Effect of Substrate Bias Voltage on the Structure and Properties of Mos2-Ti Composite Films on Titanium Alloy Surface

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Abstract. In order to discuss the effect of negative bias on the structure and properties of MoS2-Ti composite films on titanium alloy surface. In this paper, MoS2-Ti solid lubrication films were deposited on titanium alloy surface by unbalanced magnetron sputter. The effects of negative bias on the structure and properties of MoS2-Ti solid lubrication films were discussed. The morphology, phase, hardness, friction and wear resistance and wear mark morphology of solid lubricating film were analyzed and tested by scanning electron microscope, XRD, microhardness tester, friction and wear tester and surface profilometer. The results shows that when the negative bias voltage was -150V and -200V, the structure of MoS2-Ti films is compact and the bonding with the substrate is compact. With the increase of negative bias voltage, the hardness of the film increases gradually. The wear rate of the films prepared at -150V bias voltage is the lowest, which is 2.2×10^{-7}mm^3/(N×m). The MoS2-Ti composite films deposited on the surface of titanium alloy exhibit excellent tribological properties with low friction and wear resistance, which effectively improves the surface friction and wear properties of titanium alloy.

1. Introduction

High-performance aero-engine blades, compressor wheel and other important parts, due to the requirements of working conditions, strong corrosion resistance, high specific strength and stable medium-temperature performance, titanium alloy is one of the common materials to meet the above requirements [1]. However, the poor wear resistance of titanium alloy [2], especially the sensitivity of titanium alloy to fretting damage, can lead to a 35%-80% decrease in fatigue life of workpiece. Therefore, in order to prolong its service life, improve safety and reduce its use and later maintenance cost, it is more urgent to solve the problems of friction, wear and lubrication protection on the surface of titanium alloy [3-4].
MoS2, as a representative solid lubricant film for lubrication and reduction in the field of aviation [4], has been widely used in vacuum and space environments due to its lower coefficient of friction, higher wear-resistant life. But in a humid air environment, the MoS2 has high hydrophilicity and high surface energy [5], it is easy to absorb water and react with oxygen quickly to form hard MoO3 particles and corrosive H2SO4, not only increase the coefficient of friction, to deteriorate the friction and wear properties, but also corrode the substrate and accelerate the failure of the workpiece. On the basis of MoS2, scholars have deposited various materials to form MoS2-based composite membrane, and the wear resistance of MoS2 film in wet air is improved, the co-deposited materials include Ti, Cr, Zr, and so on [6-8]. Teer prepared the MoS2-Ti lubricated films by magnetron sputter, it has amorphous structure, and their friction coefficient is only 0.02 when they are used in atmospheric environment. Even under the condition of high humidity, the friction coefficient of MoS2-Ti composite film after 10^4 cycles was around 0.04, showing a unique lubricating and wear-off characteristic [9]. Among the many factors that affect the properties of MoS2-Ti composite films, the negative bias voltage of substrate is taken as the research object in this paper, the effect of the film on the structure and properties of MoS2-Ti composite films was discussed.

2. Experiment

2.1. Coating film
The coating system used in this paper is called scientific research multifunctional coating system. The purity of Ti target used in the experiment is 99.99%. The film-based growth materials selected in this paper are Ti-6Al-4V (TC4) and single crystal silicon (100), in which the TC4 substrate is cut by wire through the round rod, the round rod was cut into Φ24mm×8mm wafer, and the cut wafer was ground in turn with 400, 800, 1200, 1500 and 2000# sandpaper respectively. Before charging, the two substrate materials were washed with acetone ultrasonic in CCl4 for 10 min, and then washed with anhydrous ethanol ultrasonic for 10 min. The cleaned sample is dried in an oven at 100 ℃ for use.

Fig.1 shows the structure of MoS2-Ti composite films. In the process of film preparation, the Ti transition layer was preliminarily deposited for 20 min to improve the bonding force of MoS2-Ti film layer and TC4 substrate. On the basis of Ti transition layer, MoS2-Ti transition layer was deposited to maintain the parameters of the previous process, and MoS2-Ti composite films with different negative bias pressures were deposited. The vacuum degree is (3.0~5.9)×10^{-3} pa.

