formaldehyde (HCHO) as the reducing agent. The obtained Cu@graphene powders were then added into Cu powder to prepare self-lubricating graphene/copper composites by a traditional vacuum-sintering method. The differences in the structure and surface state between graphene and Cu@graphene powders as well as the influence of the Cu/graphene powder content on the tribological properties of the composites were investigated in detail.

2 Experimental

2.1 Materials and Method

All chemical reagents were of analytical grade, and deionized water was utilized to prepare the electroless bath. The graphene, synthesized by the oxidation reduction method, was purchased from the Sixth Element (Changzhou) Materials Technology Co., Ltd., China. In the course of the experiment, the graphene was ultrasonically dispersed in deionized water for 10 min. Subsequently, the evenly dispersed graphene was sensitized using boiling SnCl_2 acid solution (20 g/L) for 5 min, and rinsed with deionized water

to neutralize it. Later, the sensitized sample was activated by silver ammonia solution under mechanical stirring for 4 min and rinsed with deionized water to neutralize it. In a typical deposition procedure, the pre-treated graphene was immersed in the constant 40 °C electroless plating solution, under mechanical stirring for 20 min. The pH value was adjusted to 12.5 by adding sodium hydroxide solution. After complete reaction, the product was collected, rinsed with deionized water, and dried in a vacuum drying oven. The electroless copper plating bath was composed of 25 g/L of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 20 g/L of EDTA-2Na, 10 g/L of potassium tartrate, 15 mg/L of 2–2 bipyridine, 5 mg/L of potassium ferrocyanide, and proper formaldehyde served as a reducing agent.

Cu@graphene/Cu composites were prepared through powder metallurgy. Different contents of as-prepared Cu@graphene powders, namely 0, 1.5 wt%, 3 wt%, and 4.5 wt%, were mixed with Cu powders ($< 74 \mu\text{m}$) in anhydrous ethanol, under simultaneous mechanical stirring and ultrasonic dispersion. After drying in a vacuum drying oven, the well-mixed powders were cold pressed under 200 MPa into $\Phi 10$ mm circular cylinders. The obtained green bodies were vacuum sintered at 950 °C for 300 min with a heating rate of 10 °C/min, and furnace cooled to obtain the expected Cu@graphene/Cu composites.

2.2 Friction Testing

The tribological properties of the Cu@graphene/Cu composites with different contents of Cu@graphene powders were tested by a friction tester (Yihua MMU-5G, China). According to the requirements of the friction tester, the circular friction samples with an outer diameter of 54 mm, an inner diameter of 38 mm, and a height of 6 mm were prepared. 45[#] steel was used as the friction pair material. The samples were subjected to dry friction under a pressure of 70 N for 1 h at room temperature. Four groups of samples classified by Cu@graphene contents, namely 0, 1.5 wt%, 3 wt%, and 4.5 wt% were designed for the tribological properties test.

2.3 Characterization

The morphology, microstructure, and microconstitution of graphene, Cu@graphene, Cu@graphene/Cu composites, and worn surfaces of the composites were characterized by field emission scanning electron microscope (FESEM, Zeiss Ultra Plus, Germany) and transmission electron microscope (TEM, FEI Tecnai G² F20, USA). The crystal structures of graphene and Cu@graphene powder were investigated by X-ray diffraction (PANalytical X'Pert Pro, Netherlands). The structural defects of graphene and Cu@graphene powder were measured by Raman spectrometry (YNON HR800, France) using a 633 nm laser generator. The surface

functional groups of the graphene and Cu@graphene powder were investigated by Fourier transform infrared spectroscopy (Agilent-660, America) in the frequency range of 500–4000 cm^{-1} . The microhardness of Cu@graphene/Cu composites was measured by a microhardness tester (Hxd-1000tmc /LCD, China). The roughness of the worn surfaces of the composites, after friction testing, was characterized by laser confocal scanning microscope (Olympus OLS4100 3D, Japan).

