ELSEVIER Science Press

Available online at www.sciencedirect.com
ScienceDirect

Trans. Nonferrous Met. Soc. China 27(2017) 2202−2213

Transactions of
Nonferrous Metals
Society of China

www.tnmsc.cn

Effects of environment on dry sliding wear behavior of silver−copper based composites containing tungsten disulfide

Ji-si WU[1], Jing-fu LI[1], Lei ZHANG[1], Zhi-yuan QIAN[2]

1. State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China;
2. Shanghai Key Laboratory of Spacecraft Mechanism, Shanghai 201109, China

Received 28 March 2016; accepted 20 February 2017

Abstract: Silver based composites containing different amounts of WS_2 were prepared by hot-pressing method and their tribological behaviors were investigated against coin silver under humid air, dry nitrogen and vacuum on a ball-on-disk tester with normal load of 5 N. The components of composites, microstructure of debris and worn surface were characterized using XRD SEM, EDS and XPS. It is demonstrated that environmental conditions significantly affect the tribological behavior of silver based composites. The friction coefficient is the highest in humid air, and the lowest in dry nitrogen. It is found that the friction and wear behavior of the composites are strongly depended on the characteristics of the lubrication film forming in different operating environments, such as thickness and composition. In addition, it is indicated that the dominant wear mechanisms of silver based composites are abrasive wear and delamination under different conditions.

Key words: self-lubricating composites; tribological behaviors; atmosphere; wear mechanism

1 Introduction

Silver matrix composites containing solid lubricant are known as self-lubricating materials, which are widely used as precision electrical contact elements in automatic control systems and high performance motor of aerospace industry [1]. It is well known that silver possesses the highest electrical and thermal conductivity, which results in the superior current carrying capacity. However, the low mechanical property and high seizure tendency with its counterpart during dry sliding are the main obstacles for its application [2]. Transition metal disulfides (MS_2, where M is molybdenum or tungsten) are known as solid lubricant, which are featured as a laminar structure. The weak van der Waals force between layers but strong covalent bond within the layer gives rise to the easy shearing of basal plane of transition metal disulfides, which resulted in the decrease of friction [3]. Aimed at the problems appearing in the application of silver, the use of composites combining silver and transition metal disulfides is the most effective way to make full use of their advantages, and finally provides antiwear and antifriction properties to sliding electrical contacts [4]. In view of this, many research efforts have been put forth on the factors related to the operating performance of silver based self-lubricating materials, including composition [5], testing parameters [6] and rubbing conditions [7], and many valuable achievements have been obtained.

At present, with the increase of the machinery complexity as well as the broadening of operating range and serve life, the improvement of operational applicability of these materials in a wide range of testing conditions, especially the solution to avoid adverse impacts of friction on efficiency and reliability, remains an issue of high engineering and scientific interest [8]. It is common knowledge that the tribological behavior of metal based self-lubricant composite is highly related to the mechanical properties of the composites [9]. In addition, more and more dedicated investigators have realized that the enhancement of lubricating ability of solid lubricants in severe environments is likely to be a more effective way to control friction and wear-related mechanical failures. Therefore, the research of the wear mechanisms and the applicability of metal based self-lubricant composites in various testing conditions, such as elevated temperature, corrosive solution and atmosphere are gaining high momentum in order to extend the practical applications of such materials [10,11].

Corresponding author: Lei ZHANG; Tel: +86-13975801816; E-mail: zhanglei@csu.edu.cn

DOI: 10.1016/S1003-6326(17)60246-2

The tribological properties of copper matrix composites containing MoS_2 and graphite were investigated with the environmental temperature ranging from −100 °C to 100 °C and the pressures ranging from ambient to as low as 10^{-4} Pa [12,13]. It has been found that the wear mode was transformed from oxidation and mild abrasive wear to severe adhesion as the testing condition changing from air at 25 °C to vacuum at −100 °C. What's more, the mechanically mixed layer on the worn surfaces, derived from work hardening, mechanical and chemical mixing of the wear debris, played a key role in reducing friction and wear. Operating atmosphere, such as inert gas as well as humid air, was also found to have significant impact on the tribological performance of metal based self-lubricant composites. The tribological test of powder metallurgical Ag−MoS_2−G composites was conducted in the mixture atmosphere of N_2 and O_2 [14]. It has been illustrated that the friction was exacerbated with the proportion of oxygen in O_2/N_2 atmosphere increasing due to the aggravated oxidation of MoS_2. Similar oxidation behavior was also detected on sputtered MoS_2 solid lubricant films [15−17], and the oxidation resistance and the wear life of such films will increase when it is deposited by sputtering with the addition of metal in a multilayer or composite structure [18−20].

In fact, WS_2 has a higher thermal stability withstanding temperatures (100 °C) compared with MoS_2 [21], which may provide a wider range of application as a solid lubricant. Unfortunately, the systematic study on the tribological properties of metal based composites containing WS_2 in different environments has been reported rarely. In addition, the connection between the tribological behavior of such materials and testing atmosphere has not been fully understood. In this work, the tribological behaviors of silver based composites containing different amounts of WS_2 fabricated by hot-pressing method against coin silver under humid air, dry nitrogen and vacuum were investigated on a ball-on-disk tribotester. Meanwhile, the composition and formation of tribolayer under different environments were studied in detail, and this investigation can provide some valuable information to utilize the silver based composites.

2 Experimental

2.1 Material preparation

Atomized silver−copper alloy powder (2.5% copper (mass fraction), 99.9% in purity, particle size <37 μm) and tungsten disulfide powder (99.8% in purity, particle size <1 μm) were homogeneously mixed in a ball milling jar for more than 24 h. The mixtures were then hot-pressed at 25 MPa under the protection of pure nitrogen atmosphere. The sintering process was carried out at 900 °C and maintained for 20 min. The content of tungsten disulfide in the prepared composites was varied from 8% to 24% (mass fraction).

For further investigation of the mechanical and tribological properties, the sintered materials were machined into 3 mm × 3 mm × 30 mm and 3 mm × 3 mm × 10 mm in size, respectively. The density of the composites was measured by the Archimedes principle. The hardness of the sintered material was measured using a Brinell hardness tester at a load of 625 N and ball indentation of 2.5 mm. And the bending strength was evaluated by a three-point bending tester. The components of composites were characterized using X-ray diffraction. Each test was repeated at least three times and the average value was reported.

2.2 Friction and wear tests

The friction and wear properties of the prepared composites were investigated using a pin-on-disc contact geometry on a CSM tribometer (see Fig. 1). The counterpart was coin silver with a Brinell hardness of HB 120. The equipment with a closed hood would be able to control atmosphere. When being tested in dry N_2, the hood was flushed with gas for about 20 min prior to the test and with a continuous flow during the whole tests to prevent any air to enter. Tests were performed in dry nitrogen (RH <5%), humid air (RH 70%) and vacuum (10^{-5} Pa), respectively. Prior to testing, the contacting surfaces of both the coin silver disc and pin specimens were lightly ground with 800, 1200, 1500 and 2000 grit SiC papers and then cleaned with acetone. Generally, high stability and reliability are main features for silver based self-lubricant materials used in precision instrument, thus the operating conditions are characterized as low load and speed. In this work, a certain amount of exfoliated tungsten disulfide which was proportional to the wear loss was necessary in order to gain insight into its reaction with atmospheres. Therefore, the sliding wear tests for AgCu−WS_2 composite were carried out under a comparatively high normal load of 5 N and sliding speed of 1 m/s. For each sliding condition, the coefficient of friction was continually recorded during the tests and the average value was calculated for each test within the distance of 10000 m, besides each sample was weighed before and after testing by a digital microbalance (0.1 mg in precision). The wear mass loss was calculated from the difference in the mass measured. The wear rate of the composites was calculated using the following formula: $w=m/(\rho Ps)$ [22], where w is the wear rate ($m^3/(N\cdot m)$); m is the wear mass loss (g); ρ is the density of specimens (g/cm^3); P is the normal load (N); s is the sliding distance (m). In order to obtain insight into the wear mechanisms involved, the microstructures of the worn surfaces and loose wear debris were investigated using a scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) analysis of the composition of the transfer film on the worn surface was also performed.

