The effect of S/Mo ratio on structure and properties of MoS$_x$-Ti composite coatings deposited by magnetron sputtering

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Abstract

MoS$_x$-Ti composite coatings with different S/Mo ratios were prepared by varying the substrate bias voltage of magnetron sputtering. It was found that the S/Mo ratio of the as-deposited MoS$_x$-Ti coating decreased gradually from 1.7 to 1.3 as substrate bias voltage increased from $-30$ V to $-110$ V. The MoS$_{1.7}$-Ti coating exhibits a nanocrystalline and amorphous phase mixed structure while the other MoS$_x$-Ti coatings were all amorphous structured. The hardness of the MoS$_x$-Ti coatings increased from 8.8 GPa to 9.8 GPa as the S/Mo ratio decreased from 1.7 to 1.3. The MoS$_{x}$-Ti coatings with the S/Mo above 1.4 exhibit COF with values smaller than 0.07 at RH of 50% and increased wear rate in the magnitude of $\sim 10^{-7}$ mm$^3$ N$^{-1}$ m$^{-1}$. The tribological behavior of the MoS$_x$-Ti coatings were determined by the formation of the imperfect crystalline MoS$_2$ tribofilm. With the decrease of the S/Mo ratio, the increased defects in imperfect crystalline MoS$_2$ tribofilm lead to quicker consumption of the tribofilm during the trio-test, which result in a higher wear rate.

1. Introduction

Molybdenum disulphide (MoS$_2$) coatings have been used as solid lubricant coatings in aerospace applications for their ultra-low coefficient of friction in high vacuum [1–4] in the past decades. However, the pure MoS$_2$ coatings failed easily in humid environment owning to their loose structure and high chemical activity of oxygen [5, 6]. Therefore, numerous studies have been made on reducing the sensitive of MoS$_2$ coatings to moisture by doping metal elements like Ti, Cr, Pb, etc [7–13] or oxides like Sb$_2$O$_3$ [14, 15] or nitrides like TiN [16]. The tribological performance of these doped MoS$_2$ coatings has been significantly improved in ambient air. The MoS$_2$-Cr coating even exhibit a coefficient of friction (COF) and wear rate as low as $\sim 0.05$ and $\sim 2.0 \times 10^{-7}$ mm$^3$ N$^{-1}$ m$^{-1}$ in 75% relative humidity (RH) atmosphere, respectively [10]. Hence, the usage of doped MoS$_2$ coatings has been widely extended into application in atmospheric environment like gears and switches used in electromechanical system [17] and cutting/forming tools used in machining of light weight alloys [18, 19].

The doped MoS$_2$ coatings were usually fabricated by closed field unbalanced magnetron sputtering (CFUBMS) [7–16]. There is a high level of ion bombardment on growing film during deposition process of CFUBMS, which lead to preferentially re-sputtering of S atoms from the film, thereby the S/Mo ratio was smaller than 2. By using H$_2$/Ar as the sputtering gas, the S/Mo ratio can be raised to 2.8 by increasing the H$_2$/S flow rate [20, 21]. With the decrease of S/Mo ratio, the microstructure of MoS$_{x}$ coatings changed from well-crystallized MoS$_2$ structure ($x > 2$) to primarily crystalline MoS$_x$ structure with additional Mo atoms in the gap between S planes ($2 > x \geq 1.3$) to amorphous structure ($x < 1.3$) [21]. The MoS$_{x}$ coating with S/Mo ratio ranged from 1.5 $\sim$ 1.6 exhibit better lubricating properties than amorphous or well-crystallized MoS$_x$ coatings. By contrast, the doped MoS$_2$ coatings with excellent tribological performance in humid air were all amorphous structured. However, the effect of S/Mo ratio on microstructure and tribological properties of the doped MoS$_x$ coatings were seldom involved and are worth to be studied.

The S/Mo ratio of MoS$_2$-based coatings can be controlled by the changing of the negative bias voltage applied on the substrate or working pressure during magnetron sputtering deposition [22, 23]. It was found that
The chemical compositions of the as-deposited MoS$_x$-Ti coatings measured by XPS are given in Table 1. The S/Mo ratio decreased when increasing negative substrate bias voltage or decreasing the working pressure. Therefore, in this paper, MoS$_x$-Ti coatings with different S/Mo ratio were fabricated by varying the substrate bias voltage. The microstructure was investigated and the effect of S/Mo ratio on the tribological behavior of MoS$_x$-Ti coatings was discussed in details.