![Figure 1. Structure of the MoS2-Ti composite films](image)

2.2. Characterization and performance analysis
The surface and cross section morphology of MoS2-Ti composite synovium were observed by NOVA NanoSEM430 field emission scanning electron microscope. The phase of the composite film was analyzed by Japanese Rigaku SmartLab SE X-ray polycrystal diffractometer. The hardness of the composite synovium was measured by using the MH-5D micro-hardness tester. The friction and wear test of the lubricating film is carried out on the MS-T3000 ball-disc type friction and wear test machine. The test conditions for the friction and wear performance of the film are as follows: the friction pair is GCr15 steel ball with a diameter of 4 mm, the test load is 4.9 N, the experimental temperature is room temperature, and the test speed is 400 r/min. The surface morphology of the wear mark of the composite film was analyzed by S3700 scanning electron microscope, and the EDS energy spectrum analysis of the iconic region of the wear mark surface was carried out. The friction and wear morphology region was scanned and analyzed by Dektak-XT surface profiler.
2.3. The preparation parameters of MoS2-Ti films

The optimal substrate bias, deposition temperature, deposition pressure and Ti target current were studied by single factor single variable method. The content of Ti in the composite film was controlled at about 10%. The preparation parameters of MoS2-Ti films was shown in Table 1.

| Sample number | Base negative bias/ V | Pressure of deposition/ Pa | Deposition temperature/ ℃ | Ti target current/ A |
|---------------|------------------------|-----------------------------|---------------------------|---------------------|
| 1#            | -50                    | 1.0                         | 150                       | 1.0                 |
| 2#            | -100                   |                             |                           |                     |
| 3#            | -150                   |                             |                           |                     |
| 4#            | -200                   |                             |                           |                     |

3. Results and analysis

3.1. Effect of substrate bias on Surface and Cross Section Morphology of MoS2-Ti Films

Fig.2 is the SEM diagram of the surface morphology of four groups of MoS2-Ti films prepared under different substrate bias. It can be seen from the diagram that all the grains on the surface of the films are island. Fig. 1(a) is the film prepared at -50V bias, there are obvious reticular cracks on the surface of the film, the particles are loose between the particles and the particles, and the compactness of the films is poor. When the negative bias voltage is increased to -100 V, the crack width of the film surface (see Fig. 2(b)) is reduced, but the crack does not all disappear, and as the negative bias voltage continues to increase (see Fig. 2(c) and (see Fig. 2(d)), with the increase of negative bias voltage, the surface crack disappears and the compactness of the film increases obviously. With the increase of negative bias voltage, the speed of the ionized film-forming particles to reach the substrate increased, and the bombardment effect of the plasma on the surface of the film is also enhanced, the film can be uniformly and densified, the internal stress of the film is relieved [10], the formation of the MoS2-Ti film during the growth process is reduced, so that the hole of the film surfance is reduced, the crack disappears, and the surface grain is refined.

![Figure 2. Surface morphologies of MoS2-Ti films deposited at different bias voltage](image-url)
Fig. 3 shows the cross section morphology of MoS$_2$-Ti films prepared under different substrate bias. It can be found that MoS$_2$-Ti films grow in columnar crystals at different bias pressures. As shown in Fig. 3 (a), the film cross section at -50V bias pressure shows that there are obvious pores in the film, and with the increase of negative bias pressure, the pores in the films disappear to -150V (see Fig. 3(c)) and -200V (see Fig. 3 (d)), the film cross section is dense columnar crystal structure and no pores appear. At the same time, it can be observed that the thickness of the film decreases with the increase of negative bias voltage at the same deposition time. This may be due to the increase of the energy obtained by ions when the negative bias voltage increases, and the high energy ions bombarded the surface of the films to produce reverse sputter, which makes the deposition rate of the films relatively decrease and the thickness of the films decrease [11].

