Atomic Oxygen Effect on Sputtered MoS2-Ag Composite Film

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ABSTRACT

MoS2-Ag composite film was co-deposited by rf-sputtering technology and irradiated by atomic oxygen (AO) using a ground AO simulation facility. The structure, morphology, composition and tribological property of the composite films before and after the AO irradiation were investigated using X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), X-ray photoelectron spectrocope (XPS) and ball-on-disk tribometer, respectively. The results revealed that the MoS2-Ag composite film was severely oxidized by the AO irradiation and the wear resistance was declined significantly; the MoS2 phase was mainly oxidized to MoO3 and the Ag was changed to a mixture of AgO and Ag2O; and the cracking phenomenon was obvious after the AO irradiation. The oxidation behavior was mainly controlled by the Ag, not the MoS2.

INTRODUCTION

Atomic oxygen (AO) is dominant species at low earth orbit (LEO) altitudes of 200-1000 km \[1,2\], where most of spacecrafts have been served. In the LEO environment, the AO density is rather low, but can cause the oxidation, erosion and performance deterioration of many space materials \[3\]. It is well-known that the MoS2 film is an excellent solid lubricant for application in space technology. For some applications, it must withstand direct exposure in the LEO environment. Therefore, the AO effects on the MoS2 have been investigated by both ground-simulation and space-flight experiments \[4-9\]. Overall, the AO irradiation can cause the oxidation of MoS2 films, but the oxidation is restricted to the film surface. The film surface can be oxidized to form an oxide layer composed of MoO3 plus a small amount of MoO2. The oxidation layer may play a better protective function and prevent the further oxidation from the lower films. As for the change in the friction property, due to the surface oxidation the AO-irradiated MoS2 films represent a relatively high friction coefficient in run-in stage, after which it resume the normal value.

By adding metal elements (such as Au, Ag, Cu, Ti, Cr, Al and Ni, etc.), the wear-resistance of MoS2 films can be increased significantly because of the different effects such as alloy strengthening, micro-structural densification, and improvement
in film-substrate adhesion and anti-oxidation property\textsuperscript{[10-17]}. These MoS\textsubscript{2} based composite films exhibit much better wear-resistances than the pure MoS\textsubscript{2} film in vacuum environment. The anti-oxidation ability of the MoS\textsubscript{2}-Au composite film was investigated in the AO environment by the space-flight and ground-simulation methods\textsuperscript{[10]}. It was found that the AO irradiation only led to the slight surface oxidation of the MoS\textsubscript{2}-Au composite film. However, for some MoS\textsubscript{2} films composited with active metal elements (such as Ag), the anti-oxidation capability should be different from the MoS\textsubscript{2}-Au composite film. In this paper, the MoS\textsubscript{2}-Ag composite changes in the composition, morphology, phase structure and tribological performance of the sputtered MoS\textsubscript{2} films, resulted from the LEO space exposure, were investigated systematically.

EXPERIMENTAL DETAIL

Film Deposition

The MoS\textsubscript{2}-Ag films were deposited by an rf-sputtering system. One MoS\textsubscript{2}-Ag composite target was used for cathode with 85 mm in diameter. AISI 440C steel pieces were used for the substrate with 25 mm in diameter. Before the deposition, the substrate was surface-polished with abrasive papers to $R_a \leq 0.05 \mu m$ and then ultrasonically cleaned in acetone, after which it was put into the vacuum chamber and fixed on sample holder. As the vacuum chamber was evacuated to a base pressure lower than $2.0 \times 10^{-3}$ Pa, the substrate surface was etched in Ar plasma to eliminate possible contaminants under a DC bias voltage of -500 V for 15 min. Afterwards, the MoS\textsubscript{2}-Ag films were deposited under Ar pressure of $\sim 4.0$ Pa and sputtering power of 600 W. During the film deposition, the substrate was located under the MoS\textsubscript{2}-Ag target. Film thickness was determined to be $\sim 5 \mu m$.

