Tribological Performance of Sputtered MoS_2 Films in Various Environment
- influence of oxygen concentration, water vapor and gas species -

Koji MATSUMOTO and Mineo SUZUKI

NATIONAL AEROSPACE LABORATORY
Space Project and Research Center
7-44-1 jindaiji-higashi-machi Chofu, Tokyo, JAPAN 182-8522
Phone : +81-422-40-3181 / Fax : +81-422-40-3148
E-mail : kmatsu@nal.go.jp / suzukim@nal.go.jp

Abstract

Influences of oxygen, water vapor and gas species of the operating environment on the tribological characteristics of three types of sputtered MoS_2 films were examined. The tested films were RF (Radio Frequency) sputtering film, magnetron-RF sputtering film, and ECR ion beam sputtering film. The friction tests were carried out in various environments: in nitrogen + oxygen mixed gas where oxygen concentration was changed, in nitrogen or air where relative humidity was changed, and in ultra high vacuum.

All the tested films were affected similarly by oxygen and the humidity. Little effect on tribological performance was observed for all the films when the oxygen concentration was below 0.1%. However, when the oxygen concentration became over 0.1%, the wear life greatly decreased as the oxygen concentration increased. When the relative humidity was changed in air, no degradation of the wear life was observed at the relative humidity less than 15-20%. In the case of RF film, maximum wear life was obtained at the humidity of 10%. At over 20%RH, the wear life greatly decreased as the relative humidity became higher. When the humidity was changed in nitrogen gas, very different results were obtained. The relative humidity of a few percent caused degradation of the wear life, and the wear life drastically decreased as the relative humidity increased. Consequently, the wear life became shorter than in air at the relative humidity of over 20%.

The influence of the moisture on the tribological characteristics was greater than that of the oxygen, because that decrease of the wear life in the environment with humidity was bigger than that with the same mole concentration of oxygen.

When the gas species in the environment was changed, wear life of all the films was longer in the order of (in nitrogen) > (in dry air, in vacuum) > (in oxygen). The wear life in vacuum was shorter than in dry air for RF film, but longer for RF-m film. The wear life of ECR film in vacuum showed a big scatter, and it was superior to in air in some cases, but inferior in another cases. The fact that the wear life was longer in nitrogen gas than in vacuum indicates that the existence of nitrogen gas in operating environment had a beneficial influence to extend the wear life.

1. Introduction

Molybdenum disulfide (MoS_2) has been widely used as a lubricant of space equipment, because it shows good tribological characteristics in vacuum. To check the functions of space equipment including tribological components, ground tests are usually carried out before the launch. Therefore, MoS_2 films are required to show good tribological characteristics not only in vacuum but also in the ground test atmosphere. This is because that excess wear and/or deterioration of tribological characteristics of the MoS_2 film may happen during the ground tests. One of the major drawbacks of MoS_2 is that its tribological characteristics are greatly degraded in an environment with high humidity [1]. On the other hand, MoS_2 shows excellent tribological characteristics in nitrogen gas[2]. From this reason, the ground tests are often performed with nitrogen gas purging so as to allow the tribological components to be operated in nitrogen gas.

To improve the humidity resistance of MoS_2 films, extensive researches have been carried out [3-5]. It has been reported that a Mo-rich film deposited by co-sputtering of MoS_2 and Mo showed a good humidity resistance [4]. Improvement in humidity resistance has been also reported by ion implantation [5].

In another study, attempts have been made to grasp the influence of water vapor and/or oxygen on the tribological characteristics of MoS_2 films in more details. Matsumoto et al. examined the influence of the operating environment on the tribological characteristics of a MoS_2 film [6]. They carried out friction tests in moist nitrogen gas as well as in humid air, and in mixed gas of nitrogen and oxygen with various oxygen concentrations. Their results showed that the tribological characteristics were deteriorated by a slight amount of moisture, and that moisture had a much influential effect than oxygen. They also showed that the wear life in moist nitrogen gas was shorter than in moist air when the relative humidity was more than 20%. However, their results were obtained with a MoS_2 film by ECR ion beam sputtering, which was extremely Mo-rich, S/Mo ratio of 1.1-1.3.

In this study, the influences of gas species, oxygen and moisture of the operating environment on the tribological characteristics of three types of sputtered MoS_2 films were examined. Based on the test results, the influences of oxygen and moisture were compared, and the difference was discussed.

2. Test Specimens

Three types of sputtered MoS_2 films shown below were used as the test specimen:

(1) Radio Frequency sputtered film (RF film)
(2) Magnetron RF sputtered film (RF-m film), and
(3) Electron Cyclotron Resonance ion beam sputtered film (ECR film).

All the films were deposited on 440C stainless steel disk (the outer diameter of 45mm, the inner diameter of 8mm, and the thickness of 8mm) with a thickness of 1um. The sputtering conditions, appearances and S/Mo ratio of the films are described below, and the summary was listed in table 1.

