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Friction and wear properties of copper matrix composites reinforced by tungsten-coated carbon nanotubes

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Abstract

Carbon nanotubes (CNTs) were coated by tungsten layer using metal organic chemical vapor deposition process with tungsten hexacarbonyl as a precursor. The W-coated CNTs (W-CNTs) were dispersed into Cu powders by magnetic stirring process and then the mixed powders were consolidated by spark plasma sintering to fabricate W-CNTs/Cu composites. The CNTs/Cu composites were fabricated using the similar processes. The friction coefficient and mass wear loss of W-CNTs/Cu and CNTs/Cu composites were studied. The results showed that the W-CNT content, interfacial bonding situation, and applied load could influence the friction coefficient and wear loss of W-CNTs/Cu composites. When the W-CNT content was 1.0 wt.%, the W-CNTs/Cu composites got the minimum friction coefficient and wear loss, which were decreased by 72.1% and 47.6%, respectively, compared with pure Cu specimen. The friction coefficient and wear loss of W-CNTs/Cu composites were lower than those of CNTs/Cu composites, which was due to that the interfacial bonding at (W-CNTs)-Cu interface was better than that at CNTs-Cu interface. The friction coefficient of composites did not vary obviously with increasing applied load, while the wear loss of composites increased significantly with the increase of applied load.

Keywords: carbon nanotubes; tungsten layer; copper; friction coefficient; wear loss

1. Introduction

As advanced engineering materials, metallic matrix composites are used in many applications, such as electrical contact brushes, cylinder liners, artificial joints, and helicopter blades, which all require high wear resistance. Copper offers a unique combination of good toughness, formability, excellent electrical and thermal conductivity, and low cost, making copper matrix composites arouse interest in the structural and functional application fields [1-2].

Carbon nanotubes (CNTs) have drawn extensive interest since their discovery in 1991 because of their extraordinary intrinsic mechanical, electrical and thermal properties, as well as high aspect ratios [3], for example, CNTs possess the high Yong's modulus up to 1.3 TPa and tensile strength of about 100 GPa and can be used as the reinforcement of composites [4]. Many previous literatures [5-8] have been reported that the CNTs could significantly improve the tensile strength, hardness, and Yong's modulus of metallic matrix composites. Moreover, since the component of CNTs is graphite, CNTs have good self-lubricating property like graphite bulk. Therefore, it is expected that the incorporation of CNTs into Cu matrix could improve the mechanical and wear resistance properties of Cu matrix composites.

In general, the friction coefficient and wear loss of composites are often affected by microstructures of the composites. Therefore, to improve the interfacial wettability and enhance the interfacial bonding strength between CNTs and Cu matrix, a tungsten layer was deposited onto the surfaces of CNTs by metal organic chemical vapor deposition (MOCVD) in the present study. The W-coated CNTs (W-CNTs)/Cu composites were fabricated by magnetic stirring (MS) and spark plasma sintering (SPS) processes. The friction coefficient, wear loss and worn surface morphologies of W-CNTs/Cu composites were characterized in detail.

2. Experimental

Cu powder (purity> 99.7%, 10 μm in mean diameter, Beijing Xin Rongyuan Co., Ltd, China) and multi-walled CNTs (purity> 95.0%, 20-30 nm in diameter and 20-30 μm in length, Chinananotech, Co., Ltd, China) were used as

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starting materials in the present study.

The pristine CNTs were purified in a mixed solution of concentrated H_2SO_4/ HNO_3 (volume ratio 3:1) to remove the CNT catalysts and other impurities. Subsequently, the as-purified CNTs were ultrasonically cleaned for 2 h. Then the CNTs were washed with distilled water for several times and dried at 375 K in a vacuum drying chamber. The MOCVD process was used to deposit the tungsten layer onto CNTs. High-purity H_2 was used as the carrier gas and tungsten carbonyl complex ($W(CO)_6$) was selected as the precursor. The deposition temperature and holding time of MOCVD were set to 400 °C and 60 min, respectively. The reaction principle can be expressed as: $W(CO)_6 \xrightarrow[\text{CNTs}]{\Delta} 6CO + (\text{W-CNTs})$. The MOCVD process is schematically shown in Fig. 1.

