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High temperature friction and wear behavior of MoS_2/Nb coating in ambient air

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Abstract MoS_2 coatings are well-known for their solid lubricant properties and used as self-lubricants in vacuum and inert gas environments, and such coatings are not used in atmospheric conditions because of their deteriorating tribology. The tribological performance of MoS_2 solid lubricant coatings in the different atmospheres has been improved by the codeposition of a small amount of another metal. In this study, the tribological behavior of MoS_2/Nb coatings was investigated in ambient air at temperatures up to 500°C by using high-temperature pin-on-disc tribo testers and alumina balls as counterfaces. MoS_2/Nb coatings were deposited on silicon wafers and AISI 52100 steel substrate by closed-field unbalanced magnetron sputtering. The structural analyses of the coatings were performed using X-ray diffraction and scanning electron microscopy techniques. The hardness was measured using a microhardness tester.

Keywords MoS_2–Nb, Solid lubricant, High temperature, Friction, Wear

Introduction

MoS_2 solid lubricant coatings are well-established in industrial communities. Sputtering techniques are now most widely used for the deposition of MoS_2 coatings.[1] However, the resistance of MoS_2 coatings against humidity is inadequate and the tribological properties of MoS_2 coatings are degraded in humid conditions, resulting in an increase of the friction coefficient and a decrease in its working lifetime. Furthermore, MoS_2 coatings are easily oxidized at high temperatures.[2–6] Therefore, considerable efforts have been made to improve the tribological properties of sputtered MoS_2 coatings in humid environments. Researchers have indicated that the addition of metals has improved the wear resistance of MoS_2. Many metals were studied, such as Ni, Pb, Ta, Au, Ce, Cr, and especially Ti.[7–11] Recently, MoS_2–Ti coatings have provided excellent industrial results for a wide range of cutting and forming applications.

The studies of MoS_2/metal composite coatings have generally concentrated on the content of the metals selected, their structural characterization, and their tribological behavior at room temperature in atmospheric conditions. However, there are few studies on the tribological behavior of MoS_2/metal composite coatings at high temperatures in the literature. As is known, MoS_2/metal composite coatings, which are used as solid lubricant in cutting tools, are subjected to high temperatures during machining. At these temperatures, the tribological properties of the coating are negatively affected,[12] which limits the use and performance of coatings for cutting tools.

To improve the tribological performance of MoS_2 coatings in atmospheric conditions, Nb was added to MoS_2 in this study as a different additive metal than mentioned previously. To our knowledge, there are few studies on MoS_2 composite coatings with the addition of Nb in the literature.[13] Therefore, MoS_2/Nb composite coatings were deposited with the pulsed-dc magnetron sputtering technique in a closed-field unbalanced magnetron sputtering (CFUBMS) ring. The tribological performances of the coatings were evaluated at both room and high temperature.

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Experimental details

MoS_2/Nb composite coatings were deposited on AISI 52100 polished steel ($R_a \le 0.12$ μm) using CFUBMS using the pulsed-dc technique. The experimental parameters are given in Table 1. Before deposition, the samples were sputter-cleaned with an advanced energy (AE) DC magnetron driver at 900 V. MoS_2/Nb composite coatings using the CFUBMS system presented schematically in Fig. 1 were deposited by rotating these substrates between three MoS_2 targets and one niobium target in an argon atmosphere. MoS_2/Nb coatings were deposited with a niobium interlayer, followed by sputtering from three MoS_2 targets and one niobium target simultaneously. The DC power supply (AE) was run in the constant current mode and another model of pulsed supply (AE-Pinnacle plus + 5 kW) was used for comparison. Unipolar pulsed-dc power at substrate was used in this work, in which the line form of the unipolar pulses used is shown schematically in Fig. 2, and where the substrate voltage is pulsed between the normal operation voltage and the ground. The pulse parameters were fixed for all runs.