3 Results and Discussion

3.1 Characterization of Graphene and Cu@graphene

In this work, the graphene used was prepared by an oxidation–reduction method, so there is a large amount of oxygenated functional groups, which were produced during the redox process, on the surface of the graphene [25]. These functional groups on the graphene surface will reduce the excellent performance of the graphene, such as conductivity, light transmittance, thermal conductivity, and so on. The surface of the graphene was metallized by electroless plating, and the structure of the graphene before and after electroless plating was characterized by FESEM and TEM, as shown in Fig. 1. The graphene presented a two-dimensional lamellar structure with many wrinkles, as shown in Fig. 1a, b. Owing to the presence of oxygen-containing functional groups on the surface of the graphene, the hydrogen bonds acted to laminate the graphene sheets together [25]. In contrast, the morphology of Cu@graphene largely retained the original two-dimensional gravitational structure of graphene, as shown in Fig. 1c, d. According to the EDS element analysis (Fig. 1c), the surface of the graphene was completely covered with a uniform and compact copper layer. It can be seen from Fig. 1d that many dark irregular copper nanoparticles were homogeneously dispersed on the transparent graphene, which was consistent with the SEM results. Moreover, the distribution of Cu nanoparticles was closely associated with the distribution of the Ag element. Because the copper film was completely attached to the graphene surface, the thickness of the graphene increased, and the fringes of the graphene surface became weaker. The weight gain rate R of the copper coating after the electroless plating was determined via a weight gain method:

$$R = \frac{m_2 - m_1}{m_1} \times 100\%, \quad (1)$$

where m_2 is the mass of the object after electroless plating and m_1 is the initial mass of the used graphene. According to Eq. (1), the value of R was calculated as 300%, implying that

Fig. 1 FESEM image **a** and TEM image **b** of graphene, and FESEM image and element area profile **c** and TEM image **d** of Cu@graphene

the mass ratio of copper and graphene in the Cu@graphene powder was 3:1. Hence, the mass ratio of graphene in Cu@graphene powder was 25 wt%.

X-ray diffraction (XRD) analysis was employed to investigate the crystal phase. XRD patterns of graphene and Cu@graphene powder is shown in Fig. 2a. Three peaks in the XRD pattern of Cu@graphene, located at $2\theta = 45.08^\circ$, 52.22° , and 76.44° , corresponding to the (111), (200), and (220) planes of face-centered cubic copper, indicated the presence of copper on the surface of the graphene. The widths of the above three diffraction peaks were broadened, indicating that the reduced copper particles were of nanoscale and/or of low crystallinity [23]. In addition, the (002) characteristic reflection peak of graphene, located at $2\theta = 26.19^\circ$, was observed in both the graphene and Cu@graphene patterns, despite the intensity of characteristic peak of Cu@graphene obviously decreasing. This might be due to the copper coating on the surface of the graphene. Moreover, the diffraction peaks of carbon disappeared, or obviously weakened, after the electroless plating, implying that the structural defects on the surface of the graphene had been repaired to some extent. However, diffraction peaks observed at $2\theta = 36.62^\circ$, 61.57° , and 77.54° , were assigned to Cu_2O which was attributed to the following chemical side reaction during the electroless plating:

Raman scattering is extremely sensitive to the electronic structure of graphene, especially for changes in the defects. The change in the carbon structure of graphene and Cu@graphene was analyzed by Raman spectroscopy, as shown in Fig. 2b. The prominent Raman characteristic of graphene shows that the D band ($\sim 1360 \text{ cm}^{-1}$) is closely related with the vibrations of the sp^3 -hybridized carbon lattice with the presence of defects (edges, implanted atoms, grain boundaries, dislocations, or vacancies), and the G band ($\sim 1580 \text{ cm}^{-1}$) is closely related with the ordered state of the sp^2 -hybridized carbon lattice [26]. Both prominent peaks can be seen in graphene and Cu@graphene, and there was little variation in the position of each peak, indicating the same structure of graphene and Cu@graphene. In other words, the electroless plating did not change the intrinsic structure of graphene. The intensity ratio of the D band and G band (I_D/I_G) is always used to characterize the degree of graphene defects [27]. The I_D/I_G ratio decreased from 1.367 for graphene to 1.187 for Cu@graphene, which implied that the Cu@graphene has fewer defects. In the literature [22], the I_D/I_G ratio of the Cu-graphene composite coating prepared by electroless plating, i.e., reducing graphene oxide