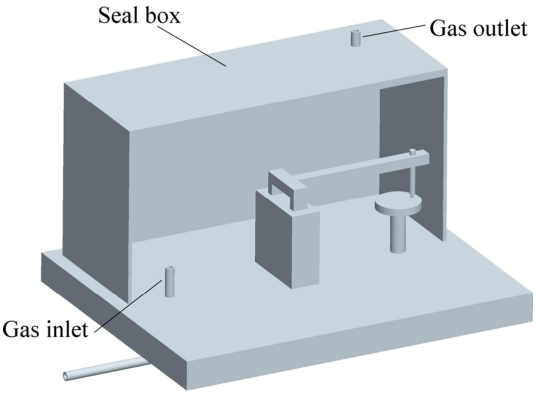

Fig. 1 Simple atmosphere control principle diagram of CSM tribotester

3 Results and discussion

3.1 XRD analyses and microstructure of composites

The XRD patterns of sliver−copper based composites in Fig. 2(a) indicate that WS_2 and Ag are dominate phases. The diffraction intensity of WS_2 is weaker than that of Ag, due to their amounts being too little. The metallographic structures of the Ag−Cu based composites with 8%, 16% and 24% WS_2 (mass fraction) are shown in Figs. 2(b), (c) and (d), respectively. The black areas in silver−copper matrix are WS_2 particles and these WS_2 particles are uniformly distributed throughout the silver−copper matrix in the form of small-sized aggregates. In addition, WS_2 aggregates grow with the increase of WS_2 content in the composites, which is resulted from the difficulty in uniformly dispersing large amount of WS_2 by ball milling. It is the evidence of weak interface bonding of silver−copper matrix composites containing relatively high amount of WS_2.

3.2 Mechanical properties of composites

The mechanical properties of the composites such as relative density, Brinell hardness and bending strength are investigated, as presented in Table 1. The relative densities of the composites are over 98%, which confirms the good sinterability of the composites.

The Brinell hardness of the composites increases from HB 57.8 to HB 68.9 due to the increasing of WS_2 content added into the composites as the reinforcement constituent. The variation of bending strength of the composites experiences a slight decrease with the increment of WS_2 content. This can be attributed to the relatively weak strength of AgCu/WS_2 interface bonding as compared to that of silver matrix, which can be

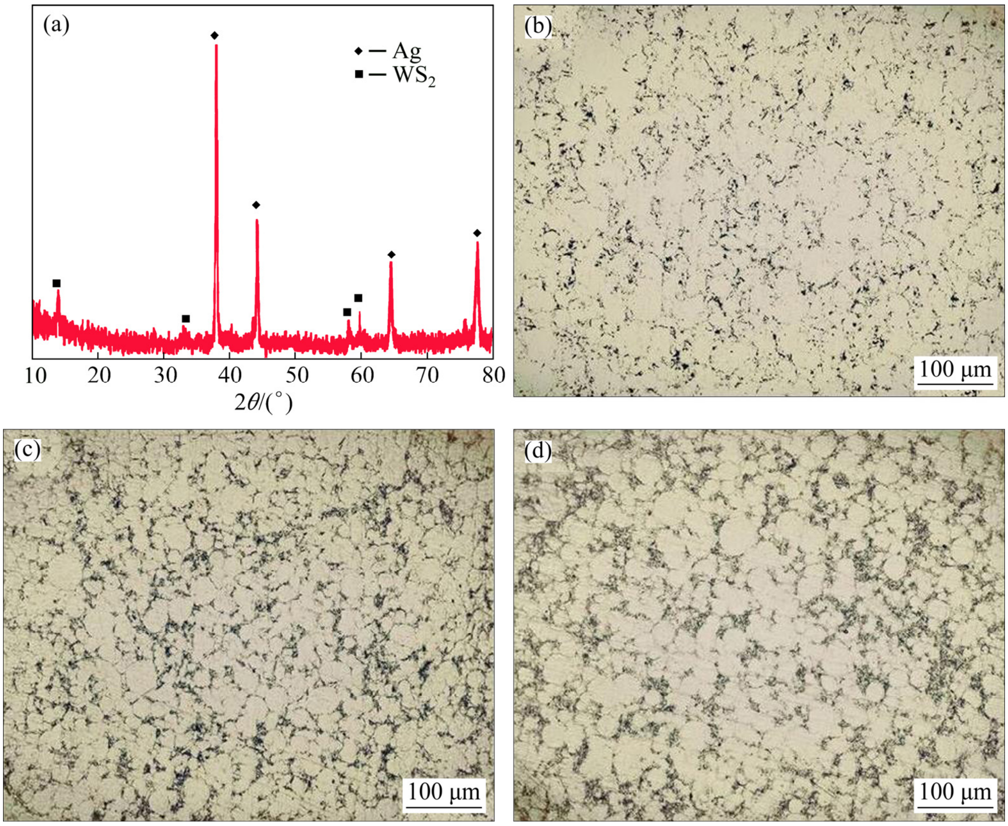

Fig. 2 XRD pattern of sliver−copper composites (a) and metallographic structures of silver−copper composites with 8% (b), 16% (c) and 24% (d) tungsten disulfide

Table 1 Physical and mechanical properties of AgCu−xWS$_2$ (x=8%−24%) composites

Mass fraction of WS$_2$/%	Relative density/%	Brinell Hardness (HB)	Bending strength/MPa
8	98.6	57.8	185
12	98.7	60.4	171
16	99.6	63.3	169
20	99.2	65.8	174
24	99.4	68.9	160

susceptible to the crack nucleation under pressure. The morphologies of fracture surfaces of the composites after the bending test are shown in Fig. 3. Pulling-out of the WS$_2$ plates can be clearly seen on the fracture surfaces. It may be concluded that the poor bonding strength of WS$_2$−AgCu interfaces is the primary factor responsible for the reduced bending strength of the composites.