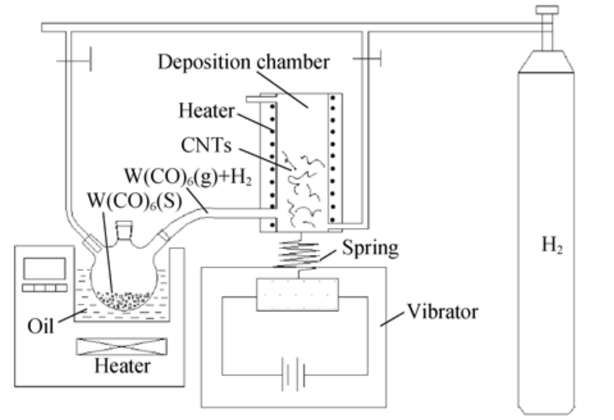

Fig. 1. Diagram of MOCVD for depositing W onto CNTs.

The as-obtained W-CNTs (0.5, 1.0, 2 and 3 wt.%) were dispersed into Cu powders using MS process with a stirring frequency of about 300 r/min. The W-CNTs were dispersed ultrasonically for 60-120 min in alcohol first. Subsequently, the Cu powders were added into the ultrasonic treated W-CNT suspension and stirred through MS for 120 min to ensure good dispersion of W-CNTs. After MS, the residual alcohol solvent was removed at 80 °C in a water-bath. The MSed powders were then consolidated by SPS (model 1050, Sumitomo Coal Mining Co. Ltd., Japan) at 850 °C with holding time of 5 min under a uniaxial pressure of 40 MPa. For comparison, the CNT/Cu composites with uncoated CNT reinforcement were fabricated by the identical processes.

The microstructure and morphology characterization were carried out on a Zeiss Supra55 field emission scanning electron micrograph (SEM) and a JEOL2100 transmission electron microscope (TEM). Actual density (ρ_{actual}) of the consolidated specimen was obtained using Archimedes' method, with distilled water as the intrusion medium. The relative density ($\rho_{relative}$) was estimated by calculating the ratio of ρ_{actual} to theoretical density ($\rho_{theoretical}$) of bulk, and the porosity of bulk was obtained as $1-\rho_{relative}$. Before friction and wear property testing, the specimens were polished using standard metallographic procedures, utilizing SiC sandpaper (300, 400, and 600 grit), followed by progressively smaller diamond slurries of 9, 3, 1, and 0.25 mm diameter. The friction coefficients of the specimens were measured by friction wear testing apparatus (WTM-2E, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences) at room temperature. The loads of 2, 3, 4 and 5 N were applied, and the sliding speed was 500 r/min. The friction counterpart was made of Si_3N_4 ceramic. The wear loss was got from the mass loss of the specimen after wear testing.

3. Results and discussion

3.1. The characterization of W-CNTs and CNTs

Fig. 2 shows the TEM morphologies of CNTs before and after purification treatment using concentrated H_2SO_4/HNO_3. As shown in Fig. 2(a), the pristine CNTs have residual metallic catalysts on their surfaces. In contrast, there are no apparent impurities on the surfaces of acid purified CNTs, as shown in Fig. 2(b). Moreover, after the concentrated H_2SO_4/ HNO_3 treatment, CNTs maintain their good surface structures. This indicates that the concentrated H_2SO_4/HNO_3 is

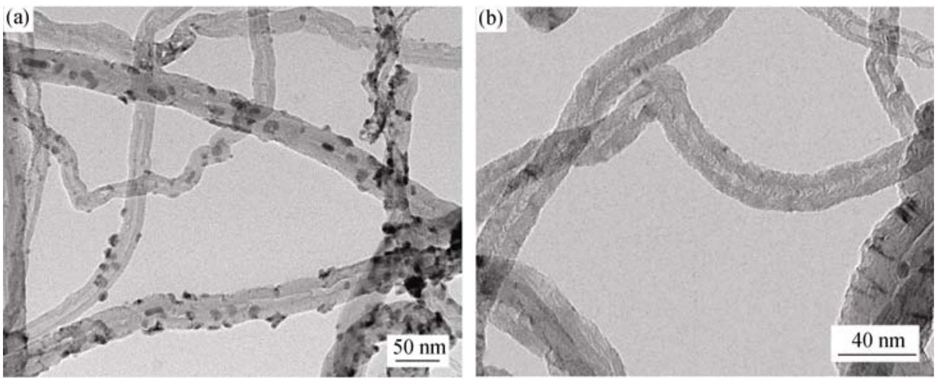

Fig. 2. TEM images of CNTs before (a) and after (b) purification treatment.

suitable for purifying the CNTs in our experiment.