(1) RF film

The sputtering conditions had been optimized through ball-on-disk friction tests in dry air [7]. First, cleaning of a 440C stainless steel substrate was performed by means of ion-bombardment by applying a DC voltage of 2kV and at an Ar gas pressure of 6.5Pa for 10 minutes. Next, RF power was applied onto the MoS_2 target to clean the surface by Ar plasma for 5 minutes. Then the sputter deposition of the film was carried out at a RF power of 220W for 30 minutes, which produced a film with a thickness of 1um. During the sputter deposition, the target and the specimen were water-cooled. Temperature of the disk specimen during the sputtering was about 60 degree C [8].

The color of the film was black. The film looked dense, and columnar structure was remarkable. The S/Mo ratio of the film analyzed by EPMA was approximately 1.7.

(2) RF-m film

This type of the film was deposited by Hosei University. The procedure of the sputtering was similar with the RF film. For substrate cleaning, a RF power was applied onto the substrate at an Ar gas pressure of 5Pa for 10 minutes. Next, the MoS_2 target was cleaned for 10 minutes by applying a RF power to the target. Then, sputter deposition of the film was carried out at an Ar gas pressure of 0.2Pa, and at a RF power density of 1.6W/cm^2 for 15 minutes, which gives a film thickness of 1um. Both the target and specimen were water-cooled during sputtering.

The film surface was silver-gray colored, and the S/Mo ratio of the film was approximately 1.4.

(3) ECR film

For this film, MoS_2 was sputtered by an ECR ion beam. Ar plasma was activated by 2.45GHz microwave and 875G magnetic field, and the Ar ions were accelerated by an electric field into the ion beam.

First, the specimen was cleaned by placing it in front of the ion beam for 3 minutes. Then the sputter deposition was carried out. Both the cleaning by the ion and sputtering were carried out at an acceleration voltage of 2.0kV, a microwave power of 100W, an Ar gas flow rate of 0.58 SCCM, and at a pressure of 2.0 x10^{-2}Pa. These conditions were optimized by friction tests in vacuum [9].

The thickness of the film depended on the position of the disk during sputtering. In order to get a film with uniform thickness, the sputter deposition was interrupted at the half the scheduled sputtering time and the disk specimen was rotated 180 degree, and then sputtering resumed[9]. The sputtering time was 90 minutes x 2, totaling 180 minutes. Both the specimen and the target were water-cooled during sputtering. The temperature of the specimen during the sputtering was about 20 degree C [8].

The film was silver-colored, and had a metallic luster. The S/Mo ratio of the film was 1.0-1.2, which was remarkably low value.

3. Experimental Details

3.1 Friction test method

Friction tests were carried out in ultra-high vacuum, in mixed gas of nitrogen + oxygen (oxygen concentration of 10ppm - 100%), and in humid nitrogen or humid air at relative humidity of 0-80%. Two friction testers, both with ball-on-disk configuration, were used. The first one is an ultra-high vacuum tribometer, which has a sorption pump, a turbo-molecular pump and an ion-sputter pump as a vacuum pumping system. The pressure of an order of 10^{-6}Pa can be attained. Another is a controlled-atmosphere tribometer, of which the test section is surrounded with an acrylic cover, and the test environment can be controlled by gas purge.

The test conditions and test specimen are listed in table 2. The counterpart ball specimen was made of 440C stainless steel, with a diameter of 7.94 mm (5/16"). The applied load was 10N and sliding speed was 0.5m/s. Wear life was defined as the time when friction coefficient exceeded 0.3.

3.2 Method of the environment control

3.2.1 Oxygen concentration adjustment

In the tests where oxygen concentration was changed, commercially available mixed gas of nitrogen + oxygen was used. The used gases were high-purity nitrogen gas (purity of 99.9995%, O_2< 0.5ppm), standard mixed gases (oxygen concentration of 100ppm, 1000ppm, 1%), dry air (oxygen concentration of 20%) and pure oxygen gas.

For the tests at the oxygen concentration of less than 1%, the ultra-high vacuum tribometer was used. First, the vacuum chamber was evacuated to a pressure of 10^{-5}Pa, and then the test gas was introduced. The gas was continuously supplied at a flow rate of 200ml/min throughout a test. At the outlet of the gas flow line, oxygen concentration was measured using a zirconia type oxygen concentration meter. We define in this study that the oxygen concentration of the test environment is the measured value by the oxygen concentration meter. The measured oxygen concentration was a little higher than that of supplied gas when the concentration was low. For example, the measured value was 10-30ppm when the high-purity nitrogen gas (specification is O_2< 0.5ppm). The friction tests were started after the measured oxygen concentration stabilized, which usually took a few hours.

