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Properties of copper/graphite/carbon nanotubes composite reinforced by carbon nanotubes

Xin-Ying Liu, Xiong-Zhi Xiang*, Fei Niu, Xiao-Jun Bai

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Abstract Electroless Cu plating was used for flake G powder and CNTs, Cu–G–CNTs (copper/graphite/carbon nanotubes) composites were manufactured by means of powder metallurgical method. The influences of CNTs on the mechanical properties, conductivity properties, friction, and wear performance of the composite were examined. The results indicate that adding a small amount of CNTs can improve comprehensive property of the composites, especially mechanical property. However, excessive CNT, which is easily winding reunion and grain boundary segregation, results in performances degradation.

Keywords Cu/G composite; Carbon nanotubes; Resistivity; Friction and wear resistance

1 Introduction

Metal matrix composite which is an integration of high specific modulus, high specific strength, good wear-resisting properties, excellent electrical conductivity, and thermal conductivity, becomes one of the most rapid development of the advanced materials at present [1–3]. Cu/G is an important metal matrix composite widely used in electrical sliding contact applications, such as electrical brushes in motors and generators. In conventional Cu/G electrical contact material, Cu matrix presents higher strength, excellent thermal and electrical conductivity; G shows impressive tribological performance [4]. But with the increase of Cu content, the electrical and thermal conductivity are improved, while lubricating and wear resistance property declined. However, with the increase of G content, its lubricating property and wear resistance property are improved, but electrical and thermal conductivity and strength declined. The dilemma limits the scope of its application [5]. Because of their extraordinary intrinsic mechanical, electrical and thermal properties, and high aspect ratios, especially high Yong's modulus makes multiwalled carbon nanotubes (MWCNTs), the ultimate high strength fibers to be used as reinforcement in composite materials [6]. In recent years, most investigations focused on MWCNTs can considerably enhance the mechanical and conductive properties of polymer and ceramic matrix, while only few investigations concerned with the properties of bulk CNTs-metal composites. In this study, the MWCNTs to Cu/G composite electrical contact performance influence were investigated, and the mechanism of action was further discussed.

2 Experimental

2.1 Materials

Raw materials used in experiments including: 38 μm dendritic electrolytic Cu powder was purchased from Beijing Nonferrous Metals Research Institute; 45 and 25 μm flake G powders were obtained from Qingdao Nanshu Hongda Graphite Products Factory; MWCNTs were purchased from Shenzhen Nano Port Co., Ltd, having a diameter range of 40–60 nm, length of 5–15 μm, a purity of 98 %, a specific surface area of 40–300 $m^2 \cdot g^{-1}$.

X.-Y. Liu, X.-Z. Xiang*, F. Niu, X.-J. Bai
Shenzhen Key Laboratory of Special Functional Materials,
College of Materials Science and Engineering,
Shenzhen University, Shenzhen 518060, China
e-mail: xiyun_cn@szu.edu.cn

2.2 Surface treatment of CNTs and preparation of composites

Owing to large ratio of length to diameter and van der Walls attraction [7], the initial CNTs were easy to twist and cluster. In order to improve the activated ability and the dispersion, and increase the interfacial bonding strength with the Cu matrix, CNTs were subjected to purification and oxidation treatments [8]. The CNTs were calcined at 580 °C for 3 h in the muffle furnace and then immersed in acetone, supersonic treatment for 2 h after furnace cooling. The purification of CNTs were dissolved in a mixed solution containing potassium dichromate and sulfuric acid, in 1:1 ratio and electromagnetic stirring for 4 h at 75 °C. After purification, oxidation, sensitization, activation, and reduction pretreatments, the CNTs were coated by Cu through electroless plating. A certain content of Cu coated MWCNTs, Cu powder, and 8 wt% Cu coated G (45 and 25 μm G in 3:2 quality ratio) were homogeneously mixed by milling [9], the pressing pressure for 150 MPa, holding pressure 10 s. After pressing the body for vacuum sintering at 800 °C, insulation 2 h. The composite material of MWCNTs containing carbon quality ratio in experiments is shown in Table 1.