The TEM morphology and energy spectrum of W-CNTs are shown in Fig. 3. As shown in Fig. 3(a), the W-CNTs obtain a dense and continuous W layer, which indicates that the MOCVD process is effective for obtaining uniform deposition of W onto CNTs. Fig. 3(b) is the energy spectrum image of W-CNTs containing W and C elements. The W and C elements are from the W layer and CNTs, respectively.

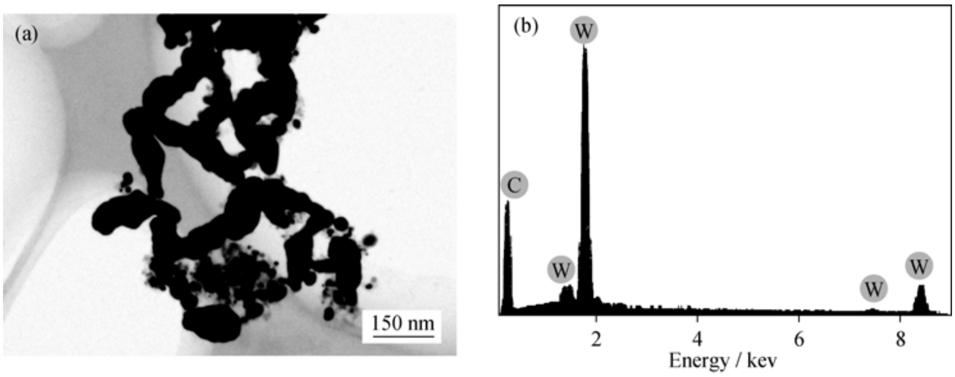

Fig. 3. TEM morphology (a) and the energy spectrum image (b) of W-CNTs.

3.2. TEM characterization of interfaces in the composites

The interfacial bonding between reinforcement and matrix plays very important role in the friction and wear properties of composites. The interfacial regions of W-CNTs/Cu and CNTs/Cu composites are characterized by TEM, and Fig. 4 shows the interfacial morphologies and diffraction spots of composites. Fig. 4(a) shows that the poor interfacial bonding with apparent pores and fissures at the CNTs-Cu interface is obtained for the CNTs/Cu composites, which is attributed to the poor interfacial wettability between CNTs and Cu matrix. Figs. 4(b) and 4(c) are the diffraction rings and spots of CNTs and Cu matrix, respectively. For the W-CNTs/Cu composites, the interfacial bonding between W-coated CNTs and Cu matrix is strong without the presence of pores or fissures. Fig. 4(e) is the high magnification image of Fig. 4(d), which further shows that the W-CNT reinforcement and Cu matrix obtain a good interfacial bonding strength. This indicates that the W layer effectively improves the interfacial wettability between CNTs and Cu matrix. Fig. 4(f) is the diffraction spots of W layer, showing no other impurities are introduced into W layer during specimen fabrication.