Table 1: The coating parameters of MoS_2/Nb deposited by CFUBMS

Process parameters	
Working pressure (Pa)	0.33
Bias voltage (−V)	−75
MoS_2 target current (A)	1.5
Nb target current (A)	1
The space between the substrates and targets	95 mm
Working gas	Argon
Substrate temperature	~150°C
Pulsed-dc	f = 150 kHz, T = 2 μs

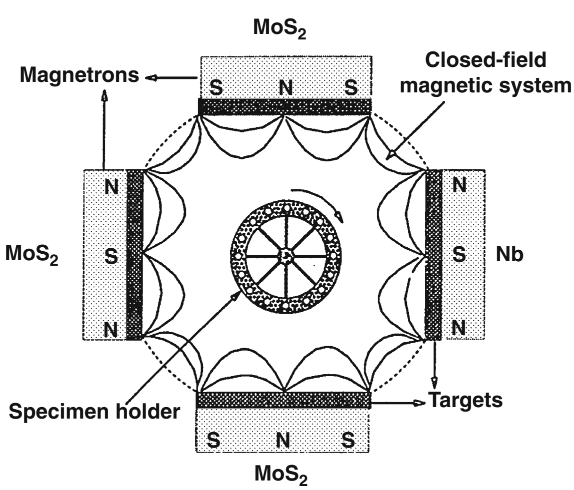

Fig. 1: Teer coating CFUBMS

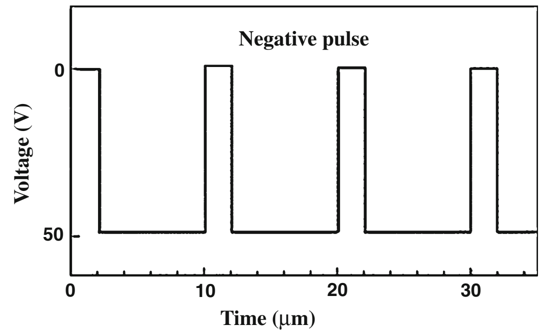

Fig. 2: Schematic diagram of the substrate voltage waveform for a pulsed-dc power in unipolar pulse mode

To investigate the phase transformations of MoS_2/Nb composite coatings as a function of temperature, in situ X-ray characterizations using high-temperature attachment were performed on an Rigaku 2200D/Max diffractometer with a Cu Kα ($\lambda = 1.5404$) radiation source. In situ X-ray diffraction (XRD) studies were carried out at room temperature and at the temperatures of 100, 300, and 500°C in a vacuum with a chamber pressure of 10^{-2} Pa. The heating duration time at each annealing temperature was 20 min, and the ramp rate was 20°C/min.

The microstructure of MoS_2/Nb composite coatings, the wear tracks, and the surface of the counterface after the wear tests were analyzed by means of a JEOL-6400 scanning electron microscopy (SEM), and the composition of coatings was determined by energy dispersive spectrometry (EDS). The high-temperature tribological behavior of MoS_2/Nb composite coatings was examined using a pin-on-disc test device (CSM high-temperature tribo-tester). All the experiments were conducted with an Al_2O_3 ball with a 6 mm diameter in sliding contact. The tests were carried out with a load of 5 N at the linear speed of 30 mm/s, and in dry sliding condition at room temperature, and at the temperatures of 100, 300, and 500°C in atmospheric conditions. Surface profiles of the wear tracks on the MoS_2/Nb composite coatings were measured by a Mitutoyo surface profilometer. The wear volume was calculated using the profiles obtained from the wear track cross section, and thus the wear rate was attained using the $K = V/(w \cdot s)$ equation, where K is the value of the wear rate, V is the worn volume, w is the normal load, and s is the distance moved.

Results and discussion

SEM micrographs of the MoS_2/Nb composite solid lubricant coatings deposited using pulsed-dc magnetron sputtering technique are given in Fig. 3. The

