Characterization and anti-friction on the solid lubrication MoS$_2$ film prepared by chemical reaction technique

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Received 14 January 2005; revised 23 February 2005; accepted 8 March 2005
Available online 23 June 2005

Abstract

To develop a new way to produce the molybdenum disulfide (MoS$_2$) solid lubrication film, the following two-step chemical reaction technique was attempted. Firstly, a Mo film was prepared by multi-arc ion plating technique, and secondly the Mo film was sulfurized by a low temperature ion sulfuration technique to obtain the MoS$_2$ solid lubrication film. This MoS$_2$ film was a composite film consisted of MoS$_2$ and Mo. The lubricant MoS$_2$ is dominant in the surface and metal Mo is dominant in the deep layer. It is an ideal frictional surface. The tribological properties showed that the solid lubrication MoS$_2$ film possessed an excellent anti-friction property.

Keywords: Inorganic compounds; Thin films; Chemical synthesis; Surface properties; Solid lubrication; Characterization

1. Introduction

The inorganic solid lubricant molybdenum disulfide (MoS$_2$) is a kind of solid lubricant, which has been applied extensively for a long time. Its crystalline microstructures, tribological properties and anti-friction mechanisms have been studied deeply. Dunn et al. [1] investigated the XRD spectrum variation of MoS$_2$ in detail. Feldman et al. [2] reported the growth pattern of MoS$_2$ which was claded with carbon nanotubes, and scientist Chhowalla [3] have studied the tribological properties of nano particles of MoS$_2$.

There are lots of techniques for preparing a MoS$_2$ film, such as magnetron sputtering [4,5], ion beam assisted deposition [6], anode oxidation combined with heat treatment [7], chemical reaction and high temperature annealing [8], as well as sol-gel method [9]. The above techniques are useful, but obviously have the disadvantages, such as inaccurate atomic ratio between sulfur and molybdenum [10] and low deposition efficiency, or oxidation after high temperature annealing, or poor bonding strength with substrate.

To develop the preparation technique for MoS$_2$ film, combined the advantages of high deposition efficiency in multi-arc ion plating, and the simpleness and low cost of low temperature ion sulfuration [11], the authors adopted a two-step chemical reaction technique. Firstly, we employed the multi-arc ion plating to prepare a layer of hard molybdenum (Mo) film on the substrate, and then used the low temperature ion sulfuration to sulfurize the Mo film, finally obtained a solid lubrication MoS$_2$ film in situ. In the present paper, the characterization and tribological properties of the MoS$_2$ film was studied in detail.

2. Experimental methods

The substrate was AISI 1045 steel with hardness HRC52 and surface roughness Ra 0.13 μm. The metal Mo film was firstly prepared on the surface of 1045 steel in the multi-arc ion plating equipment, and then the Mo film was treated by low temperature ion sulfuration in the sulfuration equipment. The details of the ion plating and ion sulfuration can be found in Refs. [11,12], respectively.

The friction tests were carried out on a ring-on-block tester under dry sliding. The upper samples were 1045 steel blocks with the MoS$_2$ coatings, with dimensions of 31 mm×6.5 mm×6.5 mm. The lower samples were 1045...
steel rings with 40 mm in outer diameter, 16 mm in inner diameter, 10 mm in width and a hardness of 55HRC. The rotating speed of 0.42 m/s was fixed. The friction coefficient was measured in the time range from 0 to 60 min. The width of worn scar was measured at the time of 7.5, 15, 22.5, 30 and 37.5 min.

As comparison, the FeS films with 6 µm thick (sulfurized 1045 steel) were also carried out under the same condition. Atomic Force Microscope (AFM) and Scanning Electron Microscope (SEM) equipped with EDS were employed to analyze the morphologies of surface, cross-section of the Mo and MoS2 films. X-ray Diffraction (XRD) was utilized to identify the phases present in the films. Scanning Auger Microprobe (AES) was adopted to detect their element variation with depth and a scratching machine tester was used to measure the bonding strength between the Mo, MoS2 film and substrate.

3. Results and analyses

3.1. Characterization and film-forming mechanism of the MoS2 film

Fig. 1(a) and (b) are the surface morphologies of the Mo and MoS2 film by AFM. In Fig. 1(a), the compact and orderly columnar grains were shown on the surface of the Mo film, revealing the Mo film grew up as the direction of perpendicularity and the shape of columnar. The size of grains on the film surface was over 100 nm. In Fig. 1(b), the obvious sharp-island shape was present. The size of each grain was under 100 nm. This is because of the influence of low temperature ion sulfuration. In the earlier stage of sulfuration, the cathode, namely the Mo film, was heated by the bombard of ions. The Mo film was continuously bombed by lots of ammonia ions, and then the surface of the Mo film became gradually sharp-island shape from columnar shape.

Fig. 2(a) is the cross-section morphology of the MoS2 film by SEM, showing the thickness was 3 µm. The bonding between the film and substrate was compact and there is no transition layer at the interface. Fig. 2(b) is the enlarged image of Fig. 2(a), in which the line distribution to the elements of oxygen, iron, molybdenum and sulfur are labeled. In the whole film, the content of molybdenum is highest. The content of sulfur is very high in the surface, and decreased gradually from surface to inside. It can be seen that near the interface between the film and substrate, there was a little element transfer between iron and molybdenum. This is believed that during ion plating Mo, the molybdenum ion beam flow washed continuously out the 1045 steel surface. The iron ions that were sputtered out were blocked by the mass of molybdenum ions, which rushed onto the substrate, and then co-deposited on the substrate surface with the molybdenum ions. The atomic diameter of Mo is 0.201 nm, is similar with the atomic diameter of Fe of 0.172 nm. Therefore, promoted by the heat due to the collision of atoms, the Mo atoms permeate into the Fe substrate with the defects or crystalline boundaries.