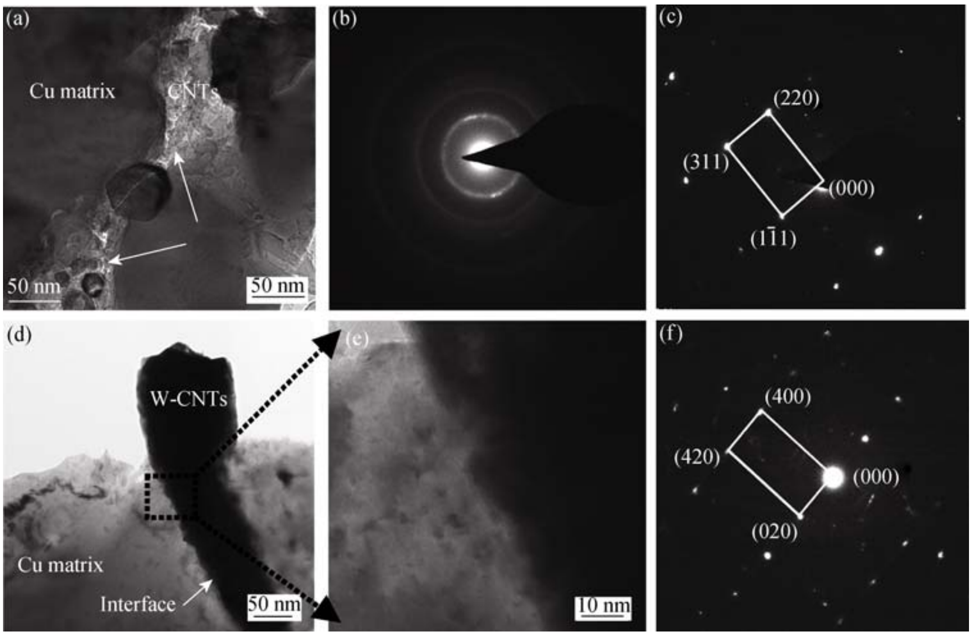

Fig. 4. TEM images of (a) CNTs-Cu interface region, (b) diffraction rings of CNTs, (c) diffraction spots of Cu matrix, (d) (W-CNTs)-Cu interface region, (e) the high magnification image of (d), and (f) diffraction spots of W layer.

3.3. The influence of W-CNT content on the friction and wear properties

Fig. 5 shows the results of friction coefficient (μ) of the 0 wt.%-3.0 wt.% W-CNTs/Cu composites. Within the range of W-CNT contents from 0 wt.% to 1.0 wt.%, the friction coefficient of W-CNTs/Cu composites decreases with increasing the W-CNT content. This may be attributed to that the increase in W-CNT content reduces the direct contact between the Cu matrix and the friction counterpart, and thus the friction coefficient of composites is reduced due to the self-lubrication of CNTs [9]. However, when the W-CNT content is up to 2.0 wt.%-3.0 wt.%, the friction coefficient begins to increase with increasing the W-CNT content, which can possibly be attributed to the high porosity of W-CNTs/Cu composites, as shown in Table 1. As reported in previous literatures [10-11], inhomogeneous microstructure with a large number of pores could result in the high friction coefficient of the composites. In addition, it can be seem in Fig. 5 that the friction coefficient of the composites with 1.0 wt.% W-CNTs is decreased by 27.9%, compared with that of pure Cu specimen, indicating the good friction coefficient reduction effect of W-CNTs.

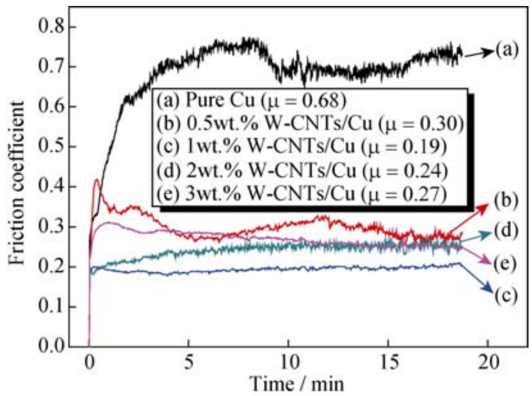

Fig. 5. The friction coefficients of W-CNTs/Cu composites containing (a) 0 wt.%, (b) 0.5 wt.%, (c) 1 wt.%, (d) 2 wt.%, and (e) 3 wt.% W-CNTs.

Table 1 shows the porosity and wear loss of W-CNTs/Cu composites with different W-CNT contents. It is obviously observed in Table 1 that the porosity of W-CNT/Cu composites is increased by increasing the W-CNTs content, and when W-CNT content reaches up to 2.0 wt.%-3.0 wt. %, the porosity is very high (2.7%-5.0%). The remarkable increase in porosity for the W-CNT/Cu composites with high W-CNT content is mostly attributed to the presence of agglomerations of W-CNTs in the composites due to the poor dispersion of 2.0 wt.%-3.0 wt.% W-CNTs [7, 12-13]. Under dry sliding wear condition, the wear loss of W-CNTs/Cu specimen is lower than that of pure Cu specimen, and the wear loss of the composite with 1.0 wt.% W-CNTs is 52.4% of that of pure Cu specimen, as shown in Table 1. This result means that the W-CMTs/Cu composite shows higher wear resistance compared with pure Cu specimen. In addition, Table 1 also shows that when W-CNT content is higher than 1.0 wt.%, the wear loss increases with increasing W-CNT content. This is because the high porosity in the composites degrades the wear resistance of composites with high contents of W-CNTs.