For the tests of oxygen concentration of 20% (dry air) and 100% (pure oxygen gas), the controlled-atmosphere tribometer was used. The test gas was supplied to the test section, which was encased with an acrylic cover, at a flow rate of 3 l/min for about 1 hour before the test was started. The gas was continued to flow at the same flow rate throughout the test. Oxygen concentration was not measured in these tests.

	RF	RF-m	ECR
Working Gas	Ar(Argon)		
Target	Hot Press	CIP	CIP
Ion-bombardment Conditions	DC 2 kV	RF 2.5 kV	Acceleration Voltage 2.0kV Microwave Power 100 W
Pressure [Pa]	6.5	5	2 x 10^{-2}
Time [min]	10	10	3
Sputtering Conditions	RF Power 220 W	Voltage 1.4 - 1.8 kV RF Power 1.6W/cm^2	Acceleration Voltage 2.0kV Microwave Power 100 W
Pressure [Pa]	6.5	0.2	2 x 10^{-2}
Time [min]	30	15	90 x 2
Color of film	black	silver-gray	metallic
S/Mo ratio	about 1.7	about 1.4	1.0 - 1.2

Table.1 Sputtering Conditions and Characteristics of the films

Load	10 N
Sliding Speed	0.5 m/s
Atmosphere	*Ultra High Vacuum (10^{-6} Pa) *N_2+O_2(O_2Conc.:10ppm-100%) *Air+H_2O (Relative Humidity:0-80%) *N_2 +H_2O (Relative Humidity:0-80%)
Ball Specimen	440C, D 7.94 mm
Disk Specimen	440C +MoS_2(thickness of about 1um)

Table.2 Test Conditions and Test Specimens

3.2.2 The humidity adjustment

For the tests where relative humidity was changed, the controlled-atmosphere tribometer was used and the test gas, generated by mixing humid gas and dry gas, was supplied to the test section. The relative humidity was adjusted by controlling the flow rates of humid gas and dry gas. The humid gas was generated by bubbling method. The relative humidity was measured using an absolute humidity sensor placed near the specimen. The sensor actually measures the change in thermal conductivity caused by the change in humidity, and it is not possible to measure the humidity in nitrogen gas. Thus in nitrogen gas tests, we supposed that the same relative humidity was set as in air tests when the flow rates of the humid gas and the dry gas were the same. No humidity measurements were made in the nitrogen gas tests. The humidity sensor has not enough accuracy for the measurements of low relative humidity of less than 10%. Therefore, humidity sensor was calibrated later using a dew-point meter, and the measured values were corrected.

The test gas was fed at a flow rate of about 3 l/min for approximately 1 hour until relative humidity was stabilized, and then friction test was started. The gas was supplied at the same flow rate throughout the test.

4. Results and Discussions

4.1 Influence of the oxygen

A relation between the wear life and the oxygen concentration is shown in figure 1. When oxygen concentration was over 0.1%, the wear life of all films was remarkably decreased as the oxygen concentration increased. In dry air (an oxygen concentration of 20%), the wear life was 1 to 2 order of magnitudes shorter than that at an oxygen concentration of 0.1%. At oxygen concentrations of below 0.1%, the RF-m film and ECR film showed longer wear life when the oxygen concentration became low. In the case of the RF film, the longest wear life was obtained at an oxygen concentration of 0.01%, and at lower oxygen concentrations, the wear life became shorter.

Figure 2 shows the friction coefficient against the oxygen concentration. At the oxygen concentration higher than 1%, the friction coefficient of all the films increased as the oxygen concentration. However, when the oxygen concentration was low, the effect of the oxygen concentration depended on the type of the films. The RF film gave higher friction coefficient at oxygen concentrations of less than 0.1%. The ECR film also gave higher friction coefficient at lower oxygen concentrations, but the threshold concentration was 10-30ppm. In contrast, the friction coefficient of the RF-m film became lower monotonously with the decrease of the oxygen concentration.

At the oxygen concentrations higher than 0.1-1%, the tribological characteristics of the sputtered MoS_2 films were deteriorated. This seems to be caused by oxidation. Tribological characteristics was also deteriorated at very low oxygen concentration in the case of the RF film. Fleishcauer et al. reported that a sputtered MoS_2 film showed the longest wear life when about 25% of the surface layer was oxidized. They suggested that a slight oxidation might cause good adhesion of the MoS_2 transfer film to the mating steel surface [10]. There is a possibility that the RF film was optimally oxidized at an oxygen concentration of about 0.01%, and thus the wear life increased. In this study, only RF film showed this phenomenon. One explanation for this is that the RF film was easily oxidized compared with the other films. Matsumoto et al. reported that the depth of the oxidized layer was about 100nm for the RF film when atomic oxygen irradiated, whereas it was a few tens nm for the ECR film. They supposed that atomic oxygen can penetrate easily into the RF film due to its film structure with higher porosity [8].