Fig. 2 XRD patterns **a**, Raman **b**, and FTIR spectra **c** of graphene and Cu@graphene

into graphene during co-deposition, was 1.280, higher than that of Cu@graphene in the study. The graphene had more folds and twists owing to the simultaneous reduction and co-deposition, which resulted in plentiful defects in the graphene. It implied the superiority of electroless plating used in this research to repair the structure of graphene. From the collected Raman spectra, the density of the defects in graphene, N_D , can also be quantified according to the following equation [28]:

$$N_D(\text{cm}^{-2}) = \frac{(1.8 \pm 0.5) \times 10^{22}}{\lambda^4} \left(\frac{I_D}{I_G} \right), \quad (3)$$

where λ is the laser wave length. The defect density increases linearly with the ratio of I_D/I_G , so the N_D of Cu@graphene was lower than that of graphene. Hence, the defect density of the graphene surface can be reduced by electroless plating.

Fourier transform infrared (FTIR) spectroscopy was used to explore the changes of the oxygen-containing

functional groups on the surface of the graphene before and after electroless plating. FTIR spectra of graphene and Cu@graphene are shown in Fig. 2c. Among the characteristic peaks shown in the infrared spectrum of graphene, a broad and strong absorption peak at around 3415 cm^{-1} was attributed to the characteristic stretching and bending vibration of the hydroxyl groups of graphene. The strong peak at 1725 cm^{-1} was due to the stretching vibration of C=O, and the peak at 2917 cm^{-1} corresponded to the stretching vibration of C-H. These characteristic peaks indicated the existence of oxygen-containing functional groups on the surface of the redox graphene. These oxygen-containing functional groups acted as an adhesive and can effectively promote the bonding strength between the graphene substrate and the Cu coating [29]. An absorption peak at 615 cm^{-1} in the infrared spectra of Cu@graphene was attributed to the stretching vibration of C-Cl, owing to the introduction of Cl^- during the electroless plating process. In addition, a disproportionation reaction

of formaldehyde occurred in the alkaline conditions is as follows [30]:

The resulting $-\text{OH}$ and $-\text{COOH}$ groups may react with the oxygen-containing functional groups on the surface of graphene. Therefore, the FTIR curve of Cu@graphene became smooth and the characteristic vibration absorption peaks of the oxygen-containing functional groups vanished, or appeared with significantly lower intensities, indicating that most oxygen-containing functional groups were successfully removed after the electroless plating. As a result, the defect content of redox graphene can be reduced by electroless plating, which agreed with the XRD and Raman results.

3.2 Microhardness of Cu@graphene/Cu Composite

The friction performance is closely associated with the surface hardness. The microhardness of Cu@graphene/Cu composite is shown in Fig. 3. Based on the mass ratio of graphene in the Cu@graphene powder being 25 wt%, the graphene content in the Cu@graphene/Cu composite was 0.375 wt%, 0.750 wt%, and 1.125 wt% when the Cu@graphene content was 1.5 wt%, 3.0 wt%, and 4.5 wt%, respectively. The microhardness of the Cu@graphene/Cu composite initially increased and then decreased with the increase in the Cu@graphene content. When the Cu@graphene content was 3.0 wt%, the microhardness of the composite reached its maximum (67.35 HV), which was about 10.72% higher than that of pure Cu. Similar hardening effect was observed for copper matrix composites reinforced with nickel nanoparticles-anchored graphene nanosheets [21]. Hence, a