Table 1. The porosity and wear loss of W-CNTs/Cu composites as a of function of varying W-CNT content

W-CNT content / wt.%	Porosity / %	Wear loss / mg
0	1.1	0.82
0.5	1.3	0.55
1.0	1.5	0.43
2.0	2.7	0.57
3.0	5.0	0.63

Fig. 6 shows SEM images of worn surfaces of W-CNTs/Cu composites with different W-CNT contents. As shown in Fig. 6(a), the severe surface failure occurs in the worn surface of the pure Cu specimen. The detachment of the wear fragments and scars of plastic deformation by ploughing are evident in the surface of pure Cu specimen. Although furrow microstructures caused by ploughing effect can still be observed on the surface of the composites with 0.5 wt.% W-CNTs, the detachment of the wear fragments almost cannot be observed, as shown in Fig. 6(b). When the W-CNT addition is up to 1.0 wt.%, the composites shows almost clear surface morphology as shown in Fig. 6(c), indicating the good wear resistance for the composite, and this is mainly due to the self-lubricating effect and good dispersion of W-CNTs.

For the 2.0 wt.% and 3.0 wt.% W-CNTs/Cu composites, however, the micro-debris is removed from the surfaces of composites, as shown in Figs. 6(d)-6(e). This can be attributed to the appearance of high porosities in the composites. Generally, the pores in composites can act as preexisting incipient crack in the material, waiting to become unstable at an appropriate stress level [11]. If the formation of big crack caused by the joining pores occurs, the in-situ delamination in the subsurface layer of the composite would take place. The higher magnification worn surface (Fig. 6(f)) clearly shows the debris delamination on the surface of composites.

3.4. The influence of interfacial bonding on the friction and wear properties

In order to investigate the influence of W-metallization of CNTs on the friction coefficient and wear loss of the consolidated composites, the CNT/Cu composites reinforced by