If the RF film can be oxidized easily, the oxidation would progress extensively under high oxygen concentrations, and thus the tribological characteristics would also be deteriorated remarkably. However the test results were very different. The RF film showed the longest wear life and low friction coefficient in pure oxygen gas environment, and it showed comparable tribological characteristics with the other films in dry air. Under the high oxygen concentrations, 440C steel of the mating ball material would be oxidized and thus the MoS_2 film rubs

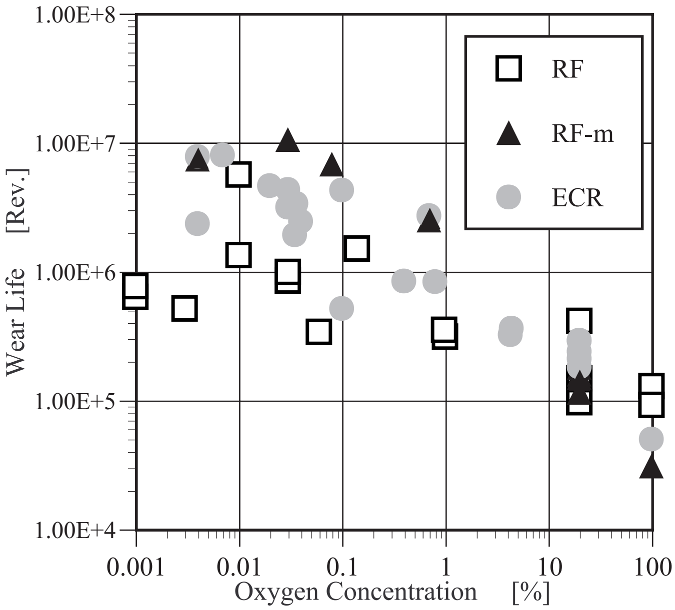

Fig.1 Wear life against oxygen concentration

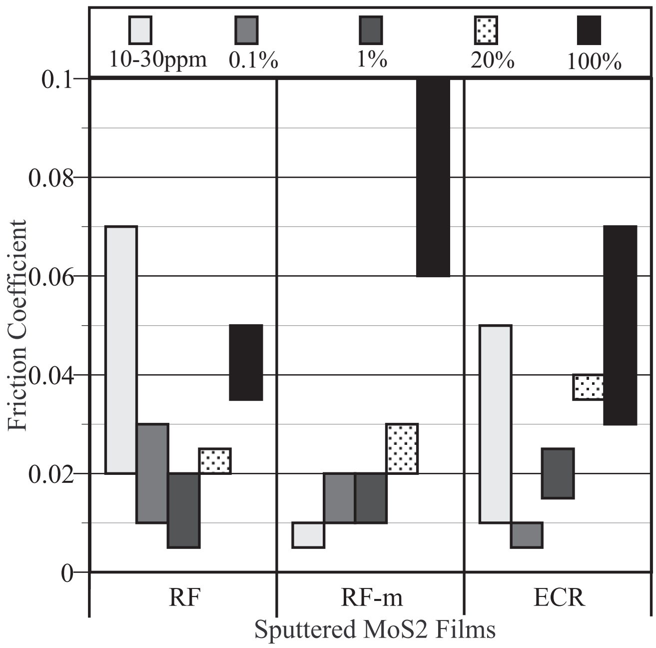

Fig.2 Friction coefficient of films in various oxygen concentration

against iron oxide, not against steel. There is a possibility that the RF film showed better tribological performance against iron oxide than the other films. Further study is needed to clarify the effect of the oxygen on the tribological characteristics of MoS_2 film.

4.2 Influence of the humidity

The wear life of the three types of MoS_2 films was plotted against relative humidity in figures 3 - 5. In the tests in air, the wear life of the RF film increased as the relative humidity increased up to 10%, but it was rapidly decreased as the humidity further increased (fig. 3). The wear life at 80%RH was 3 order of magnitude shorter than the one at 10 %RH. As for the RF-m film (fig. 4) and ECR film (fig. 5), the wear life remained almost the same at the relative humidity of below 20%, and it decreased as the humidity increased over 20%. However the decrease in wear life was smaller than the RF film, 1 order of magnitude for the RF-m film and 2 order of magnitude for the ECR film.

In contrast to the air environment, the wear life of all the films decreased dramatically in nitrogen gas tests when the relative humidity was increased. The difference in wear life was as much as 4 order of magnitude between in dry nitrogen gas and in humid nitrogen gas with a humidity of 80%. It is worthy to note that the wear life in nitrogen gas of all the films became shorter than that in air at a relative humidity of over 20%. This means that existence of 20% oxygen relieved the deterioration of the tribological characteristics by water vapor.