3.3 Friction and wear properties

The average friction coefficients of the composites with different WS$_2$ contents are shown in Fig. 4(a). When the composites are tested in humid air, the friction coefficients are reduced from 0.23 to 0.19 as the WS$_2$ content is increased from 8% to 24%. And the composites tested in dry nitrogen also exhibit a reduction from 0.15 to 0.09. The result of the reduction of friction coefficient with the increment of WS$_2$ content could attribute to the formation of a WS$_2$-rich transfer film on the worn surfaces, which can prevent direct contact of the pins with the rotating coin silver disc surface and change the nature of contact from metal–metal to metal–film–metal. More importantly, the WS$_2$ content in the transfer film is highly related to the WS$_2$ content of the composites. Hence, the composites containing higher amount of WS$_2$ have superior antifriction properties. The dynamic friction coefficients of the composites in different environments are shown as a function of sliding distance in Fig. 4(b). As can be seen in Fig. 4(b), the friction behavior depicts marked changes whenever environment is altered. For each composite, the value of friction coefficient in air is significantly higher than that in vacuum and dry N$_2$ environments. In addition, the curves of friction coefficient in air exhibit relatively larger amplitude of fluctuation. However, it is interesting to note from Fig. 4(b) that the friction coefficient curves in vacuum and dry N$_2$ environments are fairly smooth. The obtained results confirm that the efficiency of self-lubrication of WS$_2$ is influenced by testing environments, and then it displays larger self-lubrication level under vacuum and dry nitrogen than in humid air.

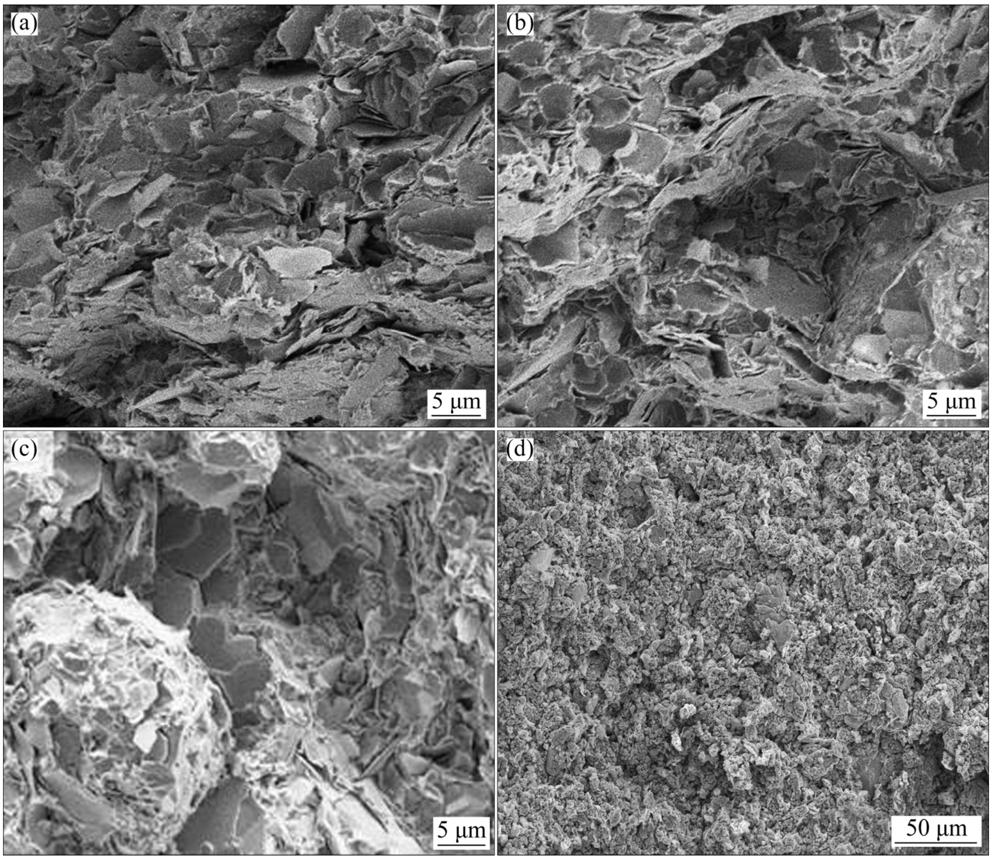

Fig. 3 SEM micrographs of fracture surfaces of silver−copper composites with different contents of tungsten disulfide: (a) 8%; (b) 16%; (c, d) 24%

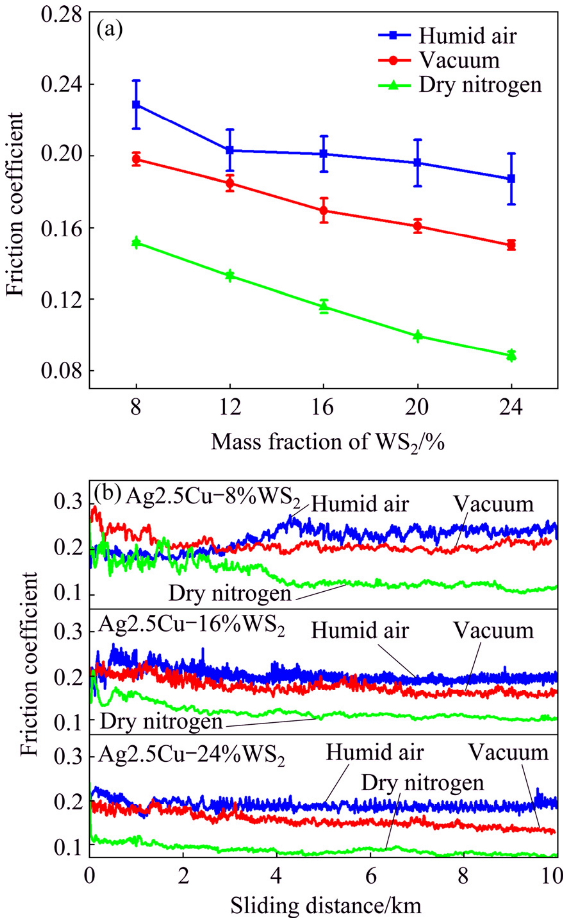

Fig. 4 Friction coefficients of AgCu−WS_2 composites in different environments: (a) Average friction coefficient; (b) Dynamic friction coefficient

The wear rates of the composite in various sliding environments are shown in Fig. 5. It can be observed that the wear rates of the composites show decreasing trends with the increment of WS_2 content in the composites. Moreover, the effect of environments on the wear behaviors is also remarkable. It is revealed in Fig. 5 that the composites present the lowest wear rate in dry N_2 environments, which might be due to the higher levels of WS_2 content. Interestingly, a relatively low wear rate is also achieved, when the composites are slipped in humid air. However, the wear rate of the composites in vacuum condition is the highest among the three testing conditions, which does not follow the variation trend of friction coefficients. Based on the above results, the friction and wear behavior of AgCu−$x$$WS_2$ (x=8%−24%) composites are thoroughly different with the variation of testing atmosphere. In addition, the effect of the environments on the friction and wear behaviors is more pronounced with the increase of WS_2 content in the composites (as shown in Fig. 4 and Fig. 5) Therefore, in the following sections, the worn surfaces and wear debris of silver−copper based composites containing high amount of WS_2 (AgCu−24%WS_2) are analyzed in order to demonstrate the relation between testing environments and tribological behaviors of the self-lubricating composites.