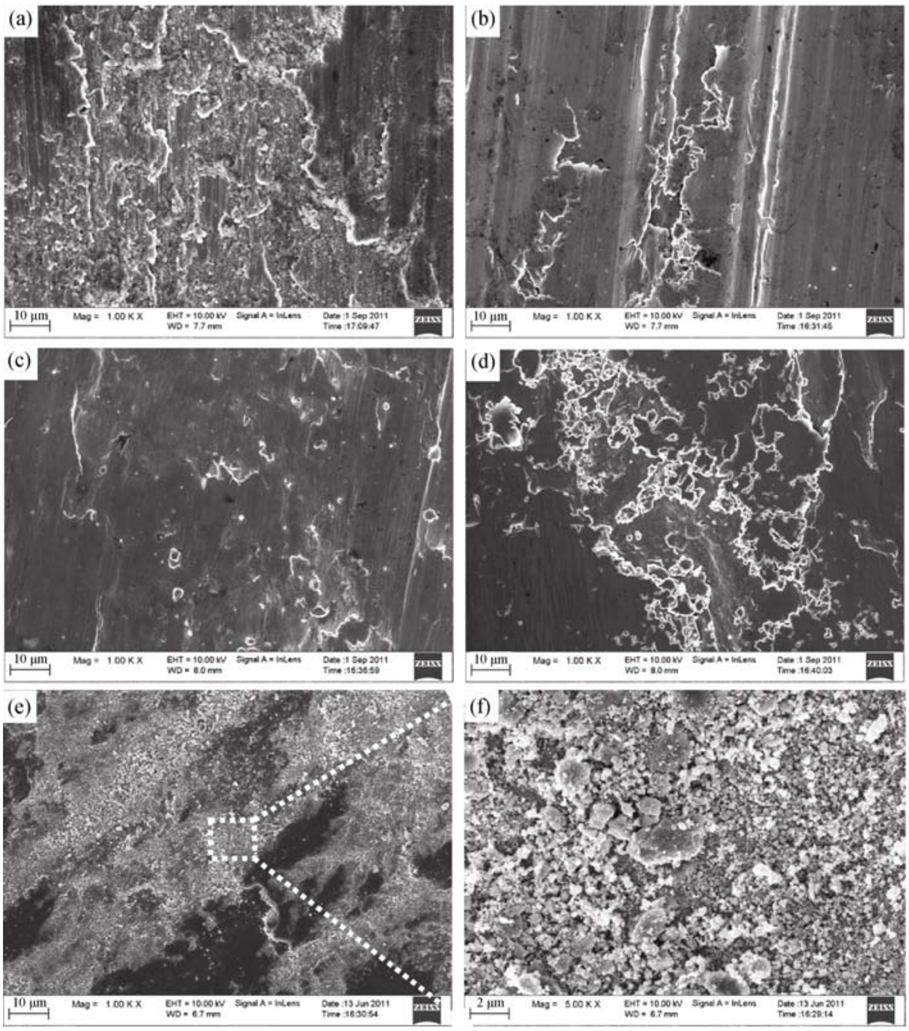

Fig. 6. Worn surface morphologies of the W-CNTs/Cu composites with different W-CNT contents: (a) 0 wt.%, (b) 0.5 wt.%, (c) 1 wt.%, (d) 2 wt.% and (e) 3 wt.%; (f) the higher magnification morphology of image (e).

uncoated CNTs were also fabricated using the same powder mixing and sintering processes. The friction coefficient and wear loss results are shown in Fig. 7 and Fig. 8, respectively. As shown in Fig. 7, the W-CNTs/Cu composites get lower friction coefficient than the CNTs/Cu composites containing the same CNT content. It is well accepted that the surface tension of Cu is about 1103 mN/m, while CNTs cannot be wetted by the materials with surface tension higher than 100-200 mN/m [14-15]. Thus, Cu and uncoated CNTs exhibit mutual insolubility, resulting in a poor interfacial bonding at their interface, as shown in Fig. 4(a). However, after the W-metallization of CNTs, the interfacial wettability between W-CNTs and Cu matrix can be improved, and thus results in an enhanced interfacial bonding between W-CNTs and Cu matrix (Figs. 4(d) and 4(e)) without the presence of pores or fissures. When the interfacial bonding is well, the CNTs can effectively reinforce the Cu matrix and exert the self-lubricating effect. However, when the interfacial bonding is weak, the debonding and pull-out of CNTs from Cu matrix can easily occur, which reduces the self-lubricating effect of CNTs. Therefore, the W-CNTs/Cu composites obtain the lower friction coefficients than the CNTs/Cu composites, as shown in Fig. 7.

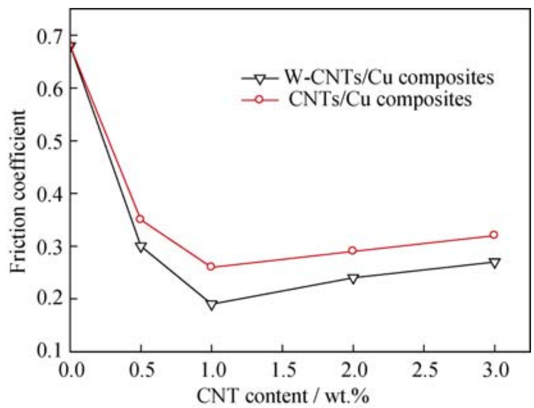

Fig. 7. Friction coefficients of W-CNTs/Cu and CNTs/Cu composites.

Fig. 8 shows the wear loss results of W-CNTs/Cu and CNTs/Cu composites. As shown in Fig. 8, the wear loss of W-CNTs/Cu composites is lower than CNTs/Cu composites with the same CNT content. This can also be attributed to the different interfacial bonding strengths for W-CNTs/Cu and CNTs/Cu composites. The presence of pores and fissures at CNTs-Cu interface can cause the formation of big cracks in the composites [11], and thus results in the flaking and spalling of Cu matrix [11]. As a result, the mass wear loss of the CNTs/Cu composites is higher than the W-CNTs/Cu composites.