The change in friction coefficient during the tests in air is shown in figure 6. In dry air, all the films showed low friction coefficient of 0.025-0.045 in a stabilized state, and little difference was found among the films. However, the difference in friction characteristics among the films became apparent when the relative humidity increased. At 10%RH, RF film and ECR film showed a little higher friction coefficient, but friction coefficient of RF-m film rose immediately at the beginning of the test, and then varied from 0.05 to 0.2. Further increase in relative humidity caused higher friction coefficient from the beginning of the test as well as bigger variation for all the films, although it cannot be seen in fig.6 due to drastic decrease in wear life.

The change in friction coefficient in the tests in nitrogen gas is shown in figure 7. All the films showed low friction coefficient of 0.025-0.05 in dry nitrogen gas, the value is almost the same as in dry air. The effect of the humidity on friction characteristics was similar with in air. Friction coefficient became a little high at the relative humidity of 10-20%, and further increase in the humidity caused higher friction coefficient from the beginning of the test. However, variation of the friction coefficient was not so big even at high relative humidity, different from the tests in air. Although the effect of the humidity on wear life was very different between in nitrogen gas and in air, the effect of the humidity on friction characteristics was similar.

These results revealed that the wear life of the sputtered MoS_2 films did not decrease when the relative humidity was below 20% in air. In the case of the RF film, the longest wear life was obtained at a relative humidity of 10%. At a higher relative humidity, RF-m and the ECR films showed better humidity resistance than the RF film. However, wear life of all the films dramatically decreased, suggesting that the film with a higher humidity resistance is required from a practical point of view. It was reported that a Mo-rich film obtained by co-sputtering with the 2 targets of Mo and MoS_2 had better humidity resistance