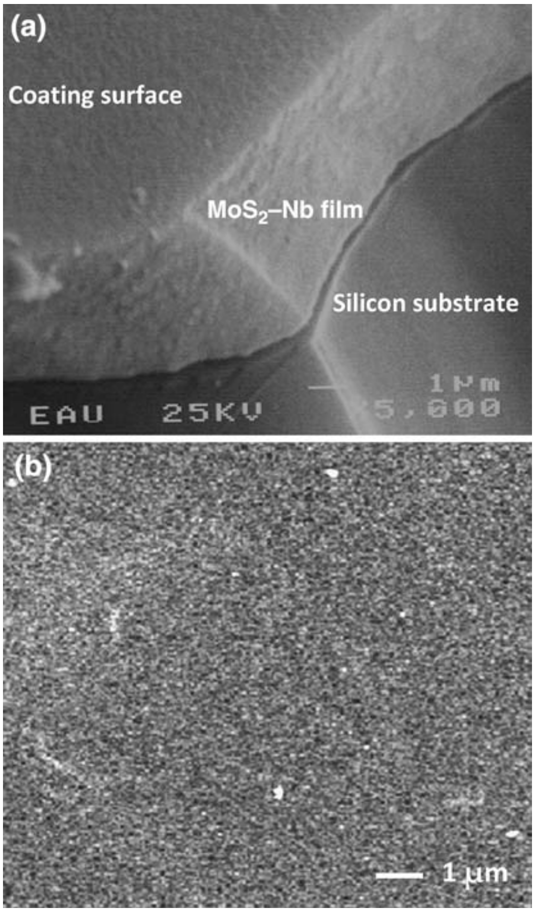

Fig. 3: SEM image showing (a) the cross section, and (b) the coating surface of the MoS_2/Nb composite solid lubricant coating

thickness of the coating was about 3 μm, depending on the process time and parameters of the coating. Since pulsed biasing of the substrate during deposition increased the grade of ionization and ion-to-neutral ratio, the composite coatings grow as dense, compact, noncolumnar structures and featureless coating surfaces as shown in Figs. 3a and 3b. The microhardness of the coating was measured as 800 HV.

The composition of MoS_2/Nb coatings was determined by EDS. The results of EDS analysis are given in Fig. 4. When the quantitative values of MoS_2/Nb coatings were evaluated, the stoichiometry ratios N_S/N_{Mo} of the number of sulfur atoms to the number of molybdenum atoms was about 1.64. This ratio shows that the coating was deposited with a composition close to MoS_2 stoichiometry.[14]

To better understand the results of the tribological tests to be carried out at higher temperatures, in situ XRD studies were performed at room temperature and the temperatures of 100, 300, and 500°C. The XRD patterns obtained from these studies are illustrated in Fig. 5. The patterns obtained at room temperature included the basal plane (002) and (001) and the (101)

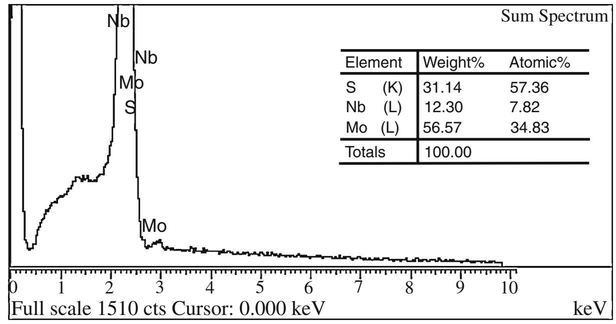

Fig. 4: EDS analysis from the surface of coatings

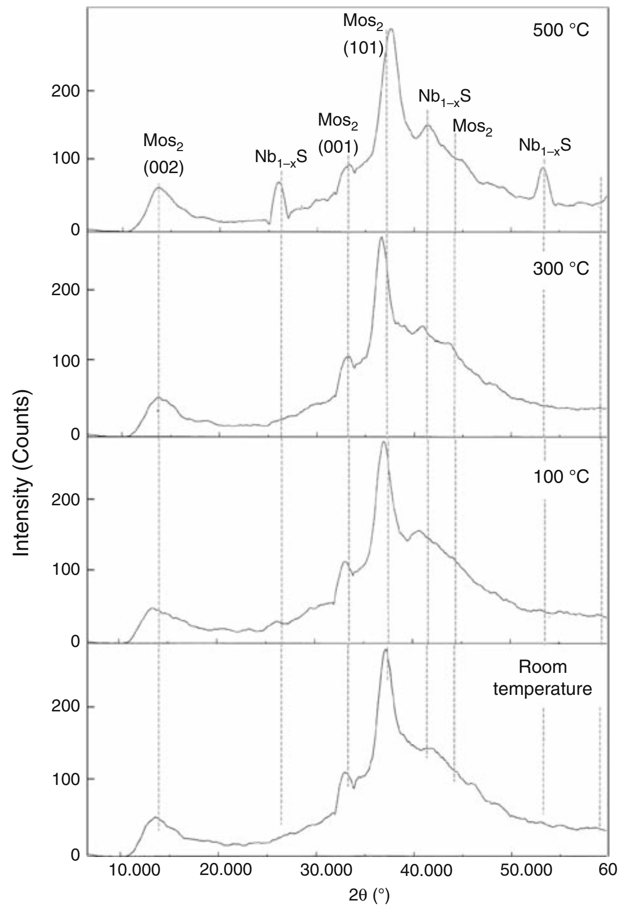

Fig. 5: In situ XRD patterns at different temperatures of the MoS_2/Nb composite solid lubricant coatings