2. Experimental details

The MoS$_x$-Ti coatings were deposited on silicon wafers (100) and steel substrates by a closed field unbalanced magnetron sputtering system. This CFUBMS system contains four rectangular unbalanced magnetrons (330 × 134 mm) installed at 90 degrees to each other around the cylindrical chamber wall. Two MoS$_2$ targets (99.9% purity) and two Ti targets (99.99% purity) were installed on magnetrons opposite each other, respectively. The silicon wafers are used for structural and chemical analysis, and the polished AISI 1045 steel disks are used for tribological test. The substrates were placed on a rotatable sample holder lying 120 mm away from the target. During deposition, the rotational speed of the sample holder was kept at 5 rpm and the working pressure was maintained at 0.11 Pa by introducing Ar with a flow rate of 15 sccm. The target power was applied on each target by AE Pinnacle power supplies using the constant current mode. The target current applied on MoS$_2$ targets and Ti targets are 1.2 A and 0.4 A, respectively. To obtain different S/Mo ratios, different negative bias voltage were applied on the substrates by an AE Pinnacle Plus power at a frequency of 250 kHz and a reverse pulse duration of 0.5 μs. The values of bias voltage used during deposition are given in Table 1. The deposition time was 90 min and the deposition temperature was generally kept at 120 °C.

The crystal structure of the coatings was studied by an x-ray diffractometer (SHIMADZU/XRD-7000S, Japan) using Cu Kα radiation (λ = 0.15406 nm) in a glancing angle mode. The glancing angle was 1°. The cross-sectional morphology of the coatings was observed by a scanning electron microscope (JEOL/JSR-6700F, Japan) and a transmission electron microscope (JEOL/TEM-3010, Japan). The chemical structure of the coatings was investigated by an XPS photoelectron spectroscopy (Kratos/AXIS Ultra XPS, UK) using Al Kα radiation (1486.6 eV). The peak fittings of XPS spectra were carried out based on the data from the NIST x-ray Photoelectron Spectroscopy Database. The hardness and elastic modulus of the coatings were measured by a nano-indenter (Agilent/G200, America). The indentation depth was 300 nm, which was less than 1/10 of the film thickness to eliminate the effect of substrate on hardness. The tribological properties of the coatings were evaluated by a ball-on-disc tester (Brucker/UMT Tribolab, America) using an AISI 52100 steel ball with a diameter of 6.35 mm as the counterpart. The tests were performed at a temperature of 23 ± 2 °C and RH of 50%. The load applied to the counterpart ball was 5 N. The sliding speed was kept at a constant of 0.2 m s$^{-1}$ for a sliding distance of 900 m. After that the wear track was studied by a confocal laser scanning microscope (Olympus/LEXT OLS4000, Japan) and the chemical composition of the counterpart ball was analyzed by energy dispersive x-ray spectrometer (EDS) attached to the SEM.

3. Results and discussions

3.1. Chemical compositions and microstructure

The chemical compositions of the as-deposited MoS$_x$-Ti coatings measured by XPS are given in Table 1. The S/Mo ratio of MoS$_x$-Ti coatings decreased from 1.7 to 1.3 as the bias voltage was increased from −30 V to −110 V. Figure 1 shows the Mo 3d, S 2p, Ti 2 s XPS spectra of the as-deposited MoS$_x$-Ti coatings. The Mo 3d spectra (Figure 1(a)) had been systematically deconvoluted into three chemical binding states corresponding to MoS$_2$ (BE = 229.2 eV), MoS$_{2-x}$ (BE = 228.6 eV [24]) and MoO$_2$ BE = 230.3 eV). The formation of MoS$_{2-x}$ peak was associated with the intentional Ar$^+$ ions bombardment during deposition [24]. With the increase of the bias voltage, the effect of Ar$^+$ ions bombardment was enhanced and hence more MoS$_{2-x}$ bond was formed.

