Friction of metal-matrix self-lubricating composites: Relationships among lubricant content, lubricating film coverage, and friction coefficient

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Abstract: Metal-matrix self-lubricating composites can exhibit excellent tribological properties owing to the release of solid lubricant from the matrix and the formation of a lubricating film on the tribosurface. The coverage of the lubricating film on a worn surface significantly influences the sliding process. However, it is difficult to quantify the film coverage owing to the thin and discontinuous character of the lubricating film and the high roughness of the worn surface. A quantitative characterization of the lubricating film coverage based on X-ray photoelectron spectroscopy (XPS) analysis was developed in this study. The friction tests of Cu-MoS₂ composites with a MoS₂ content of 0–40 vol% were conducted, and the worn surfaces of the composites were observed and analyzed. Further, the influence of the MoS₂ volume content on the coverage of the lubricating film on the worn surface was investigated. The relationships among the volume fraction of the lubricant, coverage of the lubricating film, and the friction coefficient were established. The friction model for the metal matrix self-lubricating composites was developed and verified to facilitate the composition design and friction coefficient prediction of self-lubricating composites.

Keywords: self-lubricating composites; friction coefficient; lubricating film; XPS

1 Introduction

Metal-matrix self-lubricating composites (MMSCs) are widely used in tribological applications wherein oil or grease lubrication cannot be implemented [1–3]. MMSCs are fabricated using two constituent components: a metal matrix and reinforced solid lubricant particles. Graphite, molybdenum disulfide, tungsten disulfide, and black phosphorus are widely used solid lubricants. They have a lamellar crystal structure with stacked layers weakly bonded with each other, while the bonding within the layers is quite strong. Thus, the shearing of the layers is easy [4–6]. MMSC is self-lubricating because of the transfer of the solid

lubricant to the tribosurface and its formation into a thin film, which can prevent direct contact between the two mating surfaces. As an MMSC can maintain a continuous supply of solid lubricant to replenish the lubricating film formed at the tribosurface, it could provide effective lubrication throughout a long-term frictional operation [7–9].

The solid lubricant content significantly influences the tribological performance of MMSCs. Several researchers have found that the friction coefficient of MMSCs decreases with the increase in the lubricant content and reaches a minimum at a certain critical lubricant content [10–13]. Rohatgi et al. [14] stated that when the graphite content of metal-matrix composites

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Nomenclature

V	Volume fraction of solid lubricant	μ	Friction coefficient
α_f	Area fraction of lubricating film	μ_m	Friction coefficient of metal matrix
α_m	Area fraction of metal matrix	μ_f	Friction coefficient of lubricating film
k	Lubricating efficiency of lubricant		

exceeds approximately 20 vol%, the friction coefficient approaches that of pure graphite and becomes independent of the matrix alloy. The wear resistance of MMSCs can also be greatly improved by using a certain amount of lubricant. Therefore, determining the relationship between the lubricant content and friction coefficient is essential for the design of MMSCs that provide an optimal tribological performance. Axén et al. [15] developed a model for calculating the friction of multiphase materials in abrasion. The model is based on the equal pressure or equal wear between the phases, and the total friction force is the sum of the contributions from each phase. The main limitation of the model is the consideration of only the effect of pressure and wear on the area fraction of the reinforcing phase on the worn surface. Similar models have also been proposed in other studies [7, 16]. Furthermore, the chemical composition of the surface is very different from that of the matrix after the occurrence of friction. The surface composition of MMSCs not only depends on the lubricant content, but also on the experimental conditions such as load, sliding speed, temperature, and mating surface. Hence, it is difficult to establish an accurate quantitative relationship between the composite lubricant content and the surface lubricant content.