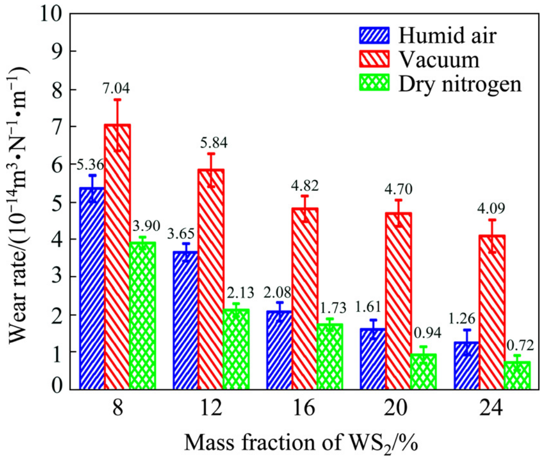

Fig. 5 Relation between testing environments and wear rate

3.4 Characterization of worn surfaces and wear debris

The typical morphologies of worn surfaces of the AgCu−24%WS_2 composite in the three testing conditions are shown in Fig. 6. There are considerable abrasive grooves and wear fragments on the worn surface tested in air, which is due to the ploughing of hard particles, such as surface asperities, and work-hardened wear debris generated during repeated sliding contact. Moreover, the high-magnification SEM image of the worn surface (Fig. 6(b)) shows the presence of cracks generated by the spalling or delamination process. Delamination is a fatigue-related wear mechanism and is created by the repeat sliding-induced subsurface cracks on the wear surface that gradually grow and eventually extend to the surface. It is believed that these cracks have a direct relation with the morphologies of wear debris and the wear loss of composite [23]. It can be observed in Fig. 6(c) that the worn surface tested in vacuum is less coarse than that in air; however, there are considerable amounts of surface damages, as shown in Fig. 6(d). The surface damage is characterized as delamination scars and many voids filled by fine fragments, which indicates the strong adhesion and seizure between the two contact surfaces. Sliding test performed under vacuum allows the preparation of the surface of low degree contamination, thus the surface of the composites will be covered by an oxide film which may be only a few nanometers thick [15]. Adhesion between the composites and the coin silver surfaces becomes very large when this thin oxide film is melt off by the frictional heat at the beginning of the sliding, which aggravates the wear loss of the composites in vacuum. Figures 6(e) and (f) exhibit

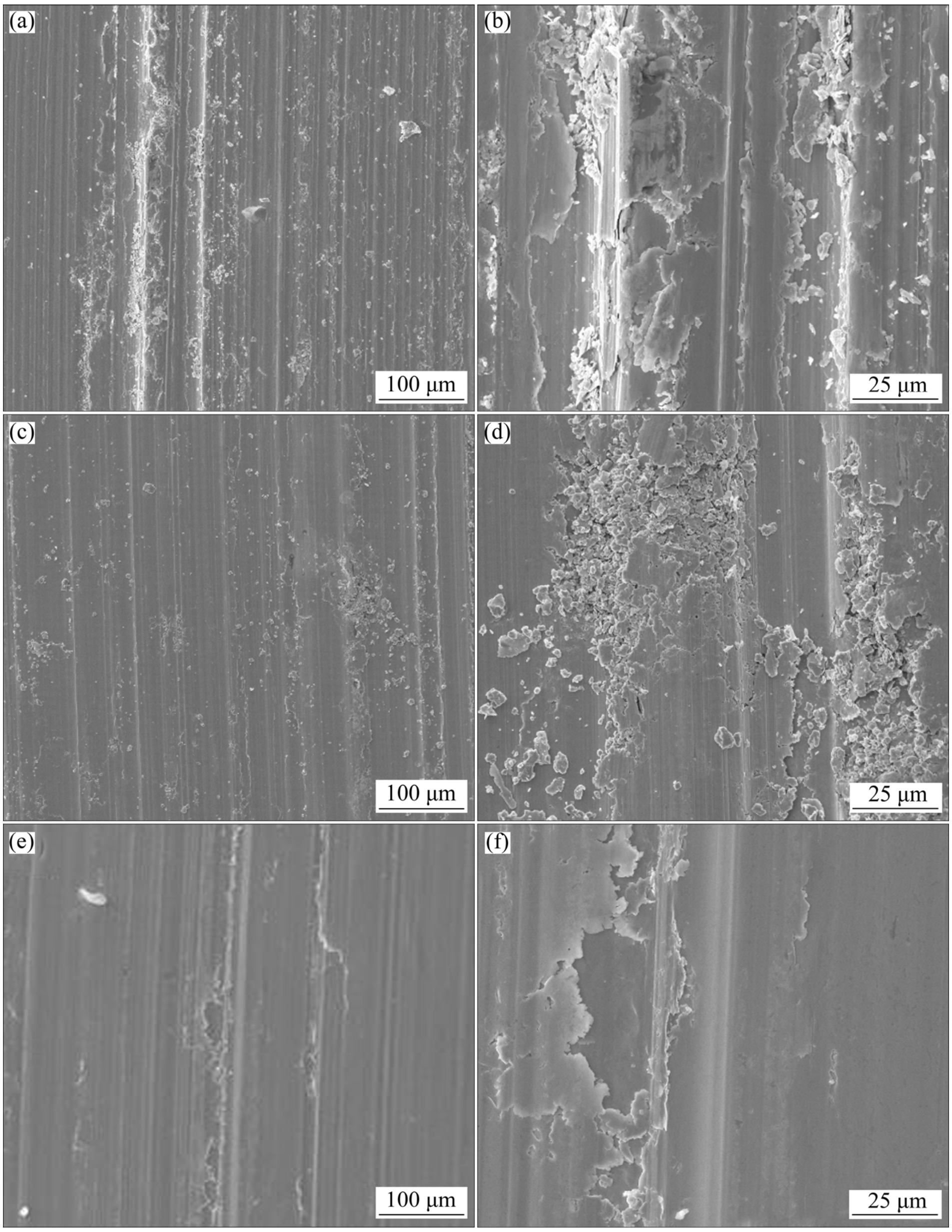

Fig. 6 Low and high magnification images of worn surfaces of AgCu−24%WS_2 tested in different environments: (a, b) Humid air; (c, d) Vacuum; (e, f) Dry nitrogen

the worn surface of the composite tested in dry N_2 environment. As can be seen, the surface has a high flatness, although a few abrasive grooves can also be observed; moreover, it should be noted that no obvious breakage is found on the worn surfaces. The superior tribological properties of the composites in N_2 condition indicate the protective effect of N_2 during sliding.

The types of wear debris offer clues to the wear mechanisms involved. Figure 7 shows the typical SEM micrographs of the collected wear debris of AgCu−24%WS_2 composite in three testing environments. Thin sheet-like debris along with ribbon-like, long wear debris collected on the worn surfaces of the composites sliding in air, as shown in Fig. 7(a), is typical of delamination and abrasive wear. However, fine equiaxed particles and large layered sheet-like debris are observed while sliding in vacuum. It has been reported previously [24] that when two clean solid surfaces brought into contact in vacuum environment, micron-sized contact junctions exhibiting strong adhesion between contacting metals would be formed, which may be responsible to the initial high friction coefficients of the composites sliding in vacuum (Fig. 4(b)). The generation of fine equiaxed wear debris might be attributed to the breakage of these adhesion junctions between the contact surfaces by tangential stress, and the large layered sheet-like debris indicates the occurrence of delamination-related wear on the composite. In the case of sliding in dry N_2, the wear process of the composite generally tends to form relatively small size wear debris, which is similar to the fine-equiaxed particles collected on the worn surfaces tested in vacuum. Besides, thin sheet-like debris also appeared but the amount and size of the wear debris were much less than those in other two testing environments. The above findings about the morphologies of wear debris together with the worn surfaces sliding in dry N_2 (Figs. 6(e) and (f)) illustrate that the plastic deformation of the composite during repeated sliding is comparatively slight, and the dominant wear mechanisms of the composite sliding in N_2 are mild adhesion and delamination.