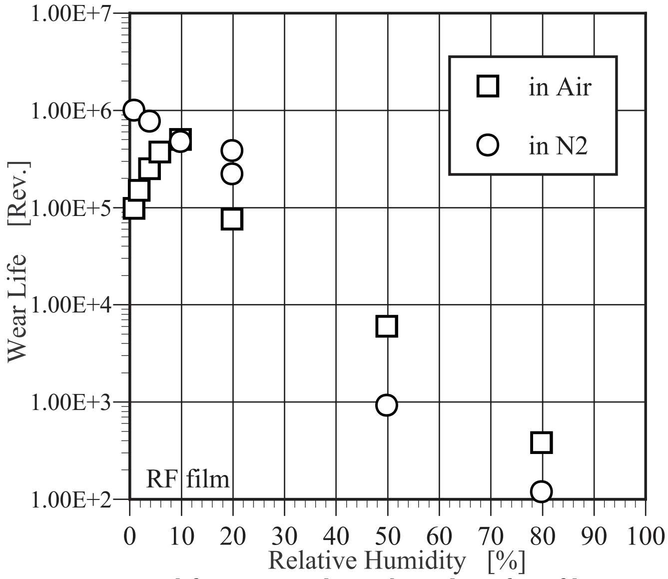

Fig.3 Wear life against relative humidity of RF film

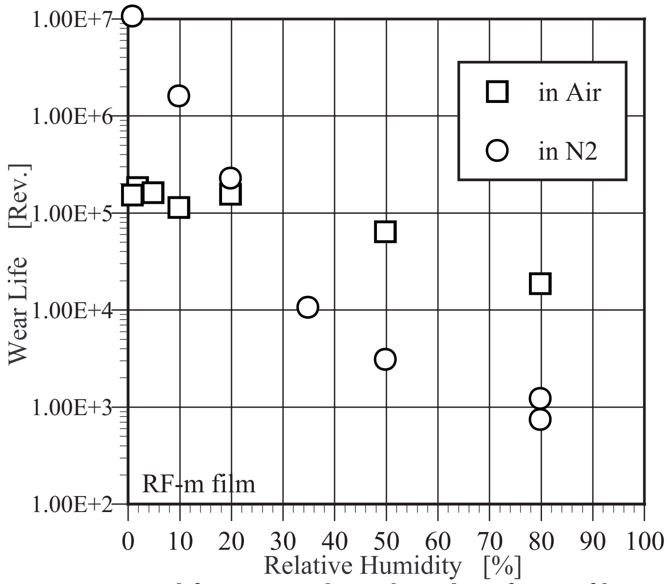

Fig.4 Wear life against relative humidity of RF-m film

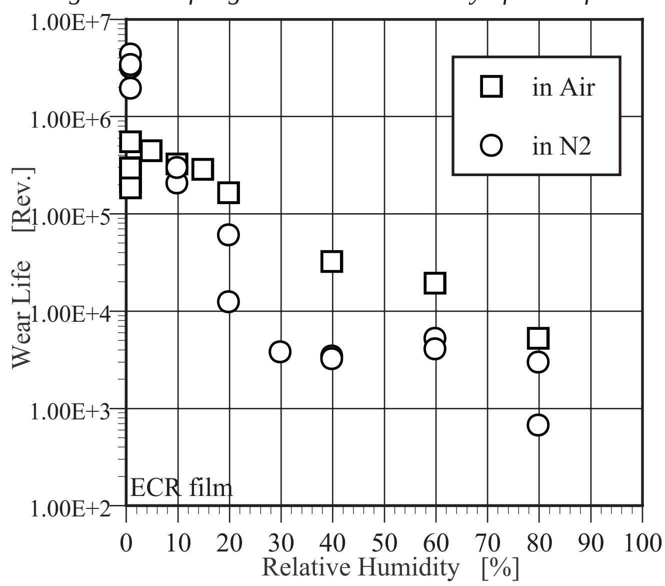

Fig.5 Wear life against relative humidity of ECR film

when tested in air. The S/Mo ratios of the films tested in this study were about 1.7 for the RF film, about 1.4 for the RF-m film, and 1.0-1.2 for the ECR film. Both results support that Mo-rich films had better humidity resistance.

All the tested films showed monotonous, drastic decrease in wear life as the relative humidity increased when tested in nitrogen gas, even in low humidity conditions. The wear life in nitrogen gas was longer than in air at low relative humidity of below 10-20%, but shorter at higher humidity. This implies that tribological characteristics were deteriorated by different mechanism between the cases in humid nitrogen gas and in humid air. This is also supported by the fact that the effect of the moisture on the wear life was more serious than that of oxygen. Relative humidity of 20-80% at room temperature corresponds to the mole concentration of 0.6-2.5%. Existence of 1.5% oxygen in the operating environment caused a little difference in wear life, however existence of 1.5% H_2O (relative humidity 50%) resulted in remarkable decrease in the wear life. After the tests at oxygen concentrations of 20% and 100%, red brown wear particles, probably Fe_2O_3, was observed on the rubbing track of the disk, while black wear particles, mixed with the red brown ones, were found on the rubbing track when tested at the relative humidity of 80%. This suggests that the oxides produced by moisture was different from ones by oxygen. Further study is needed to clarify what kinds of oxides are produced by oxygen and/or moisture, and how these oxides affect tribological characteristics of MoS_2 films.

4.3 Influence of the gas species

Wear life was longer in the order of in nitrogen > in dry air > in oxygen for all the films. This suggests that the wear life decreased with the amount of oxygen in the operating environment. If so, one can expect that the wear life in vacuum is as long as that in nitrogen gas. Figure 8 compares the wear life in vacuum with that in the other environments. In the figure, the results are chronologically presented in recent 5 years experiments.

It was commonly observed that the wear life was longer in the order of in nitrogen > in vacuum > in oxygen. However, it depended on the type of the films whether the wear life in vacuum was superior or inferior to the life in dry air. The RF film showed shorter wear life in vacuum than in dry air, whereas the RF-m film gave the reversed result. In the case of the ECR film, the wear life in vacuum