During dry sliding, the subsurface metal undergoes severe deformation under the combined action of a normal force and friction force. The solid lubricant particles embedded in the matrix are then squeezed out and smeared to the tribosurface. The continuously smeared lubricant layers form a lubricating film on the tribosurface. It is well known that the formation of a lubricating film greatly depends on the solid lubricant content in the composite. As the lubricant content increases, a greater number of lubricant particles are released, which aids in the formation of a continuous lubricating film. Many experiments and simulations have been focused on the study of

lubricating film thickness. Song et al. [17] presented a model that could predict the thickness of the lubricating film under the condition that the ceramic composite behaves macroscopically elastically, while the inclusions in the second phase material undergo locally plastic deformation. Valefi et al. [18] proposed a physical model for the process of the formation and removal of the soft layer. The model was developed based on the mechanical stresses in the soft second phase and the elastic-plastic contact between the rough and flat surfaces. Based on this model, the thickness of the soft surface layer on a ceramic substrate was predicted. Xu et al. [19] developed an approximate model for the migration of a solid lubricant on MMSCs. The mechanism of solid lubricant migration was investigated, and the thickness of transferred film onto the worn surface was calculated under various parameters. However, the research on the coverage of a lubricating film has progressed slowly.

Bowden et al. [20] proposed that friction was a linear function of the boundary film area fraction. Hence, the coverage of the lubricating film is an important parameter in tribology [21–24]. The film coverage has been defined as an area ratio of the tribosurface covered by the lubricant to the total tribosurface. Many works have identified that the tribosurfaces of self-lubricating composites are rich in lubricant, but the exact coverage fraction of the lubricating film on the tribosurface is unknown [13, 14]. In order to study the influence of the lubricating film on the friction coefficient, the coverage of the lubricating film has to be quantitatively characterized. The difficulty in the characterization of the film coverage lies in the thin and discontinuous character of the lubricating film and rough worn surface. The majority of qualitative analyses of the coverage of the surface film was performed using optical or electron microscopy [25, 26]. However, a high image contrast is required between the area that is covered and not

covered by the lubricant film. Our previous works have demonstrated that X-ray photoelectron spectroscopy (XPS) is an effective and reliable analytical method for lubricating film characterization [27, 28]. XPS has also been applied for analyzing the chemical composition and thickness of the lubricating film [29, 30].

Therefore, the main aim of this work is to establish the relationships among the lubricant content, lubricating film coverage, and friction coefficient for understanding the friction behavior of self-lubricating composites. A new method that can be used to quantitatively characterize the coverage of the solid lubricating film on the tribosurface of the self-lubricating composites was developed. The friction behavior of Cu-MoS₂ composites with a MoS₂ content of 0–40 vol% was investigated. To identify the MoS₂ lubricating film formed, the worn surfaces of Cu-MoS₂ composites were observed and analyzed using scanning electron microscopy (SEM) and XPS. Based on the developed XPS analysis method, the MoS₂ film coverage on the worn surfaces of Cu-MoS₂ composites was quantitatively characterized. The friction model for the MMSCs was developed.

2 Method for quantifying lubricating film coverage

2.1 Lubricating film formation and friction model

A MMSC contains a certain amount of solid lubricant with particles homogeneously filled in the matrix. The evolution of the lubricating film on its contacting surface during sliding is illustrated in Fig. 1. Before sliding, the contact surface of the MMSC is partially

covered by a solid lubricant of area fraction of α_f , which is equal to the volume fraction of the solid lubricant (V) in the composite. During sliding, the metal matrix undergoes severe plastic deformation that is induced by the applied load and friction force. The solid lubricant particles are then squeezed out from the matrix and smeared onto the tribosurface, thus forming a lubricating film. Owing to the smearing of the lubricant particles, the coverage area of the lubricant on the tribosurface increases from V to $2V$ and even to kV . In addition, the structure of the subsurface layer also changes, and the lubricant content in it shows an increasing trend from the composite matrix to the outmost worn surface. The outmost worn surface may not be totally covered by the lubricating film. Generally, the greater the lubricant content, the greater the amount of lubricant that is released and the larger the area fraction of the lubricating film. Hence, the area fraction of the lubricating film (α_f) on the tribosurface greatly depends on the volume fraction of the solid lubricant (V) in the composite, which is represented as follows:

$$\alpha_f = kV \quad (1)$$

where k represents the lubricating efficiency of the lubricant; it indicates the ability of the solid lubricant to form a lubricating film on the worn surface during sliding. The area fraction of the metal matrix (α_m) can be expressed as

$$\alpha_m = 1 - \alpha_f \quad (2)$$

Generally, the friction coefficient of MMSCs is expressed by the rule of mixture as the sum of the