Fig. 3(a) and (b) are the XRD patterns of the Mo and MoS2 film. Fig. 3(a) exhibits peaks from polycrystalline Mo film and Fe substrate. Fig. 3(b) exhibits the peak of MoS2 in addition to Mo and Fe, showing that the solid lubricant MoS2 was undoubtedly formed as a result of the reaction between the active sulfur atoms and the molybdenum atoms. The intensity of the peaks for Mo is much higher than that of MoS2. It indicates that although parts of Mo atoms in the Mo film were transferred to be MoS2, majority of them was still simple substance. In Fig. 3(b), the texture of Mo changed at the degree of 58.6°, the peak of crystal plane (121) disappeared. It is considered that the solid lubricant MoS2

![Fig. 1. Surface morphologies of the films observed by AFM. (a) Mo film, (b) MoS2 film.](image1)

![Fig. 2. SEM cross-section image and composition line scanning of the MoS2 film. (a) SEM cross-section morphology, (b) composition line scanning.](image2)
and simple substance Mo co-exist, but Mo is dominant in the MoS$_2$ film.

Fig. 4(a) and (b) show the chemical valence states of the molybdenum and sulfur elements on the MoS$_2$ film (before testing, 3 min sputtering to film needed) analyzed by XPS. Peaks of Mo can be seen at the bonding energy of 228.12 and 229.43 eV, while a peak of S appeared at the bonding energy of 162.25 eV. According to the standard bonding energy spectrogram, the bonding energy of the simple substance molybdenum is reported as among 227.65 and 228.20 eV, whereas that of the positive four state molybdenum (Mo$^{4+}$) is in the range of 229.0–229.85 eV. On the other hand, the bonding energy of the negative two state sulfur ($S^{2-}$) is among 160.3 and 163.9 eV. Therefore, it is concluded that there are two phases co-existing in the MoS$_2$ film. One is simple substance molybdenum, being dominant; another is some solid lubricant MoS$_2$, being much more near the film surface.

Fig. 5(a) and (b) are the AES depth composition profiles for the Mo film and MoS$_2$ film, respectively. In Fig. 5(a), molybdenum was evenly distributed along the depth direction from sub-surface. The existence of oxygen is probably due to the air preservation of the samples. In Fig. 5(b), the content of sulfur in the MoS$_2$ film was high, but decreased with the increase of depth, the content of molybdenum was low in the surface, but increased with the increase of depth. The trend showed that the solid lubricant MoS$_2$ exists much more in the near surface region of the film. In the depth of the film, the simple substance molybdenum is dominant and the solid lubricant MoS$_2$ is subsidiary.

Fig. 6(a) and (b) are the bonding strengths between the Mo, MoS$_2$ film and substrate, respectively, measured by a scratch tester. The peak occurred suddenly meant that the bonding was destroyed. The two coatings’ bonding strengths were up to 68.6 and 59.7 N, meaning that the adhesive strength between ion-plated Mo and substrate is sufficiently high. On the other hand, the MoS$_2$ film showed
lower bonding strength probably due to the formation of MoS₂, disturbing the continuity of interaction between Fe and Mo atoms.

3.2. Tribological properties of the solid lubrication MoS₂ film

Fig. 7(a) and (b) are the variation curves of the friction coefficient and worn scar with time of the MoS₂ film, FeS film prepared directly by low temperature ion sulfuration and 1045 steel under dry sliding, respectively. It can be seen in Fig. 7(a) that the friction coefficient increases with increasing time for all the films. The friction coefficient of the MoS₂ film was evidently lower than that of the FeS film and 1045 steel surface. From Fig. 7(b), the worn scar of the MoS₂ film increased with time, but the value of worn scar was also obviously lower than that of the FeS film and 1045 steel surface. It is concluded that due to its excellent solid lubrication effect, the MoS₂ film has the remarkable tribological properties.

It is widely accepted that the excellent anti-friction of the MoS₂ film is associated with the layered crystal structure of the solid lubricant MoS₂ [13]. MoS₂ has a close-packed hexagonal structure with lattice constant of \(a = 0.316 \text{ nm}, c = 1.229 \text{ nm}\). In the crystal lattice the close-packed groups consisting of three layers of S, Mo, S are formed. The thickness of the group is 0.625 nm, and the bonding between the MoS₂ layers is weak. Therefore, slippage happens easily along the close-packed plane, resulting in the remarkable anti-friction performance is shown.

4. Conclusions

(1) The solid lubrication composite MoS₂ film was successfully prepared by a two-step chemical reaction method, namely multi-arc ion plating plus low temperature ion sulfuration on the 1045 steel. The solid lubricant MoS₂ is much more on the film surface, and becomes less and less with the increase of depth.

(2) The obvious sharp-island shape was presented on the MoS₂ film, and the diameter of each island-shape crystal grain was less than 100 nm. The thickness of the MoS₂ film was about 2 μm, and the bonding strength with substrate was strong.

(3) The solid lubrication MoS₂ film possessed the excellent anti-friction property. It is a kind of outstanding solid lubrication film in the future.

Acknowledgements

This research was founded by National Natural Science Foundation of China (No. 50235030) and ‘863’ Project (2003AA331130).
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