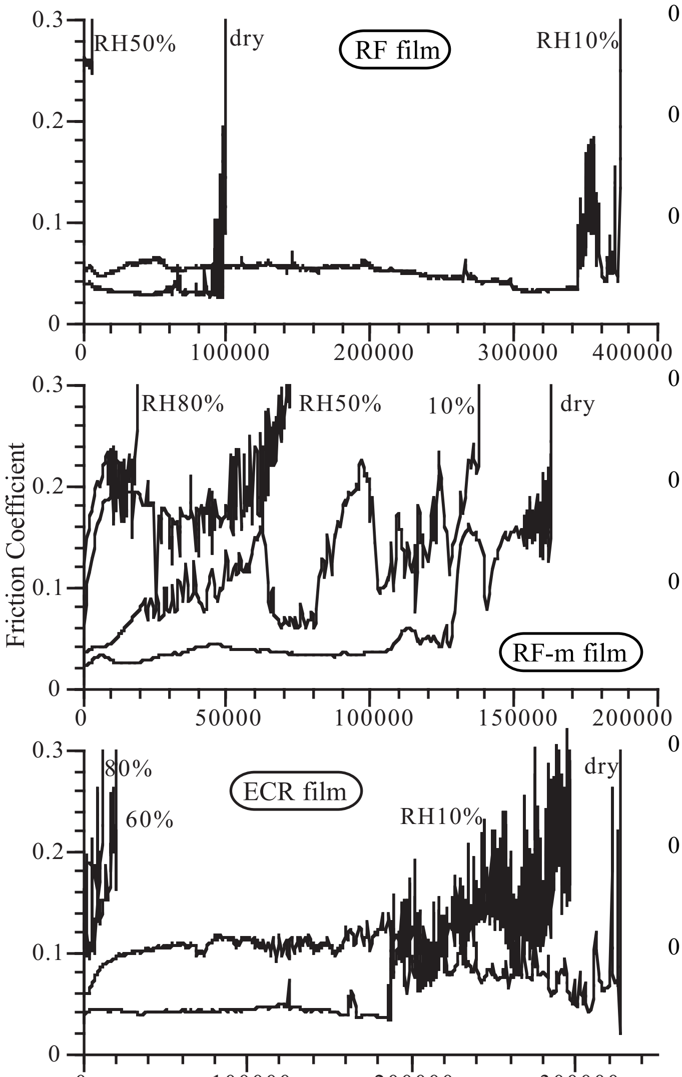

Fig.6 Change in Friction Coefficient in Air

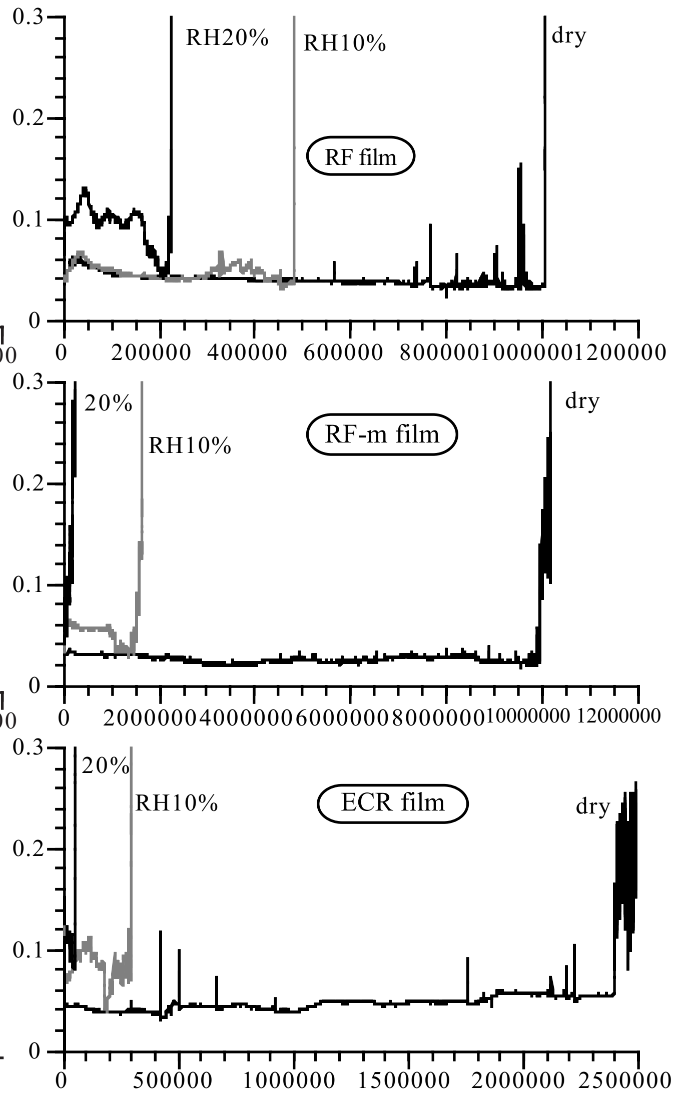

Fig.7 Change in friction Coefficient in N2

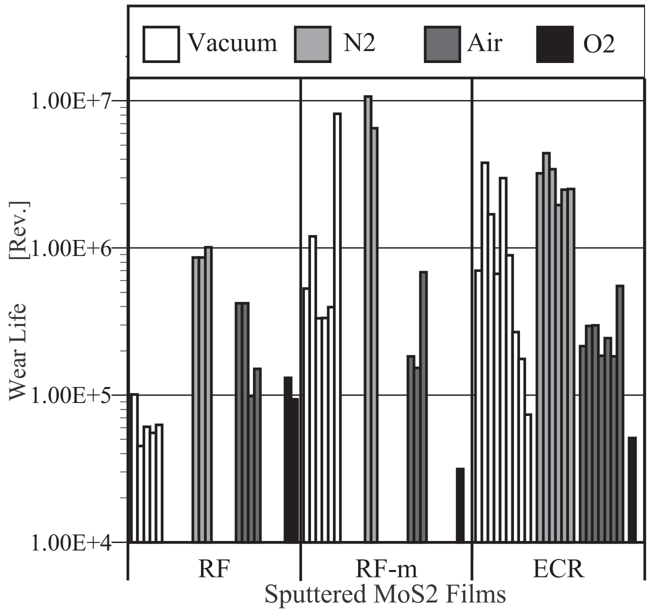

Fig.8 Wear life of three types of films in various environment

was longer than in dry air a few years ago [6], however, it decreased to a shorter level than in dry air as the sputtering was carried out repeatedly.