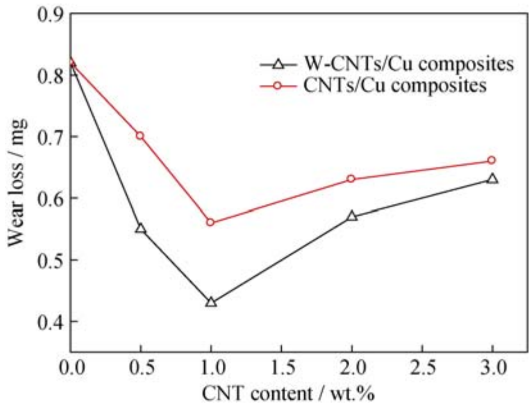

Fig. 8. The influence of interface on the wear loss for composites.

3.5. The influence of applied load on the friction and wear properties

The friction coefficients and wear losses of the W-CNTs/Cu composites containing 0 wt.%-3.0 wt.% W-CNTs at various loads (2N, 3N, 4N and 5N) were studied. Fig. 9 shows the friction coefficients of the composites, and it can be seen that the friction coefficients of the pure Cu specimen and W-CNTs/Cu composites slightly increase with increasing applied load. This indicates that the applied load has small influence on the friction coefficient of pure Cu specimen and Cu matrix composites.

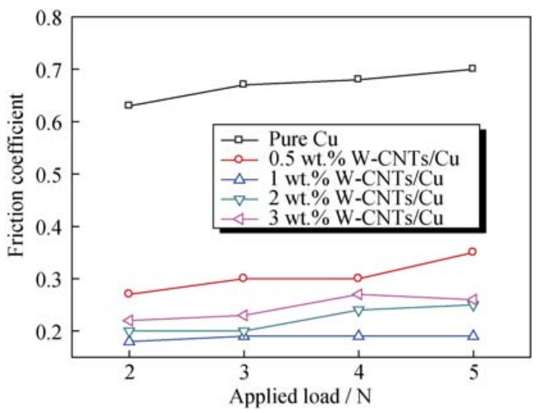

Fig. 9. The influence of applied load on the friction coefficient of W-CNTs/Cu composites.

Fig. 10 is the wear loss results of composites under different applied loads. As shown in Fig. 10, the wear loss of the W-CNTs/Cu composites increases with increasing applied load. According to Archard's formula [16]:

$$V = k\left(\frac{LS}{H}\right) \tag{1}$$

where V is wear loss of composites and k is a constant called wear coefficient. L and S stand for applied load and sliding distance, respectively, and H denotes the hardness of composites. The wear loss of composites would increase linearly with increasing applied load. In our case, the experimental wear loss results are consistent with Archard's theoretical results. In addition, the pure Cu specimen gives a greater rate of increase in wear loss than the composite, as shown in Fig. 10. This also indicates that the W-CNTs/Cu composite has excellent wear resistance in our case.

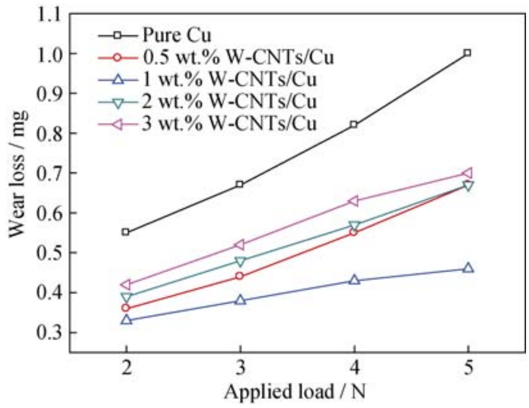

Fig. 10. The relationship between applied load and wear loss.

4. Conclusions

(1) When the W-CNT content was 1.0 wt.%, the W-CNTs/Cu composites got the minimum friction coefficient and wear loss. The friction coefficient and wear loss of W-CNTs/Cu composites containing 1.0 wt.% W-CNTs were decreased by 72.1% and 47.6%, respectively, compared with pure copper specimen.

(2) The interfacial bonding situations at reinforcement-matrix interfaces could affect the friction coefficient and wear loss of the composites. The friction coefficient and wear loss of W-CNTs/Cu composites were lower than those of CNTs/Cu composites, which was due to that the interfacial bonding at (W-CNTs)-Cu interface was better than that at CNTs-Cu interface.

(3) The friction coefficient and wear loss of the composites could be affect by the applied load. The friction coefficient of the composites did not vary obviously with increasing applied load, while the wear loss of the composites increased significantly with the increase of applied load.

Acknowledgements

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