Fig. 1 Schematic showing the evolution of lubricating film on worn surface of MMSC.

friction coefficients acting on each phase [31],

$$\mu = \alpha_m \mu_m + \alpha_f \mu_f \quad (3)$$

where μ_m and μ_f are the friction coefficients of the metal matrix and lubricating film, respectively. However, this equation cannot be used to describe the real phenomenon, because a transfer layer with the same composition as an MMSC is often generated on the counter surface during sliding [32].

Accordingly, the friction of the MMSC includes three contact models: metal–metal contact, metal–lubricating-film contact, and lubricating-film–lubricating-film contact [33]. The three contact models along with the related contact rates and friction coefficients of the MMSC are illustrated in Table 1. According to the classical theory of Bowden and Tabor [20], friction force is determined by the real contact area and the shear strength of the lubricant material. Therefore, the friction force of the metal–lubricating-film contact is almost equal to that of the lubricating-film–lubricating-film contact. As a result, it can be justifiably assumed that the latter two models produce the same friction coefficients as that of the lubricating film (μ_f). Moreover, based on the results reported in the literatures, the counter surfaces of MMSCs are usually covered with continuous transfer layers, which have the same chemical composition as MMSCs; thus, the lubricating film on the transfer layer can be assumed to have an area fraction equivalent to that of the worn surface of the composite [13, 28]. The contact rates for the metal–metal contact, metal–lubricating-film contact, and lubricating-film–lubricating-film contact are $\alpha_m \alpha_m$, $2\alpha_m \alpha_f$, and $\alpha_f \alpha_f$, respectively. Therefore, the friction coefficient of the MMSCs can be expressed as

$$\mu = (\alpha_m^2) \mu_m + 2(\alpha_m \alpha_f) \mu_f + (\alpha_f^2) \mu_f \quad (4)$$

On combining Eqs. (2) and (4), we obtain

$$\mu = (1 - \alpha_f)^2 \mu_m + (1 - (1 - \alpha_f)^2) \mu_f \quad (5)$$

On combining Eqs. (1) with (5), we obtain the friction coefficient of the MMSCs:

$$\mu = (1 - kV)^2 \mu_m + (1 - (1 - kV)^2) \mu_f \quad (6)$$

2.2 Quantification of lubricating film coverage using XPS

The quantitative characterization of the lubricating film coverage is obtained using XPS. XPS is an effective and reliable analytical method for elemental identification and the quantification of the chemical states of active surface atoms because it is surface-sensitive and non-destructive. XPS analysis is performed by irradiating a sample with monoenergetic soft X-rays and energy analyzing the electrons emitted. The spectrum obtained is a plot of the number of emitted electrons per energy interval versus their kinetic energy. Each element has a unique elemental spectrum, and the spectral peaks from a mixture are approximately the sum of the elemental peaks from the individual constituents. The quantitative data of elements can be obtained from the peak areas. As the mean free path of the electrons is very small, the electrons that are detected originate only from the top few atomic layers. The sampling depth (3λ for Al K α radiation) for the XPS is 3 nm–10 nm, and the sampling spot size can be 15 μm –500 μm . As the thickness of the lubricating film can reach hundreds of nanometers, sputter depth profiling was often used along with XPS. The compositional in-depth distribution of thin films and coatings can be directly determined using depth profiling [34–36].