AO Irradiation Procedure

The AO irradiation was carried out by a ground-based AO simulation facility. A microwave power source was used as a exciter to produce the oxygen plasma. The oxygen plasma would become a beam under the effect of an electromagnetic field, and then be accelerated towards a molybdenum plate with a negatively charged electric field. The accelerated oxygen positive ions collided with the plate, and were neutralized by the negative charges on the plate and rebounded to form a neutral AO beam with an average impingement kinetic energy of 5 eV and an flux of $5.8 \times 10^{15}$ atom·cm\textsuperscript{-2}·s\textsuperscript{-1} at the sample position. The irradiation period was set to 120 h for the MoS\textsubscript{2}-Ag composite film.

Characterization

Chemical composition was analyzed using X-ray photoelectron spectroscopy (XPS, PHI Quantera Scanning X-ray Microprobe) equipped an Ar ion sputtering gun with a monochromatic Al Ka X-ray source of 1486.6 eV (hv). The sputter was implemented by a 2 keV Ar ion gun, whose etching speed was $\sim 29$ nm/min for SiO\textsubscript{2} film. The spectra were referenced with respect to C 1s line at 284.6 eV. Phase structure were analyzed using grazing incidence X-ray diffraction (XRD, Philips
X’Pert Pro) with Cu Ka radiation (40 kV, 30 mA) under an incident beam angle of 1°. Surface morphology was observed by scanning electron microscope (SEM, JEOL JSM-6701F). Friction and wear behavior were performed using a ball-on-disk tribometer. The disk was the MoS$_2$-Ag coated samples. The counterpart was AISI 440C steel balls (HRC ~60) with 8 mm in diameter. The friction and wear tests were carried out at room temperature in vacuum ambient (below $5 \times 10^{-3}$ Pa), the normal load was 2 N, and the rotational speed was 1 000 r/min. After the friction tests, the morphology and element composition of the wear tracks were analyzed by scanning electron microscope (SEM, JEOL JSM-6701F).

RESULTS AND DISCUSSION

Fig. 1(a) shows the SEM micrograph of the MoS$_2$-Ag composite film before the AO irradiation. The composite film mainly exhibited a dentrite-like surface morphology along with some cauliflower-like protuberances. This surface morphology was normally observed from the MoS$_2$-metal composite film [18]. The growth mechanism was clarified for the rf-sputtered pure MoS$_2$ film [19-25]. Some investigations revealed that in the nucleation process, two types of MoS$_2$ nuclei appeared. For the first type, the basal plane was perpendicular to the substrate surface. For the second, the basal plane was parallel to the substrate surface. However, the MoS$_2$ crystal would have a much faster growth rate in the edge direction than in the basal direction due to its anisotropy. Therefore, the growth in the edge directions along the substrate surface appeared to be stopped by the impingement of the islands. The localized edge islands merged and evolved into columnar plate morphology. From the MoS$_2$-Ti composite film [18], it was found that with the increase of Ti content, the film morphology was gradually changed from a dentrite-like surface, to a fiber-like surface, then to a cauliflower-like surface, and finally to a featureless surface. In this paper, the Ag content in the composite film was determined to be ~16 at.% by XPS analysis. Perhaps, at this Ag content, the suppression of Ag atoms to the growth of MoS$_2$ crystallites was limited, and hence the composite film developed into this surface feature, as shown in Fig. 1(a). Clearly, the obvious change in the film morphology was observed from the AO-irradiated film, shown in Fig. 1(b). After the AO irradiation, the dentrite-like surface disappeared, while some cracks occurred. This change was different from the pure MoS$_2$ film, and MoS$_2$-Au and MoS$_2$-Sb$_2$O$_3$-Au composite films [10]. Previous space exposure experiments revealed that the film surfaces were not changed before and after the AO exposure for the pure MoS$_2$ film and the MoS$_2$-Au and MoS$_2$-Sb$_2$O$_3$-Au composite films. This difference was mainly related to the chemical activity of adding metal elements.