edge planes of the hexagonal crystal structure. The XRD examinations at room temperature indicated that randomly oriented coatings were deposited on the substrate. The reflection at about $2\theta = 13°$ showed the basal plane (002) that was parallel to the substrate. Fleischauer[15] indicated that this plane provides a low-friction coefficient among sliding surfaces to each other. However, the broad reflection peaked at about $2\theta = 33°$, which corresponded to the (001) and to (101) reflections at about $2\theta = 37°$, was observed in MoS_2/Nb

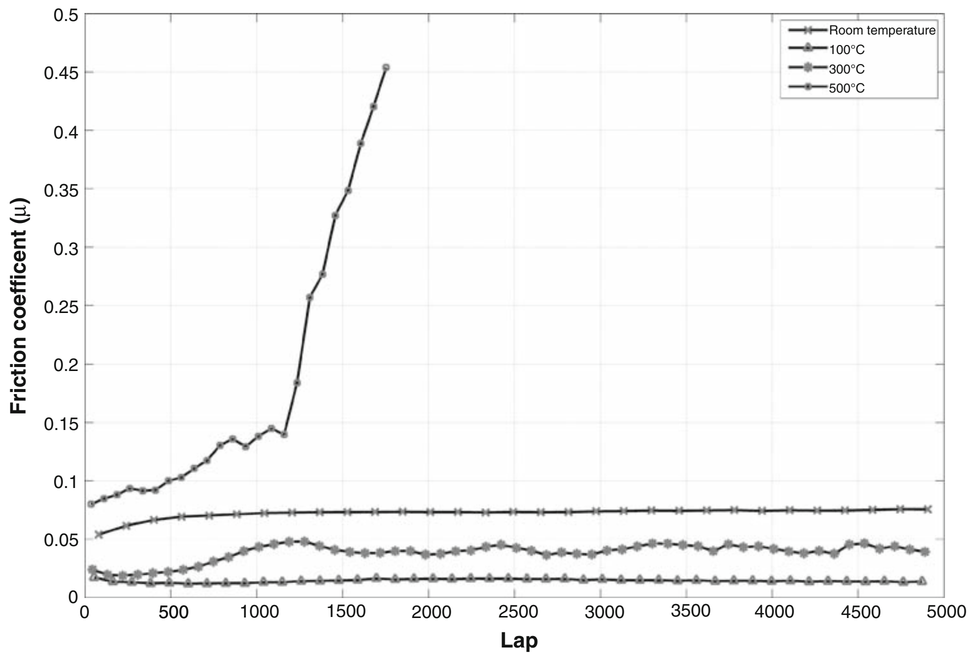

Fig. 6: Changes in the friction coefficients at high temperatures of the MoS_2/Nb composite solid lubricant coatings as a function of lap

coatings for room temperature. In addition, a relatively broad $Nb_{1-x}S$ peak was observed in the XRD examination at room temperature. On the other hand, there were not any Nb peaks in the XRD patterns. This condition is similar for MoS_2 with Ti added as indicated in the literature,[6] where Nb replaces molybdenum in the MoS_2 matrix and/or becomes a interstitial solid solution of Nb in the direction of the lattice parameter of MoS_2.

In in situ XRD studies at 100, 300, and 500°C, it was detected that the peaks obtained at room temperature changed, and new peaks formed. The basal plane (002) at these temperatures shifted to smaller angles, and the (001) peak reduced. However, there was not a significant change for the (101) peak. On the other hand, some significant changes were observed for the X-ray pattern at 500°C as the peaks of $Nb_{1-x}S$ crystals reflected at about $2\theta = 27°$ and $2\theta = 53°$. This caused the formation of a new phase by combining sulfur atoms diffused depending on the temperature of Nb atoms.