The schematic of the method used for the quantitative

Table 1 Contact models of MMSC.

Contact model	Metal–metal	Metal–film	Film–film
Schematic
Contact rate	$\alpha_m \alpha_m$	$2\alpha_m \alpha_f$	$\alpha_f \alpha_f$
Contact rate	$(1 - kV)^2$	$2(1 - kV)kV$	$(kV)^2$
Friction coefficient	μ_m	μ_f	μ_f

characterization of the lubricating film coverage using XPS analysis developed in this research is illustrated in Fig. 2. The first step of the measurement is to immediately place the samples of MMSC into the XPS instrument after the friction testing and evacuate for testing. Secondly, the first XPS analysis on the typical region of the worn surface is conducted followed by ion etching at the same position of the surface using an argon ion gun. After a few dozens of nanometers of atoms are etched from the surface, the second XPS analysis is performed on the etched area. In this manner, the processes of analysis and etching are repeated several times until no obvious change in XPS spectra is obtained. The surface layer has then been totally sputtered, and the internal microstructure of composite is exposed. No further changes in chemical composition will be observed in the depth profiling. Thus, a continuous analysis of the composition from the outmost worn surface to the internal material is achieved. The evolution of the lubricating film on the worn surface during Ar^+ sputtering is shown in Figs. 2(a) and 2(b). Thirdly, based on the XPS spectra, the atomic percentage of the elements on the surface can be obtained using Avantage software. The atomic percentage of elements is multiplied by the relative atomic mass to obtain the weight percentage of the elements. The weight percentages of the elements of the same compound are summed and then divided by the density of the compound. The volume fraction

of the materials on the worn surface can then be obtained. The expected obtained XPS result is shown in Fig. 2(c). Finally, the XPS results of the lubricant content are compared in the unchanged stage with the filled lubricant content to check the accuracy of the XPS analysis. The value of the coverage fraction of the lubricating film is equal to the volume fraction of the lubricant detected on the worn surface. Therefore, the lubricating film coverage of the MMSCs can be successfully characterized using XPS analysis.

3 Experimental details

3.1 Materials

The Cu-MoS₂ composites with various volume fractions of MoS₂ were prepared using the powder metallurgy route with hot-pressing. The copper powder was first mixed with MoS₂ powder having an average particle size of 5 μm using a planetary mill. The mixed powder was then hot-pressed in a graphite die at a sintering temperature of 850 $^{\circ}\text{C}$ and pressure of 25 MPa for 40 min. The furnace was filled with nitrogen as a protective gas. The Cu-MoS₂ composites with MoS₂ contents of 0, 5 vol%, 10 vol%, 20 vol%, 30 vol%, and 40 vol% were prepared using this method. The microstructure of the prepared Cu-MoS₂ composites is shown in Fig. 3. The gray areas are the MoS₂ particles, and the bright area is the copper matrix. It can be observed that the MoS₂ particles have a flake-like

Fig. 2 Schematic illustrating the evolution of lubricating film on worn surface during Ar^+ sputtering process, (a) cross section of worn surface, (b) worn surface, (c) XPS analysis results.

Fig. 3 Microstructure of Cu-MoS₂ composites with MoS₂ content of (a) 10 vol%, (b) 20 vol%, (c) 30 vol%, and (d) 40 vol%.

shape. The MoS₂ particles are uniformly distributed throughout the copper matrix.

3.2 Friction testing

The friction experiments were performed using a tribometer (UMT-2, Bruker Instrument, USA) with a pin-on-disc configuration. The sample pins had a circular arc profile with a radius of 25 mm. The counter disc was fabricated from beryllium copper with a diameter of 60 mm and hardness of 361 HV1. The pins and discs were polished and cleaned before the testing. Sliding tests were performed at a constant normal load of 5 N. The rotational speed was 200 rpm, and the rotational radius was set to 20 mm. The corresponding linear speed was approximately 0.42 m/s. The sliding distance was set as 15 km. The tests were performed in an ambient environment with an approximate temperature of 20 °C and relative humidity of 60%. Three parallel tests were performed.