Fig. 3 Microhardness of Cu@graphene/Cu composite with different Cu@graphene contents

considerable strengthening effect was exhibited due to the addition of graphene. Figure 4 shows the morphologies of the Cu@graphene/Cu composite with 3.0 wt% and 4.5 wt% Cu@graphene content. As shown in Fig. 4a, the graphene can be uniformly dispersed in the Cu matrix, and mostly located at the boundaries of Cu grains when the Cu@graphene content was 3.0 wt%. The interface microstructures of Cu@graphene/Cu composite with 3.0 wt% Cu@graphene were investigated by TEM, as shown in Fig. 4c, d. It can be seen from the TEM image as shown in Fig. 4c that the graphene was located at the boundary of the Cu grains. The HRTEM image of the composite, as shown in Fig. 4d, displayed clearly a graphene/Cu interface without visible impurities, voids, and gaps, indicating an interfacial adhesion by mechanical interlocking. It confirmed that a coherent interface between copper and graphene can be obtained in the process of electroless plating. The similar interface between copper and graphene was observed by electroless plating [24]. The dislocation density notably increased due to the thermal expansion mismatch between copper and graphene. Moreover, according to the theory of dislocation strengthening, the uniformly dispersed Cu@graphene in the Cu matrix can effectively block the dislocation movement during deformation process and can act as an extraneous hard point to play the role of pinning dislocation. The dislocation pileup formed near the grain boundaries could result in a strengthening effect [31]. As a result, the Cu@graphene/Cu composite was significantly strengthened, and the microhardness obviously increased. When the Cu@graphene content reached 4.5 wt%, the Cu@graphene powders agglomerated at the copper grain boundaries and the agglomeration of graphene hindered the combination in the sintering process. As a result, big pores (marked by blue dotted circle in Fig. 4b) were formed in the sintered Cu@graphene/Cu composite, decreasing their hardening effect. Hence, the microhardness of the composite with 4.5 wt% Cu@graphene decreased.

3.3 Tribological Properties of Cu@graphene/Cu Composites

The coefficients of friction and friction surface roughness of the Cu@graphene/Cu composite with different Cu@graphene contents are given in Fig. 5. With increasing Cu@graphene content, the coefficients of friction and friction surface roughness of the Cu@graphene/Cu composite both initially decreased and then increased. Similar evolution of the coefficients of friction as a function of self-lubricating reinforcement was reported in graphene/Cu composites [18]. When the Cu@graphene content was 3.0 wt%, the coefficient of friction and friction surface roughness of the Cu@graphene/Cu composite reached their minimums, which were about 29.47% and 37.29% lower than that of pure Cu, respectively. In addition, according to the error bar, the tendencies of the

Fig. 4 Characterizations of Cu@graphene/Cu composite: SEM images of composite with 3 wt% Cu@graphene **a** and 4.5 wt% Cu@graphene **b**; TEM **c** and HRTEM **d** images of composite with 3 wt% Cu@graphene [**d** is the local magnification image of the blue box area marked in **c**]

Fig. 5 Coefficients of friction **a** and friction surface roughness **b** of Cu@graphene/Cu composites with different Cu@graphene contents

variation ranges of the coefficients of friction and friction surface roughness were similar to those of the coefficients of friction and friction surface roughness, indicating that the suitable addition of Cu@graphene can make the friction performance of Cu@graphene/Cu composites more stable. When the Cu@graphene content was increased to 4.5 wt%,

the coefficients of friction and friction surface roughness of the Cu@graphene/Cu composite obviously increased, which was closely related with the structure of Cu@graphene/Cu composite, as shown in Fig. 4b. The existence of pores rooted in the agglomeration of graphene increased the coefficients of friction and friction surface roughness.