| Sample ID | Bias voltage (V) | Mo (at.%) | S (at.%) | Ti (at.%) | S/Mo ratio | Coating thickness (μm) | H/E | H/E$^2$ |
|-----------|-----------------|-----------|---------|---------|------------|-----------------------|-----|--------|
| MoS$_{1.7}$-Ti | −30 | 34.3 | 57.3 | 8.4 | 1.7 | 3.82 | 0.080 | 0.049 |
| MoS$_{1.4}$-Ti | −50 | 35.8 | 55.5 | 8.7 | 1.6 | 3.59 | 0.077 | 0.046 |
| MoS$_{1.5}$-Ti | −70 | 36.5 | 54.0 | 9.5 | 1.5 | 3.46 | 0.074 | 0.043 |
| MoS$_{1.6}$-Ti | −90 | 37.7 | 52.5 | 9.8 | 1.4 | 3.28 | 0.075 | 0.046 |
| MoS$_{1.8}$-Ti | −110 | 39.2 | 50.6 | 10.2 | 1.3 | 3.27 | 0.074 | 0.046 |
corresponding to that more MoS$_{2-x}$ bond was formed in MoS$_x$-Ti coatings with lower S/Mo ratio. The S 2p spectra (figure 1(b)) was composed of Mo-S ($S^2^-$, as marked in the figure 1(b), BE = 162.7 eV) and Mo(Ti)S$_x$ composite ($S^2^-$-(Mo,Ti), as marked in the figure 1(b), BE = 163.4 eV [24]) binding states. The existence of Mo(Ti)S$_x$ composite implies that Mo in the MoS$_x$ matrix has been partially substituted by Ti. The S 2p spectra of MoS$_x$-Ti coatings with S/Mo ratio between 1.7 ∼ 1.4 was almost the same to each other. By contrast, there was a noticeable increment in the intensity ratio of Mo(Ti)S$_x$/Mo-S in MoS$_{1.3}$-Ti coating, indicating more Ti-S bond was formed. Similarly, the higher Ti-S/TiO$_2$ ratio of the MoS$_{1.3}$-Ti coating in Ti 2p spectra (figure 1(c)) compared to the other coatings also confirmed that more Mo-S has been replaced by Ti-S in MoS$_{1.3}$-Ti coating although the difference in Ti content was small.

Figure 2 shows the XRD patterns of the as-deposited MoS$_x$-Ti composite coatings. The MoS$_{1.7}$-Ti coating exhibit a broadened diffraction peak around 13°, which can be corresponded to (002) reflection of MoS$_2$ phase (JCPDF 17-0744). The broadened diffraction peak could be related to two reasons: on one hand, the additional Ti and Mo atoms incorporated into the gap between S planes of crystalline MoS$_2$ lead to the increment of lattice distance of (002) planes, on the other the Mo was partially substituted by Ti with larger atomic radius. As the S/
Mo ratio was smaller than 1.6, the as-deposited MoS$_x$-Ti composite coatings all transform to amorphous structure.

The microstructure of the as-deposited MoS$_x$-Ti coatings was further investigated by TEM. Figure 3 shows the cross-sectional TEM micrograph of MoS$_{1.7}$-Ti coating and MoS$_{1.5}$-Ti coating. In figure 3(a), a dense Ti interlayer, a columnar Ti-MoS$_x$ grade layer and MoS$_x$-Ti composite layer can be observed. The HRTEM micrograph (figure 3(b)) shows that the MoS$_x$-Ti composite layer of MoS$_{1.7}$-Ti coating was composed of a mixture of amorphous phase and nanocrystalline MoS$_2$. The lattice distance between the MoS$_2$ lamellae ranged from 0.609 nm $\sim$ 0.675 nm and the (002) basal plane of MoS$_2$ was generally perpendicular to the film growth direction, thus two diffraction spots can be observed in select area electron diffraction (SAED). The TEM micrograph (figure 3(c)) of MoS$_{1.5}$-Ti coating exhibits a homogenous structure without any voids. The SAED pattern of the coating is a typical amorphous halo and none MoS$_2$ lattice fringe can be identified from the HRTEM. It confirmed that the MoS$_{1.5}$-Ti coating was amorphous structured.