2.3 Methods

Material bending strength was tested with a microcomputer-controlled universal testing machine; resistance was evaluated by HK35400-1 type DC resistance tester with a four-terminal method; electrical friction and wear tests were measured by EMM—type 1 friction and wear tester of Shanghai Shenrui Instrument Co., Ltd; sliding friction and wear tests, griding crack surface morphology, and microstructure were carried out using 100T type friction and wear morphology tester of Japan Sciland, OLYMPAS GX71 metallographic microscope, Hitachi S4700 type FESEM, respectively.

3 Results and discussion

Figure 1 illustrates a good plating effect for Cu particles sequence deposited in the wall with a high coverage rate. Figure 2 shows CNTs are dispersed relatively uniform in the matrix, without obvious aggregation of large particles, which guarantees a good self-lubricating property.

Table 1 Cu/G/CNTs composite components content (wt%)

Nos.	N1	N2	N3	N4	N5	N6
Cu	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
G	8.00	8.00	8.00	8.00	8.00	8.00
CNTs	0.05	0.10	0.15	0.20	0.25	0.30

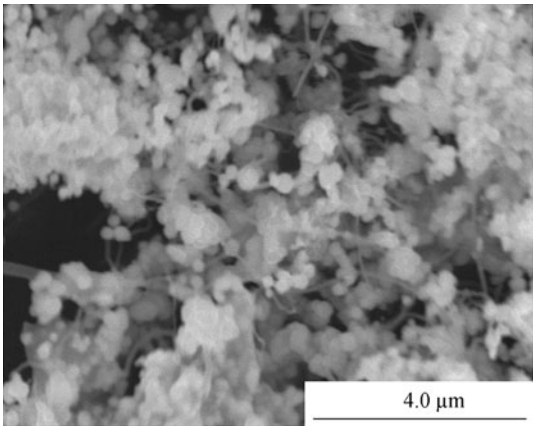

Fig. 1 SEM image of copper coated CNTs

3.1 Influence of CNTs content on bending strength

According to Fig. 3, the bending strength is increased slightly first and then declined sharply with the increase of CNTs content. Combined with SEM image (Fig. 4), we can conclude that the strength can be improved to a certain extent when add small content of CNTs (0.05 %), since the excellent mechanical properties and tubular structure of CNTs [10, 11] can connect the crackle of both sides; and the bonding strength between Cu coated CNTs and matrix enhanced by electroless can prevent crack propagation. But with the further increasing CNTs content, not only the material porosity increases, mostly are irregular open pore which lead to stress concentration intensified, but also most of the CNTs partial gathered at the grain boundaries (as shown in the fracture morphology of the samples of 0.30 %) fails to play a strength effect, cause bending strength declined.