3.3 Film characterization

The morphologies of the structure and worn surfaces of the Cu-MoS₂ composites were investigated using a field-emission SEM (Supra 55, Zeiss, Germany) in backscatter mode to differentiate between the phases by relative density. The element distribution in the worn surfaces was analyzed using energy-dispersive X-ray spectroscopy (EDS) equipped in SEM. The worn surfaces of the Cu-MoS₂ composites were investigated using XPS (Escalab 250Xi system, Thermo Fisher, UK) with a monochromated Al-K α X-ray source (excitation energy = 1486.6 eV). The XPS analysis chamber was evacuated to a pressure of 10 Pa–6 Pa before the analysis. An X-ray spot size diameter on the sample of approximately 500 μ m was adopted. Survey spectra were acquired from 0 eV–1200 eV in the constant-analyzer-energy mode with a pass energy of 100 eV and energy-step size of 0.5 eV. Two scans were averaged in the measurement of one spectrum. The binding energies were corrected relative to the C1s signal at 284.8 eV. The thickness of the lubricating film reached hundreds of nanometers. However, the XPS analysis could only analyze the surface with a maximum depth of 10 nm. In order to perform the depth profiling of the worn surfaces, Ar⁺ ions produced by the affiliated ion gun with an energy of 3 keV

were used for the sputtering procedure. The sputtering rate was approximately 0.33 nm/s, which was calibrated against a reference silicon oxide thin film on the silicon substrate. The sputtered area of 2.5 mm $\times$ 2.5 mm was much larger than the X-ray spot size. The accumulated etch time was set as 0 s, 25 s, 50 s, 75 s, 100 s, 150 s, 200 s, 300 s, 500 s, 700 s, 900 s, and 1000 s, and after each etching process, a survey spectrum was collected to detect the element content. XPS data acquisition and analysis were completed using Avantage software supplied by the equipment manufacturer. Concentration quantification was performed using standard single element sensitivity factors.

4 Results and discussion

Figure 4 presents the backscattered electron (BSE) images and EDS mapping images of the worn surfaces of the Cu-MoS₂ composites with various MoS₂ contents. The dark areas in the BSE images are covered by MoS₂ films of a low thickness, while the bright areas are copper matrices. The distribution of the MoS₂ film on the worn surfaces is also confirmed using EDS mapping. The BSE and EDS images reveal that the MoS₂ film area clearly increases as the MoS₂ content increases in the composites. The grooves and plastic deformation in the worn surfaces are reduced by the formation of the lubricating film. To clearly observe the distribution of the MoS₂ crystals on the worn surface, a field emission SEM (FE-SEM) observation was performed, and the image of the worn surface of Cu-30-vol%-MoS₂ composite is shown in Fig. 5. The worn surface is covered by a large number of MoS₂ lamellae of size less than 200 nm. Some of the MoS₂ lamellae are indicated by black arrows in Fig. 5. The MoS₂ lamellae have distinct edges and corners. However, these MoS₂ lamellae are very thin owing to the lamellar crystal structure. Therefore, it is difficult to characterize the coverage of the lubricating film quantitatively using the image method.

The composition evolution of the worn surfaces of the Cu-MoS₂ composites in depth was monitored using XPS through Ar⁺ sputtering. The XPS survey spectra collected from the worn surfaces of the Cu-MoS₂ composites with various MoS₂ contents are shown in Fig. 6. The survey spectra can provide elemental

Fig. 4 BSE and EDS mapping images of worn surfaces of Cu-MoS₂ composites with MoS₂ content of 10 vol% for (a) and (b), 20 vol% for (c) and (d), 30 vol% for (e) and (f), and 40 vol% for (g) and (h).