3.2. Mechanical and tribological properties

The hardness and elastic modulus of the as-deposited MoS$_x$-Ti composite coatings is shown in figure 4. With the decrease of S/Mo ratio from 1.7 to 1.3, the hardness of MoS$_x$-Ti coatings increased gradually from 8.8 GPa to 9.8 GPa. The hardness enhancement of the MoS$_x$-Ti coatings could be related to the densification of the coating structure and distortion of the MoS$_2$ bonding structure. On one hand, with the increase of bias voltage, the adatom mobility during coating growth could be accelerated as a result of increased energetic ion bombardment. Higher adatoms mobility promotes formation of denser coating structure. On the other hand, it can be found from the XPS analysis that more distorted MoS$_{2-x}$ bonding were formed with the decrease of S/Mo ratio. Denser structure and more distorted MoS$_{2-x}$ bonding have a benefit on improving the hardness.

The coefficient of friction of the as-deposited MoS$_x$-Ti coatings sliding against steel ball at room temperature in the atmosphere of 50% RH is shown in figure 5. All of the MoS$_x$-Ti coatings with S/Mo ratio above 1.5 exhibit low COF with values below 0.07, which are close to the results of other research about MoS$_2$-Ti coating tested under similar conditions [10]. As the S/Mo ratio decreased below 1.4, the COF of the MoS$_x$-Ti coatings increased with the decrease of S/Mo ratio. The COF value of MoS$_{1.3}$-Ti coating even increased to 0.37.

The wear track images of the as-deposited MoS$_x$-Ti coatings sliding against steel ball for 900 m are shown in figure 6. It can be seen that the width of the wear track increased gradually with the decrease of S/Mo ratio and the MoS$_{1.6}$-Ti coating exhibits the narrowest wear track than the other coatings. The MoS$_{1.4}$-Ti coating was
partially worn out and the steel substrate can be observed in the center of wear track. The MoS$_{1.5}$-Ti coating was completely worn out and the width of the wear track was about 5 times larger than that of MoS$_{1.6}$-Ti coating. Grooves along the sliding direction can be observed on these wear tracks, implying that abrasive wear happened during the tribo-test for all of the as-deposited coatings.

The SEM wear track images of the counterpart ball and corresponding EDS spectrum of the wear debris existed on the wear track are shown in figure 7. As shown in figures 7(a) and (b), the counterpart ball sliding
against MoS$_{1.7}$-Ti and MoS$_{1.6}$-Ti coating was hardly worn and sheet-like wear debris existed on the contact regions. By contrast, there were noticeable wear scars on the counterpart balls sliding against the other MoS$_x$-Ti coatings (figures 7(c) and (d)). With the decrease of S/Mo ratio from 1.5 to 1.4, the wear scar of counterpart ball enlarged and thicker sheet-like wear debris was formed. The counterpart ball sliding against MoS$_{1.3}$-Ti coating

Figure 5. Coefficient of friction of the MoS$_x$-Ti coatings with different S/Mo ratio as a function of sliding distance.

Figure 6. Wear track morphologies of the as-deposited MoS$_x$-Ti coatings (a) MoS$_{1.7}$-Ti, (b) MoS$_{1.6}$-Ti, (c) MoS$_{1.5}$-Ti, (d) MoS$_{1.4}$-Ti, (e) MoS$_{1.3}$-Ti.