![Figure 1](image_url)

**Figure 1.** SEM surface micrographs of the MoS$_2$-Ag composite films: (a) as-deposited film and (b) the AO-irradiated film.
Fig. 2 shows the XRD patterns of the non-irradiated and AO irradiated MoS$_2$-Ag composite films. The non-irradiated composite film exhibited both 2H-MoS$_2$ and face-centred cubic Ag phases. The MoS$_2$ phase mainly showed (002), (100) and (110) peaks. The Ag phase mainly presented (111), (200) and (220) peaks. After the AO irradiation, the intensities of the peaks corresponding to the 2H-MoS$_2$ and Ag phases were significantly decreased, while several new peaks appeared at $2\theta$ of 20-30°, suggested that the film might be oxidized by the AO irradiation.

![XRD patterns of the AO-irradiated and non-irradiated composite films.](image)

Table 1 gives the element composition of the AO-irradiated MoS$_2$-Ag composite film at different sputter depth. The non-irradiated MoS$_2$-Ag composite film was also analyzed, and the atomic concentration of Mo, S, O and Ag was ~31, 42, 11, and 16 at.%, respectively. Comparatively, the AO-irradiated MoS$_2$-Ag composite film showed much higher O content and lower S content either at the film surface or the film inner. The O content was increased from 11 at.% for the non-irradiated film to 54-64 at.% for the irradiated film, while the S content was decreased from 42 to 3-4 at.%. This indicated that the AO irradiation caused the remarkable loss of S element for the MoS$_2$-Ag composite film.

| Sample                  | Sputter time (min) | Atomic concentration (%) |
|-------------------------|--------------------|--------------------------|
|                         |                   | Mo   | S    | O    | Ag   |
| AO-irradiated film      | 0                 | 19   | 4    | 64   | 13   |
|                         | 10                | 23   | 3    | 57   | 17   |
|                         | 20                | 24   | 3    | 54   | 18   |
| Non-irradiated film     | 1                 | 31   | 42   | 11   | 16   |

Fig. 3 presents the XPS Mo 3d spectra obtained from the AO irradiated MoS$_2$-Ag composite at the surface and inner. It can be seen that at the film surface, the Mo 3d spectra showed two peaks at the binding energy of 232.6 and 235.8 eV, which were corresponding to the Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ of MoO$_3$, indicating that the MoS$_2$ was fully oxidized to MoO$_3$. In the film inner, the XPS Mo 3d spectra showed a very broad peak formed by the superposition of the Mo (IV) and Mo (VI) doublets. Based on the position of both Mo (VI) 3d$_{5/2}$ and Mo (VI) 3d$_{3/2}$ peaks, it was seen that the Mo (VI) was dominant even after the sputter time of 20 min, suggested that most of the MoS$_2$ was also oxidized to MoO$_3$. 

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Figure 3. XPS Mo 3d spectra of the AO-irradiated MoS$_2$-Ag film at different sputter depth.

Fig. 4 shows the XPS Ag 3d$_{5/2}$ spectra obtained from the AO irradiated MoS$_2$-Ag composite film at the surface and inner. For the AO irradiated MoS$_2$-Ag composite film, the binding energy of Ag 3d$_{5/2}$ peak was located at 367.4 eV, corresponding to AgO. In the film inner, the Ag 3d$_{5/2}$ spectra showed a peak with a binding energy about 367.8 eV, corresponding to Ag$_2$O. That indicated that the Ag was mainly oxidized to AgO at the film surface, and to Ag$_2$O in the film inner. These results were very different from the pure MoS$_2$ and MoS$_2$-Au composite films after the AO irradiation or space exposure, which presented an oxidation layer with a thickness of several nanometers.

Figure 4. XPS Ag 3d spectra of the AO-irradiated MoS$_2$-Ag film at different sputter depth.