Figure 6 shows the SEM micrographs of the worn surfaces of Cu@graphene/Cu composites with different Cu@graphene contents. As indicated in Fig. 6a, b, which showed the pure Cu-sintered specimen with low and high magnification, respectively, its worn surface exhibited a coarse and lamellar appearance characterized with a lot of large wear debris, fracturing, abrasive grooves, and typical plastic deformation. The adjacent Cu particles presented adhesion during the friction process. The worn surface metal was oxidized due to the high contact temperature, and the movement of the dislocations was restricted by the as-formed metallic oxide, resulting in some areas of the worn surface with high stress. The stress concentration cannot be released by repeated sliding because no contributing protective film was formed on the surface of the pure Cu sample. In the following sliding process, surface fracturing occurred once local stress reached the fracture strength, leading to large wear loss. Hence, large wear debris and abrasive grooves were formed on the worn surface of pure Cu-sintered specimen. All these observations suggested that the pure Cu-sintered specimen suffered from both adhesive wear and abrasive wear, which was in agreement with the higher coefficient of friction and friction surface roughness of pure Cu. Figure 6c, d shows the SEM micrographs of the worn surface of 1.5 wt% Cu@graphene/Cu composite at low and high magnification, respectively. It can be clearly seen that the worn surface was relatively smoother than that of pure Cu but was accompanied with obvious abrasive grooves and delaminated regions. Moreover, smaller and less wear debris were observed again because the addition of graphene can prohibit the adjacent Cu particles from forming adhesion. These results indicated that the significant wear mechanism changed to adhesive wear and delamination wear. However,

the worn surface of this composite was still relatively rough, and a certain amount of debris can be observed. The SEM micrographs of the worn surface of Cu@graphene/Cu composite with 3.0 wt% Cu@graphene content are shown in Fig. 6e, f. The appearance of the worn surface was rather smooth with shallow and narrow grooves along the sliding direction. This demonstrated that uniformly dispersed graphene limited the plastic deformation of the Cu matrix and can effectively decrease the stress concentration in the friction process. As a result, the lowest coefficients of friction and friction surface roughness of the Cu@graphene/Cu composite were obtained. All the results indicated that the main wear mechanism was mild adhesive wear. When the Cu@graphene content was further increased to 4.5 wt%, the worn surface of Cu@graphene/Cu composite became rough with large debris and fracturing (as shown in Fig. 6g, h). Thus, the coefficients of friction and friction surface roughness of the Cu@graphene/Cu composite seriously increased during the tribological test. This can be explained by the poor sintering ability of this Cu@graphene/Cu composite due to the agglomeration of graphene, as shown in Fig. 4b.

To explore the reason for the reduced friction for Cu@graphene/Cu composite, the characteristics of the wear track were studied by EDS, FTIR, and Raman. As shown in Fig. 7, the C and O contents of the wear track of the Cu@graphene/Cu composite after the sliding test and the wear scar both increased, while the Cu reduced with respect to the Cu@graphene/Cu composite before the sliding test, indicating that the worn surface metal was oxidized due to the high contact temperature in the continuous sliding process. According to the FTIR surveys (Fig. 8a), this showed that more oxygen-containing functional groups appeared on the surface of Cu@graphene/Cu composite after the sliding test. Also, both

Fig. 6 SEM micrographs of worn surfaces of the Cu@graphene/Cu composite with different Cu@graphene contents: **a, b** 0 wt%; **c, d** 1.5 wt%; **e, f** 3 wt%, and **g, h** 4.5 wt%. Images **b, d, f**, and **h** are corresponding partial (marked by blue dotted rectangle) enlarged images in **a, c, e**, and **g**, respectively

Fig. 7 EDS and atom percent of Cu@graphene/Cu composite before sliding test **a**, wear track of Cu@graphene/Cu composite after sliding test **b**, and wear scar on steel friction pair **c**

Fig. 8 FTIR **a** and Raman **b** spectra of Cu@graphene/Cu composites before and after sliding test and wear scar on steel friction pair