The graphic showing the relationship between the friction coefficient and lap at room temperature and different temperatures is given in Fig. 6 for MoS_2/Nb composite coatings. From the studies of the pin-on-disc tribo test carried out to determine the tribological behavior of the coatings at high temperature, it was observed that the friction coefficient significantly changed depending on the temperature. It was also determined that while a very stable friction coefficient was measured at about $\mu = 0.072$ from the wear tests performed at room temperature, an unstable friction coefficient was observed from the tests carried out at 300°C. This unstable friction coefficient changed between 0.035 and 0.061. The reason for this unstable behavior of the friction coefficient was associated with the formation of MoO_x by rapid oxidation of the MoS_2 (001) plane, which is sensitive to oxidation with an increase in temperature. Furthermore, the formation of the $Nb_{1-x}S$ phase, which has a lower solid lubricant property compared with that of MoS_2[16,17] caused unstable wear. It was observed from the high-temperature tribological test performed at 500°C that the coating showed a rather insufficient tribological behavior. The friction coefficient at this temperature, which was measured as 0.19 at the beginning depending on the hertzian contact, gradually increased up to about 1000 laps. In this interval, it was observed that the friction coefficient of the coating increased from 0.067 to 0.14. The coating was completely detached from the substrate after about 1000 laps. On the other hand, the most stable and lowest friction coefficient was determined in this study from the tribo test performed at 100°C. The mean friction coefficient at this temperature was $\mu = 0.014$. This low friction coefficient might be attributed to the nonexistence of a $Nb_{1-x}S$ phase at this temperature. From the observation of in situ XRD patterns (although $Nb_{1-x}S$ phases formed at 300°C and intensively at 500°C), sulfur did not diffuse into the coating at 100°C, and thus the $Nb_{1-x}S$ phase did not form. Depending on this, the fact that the $Nb_{1-x}S$ phase did not form at this temperature resulted in a stable and low friction coefficient.

The stable and unstable behavior of the friction coefficients were also supported by the wear track images and ball surfaces. The wear track images and

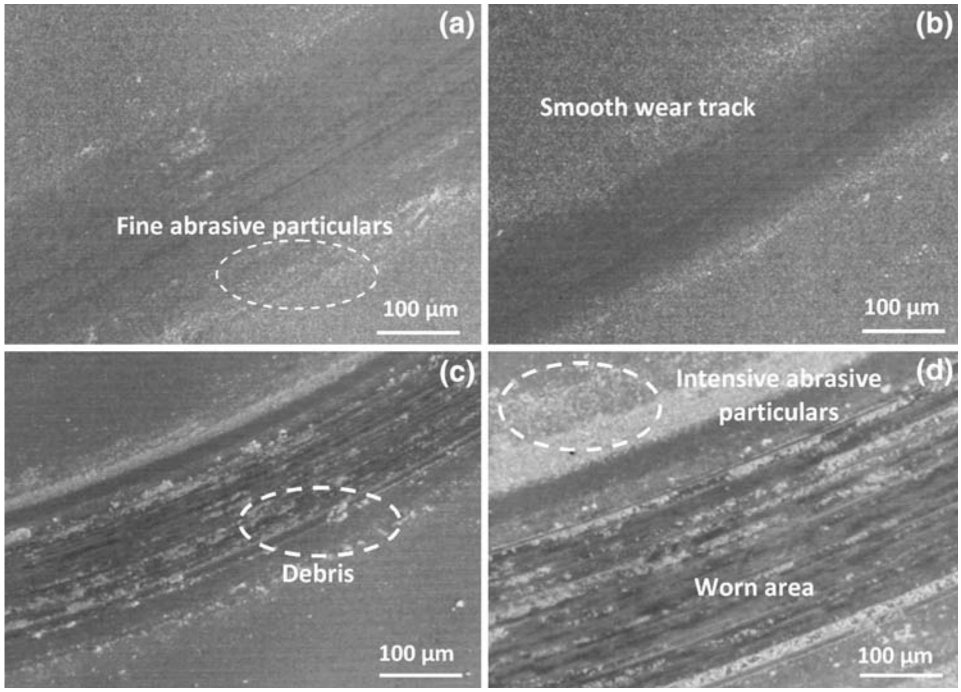

Fig. 7: SEM images of the wear tracks on the MoS_2/Nb coatings: (a) room temperature; (b) 100°C; (c) 300°C; and (d) 500°C