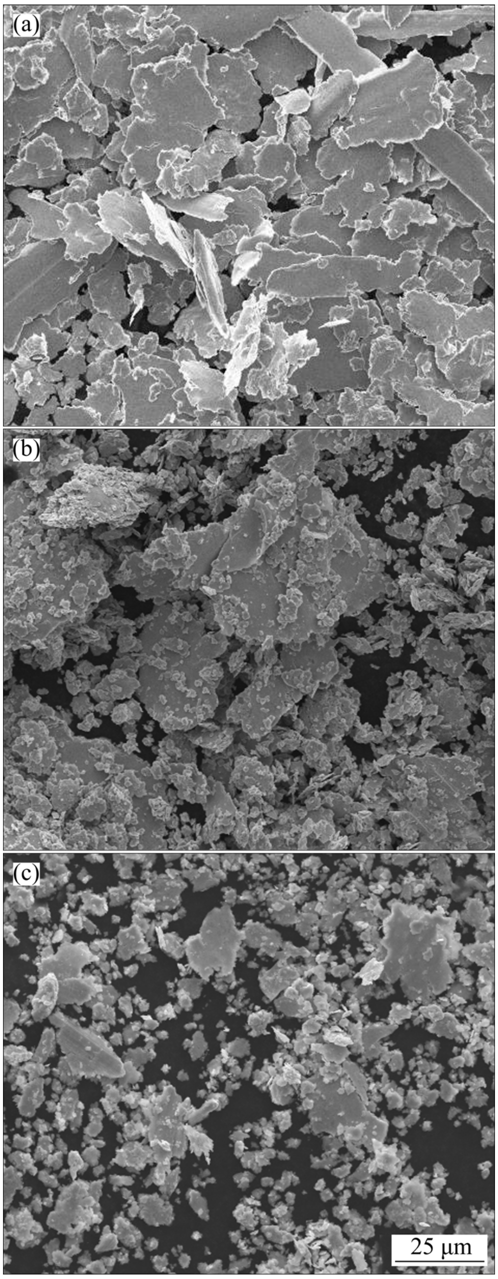

Fig. 7 Typical SEM images of wear debris of AgCu−24%WS_2 tested in different environments: (a) Humid air; (b) Vacuum; (c) Dry nitrogen

3.5 XPS analysis of worn surfaces

In order to obtain insight of the characteristics of the transfer film formed on the worn surfaces, XPS analyses of the worn surfaces are conducted and illustrated in Fig. 8. The intensity of the W 4f, and S 2p peaks which is proportional to the relative molar fraction of these elements on the outermost worn surface is much higher than that in the matrix, which confirms the accumulation of WS_2 on the worn surface during sliding. An ion etching technique affiliated with XPS was also used to measure the thickness of the transfer film. The accumulated ion etching time was in the range of 0−90 s and the ion etching speed was about 0.7 nm/s. The variation of relative molar fraction with etching time is given in Table 3. According to the method [9] to determine the area fraction of the solid lubricant on the worn surface, it can be calculated that about 58% and 83% of the worn surface area was covered by WS_2 transfer film when the composite slide in dry N_2 and vacuum, respectively, compared to only 30% in the composite. And for the composite sliding in humid air, about 44% (molar fraction) of oxygen was detected on the worn surface, which demonstrates the formation of an oxidation film on worn surface. The thickness of the transfer film can be also calculated, according to Table 3. The molar fractions of W and S elements experience a decreasing trend with the increment of etching depth. For the composite tested in dry N_2, the molar fractions of W and S elements were reduced to 6.26% and 8.95%, respectively, as the accumulated etching time reached 90 s, which is consistent with the WS_2 content in the matrix; hence, the thickness of WS_2 film is about 60 nm. However, when the composite slide in vacuum, the relative molar fraction of W and S elements almost stayed constant as the etching time exceeded 30 s; thus, the thickness of the WS_2 film is less than 20 nm.

Figure 9 shows the typical XPS spectra of W 4f of AgCu−24%WS_2 composite on the outermost worn surface tested in various environments. A marked change of the spectrum shape can be observed when the test condition varies from air to dry N_2 environment and the unremarkable variation between the composite tested in contamination-free environments (without water vapor and oxygen) and the as-prepared composite indicates the ratios of various W valence states vary with the test environment due to the formation of W oxides. As previously reported [25,26], the binding energy of W 4f will be shifted to the higher energy side as the WS_2 is oxidized, and the binding energies of W 4f from WS_2, WS_xO_y and WO_3 are located at 32.7, ~33.8 and ~35.3 eV, respectively. The low sulfur compounds of WS_xO_y and WO_3 are the oxidation products of WS_2 which might be formed during the fabrication and sliding process of the composites. To precisely identify the change of tungsten