Raman spectra (Fig. 8b) obtained from the wear track on Cu@graphene/Cu composite, and the wear scar on the steel friction pair, showed increased intensity ratios (I_D/I_G), e.g., 1.416 at the wear track and 1.443 at the wear scar, in comparison with Cu@graphene/Cu composite before the sliding test (1.213). This implied that more defects were generated on the graphene surface during the sliding process. All these changes suggested that the graphene in the Cu matrix had been modified during the sliding process. One possible reason was that the sliding-induced unsaturated C atoms in the graphene, which were passivated by H and OH dissociated from water molecules during the sliding process [32, 33]. In addition, the as-formed oxide inclusions restricted the movement of the dislocations generated by the plastic deformation at the interface and thus caused an area with high stress and great strain at the sub-surface [16, 34], resulting in defects on the graphene surface. Analogous to the graphene/metal matrix composites, it was proposed that the graphene could be transported to the contact surface by the synchronized deformation of the bulk, forming a graphene-rich tribolayer on the contact surface [33], which resulted in an increase in

C content and decrease in Cu content. Once an integrated graphene-rich tribolayer was formed on the wear tracks, the relative sliding between the counterparts was proceeded in the tribolayers. As the shear strength of graphene-rich tribolayer was considerably low, the friction effectively reduced, e.g., the coefficient of friction availably decreased. When the Cu@graphene content was 1.5 wt%, the thin and discontinuous graphene-rich tribolayers were quickly worn out by friction. As a result, the decrease in coefficient of friction was unobvious. As the Cu@graphene content increased to 3.0 wt%, the graphene-rich tribolayers became thicker and continuous. So the coefficient of friction distinctly decreased.

Based on the above observations, the friction mechanism of Cu@graphene/Cu composite with 3.0 wt% Cu@graphene content is proposed as follows. The initially embedded graphene are squeezed out from the copper matrix due to the effect of tribological stress, and then mechanically mixed with the detached debris during the sliding process, gradually forming a well-consolidated graphene-rich lubricious tribolayer on the worn surface of the Cu@graphene/Cu composite. This graphene-rich lubricious tribolayer can be

easily transferred to the steel friction pair as a transfer layer covering the surface of the steel friction pair. Effectively, the graphene-rich lubricious tribolayer not only prevents the direct metal-to-metal contact of the tribo-pair and the Cu matrix from oxidation but also decreases the direct contact area between the Cu@graphene/Cu composite and the steel friction pair, reducing interatomic junctions across the interface and resulting in adhesive wear. What's more, according to Archard's theory for adhesive wear, the wear resistance of a material is proportional to its hardness [33]. The incorporation of Cu@graphene can significantly improve the microhardness of Cu@graphene/Cu composites, as shown in Fig. 3. These two factors work together to enhance the tribological properties of Cu@graphene/Cu composite yielding a lower and more stable coefficient of friction.

4 Conclusion

Self-lubricating Cu@graphene/Cu composites with enhanced tribological properties have been prepared by electroless plating and powder metallurgy. The characterization of Cu@graphene indicates that the surface of the graphene is completely covered with a uniform and compact copper layer with many copper nanoparticles and the oxygen functional groups and defects on the surface of the redox graphene can be reduced through the electroless plating process.

Tribological tests suggest that the coefficients of friction and friction surface roughness of Cu@graphene/Cu composites initially decrease, and then increase with the increase in Cu@graphene content. When the Cu@graphene content is 3.0 wt%, the coefficient of friction and friction surface roughness of the Cu@graphene/Cu composite reach their minimums, which are about 29.47% and 37.29% lower than those of pure Cu, respectively. Such an improved tribological performance of the Cu@graphene/Cu composite can be attributed to the formation of a well-consolidated graphene-rich lubricious tribolayer at the contact surface, and a higher microhardness. This demonstrates that graphene has an obvious reinforcement effect for potential applications as an ideal reinforcement in copper matrix composites.

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