If oxidation due to the existence of oxygen caused the result that the wear life was longer in the order of in nitrogen > in dry air > in oxygen, the wear life in vacuum must be as long as that in nitrogen gas. The fact that the wear life in nitrogen gas was longer than in vacuum indicates that existence of inert gas in operating environment had a beneficial effect to extend the wear life. Suzuki reported that a good transfer film was formed on the mating ball surface in nitrogen gas environment compared with in vacuum, and he attributed this for the reason of the increase in wear life [11].

The repeatability of the wear life in vacuum was worse than in gas environment. Especially with the ECR film, we have experienced drastic decrease in wear life in only 2 years even at the same sputtering conditions. Exchange of the target and cleaning of the vacuum chamber could not improve the wear life. A minute difference in the sputtering conditions might affect the tribological characteristics. If this is true, there remains another question why the dif ference caused reduction of wear life only in vacuum. Further investigation is needed to clarify these points.

5. Conclusions

The friction tests were carried out with three types of sputtered MoS_2 films (RF, RF-m and ECR) in various gas environments. The results obtained are summarized as follows;

(1) All the tested films were affected almost similarly by oxygen and water vapor.

(2) When the oxygen concentration was over 0.1%, the wear life of all the films decreased as the oxygen concentration increased. However, little degradation in wear life was observed at the oxygen concentrations of below 0.1%.

(3) When the relative humidity was changed in air, no degradation of the wear life was observed at the relative humidity less than 15-20%. At over 20%RH, the wear life greatly decreased as the relative humidity became higher. In nitrogen gas environment, the effect of moisture on the wear life was greater than in air. The wear life decreased even by a slight amount of moisture, a few percent in relative humidity, and it decreased drastically as the humidity increased. As a consequence, the wear life in nitrogen became shorter than in air at over 20%RH. The friction coefficient of all the films became higher with the relative humidity both in air and in nitrogen.

(4) The influence of the water vapor on the tribological characteristics was greater than that of the oxygen, because that decrease in wear life caused by moisture was bigger than that by the same mole concentration of oxygen.

(5) The wear life of all the films was longer in the order of (in nitrogen) > (in vacuum, in dry air) > (in oxygen). It depended on the type of the films whether the wear life in vacuum was superior or inferior to the life in dry air.

6. References

1) Y. Miyakawa, K. Seki and M. Nishimura, Effect of Moisture and Pin Holder Rigidity on Wear, Journal of Japanese Society of Lubrication Engineers, 18 No.4 (1978) 323-334

2) M. Nishimura, M. Nosaka, M. Suzuki and Y. Miyakawa, The Friction and Wear of Sputtered Molybdenum Disulfide Films in Sliding Contact, Proc. 2nd Int. Conf. On Solid Lubrication, ASLE SP-8 (1978) 128-138

3) P. Niederkaeuser, M. Maillat and H.E. Hintermann, Moisture Resistant MoS_2-based Composite Lubricant Film, Proc. 1st European Space Mechanisms & Tribology Symp., ESA SP-196 (1983) 119-123

4) S. Hamasaki, R. Shibata, M. Nishimura and K. Seki, Tribological Properties of Alternately-Sputtered MoSx-Mo Films, Proc. Chinese Int. Symp., (1992)

5) N. Abe, K. Yasumoto, N. Watanabe and M. Nishimura, Tribological Characteristics of MoSx Films Improved by High Energy Ga Ion Implantation, Rep. Res. Cent. Ion Beam Technology, Hosei Univ. No.15 (1997) 133-136

6) K. Matsumoto and M. Suzuki, Influence of Oxygen and Water Vapor in Operating Environment on Wear Life of an MoS_2 Film, Proc. Int. Tribology Conf. Yokohama (1995) 1165-1169

7) M. Nishimura, M. Nosaka, M. Suzuki, K. Seki and Y. Miyakawa, Lubrication Properties of Molybdenum Disulfide Films Deposited by RF Sputtering Method, Tech. Rep. of National Aerospace Lab. TR-903 (1986)

8) K. Matsumoto and M. Suzuki, Evaluation of Tribological Characteristics of Sputtered MoS_2 Films Exposed to LEO Environment, Int. Symp. on Space Technology and Science (1998) 502-507

9) K. Matsumoto, M. Kawamura, M. Suzuki and M. Nishimura, Tribological Characteristics of MoS_2 Films Sputtered by ECR Ion Gun, Proc. 4th Int. Tribology Conf. (AUSTRIB ‘94) (1994) 343-349

10) P.D. Fleischauer and R. Bauer, The Influence of Surface Chemistry on MoS_2 Transfer Film Formation, ASTE Trans., 30 (1987) 160-166

11) M. Suzuki, Comparison of Tribological Characteristics of Sputtered MoS_2 Films Coated with Different Apparatus, Proc. 1st World Tribology Congress, (1997)