Based on the XRD, SEM and XPS results, it can be seen that the AO irradiation caused the severe oxidation of MoS$_2$-Ag composite film. The MoS$_2$ was oxidized to mainly MoO$_3$ and Ag was oxidized to AgO at the film surface layer. In the sub-layer, the MoS$_2$ was oxidized to mainly MoO$_3$ and Ag was oxidized to Ag$_2$O. Meantime, the remarkable loss of S and cracking phenomenon were observed. These results indicated that the oxidation behavior was different from the pure MoS$_2$ film and the MoS$_2$ films composited with the inert metal (e.g., Au) and oxides (e.g., Sb$_2$O$_3$). Previous studies revealed that the AO irradiation could lead to the loss of S element for the pure MoS$_2$ film, but it was restrained in the film surface layer. It was found from the rf-sputtered MoS$_2$ film exposed in the AO environment that the surface was oxidized to form an oxide layer of Mo oxides, and the thickness ~ 10-30 monolayers [4]. Cross et al. [5] revealed that at the atomic oxygen exposed surface of the sputtered MoS$_2$ film, the S was lost as volatile products (SO or SO$_2$), but the effect depth of atomic oxygen exposure was restricted within 3 nm due to the protective function of Mo oxide layer. However, in this paper, for the MoS$_2$-Ag composite film, the oxidation from the AO irradiation occured not only at the film surface, but also in the
film inner. The sputter time of 20 min was corresponding to a depth of 580 nm for the reference SiO$_2$ film. For the MoS$_2$ films compositied with Au and Sb$_2$O$_3$, the surface morphology was consistent before and after the ground AO irradiation or space exposure. Similar to the pure MoS$_2$ film, the oxidation of the MoS$_2$ composite films with Au or Sb$_2$O$_3$ was restricted within the surface layer. This might be attributed to the chemical inertness of Au and Sb$_2$O$_3$ [10].

Compared to the Au and Sb$_2$O$_3$, the Ag is an active element, and can be oxidized by the AO irradiation and space exposure. It was found that that Ag surface is easy oxidized as exposed in the AO environment and causes the formation of an oxide layer [26-31]. Due to the mismatch in volume between the Ag oxides and Ag, the internal stress would occur in the oxide layer and result in the flaking and cracking of the oxide layer [27]. Reasonably, the fresh surface of Ag is bare and oxidized again. So repeated, the very severe oxidation occurs. Rooij reported that the erosion thickness was about 300 μm per year for the Ag as exposed in the space environment at orbit altitude of 400 km [27].

In this study, XRD revealed that the MoS$_2$-Ag composite film had both 2H-MoS$_2$ and face-centred cubic Ag phases. During the AO irradiation, both the MoS$_2$ and Ag were oxidized. Due to the expansion in volume from the oxidation, the MoS$_2$ platelets and the oxidation layer might be cracked, resulting that the oxidation layer lost its protective function to the lower film. This oxidation behavior was like to that of pure Ag film. Therefore, the MoS$_2$-Ag composite film showed a severe oxidation as compared with the pure MoS$_2$ and MoS$_2$ composite films with Au or Sb$_2$O$_3$. Due to the oxidation, the AO irradiated MoS$_2$-Ag composite film showed a much higher initial friction coefficient and a much shorter wear life than the non-irradiated film. The initial friction coefficient was increased from 0.07 to 0.32 and the wear life was declined from $8.9 \times 10^5$ to $9.1 \times 10^4$ r. For the AO irradiated and non-irradiated MoS$_2$-Ag composite films, the vacuum sliding friction curves were shown in Fig. 5.

![Figure 5. Sliding friction curves of the MoS$_2$-Ag composite films: (a) no-irradiated film and (b) AO-irradiated film.](image-url)
CONCLUSION

The rf-sputtered MoS$_2$-Ag composite film, composed of both 2H-MoS$_2$ and face-centred cubic Ag phases, were irradiated by the AO. The results revealed that the MoS$_2$-Ag composite film was severely oxidized by the AO irradiation and the wear resistance was declined significantly; the MoS$_2$ phase was mainly oxidized to MoO$_3$ and the Ag was changed to a mixture of AgO and Ag$_2$O; and the cracking phenomenon was obvious after the AO irradiation. For the MoS$_2$-Ag composite film, the oxidation behavior was mainly controlled by the Ag, not the MoS$_2$.

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