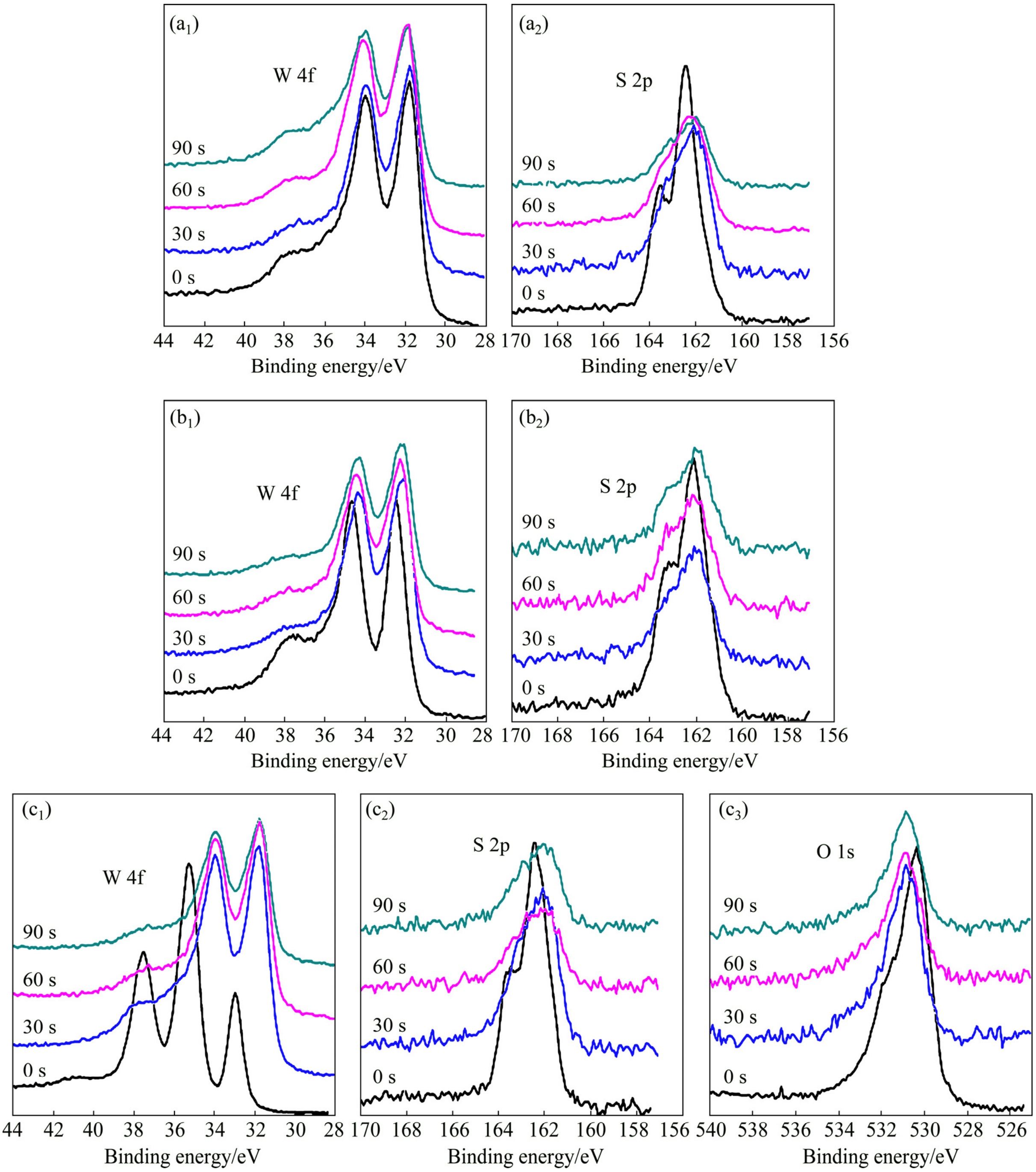

Fig. 8 XPS spectra of W 4f, S 2p and O 1s of composite tested in different environments: (a_1, a_2) Dry nitrogen; (b_1, b_2) Vacuum; (c_1, c_2, c_3) Humid air

Table 3 Relative molar fractions (%) of partial elements with variation of etching time

Etching time/s	In humid air			In dry nitrogen		In vacuum	
	W	S	O	W	S	W	S
0	11.30	19.10	44.06	19.74	28.33	18.22	30.33
30	12.72	15.52	25.21	12.22	20.80	7.23	9.30
60	10.43	11.18	14.27	8.68	14.87	5.19	7.87
90	7.78	10.80	8.00	6.26	8.95	5.67	8.01

containing compound in different conditions, the W 4f spectra were fitted using the Lorentzian–Gaussian function, as illustrated in Fig. 9. The results show that the tungsten valence states of as-prepared composite consist of a great deal of W^{4+} as in WS_2 along with a few of W^{n+} as in WS_xO_y, while only a small fraction (less than 10%) of W^{6+} as in WO_3 is detected which is due to the slight oxidation of WS_2 during sintering processes. Similar results about the tungsten valence states have been detected on the worn surface of the composite sliding in

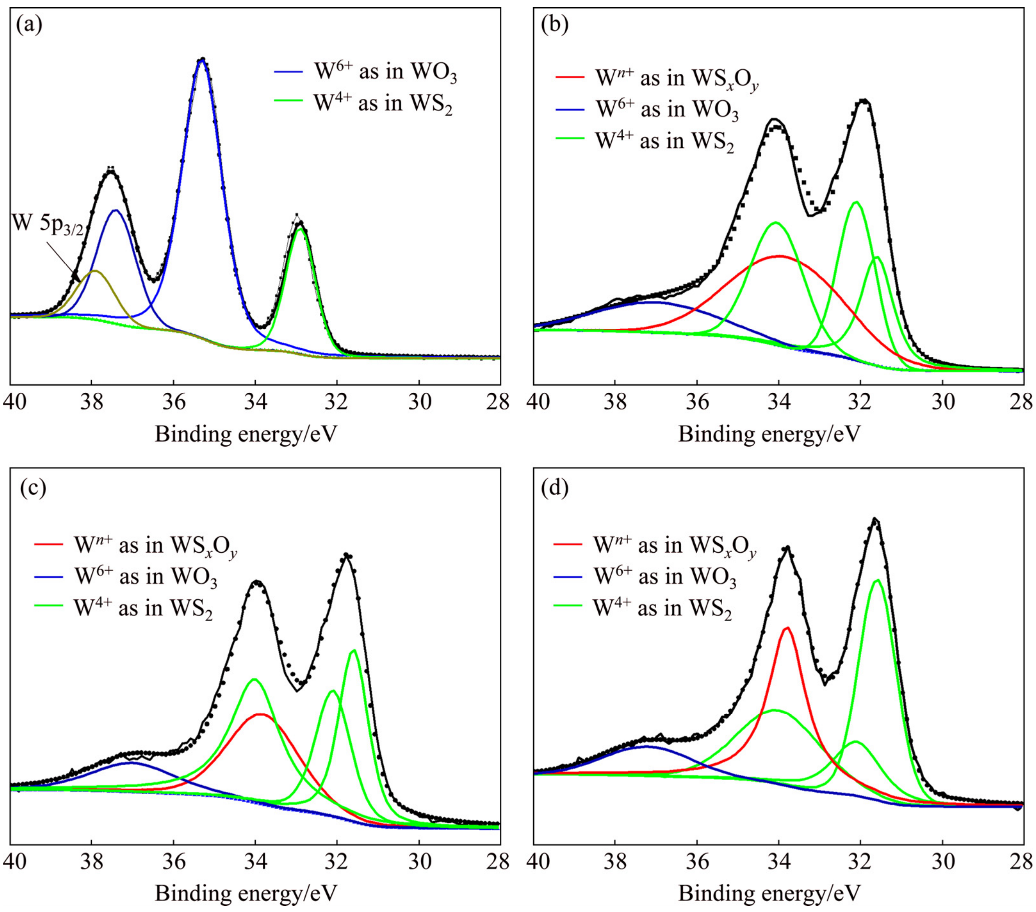

Fig. 9 Fitted XPS spectra of W 4f of AgCu−24%WS_2 composite tested in different environments: (a) Humid air; (b) Vacuum; (c) Dry nitrogen; (d) As-prepared composite

dry N_2 and vacuum environments, which demonstrates that the laminar WS_2 is largely retained after sliding. Similar oxidation behavior has been detected on the WS_2 film by GUSTAVSSON et al [27]. However, the worn surface sliding in air was seriously oxidized, and the relative molar fraction of W^{6+} as in WO_3 is about 83% which is 4 times higher than that of W^{4+} as in WS_2. This means that most of the laminar WS_2 on the contact area is transformed into WO_3 which displays almost no lubricating effect; in other words, there remains only a small amount of WS_2 which is much less than the nominal content in the composites, acting as lubricant. The above findings demonstrate that the lubricating ability of WS_2 is largely restricted in humid air, which explains the higher fluctuation and value of friction coefficients tested in air than those tested in other two contamination-free environments.