Figure 7. SEM wear track images of the counterpart ball and EDS spectrum of the wear debris existed on the wear track, (a) and (f) MoS$_{1.7}$-Ti, (b) and (g) MoS$_{1.6}$-Ti, (c) and (h) MoS$_{1.5}$-Ti, (d) and (i) MoS$_{1.4}$-Ti, (e) and (j) MoS$_{1.3}$-Ti.
exhibit a smooth wear scar with hardly any wear debris. The chemical composition of selected zones (white rectangles marked in figures 7(a)∼(e)) on wear track of counterpart ball analyzed by EDS is also presented in figures 7(f)∼(j), respectively. From the EDS images, Mo, S and Ti elements can be found on the wear track of counterpart ball sliding against the MoS$_x$-Ti coatings with S/Mo ratio above 1.4. By contrast, there was hardly any of these three elements can be found on counterpart ball sliding against MoS$_{1.3}$-Ti coating. The content of Mo, S and Ti on wear track of the counterpart ball were positively correlated with the COF. Considering the limited content of Mo, S and Ti element in 52100 steel (the chemical content of Mo, S and Ti element in 52100 steel was smaller than 0.2 at.%, 0.02 at.% and 0, respectively), it can be reasonably deduced that the wear debris came from the MoS$_x$-Ti coatings. It has been well documented that lubricating properties of amorphous MoS$_2$-based coatings was attributed to a self-mated crystalline MoS$_2$ tribofilm transformed from amorphous phase during friction [15, 25]. Therefore, imperfect self-mated crystalline MoS$_2$ tribofilm could be formed owing to lack of S atoms and with the decrease of the S/Mo ratio, more additional Mo atoms incorporated into the gap between S planes of crystalline MoS$_2$, hence thicker transfer film can be observed with the decrease of S/Mo ratio. As the S/Mo ratio was below 1.3, the lamellar structured MoS$_2$ tribofilm could not be formed and then the MoS$_{1.3}$-Ti coating lose the lubricating properties.

Based on the width and depth of the wear track, the specific wear rate was calculated and presented in figure 8. It showed that the MoS$_x$-Ti coatings deposited with S/Mo ratio above 1.4 exhibit wear rate with values in the magnitude of $\sim 10^{-7}$ mm$^3$ Nm$^{-1}$ while the MoS$_{1.3}$-Ti coating was completely worn out. The wear rate of amorphous MoS$_x$-Ti coating increased with the increase of bias voltage. The changes in wear rate of the as-deposited MoS$_x$-Ti coatings could be explained from the difference of wear mechanism. The analysis of the wear track on both of the coating and counterface showed that abrasive wear and adhesive wear occurred during the tribo-test. It has been well suggested that abrasive wear, the resistance of coating surface to mechanical degradation and failure, can be evaluated by $H/E$ ratio and $H/E^{0.2}$ ratio [26, 27]. Considering that $H/E$ ratio and $H/E^{0.2}$ ratio of the as-deposited coatings were close to each other in values as presented in table 1, the abrasive wear of the as-deposited coatings would be similar. The adhesive wear of the MoS$_x$-Ti coating was a process of the formation of the crystalline MoS$_2$ tribofilm on the contact surface and transfer of the tribofilm to the counterface. Thicker transfer film was formed during tribo-test of the MoS$_x$-Ti coating with lower S/Mo ratio, which means a quick consumption of the tribofilm, corresponding to a higher wear rate.

4. Conclusions

MoS$_x$-Ti composite coatings with different S/Mo ratios were prepared by varying the substrate bias voltage of magnetron sputtering. The S/Mo ratio decreased from 1.7 to 1.3 as the substrate bias voltage was increased from $-30$ V to $-110$ V. The MoS$_{1.7}$-Ti coating exhibits a nanocrystalline and amorphous mixed structure. With the decrease of S/Mo ratio, the MoS$_x$-Ti coating transformed to amorphous structured. The hardness of MoS$_x$-Ti coating increased from 8.8 GPa to 9.8 GPa with S/Mo ratio decreased from 1.7 to 1.3. The hardness
enhancement can be attributed to densification of the structure and formation of distorted MoS$_2$—$\gamma$ bonds, both of which are related to the decrease of S/Mo. The MoS$_x$—Ti coatings with S/Mo ratio above 1.5 all exhibit low COF with values smaller than 0.07 at RH of 50%. By contrast, with the further decrease of S/Mo ratio to 1.3, the COF values increased remarkably to 0.37. The wear rate of the MoS$_x$—Ti coatings with S/Mo ratio above 1.4 was in the magnitude of $\sim$10$^{-3}$ mm$^3$/Nm and increased slightly with the decrease of S/Mo ratio. The tribological behavior of the MoS$_x$—Ti coatings were determined by the formation of the imperfect crystalline MoS$_2$ tribofilm. With the decrease of the S/Mo ratio, the increased defects in imperfect crystalline MoS$_2$ tribofilm lead to quicker consumption of the tribofilm during the trio-test, which result in higher wear rate.

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