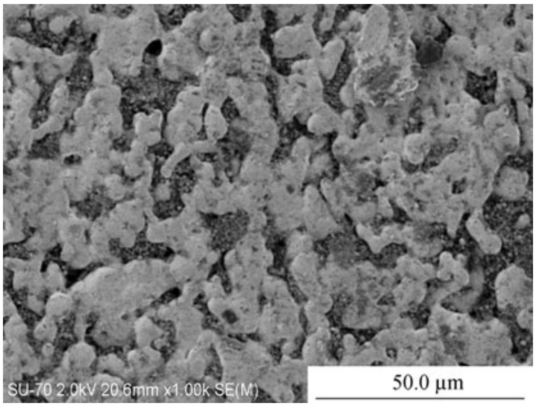

Fig. 2 Fracture SEM image of composite material

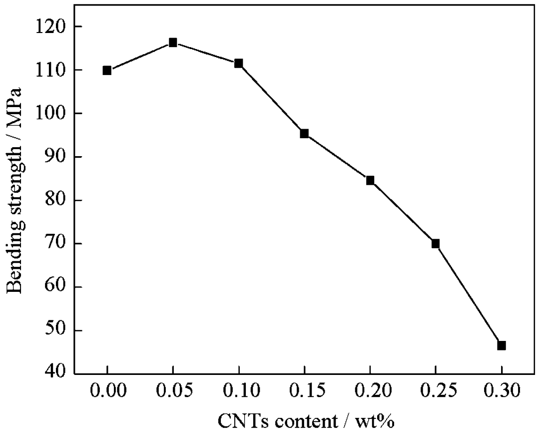

Fig. 3 Influence of CNTs content on bending strength

3.2 Influence of CNTs content on resistivity

The resistivity of composite increases with the increase of CNTs contents and the growth rate also gradually increases. Figure 5 presents that adding a small amount of CNTs has no apparent impact on the resistivity, which is due to CNT intrinsic excellent electrical conductivity [12]. After Cu plating processing, CNTs possess a good adhesion of Cu and G surface, not excessively affect the electronic conductivity. However, electron scattering increases as the CNTs contents increase, resulting in a sharp increase in resistivity.

3.3 Influence of CNTs content on mechanical friction and wear properties

Figure 6 shows a certain content of CNTs (0.1 %–0.15 %) can improve the friction and wear properties of the composite. The one reason is that CNTs are fairly well distributed in the composites, present a network cross-linked state, have a function of dispersion strength, enhance flow resistance, and plow resistance of the friction wear surface is difficult to fall off during wear process, so as to increase the wear resistance. The other reason is that CNTs surface grains raise on the layer of Cu matrix, which may take support loading "ball bearing" effect and reduce the actual contact area between the friction surface and the friction pair. During friction and wear process, these raised grains break into debris, debris accumulates and gradually spreads out of the contact interface, forming a layer of dense lubricating film, which contributes to decrease friction coefficient of composites [13]. Furthermore, according to Refs. [14, 15], the structure of contact region between the CNTs and the G determines the movement and the friction behavior of the CNTs. Incommensurate, CNTs sliding on the substrate do not have periodic translational energy and friction force. At this moment the friction is lower than commensurate, thus improve the friction and wear. As CNTs content continues to increase, the friction and wear properties of the composite decrease, present the similar wear rate variation trend, which is caused by other nanoparticles additive content. The first reason is the excessive addition of CNTs can destroy the continuity of the lubricating film of the friction pair surface, which causes the film local disturbance and some destruction, and the friction pair surfaces directly contacting each other can occur in plow phenomenon. The second reason is that higher

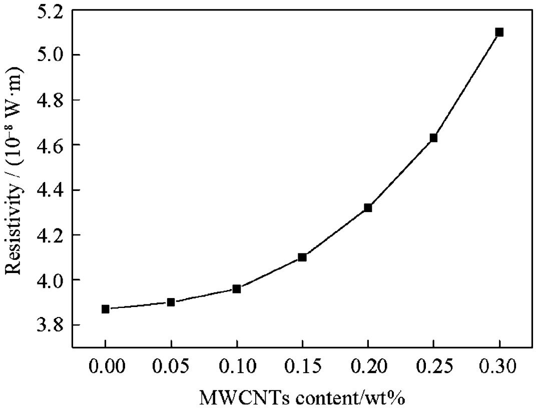

Fig. 5 Influence of MWCNTs content on resistivity

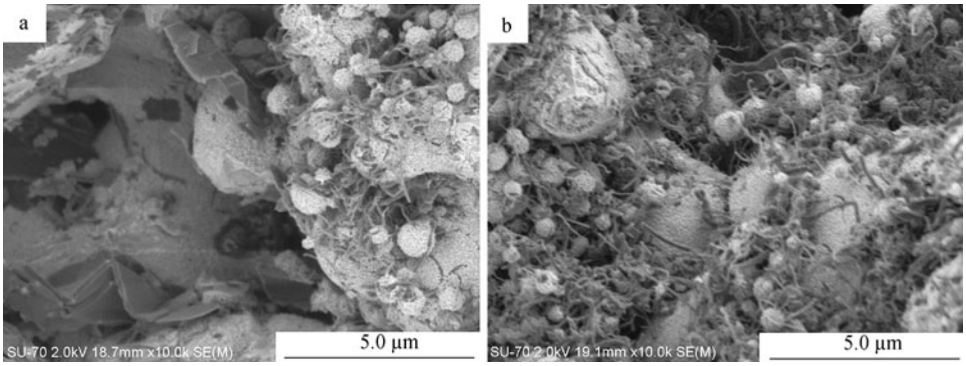

Fig. 4 Fracture SEM images of samples: **a** carbon quality 0.05 % of CNTs and **b** carbon quality 0.30 % of CNTs