Fig. 5 FE-SEM image of worn surface of Cu-30-vol%-MoS₂ composite.

information from the surface and can be useful in identifying the lubricating film or sample compositions. As can be observed in Fig. 6, the elements of Cu, Mo, S, and O are identified in the worn surfaces, and the corresponding characteristic peaks of Cu2p (932.4 eV), Mo3d (228.7 eV), S2p (162.2 eV), and O1s

(530.3 eV) are marked. It is evident that the intensities of the S2p and Mo3d peaks increase as the content of MoS₂ increases in the composites. The survey spectra of all the composites shift in the first few hundreds of seconds of etch time and then remain mostly unchanged with further etching. This indicates that the composition of the outmost surface is vastly different from that of the internal surface. Hence, it is confirmed that there is a MoS₂ lubricating film formed on the worn surfaces of the Cu-MoS₂ composites. In order to quantitatively study the elemental evolution at the surface, the survey spectra from the original data set of 7–11 scans were then peak fitted at each etch level to obtain a full atomic percent quantification throughout the sample depth.

The quantitative analysis of the elements in the worn surface distributed in the depth direction is presented in Fig. 7. It can be observed in Fig. 7(a) that the atomic percentage of Cu increases to a maximum value and then remains constant as the etch time increases, while the content of O changes in the opposite direction. The reason for the high oxygen content in the outmost surfaces is the oxidation of copper matrix and MoS₂ during friction under atmosphere environment. It is interesting to note in Fig. 7 that the atomic percentage of Mo and S greatly increases first and then gradually decreases with the increase in etch time; this is especially evident in Figs. 7(d) and 7(e). The low content of Mo and S in the outmost surface may be attributed to the high content of O. It is well known that the sputtering rate of different elements varies greatly [37, 38]. In the majority of cases, the greater the atomic mass of the element is, the lower the sputtering rate. The sputtering rate of S is higher than that of Cu and even higher than that of Mo. Hence, sputtering may result in a modification of the surface composition. However, the previous investigation on MoS₂ sputtering showed that the S concentration decreased from 67 at% to 63 at% after a sputtering time of 20 mins with a 3-keV Ar⁺ ion beam [37]. This indicates that the sputtering has a low impact on the surface composition of Cu-MoS₂ composites considered in this study. As the MoS₂ content increases from 5 vol% to 40 vol%, the atomic percentages of Mo and S clearly increase, and the maximum value is obtained at a longer etch time. The maximum contents

Fig. 6 Evolution of depth profile survey spectra of Cu-MoS₂ composites with MoS₂ content of (a) 10 vol%, (b) 20 vol%, (c) 30 vol%, and (d) 40 vol%.

of Mo and S in Cu-5-vol%-MoS₂ and Cu-10-vol%-MoS₂ composites are obtained after approximately 50 s of etching as shown in Figs. 7(a) and 7(b), which to 100 s for Cu-20-vol%-MoS₂, Cu-30-vol%-MoS₂, and Cu-40-vol%-MoS₂ composites as shown in Figs. 7(c) and 7(d). These results indicate that the worn surfaces of Cu-MoS₂ composites are enriched in MoS₂. However, the volume fraction or the area coverage of the MoS₂ lubricating film on the worn surfaces is yet to be determined, which is an essential characteristic for self-lubricating composites.

As the atomic percentages of all the elements in the surface of each etched layer are known, the volume fraction of each component can be calculated based on the following steps. Firstly, the weight of Cu, Mo, and S atoms can be determined by multiplying their atomic percentages by their relative atomic mass (63.5, 96, and 32, respectively), and the weight percentages of Cu, Mo, and S can then be calculated by dividing the weight of each atom by the total weight. Secondly, the volume of MoS₂ was calculated by dividing the sum of the weight percentages of Mo and S by the density of MoS₂ (4.8 g/cm³), and the volume of Cu was calculated by dividing the weight percentage of Cu by the density of copper (8.9 g/cm³). Finally, the