4 Discussion

The distinct tribological behaviors of the composites in the three testing environments demonstrate that the lubricating ability of WS_2 is significantly affected by the chemical/physical reaction between WS_2 and the test atmosphere (water vapor, oxygen and nitrogen). Figure 10 shows the schematic diagram of possible reactions between WS_2 and atmosphere. It is well known that good lubricating property of the lamellar solid lubricants such as WS_2, MoS_2 and graphite is due to the lamellar crystal structure, the weak van der Waals bonding between the lamellae and the low shearing force of the layers responsible for the low friction. In the present work, as the sliding goes on, the wear of the metal matrix occurs, and meanwhile, WS_2 particles are also squeezed out from the subsurface of the matrix to the sliding surface. The integrity of the crystalline of WS_2 is partially destroyed by friction force; thus, active sulfur atoms or dangling covalent bonds at the newly exposed edges are formed. In the case of humid air, the presence of humidity and oxygen can lead to considerable deterioration of the lamellar structure of WS_2. As reported previously [28,29], water molecules in the humid air will adhere to dangling bonds and active sulfur atoms of WS_2 at edge sites and defects, and this adhesion will alter the electron distribution in the crystallites by attracting electrons, which results in reduced repulsion or even attraction between the lamellae and thus significantly high shear strength. This leads to an increased friction. The water is also suggested to form hydrogen bonds between the planes [27]. The H-bond will connect the lamellae together and strengthen the adhesion. Oxygen is another factor causing the structure deterioration of WS_2 by oxidizing or substituting of sulfur within WS_2 by oxygen (as schematically illustrated in Fig. 10), because of the generation of low sulfur compound of WS_xO_y and WO_3. When being tested vacuum and dry N_2, the composites exhibit lower friction coefficients, which indicates the superior friction-reducing ability of WS_2 in vacuum and dry N_2. More importantly, owing to the physical absorption of N_2 to the active sulfur atoms and the gap between two basal planes [15], the passivation of dangling covalent bonds occurs which allows easy slip of the two basal planes; hence, the lubricating efficiency of WS_2 is largely enhanced. As a consequence, the low friction coefficient is obtained by the composites sliding in dry N_2 even though the minimum amount of WS_2 is smeared on the sliding surface (Fig. 11(a)). In addition, Ag phase was dispersed in the thick WS_2 film during the friction and wear process, and the Ag-rich surface layer is formed due to the plastic flow of Ag on the film surface, which can prevent the shearing deformation of WS_2 film and improve the resistance of crack initiation and propagation [30,31]. As a result, the tribological properties of sliver−copper based composites are improved and wear life of composites is extended.

There are considerable factors related to the wear loss of the silver self-lubricating composites, such as hardness of the matrix [32], the coverage area and adhesion ability of lubricating film on the worn surfaces [33]. According to the distinct wear behaviors of the composites tested in the three different environments in this work, sliding atmosphere also has a major impact on the wear rates by changing the nature of transfer film on the worn surface. In vacuum environment (Fig. 11(b)), as mentioned before, the strong adhesion between the contacting samples aggravates the wear; besides, during sliding the temperature of contacting surfaces is high because there is no air convection for cooling during sliding, and the high flash temperature may soften the formed transfer film which might be quickly removed by the sweeping action of sliding surfaces [22]. Thus, the detected film thickness in vacuum is below 20 nm which is much thinner than that formed in dry nitrogen. As a consequence, the transfer film would be self-healed to maintain dynamical equilibrium of the sliding contact in the expense of severe wear of the softer AgCu−WS_2 composites. Similar observations were reported on Cu−MMC operated in vacuum [12]. In humid air, the accumulation and compaction of the wear debris as well as the oxidation of the worn surface can give rise to the formation of a continuous protective film (the dark area in Fig. 11(c)) which is derived from work hardening, mechanical and chemical mixing of the wear debris and other contaminants in the surface material, therefore, mild wear of the composites sliding in humid air is observed.

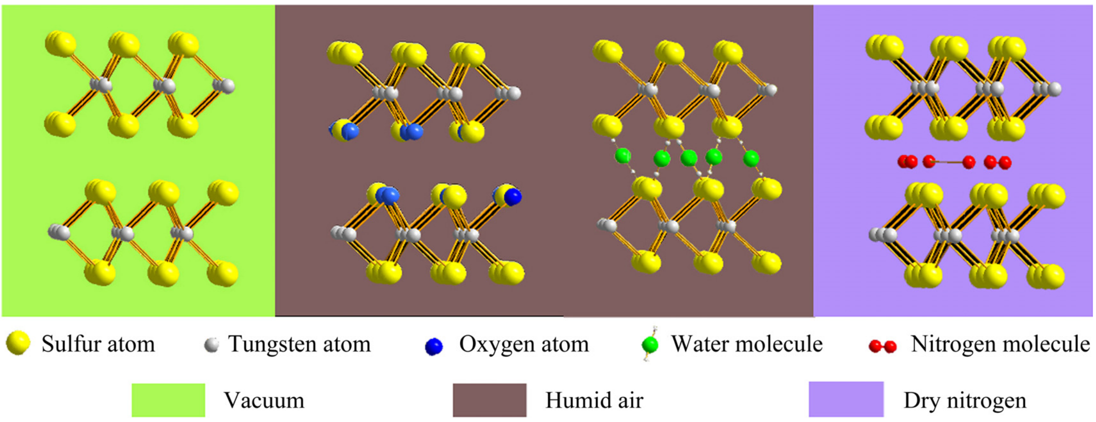

Fig. 10 Schematic illustration of interaction between WS_2 and atmosphere during sliding

Fig. 11 Optical images of wear tracks of coin silver tested in different environments: (a) Dry nitrogen; (b) Vacuum; (c) Humid air

5 Conclusions

1) The analysis of the features of the transfer film on the worn surface tested in various environments reveals the enrichment of WS_2 on the worn surfaces during sliding, and the WS_2 content on the worn surfaces is a dominant factor directly related to the friction coefficient and wear rate of self-lubricating composites.

2) In humid air, higher friction coefficients and fluctuations of are obtained. However, the wear resistance of the composites is improved due to the protection of the oxidation film formed on the worn surfaces. When being tested in dry N_2, the lubricating efficiency of WS_2 is largely improved, therefore, reduced friction coefficients and wear rate are obtained. In vacuum, the friction coefficients of the composites are also at a relatively low level but the wear rate is the highest, due to the weak adhesion of transfer film to the worn surfaces.

3) The prominent wear mechanism of the composites sliding in humid air is abrasive wear as well as delamination. In addition, strong adhesion is observed on the worn surfaces tested in vacuum; while in dry N_2, mild adhesion and delamination are dominant.

References

[1] ROBERTS E W. Space tribology handbook [M]. 3rd edition. Warrington, UK: AEA Technology Plc, 2002: 72−76.

[2] HE Da-hai, MANORY R. A novel electrical contact material with improved self-lubrication for railway current collectors [J]. Wear, 2001, 249: 626−636.

[3] WINDOM B C, SAWYER W G, HAHN D W. A Raman spectroscopic study of MoS_2 and MoO_3: Applications to tribological systems [J]. Tribology Letters, 2011, 42: 301−310.

[4] BRATERSKAYA G N, ZATOVSHII V G. Wear resistance of sliding electrical contacts of silver-base composite materials [J]. Poroshkovaya Metallurgiya, 1984, 5: 75−79.

[5] JOHNSON R L, SWIKERT M A, BISSONI E E. Friction and wear of hot-pressed bearing materials containing molybdenum disulfide [R]. Washington, USA: NASA Technical Note, 1950, TN 2027.

[6] TYAGI R, XIONG Dang-sheng, LI Jian-liang. Effect of load and sliding speed on friction and wear behavior of silver/*h*-BN containing Ni-base P/M composites [J]. Wear, 2011, 270: 423−430.

[7] LIU Hsing-pang, CARNES R W, GULLY J H. Effect of temperature on wear rate of homopolar pulse consolidated electrical brushes [J]. Wear, 1993, 167: 41−47.

[8] DONNET C, ERDEMIR A. Solid lubricant coatings: Recent developments and future trends [J]. Tribology Letters, 2004, 17: 389−397.

[9] CAO Hui-quan, QIAN Zhi-yuan, ZHANG Lei, XIAO Jin-kun, ZHOU Ke-chao. Tribological behavior of Cu matrix composites containing graphite and tungsten disulfide [J]. Tribology Transactions, 2014, 57: 1037−1043.