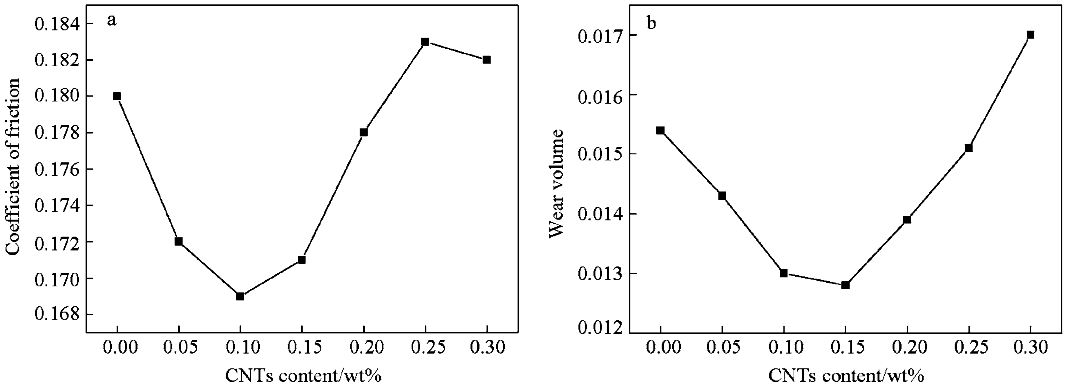

Fig. 6 Influence of CNTs content on friction and wear properties: **a** coefficient of friction and **b** wear volume

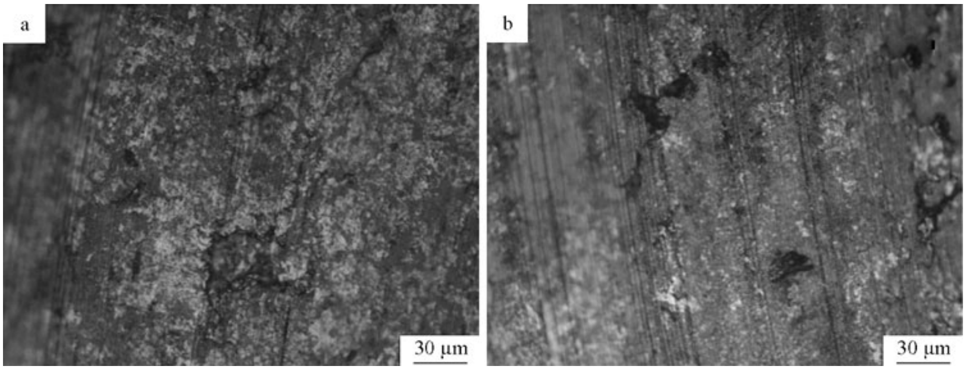

Fig. 7 Metallographic images of wear scar: **a** N2 and **b** N3

amount of CNTs may lead to twist and cluster, have no action on the matrix, which may cause the antifriction effect and wear resistance decrease. Figure 7 indicates that when the CNTs content is 0.15 %, the composites surface lubrication film asymmetries; the naked Cu comes into being finally. According to the above results, the Cu/G/0.1 %CNTs comprehensive performance is optimal.

3.4 Influence of CNTs content on electrical friction and wear properties

Electrical sliding contact materials wear is inferred to be caused by the mechanical wear and the electrical wear. Therefore, the friction and wear characteristics were surveyed in an energized state considering the contact voltage drop and wear loss. The electrical friction and wear properties of pure Cu, Cu/G, Cu/G/0.1 %CNTs samples were compared.