volume fraction of MoS₂ and Cu can be computed by dividing each volume by the sum volume of them. Figure 8 shows the evolution of the volume fraction of MoS₂ in the worn surfaces as a function of the etch time. From the outmost surface to the subsurface, the MoS₂ content first increases rapidly and then decreases slowly. The greatest content of MoS₂ was obtained at the subsurface (10 nm–30 nm off the surface) and reached 26 vol%, 34 vol%, 41 vol%, 64 vol%, and 65 vol% for the Cu-MoS₂ composites with MoS₂ contents ranging from 5 vol%–40 vol%. The content of MoS₂ in the subsurface layer is apparently significantly higher than that in the composites. When the worn surfaces were etched for approximately 700 s (230 nm), the content of the MoS₂ was beginning to stabilize. At the end of the etching, the content of MoS₂ reaches 10 vol%, 12 vol%, 22 vol%, 31 vol%, and 45 vol% for the Cu-MoS₂ composites with MoS₂ contents of 5 vol%–40 vol%. Except for the Cu-5-vol%-MoS₂ composite, the MoS₂ content of the other composites measured using XPS is very close to the actual added content, and the corresponding error is less than 8%. Therefore, it can be demonstrated that the quantitative analysis of the coverage of the lubricating film or content of lubricant on the worn surface using XPS

Fig. 7 Evolution of elemental atomic percentages in depth for Cu-MoS₂ composites with MoS₂ content of (a) 5 vol%, (b) 10 vol%, (c) 20 vol%, (d) 30 vol%, and (e) 40 vol%.

is feasible and reliable. The region with the highest content of MoS₂ does not appear at the outmost surface as expected in Fig. 2 because the surface oxidation and adsorbed gas reduce the relative content of MoS₂. The highest content of MoS₂ appears at the depth of 10 nm–30 nm from the surface, and the depth tends to increase with the increase in the MoS₂ content. The high content of MoS₂ in the worn surface is due to the split of the lamellar structure of the MoS₂ crystal during sliding, which results in the formation of many more and thinner MoS₂ crystals and increases their surface area. Hence, a MoS₂ lubricating film is formed on the

worn surface in the form of MoS₂ lamellae with a thickness from tens to hundreds of nanometers. During the etching process, the MoS₂ lamellae of a few or tens of nanometers are preferentially etched, such that the MoS₂ lamellae on the surface are gradually reduced. When the thin MoS₂ lamellae produced by friction have been etched by Ar⁺ ions, the MoS₂ content on the surface approaches that added to the composite. The evolution of the MoS₂ content with the etch depth shown in Fig. 8 is in good agreement with the expected trend shown in Fig. 2(c).

Although it is well known that the coverage of the

Fig. 8 Evolution of MoS₂ content with depth for Cu-MoS₂ composites.

lubricating film on the worn surface increases as the lubricant content increases, it is still unclear whether their relationship follows a linear law. Here, the content of MoS₂ on the outmost surface was predicted according to the changing trend as indicated in Fig. 8. The MoS₂ contents in the outmost surfaces are expected to be 31 vol%, 42 vol%, 53 vol%, 72 vol%, and 73 vol% (indicated by the solid dot in Fig. 8) for Cu-MoS₂ composites with a MoS₂ content of 5 vol%–40 vol%. The MoS₂ content on the outmost surface is equal to the coverage of the MoS₂ lubricating film. Figure 9 illustrates the influence of the volume fraction of MoS₂ in the composites on the coverage of MoS₂ film on the worn surfaces. With the increase in the MoS₂ content in the composites, the coverage of the MoS₂ film on the worn surface increases gradually, but the increasing rate reduces. In order to discover the relationship between the MoS₂ content in composite and the MoS₂ content in worn surface, Origin 9 software was used to fit the experimental data. The fitted line is presented in Fig. 9, and it satisfies the exponential equation of $\alpha_f = 22V^{0.33}$. Thus, the coverage of the lubricating film does not have a linear but an exponential relationship with the lubricant content. Apparently, when the composites have a relatively low content of MoS₂ (5 vol% or 10 vol%), the copper matrix surface can supply sufficient space for the slip and adhesion of MoS₂ lamellae, which contributes to the formation of a large area of the lubricating film. The included MoS₂ then exhibits a very high efficiency of lubrication. For