[10] ZHENG X H, TU J P, LAI D M, PENG S M, GU B, HU S B. Microstructure and tribological behavior of WS_2–Ag composite films deposited by RF magnetron sputtering [J]. Thin Solid Films, 2008, 516: 5404−5408.

[11] ZABINSHI J S, BULTMAN J E, SANDERS J H, HU J J. Multi-environmental lubrication performance and lubrication mechanism of $MoS_2/Sb_2O_3/C$ composite films [J]. Tribology Letters, 2006, 23: 155−163.

[12] XIAO Ye-long, YAO Ping-ping, ZHOU Hai-bin, ZHANG Zhong-yi, GONG Tai-min, ZHAO Lin, ZUO Xiao-ting, DENG Min-wen, JIN Zong-xiang. Friction and wear behavior of copper matrix composite for spacecraft rendezvous and docking under different conditions [J]. Wear, 2014, 320: 127−134.

[13] LI Jing-fu, ZHANG Lei, XIAO Jin-kun, ZHOU Ke-chao. Sliding wear behavior of copper-based composites reinforced with graphene nanosheets and graphite [J]. Transactions of Nonferrous Metals Society of China, 2015, 25: 3354−3362.

[14] CHEN Fan-yan, FENG Yi, SHAO Hao, ZHANG-Xue-bin, CHEN Jie, CHEN Nan-nan. Friction and wear behaviors of $Ag/MoS_2/G$ composite in different atmospheres and at different temperatures [J]. Tribology Letters, 2012, 47: 139−148.

[15] GARDOS M N. Anomalous wear behavior of MoS_2 films in moderate vacuum and dry nitrogen [J]. Tribology Letters, 1995, 1: 67−85.

[16] EFEOGLU I, BARAN Ö, YETIM F, ALTINTASl S. Tribological characteristics of MoS_2–Nb solid lubricant film in different tribo-test conditions [J]. Surface and Coatings Technology, 2008, 203: 766−770.

[17] VIERNEUSEL B, SCHNEIDER T, TREMMEL S, WARTZACK S, GRADT T. Humidity resistant MoS_2 coatings deposited by unbalanced magnetron sputtering [J]. Surface and Coatings Technology, 2013, 235: 97−107.

[18] KAO W H. Tribological properties and high speed drilling application of MoS_2−Cr coatings [J]. Wear, 2005, 258: 812−825.

[19] JING Yang, LUO Jian-bin, PANG Si-pin. Effect of Ti or TiN codeposition on the performance of MoS_2-based composite coatings [J]. Thin Solid Films, 2004, 461: 288−293.

[20] ARSLAN E, BVLBVL F, ALSARAN A, CELIK A, EFEOGLU I. The effect of deposition parameters and Ti content on structural and wear properties of MoS_2 Ti coatings [J]. Wear, 2005, 259: 814−819.

[21] XU Shu-sheng, GAO Xiao-ming, HU Ming, SUN Jia-yi, JIANG Dong, ZHOU Feng, LIU Wei-min. Nanostructured WS_2–Ni composite films for improved oxidation, resistance and tribological performance [J] Applied Surface Science, 2014, 288: 15−25.

[22] HUANG Shi-yin, FENG Yi, LIU Hong-juan, DING Ke-wang, QIAN Gang. Electrical sliding friction and wear properties of Cu–MoS_2–graphite–WS_2 nanotubes composites in air and vacuum conditions [J]. Materials Science and Engineering A, 2013, 560: 685−692.

[23] ZHANG Lei, XIAO Jin-kun, ZHOU Ke-chao. Sliding wear behavior of silver−molybdenum disulfide composite [J]. Tribology Transactions, 2012, 55: 473−480.

[24] BRAUNOVIC M, MYSHKIN N K, KONCHITS V V. Electrical contacts: Fundamentals, applications and technology [M]. Columbus, USA: CRC Press, 2010.

[25] XU Shu-sheng, GAO Xiao-ming, HU Ming, SUN Jia-yi, JIANG Dong, WANG De-sheng, ZHOU Feng, WENG Li-jun, LIU Wei-min. Dependence of atomic oxygen resistance and the tribological properties on microstructures of WS_2 films [J]. Applied Surface Science, 2014, 298: 36−43.

[26] MARTIN-LITAS I, VINATIER P, LEVASSEUR A, DUPIN J C, GONBEAU D, WEILL F. Characterisation of rf sputtered tungsten disulfide and oxysulfide thin films [J]. Thin Solid Films, 2002, 416: 1−9.

[27] GUSTAVSSON F, SVAHN F, BEXELL U, JACOBSON S. Nanoparticle based and sputtered WS_2 low-friction coatings−Differences and similarities with respect to friction mechanisms and tribofilm formation [J]. Surface and Coatings Technology, 2013, 232: 616−626.

[28] FLEISCHAUER P D. Fundamental aspects of the electronic structure, materials properties and lubrication performance of sputtered MoS_2 films [J]. Thin Solid Films, 1987, 154: 309−322.

[29] FLEISCHAUER P D, LINCE J R, BERTRAND P A, BAUER R. Electronic structure and lubrication properties of molybdenum disulfide: A qualitative molecular orbital approach [J]. Langmuir, 1989, 5: 1009−1015.

[30] WANG H D, XU B S, LIU J J. Micro and nano sulfide solid lubrication [M]. Beijing: Science Press, 2012: 274−278. (in Chinese)

[31] LAI D M, TU J P, ZHANG S C, WANG Q, PENG S M, HE D N. Friction and wear properties of sputtered WS_2/Ag nanocom posite films in different environments [J]. Tribology, 2006, 6: 515−519.

[32] RUPERT T J, SCHUH C A. Sliding wear of nanocrystalline Ni–W: Structural evolution and the apparent breakdown of Archard scaling [J]. Acta Materialia, 2010, 58: 4137−4148.

[33] RAJKUMAR K, ARAVINDAN S. Tribological behavior of microwave processed copper–nanographite composites [J]. Tribology International, 2013, 57: 282−296.

不同氛围下 AgCu−WS_2 复合材料的干摩擦磨损行为

吴集思 [1]，李景夫 [1]，张 雷 [1]，钱志源 [2]

1. 中南大学 粉末冶金国家重点实验室，长沙 410083；
2. 上海宇航系统工程研究所，上海 201109

摘　要：通过粉末冶金热压法成功制备出了具有不同 WS_2 含量的银基复合材料，并对其进行了对偶材料为银盘，湿大气、干氮气和真空条件下，载荷为 5 N 的球盘式摩擦磨损试验。通过 X 射线衍射(XRD)、扫描电镜(SEM)、能量色谱(EDS)和 X 射线光电子能谱对材料的组成，磨屑及磨损表面分别进行表面形貌表征、表面元素分析和元素价键分析。研究表明，摩擦氛围对此类银基复合材料的摩擦学行为具有较大影响，在湿大气中呈现出较高的摩擦系数，而在干氮气中摩擦系数最小。进一步研究表明，摩擦环境对材料摩擦过程中润滑膜的形成具有重要影响，主要是膜的厚度与组成。此外，不同的摩擦环境下，磨粒磨损和分层是此类银基复合材料的主要磨损机制。

关键词：自润滑复合材料；摩擦学行为；气氛；磨损机制

(Edited by Bing YANG)