3.4.1 Contact voltage drop

The measured variation of a pair of contact voltage drop actually reflects the lubricating film voltage drop variation and its degree of stability. The positive and negative brush contact voltage drop of Cu, Cu/G, Cu/G/0.1 %CNTs were measured, respectively. In order to make the current not produce serious arc erosion to samples, ensure the reliability of the test data, the current density is 5 A·cm^{-3}. In addition, the increase of the actual contact pressure can reduce shrinkage resistance, experiments using a constant load of 5 N.

From Fig. 8, we can see, the negative brush contact voltage drop is always greater than that of positive brush for these three kinds of materials. This is because the contact voltage drop may be caused by the contact resistance between brush and commutator, the larger the contact resistance, the greater the contact voltage drop. According to Refs. [16–18], on the one hand, negative brush has larger surface roughness, and collector ring has lesser actual contact area, so negative brush contraction resistance value is greater than that of positive brush. On the other hand, collector ring surface form a Cu oxide film results from the presence of water in the air and the increase of temperature, which is caused by mechanical wear and electric energy loss release heat energy, and only negative brush is under the action of electric field force, Cu cation can migrate from collecting ring to negative brush which causes oxidizing thickness increased, results in negative brush

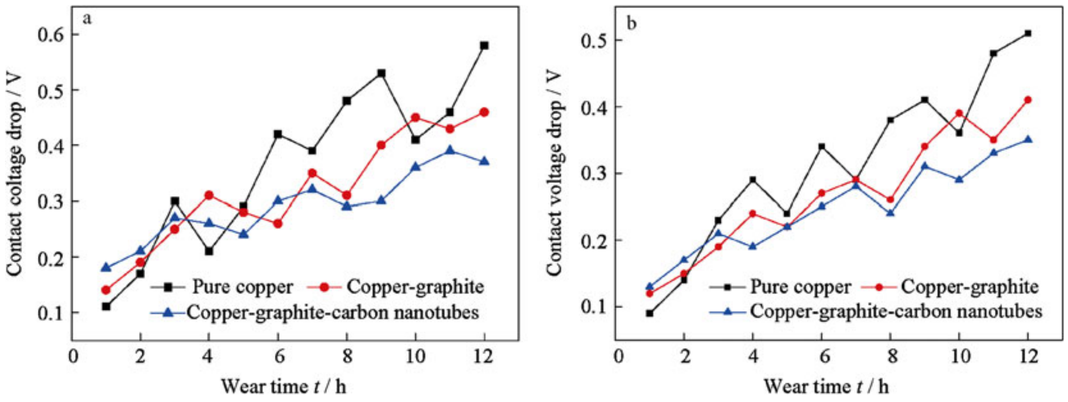

Fig. 8 Relationship between voltage drop of composite brush and wear time: **a** negative brush and **b** positive brush

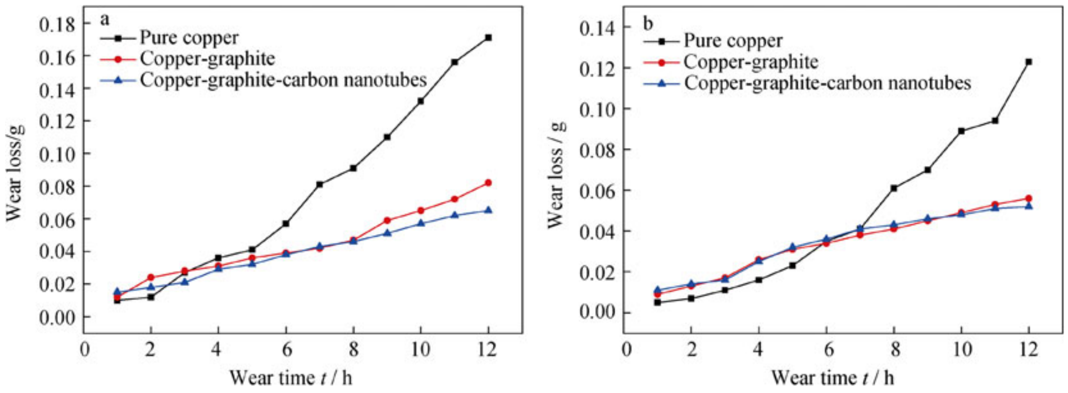

Fig. 9 Relationship between wear loss of composite material and wear time: **a** mechanical friction and wear and **b** friction and wear with power