Fig. 9 Influence of volume fraction of MoS₂ in composites on MoS₂ film coverage on outmost worn surfaces.

composites of high MoS₂ content (20 vol%–40 vol%), a further addition of MoS₂ cannot be effective in generating more new MoS₂ lamellae, and the rate of increase in the coverage of the MoS₂ film is then reduced. To directly demonstrate the lubricating effect of MoS₂, the ratio of the film coverage to the volume fraction of the lubricant (k) is calculated using Eq. (1). The value of k decreases from 6.2 to 2.9 when the MoS₂ content increases from 5 vol% to 40 vol%. This result confirms that the lubricating efficiency of the lubricant decreases with the increase in the lubricant content in the composite.

The friction coefficients of the Cu-MoS₂ composites with various MoS₂ contents were obtained in the friction tests. The coverage of the MoS₂ film in the outmost surfaces was also acquired using XPS, as illustrated in Fig. 7. Hence, the relationship between the friction coefficient and MoS₂ film coverage could be established, and it is shown in Fig. 10(a). With the increase in the coverage area of the MoS₂ film on the worn surface, the surface friction is alleviated, and the friction coefficient decreases. The solid line in Fig. 10(a) was plotted based on Eq. (5) with the equation of $\mu = (1-\alpha_f)^2 \times 0.76 + (1-(1-\alpha_f)^2) \times 0.1$. The value of μ_m in Eq. (5) is selected from the friction coefficient of pure copper (0.76), and the value of μ_f is assigned as 0.1 as the friction coefficient of the MoS₂ pin according to some literatures [12, 13, 28]. It can be observed that the experimental data agrees well with Eq. (5). Figure 10(b) presents the influence of the volume fraction of MoS₂ on the friction coefficient of the composites. The friction coefficient decreases quickly

Fig. 10 Variations of friction coefficient of Cu-MoS₂ composites with (a) MoS₂ film coverage and (b) volume fraction.

from 0.76 of pure copper to Cu-20-vol%-MoS₂ of 0.18 and decreases slowly with the further addition of MoS₂ in the composite. The solid line in Fig. 10(b) was plotted according to Eq. (6) with the equation of $\mu = (1-22V^{0.33})^2 \times 0.76 + (1-(1-22V^{0.33})^2) \times 0.1$. The values of μ_m and μ_f in Eq. (6) are the same as those in Eq. (5). The experimental data is in good agreement with the equation. The variation of the friction coefficient with the lubricant content is also in agreement with many other MMSCs [10, 11, 13]. Therefore, the relationships among the friction coefficient, coverage of lubricating film, and volume fraction of the lubricant can be successfully established via the quantitative characterization of the worn surface using XPS.

5 Conclusions

The present study is focused on the development of a friction model for MMSCs. An XPS analysis with depth profiling was developed and successfully implemented for quantitatively characterizing the

coverage of the lubricating film. The MoS₂ lubricating film on the worn surface of Cu-MoS₂ composites comprises several MoS₂ lamellae of size less than 200 nm. The MoS₂ content gradually decreases from the outmost surface to the matrix, and the coverage of the MoS₂ film on the outmost surface is 2.9–6.2 times that of the matrix. The coverage of the MoS₂ film has an exponential relationship with the MoS₂ volume content, which can explain why adding too much lubricant does not significantly reduce the friction coefficient. Based on the quantitative characterization of the film coverage, the relationships among the friction coefficient, coverage of lubricating film, and volume fraction of lubricant are successfully established, and the developed friction model for the MMSC is verified.

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