![Figure 3. Cross sectional morphologies of MoS$_2$-Ti films deposited at different bias voltage](image)

3.2. Effect of substrate bias on Phase composition of MoS$_2$-Ti Films

Fig. 4 is the XRD diffraction pattern of MoS$_2$-Ti films prepared under different bias pressures. It can be seen that there are only (002) diffused diffraction peaks in the films, no (100), (110) diffraction peaks, indicating that the films are amorphous or nanocrystal, and the (002) plane is parallel to the substrate surface. With the increase of bias voltage, the peak strength of (002) base surface of MoS$_2$ begins to weaken and shifts to a lower level. The results of energy spectrum test shows that the increase of negative bias voltage slightly increases the content of Ti elements in MoS$_2$ films, so the shift of peak to low angle is due to the increase of Ti content, while more Ti atoms are dissolved in MoS$_2$ lattice to cause lattice expansion, and finally lead to the deviation of diffraction peak. At the same time, a strong α-Ti crystal peak appears in the XRD diffraction pattern under different bias voltage, which may be derived from the doping Ti in the film layer, and may also be derived from the Ti transition layer.
Figure 4. XRD patterns of MoS$_2$-Ti films deposited at different bias voltage

3.3. Effect of substrate bias on hardness and bonding strength of MoS$_2$-Ti Films

Fig. 5 shows the relationship between hardness and bias voltage of MoS$_2$-Ti films prepared under different bias pressures. It can be seen that with the increase of the negative bias voltage, the hardness of the film is increased, and the hardness of the film can reach 400 HV under the bias of -200V. Combine with the fracture morphology of the MoS$_2$-Ti film, it can be found that the increase of the negative bias results in the increase of the ion bombardment and the increase of the density of the film, eventually, it leads to an increase in the hardness of the film [12].

Figure 5. The hardness of MoS$_2$-Ti films deposited at different bias voltage

The Rockwell indentation profile of the MoS$_2$-Ti films prepared under different bias voltages is shown in Fig. 6. It can be seen that with the increase of negative bias voltage, the evaluation level of MoS$_2$-Ti film is HF3, HF3, HF2, and HF1. With the increase of negative bias voltage, the bonding strength and toughness of MoS$_2$-Ti films are improved. Combined with the cross-section morphology and hardness of the film, it can be seen that the increase of negative bias voltage increases the bombardment energy and quantity of the film by plasma, and the bonding strength and toughness of MoS$_2$-Ti films are obviously improved.
3.4. Friction and wear tests

3.4.1. Effect of substrate bias on sliding friction and Wear Properties of MoS$_2$-Ti Films. The friction and wear curves of MoS$_2$-Ti films prepared under different bias pressures are shown in Fig.7. Under the condition of 12000r cyclic friction experiment, it can be seen from the diagram that the friction coefficient curves vary similarly under different bias pressures, and the friction coefficients fluctuate in a small range with the passage of time. Under the 12000r cycles, the friction coefficient increases first, then decreases, at last tends to stabilize, their mean values are about 0.06~0.09. Among the four bias voltages, when the bias value is -150 V, the average is the smallest, with a value of 0.65. The friction coefficients are stable and the fluctuation range is not large, showing relatively stable excellent friction and wear properties.

Figure 6. SEM micrographs of indentations of MoS$_2$-Ti films deposited at different bias voltage
3.4.2. Morphology and composition analysis of wear marks. The wear marks of the film after the friction and wear test for 30 min were observed microscopically, as shown in Fig. 8. The surface topography of the film after wear under the bias of -50V can be seen in Fig. 8(a). It can be seen that after the wear experiment of 12000r, a large amount of micro-cracks appear on the edge of the film sample, the center of the film sample has a deep crack due to contact fatigue, and a large amount of grinding debris is accumulated in the vicinity of the grinding mark. Compared with the film prepared under the rest bias, it can be seen that after the 12000r ball-disc wear test, the grinding mark is similar, the damage to the surface of the sample is slight, and the deeper plough groove and the wear crack are not observed, except that there is a difference in the width of the grinding mark.