resistance larger. So negative brush has higher contact voltage drop. Figure 8 also shows both brushes contact voltage all increase firstly and then trend to be stable. But pure Cu sample volatility and contact voltage drop are the largest. Comparing the samples of Cu/G and Cu/G/0.1 %CNTs, it is known that the drop of contact voltage of Cu/G/0.1 %CNTs is higher in the initial stage of wear, then lower than that of Cu/G over time and tend to be more stable. The reason is pure Cu seriously wearing in the friction process, and wearing will change the surface state of contact element. This causes contact resistance increase. Since work hardening will make this area difficult to deformation, contact area reduced, and the resistivity of hardened metal will increase, thus the drop of contact voltage increases sharply. The G in composite can gradually form a complete lubrication film on brush friction surface, so that the contact between brush and slip ring become a metal—lubricating film—metal contact, though voltage drop also increases, but less than pure Cu sample. When the lubricating film is in a dynamic equilibrium, the contact voltage drop of Cu/G/0.1 %CNTs brush sample is minimum, and tends to be stable.

3.4.2 Friction and wear with power quantity

As shown in Fig. 9, positive brush wear mass loss of three kinds of samples were measured, the current density is $5\ \mathrm{A{\cdot}cm^{-3}}$. The results show that the three samples wear are greater than those of mechanical wear, which indicates that current brings into electrical wear which aggravates the material wear. During electrical wear process, contact site area, where current concentration through is small, which leads to the increase of the site temperature, emerges temperature gradient, produces large internal stress of the contact points. And as collector ring constantly rotating, electrical contact points continuously transform, internal stress uninterruptedly produce and ease, bonding force between particles reduces, wear exacerbates. Moreover, the presence of current more or less causes arc wear between the brush and slip ring. When the spark energy leaps, arc and brush direct contact leads to severe burning, which makes the brush wear increase dramatically.

Pure Cu sample has the maximum electric friction and wear mass loss. In the process of electricity, in the role of elevated temperature, metal sliding with its crystal lattice surface directly contact, easy to produce adhesive wear which is caused by the elastic–plasticity deformation micro peaks of adhesion force [19]. So pure Cu sample exists the largest metal transfer in the process. For Cu/G sample, wear rate is larger in the initial stage, which results in forming a lubricant film over time. Metal spaced sliding depends on several atomic layer of the lubricating film, which greatly reduce the adhesion force and adhesive wear, thus the abrasion loss is reduced. The wear of Cu/G/0.1 %CNTs sample is slightly larger than Cu/G sample in the initial stage of wear, after a certain time its wear is lower than that of Cu/G, slow growth and trend to be stable. This is because the appropriate content of CNTs can improve material strength of the material, and then effectively restrain the plow cut. In addition, CNTs with nanometer size and specific surface area, a part of heat caused by electricity situation can be absorbed by CNTs, which effectively reduce the friction pair of surface temperature, inhibition of Cu adhesive wear.

4 Conclusion

The bending strength of the composite material is enhanced to a certain level, and then decreased with the increase of CNTs content, which is because with the increase of material porosity, stress concentration, and the segregation of most CNTs at the grain boundary, strengthening effect cannot be played.

Owing to the electron scattering enhanced with increase of CNTs content, CNTs have a negative influence on resistivity.

Certain content of CNTs can improve the friction and wear properties of the composites. The addition of CNTs can improve the electrical friction and wear properties of electrical contact composite. In the process of electrical sliding friction and wear, the grinding action of CNTs can prevent lubricating film further thickening, make the film in a state of dynamic equilibrium. In addition, CNTs significant endothermic effect can effectively reduce the temperature of the friction pair surface, inhibit adhesive wear. But excess CNTs will destroy the integrity of the friction surface lubrication film and be easy to produce winding reunion, which has no reinforcement effect on matrix.

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