(a)-50V; (b)-100V; (c)-150V; (d)-200V

Figure 7. Comparison of friction coefficients by ball-on-disk tests of MoS2-Ti films deposited at different bias voltage

(a)-50V; (b)-100V; (c)-150V; (d)-200V

Figure 8. Images of contact tracks of the surface of MoS2-Ti films deposited at different bias voltage
The energy spectrum of the inner and outer regions of the above-mentioned grinding marks shows that the content of elements in the inner and outer regions of all the films changed little before and after the wear test, so that only the content of the elements inside and outside the wear mark of the -50V film is set forth in Table 2. It can be concluded from Table 2 that a small amount of Fe elements appear in the wear mark, which mainly comes from the transfer after wear of GCr15 friction pair. The content of Mo, Ti, S, O element inside and outside the wear mark does not change much, and 11.21% oxygen appears outside the wear mark, which may be due to the oxidation of the film after long-term placement. The oxygen content of the film in the wear mark is 16.76%, which is higher than that of the film surface without friction and wear, this means that the film will oxidize to a certain extent during sliding friction and wear.

Table 2. The chemical compositions of area 1, 2 in the Fig.8

|   | O     | Fe   | Mo   | S     | Ti  |
|---|-------|------|------|-------|-----|
| 1 | 16.76 | 0.53 | 47.28| 24.73 | 10.69|
| 2 | 11.22 | —    | 48.91| 26.89 | 12.48|

The two-dimensional wear mark is scanned by DEKTAK-XT profiler, and the two-dimensional profile diagram of wear mark is shown in Fig. 9(a). On this basis, the relationship between wear rate and bias voltage is calculated as shown in Fig. 9(b). It can be seen from Fig.9(a), after 12000r sliding friction and abrasion test, the depth of the maximum grinding mark of the film is 3.26 μm under the bias of -50V, the total film thickness in the effective region of the film is about to reach the total thickness of the film, and the film is about to fail. As the bias continues to increase, the maximum wear depth of the film is increased, at the bias of -150 V, the maximum wear depth is only 0.9 μm. The wear rate is also consistent with the change trend of the maximum wear depth (see Fig.9 (b)), the wear rate of the films prepared at -50V bias voltage is the highest, which is $8.4 \times 10^{-7}$ mm$^3$/(N×m). When the bias voltage increases to -100V, the wear rate decreases rapidly. The wear rate of the films prepared under-150V bias voltage is the lowest, which is $2.2 \times 10^{-7}$ mm$^3$/(N×m), and the wear rate increased slightly at -200 V.

Figure 9. Wear tracks profile (a) and volume wear rate (b) of MoS$_2$-Ti films deposited at different bias voltage after 12000r wear test

4. Conclusion

(1) MoS$_2$-Ti composite film was prepared under different substrate bias by magnetron sputtering, and the surface of the film was in a granular structure. With the increase of negative bias voltage, the structure of MoS$_2$-Ti composite film is denser and the hardness of the film is also increases. MoS$_2$-Ti films prepared under different bias voltages can see that only (002) diffuse diffraction peaks, which time the film exhibits an amorphous or nanocrystalline feature.
(2) The friction and wear curves of the MoS$_2$-Ti composite film were similar under different bias, and the friction coefficient of the composite film was about 0.07 at the cycle of 12000r. The maximum wear depth is 3.26 μm at the negative bias of -50V, with the increase of the negative bias, the depth of the maximum wear mark is increased, and at the negative bias of -150V, the depth of the maximum grinding mark is only 0.9 μm.

(3) The maximum wear rate of the MoS$_2$-Ti composite film under -50 V bias is $8.4 \times 10^{-7}$ mm$^3$/(N×m), the wear rate is rapidly reduced when the bias is increased to -100V, and the wear rate of the film prepared under the -150 V bias is the lowest, the wear rate is $2.2 \times 10^{-7}$ mm$^3$/(N×m), the wear rate of the films increased slightly at the negative bias of -200V. The MoS$_2$-Ti composite films prepared at -150V bias showed excellent friction and wear resistance.

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