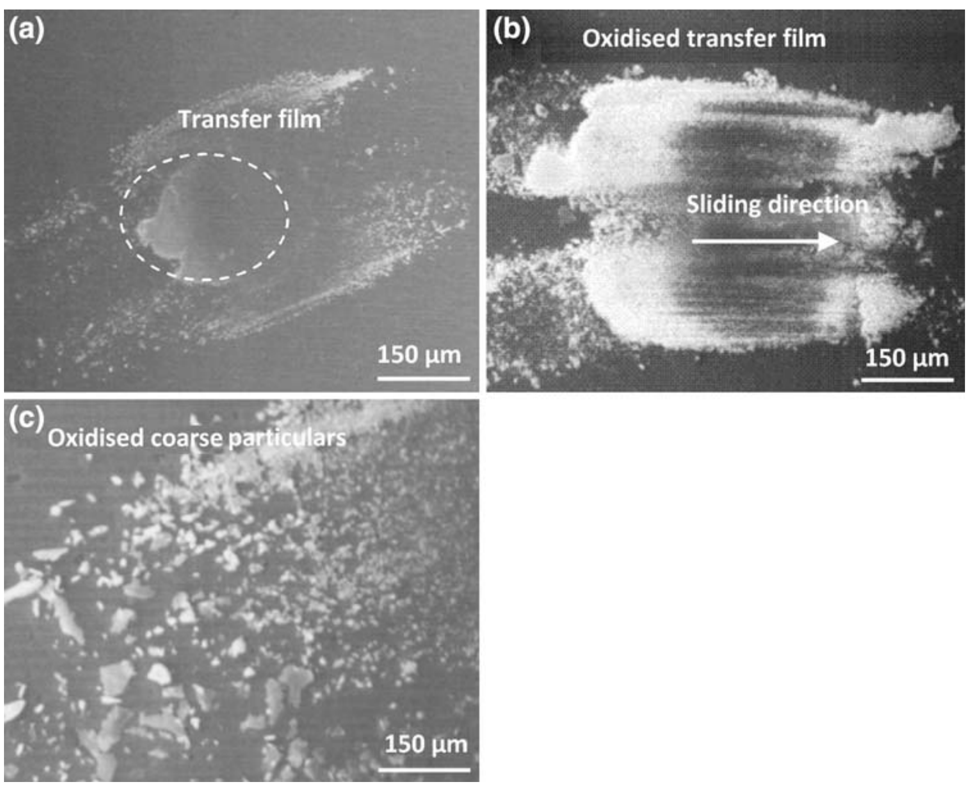

Fig. 8: SEM images from the contacting area on the ball for (a) room temperature, (b) 300°C, and (c) 500°C

ball contact area images at different temperatures are given in Figs. 7 and 8, respectively. It was observed that the wear tracks at room temperature and at 100°C were quite smooth and without any debris. Very few fine abrasive particles were determined along the tracks (Figs. 7a and 7b). Additionally, while a thin and uniform film was observed on the Al_2O_3 ball after the pin-on-disk tribo test at room temperature, no transfer film was detected at 100°C (Fig. 8). On the other hand, the wear tracks broadened at 300 and 500°C as seen in Figs. 7c and 7d. Dense debris was detected in the tracks for 300°C, which resulted in the increase of the friction coefficient (Fig. 7c). A quite dense and nonuniform transfer film on Al_2O_3 balls was observed at this temperature (Fig. 8b). For 500°C, intensive abrasive particulars along the wear tracks and dense debris in the tracks were observed, and the coating detached from the substrate (Fig. 7d). Furthermore, from the ball image in Fig. 8c given for this temperature, a transfer film that was made of randomly dispersed coarse grains and not adhered to the surface was determined. Those grains, which increased the abrasive effect between the coating and ball, caused detachment of the coating from the surface in a short time, and rapid increase of the friction coefficient. On the other hand, depending on the test temperature, different values were obtained for the wear rates. A sample wear-track profile and the wear rates at different temperatures are presented in Fig. 9 as a graphic. The changes in the wear rates were also seen by the values of the friction coefficients, wear track images, and ball images. The lowest wear rate at the end of 5000 laps was determined for the tests performed at 100°C. The wear rate also increased for room temperature and 300°C. On the other hand, in the tests performed at 500°C, the coating detached from the substrate after 1000 laps, and thus the wear rate of the coating could not be calculated since the ball wore out the substrate until about 2000 laps.

In addition, a comparison between this study and pure MoS_2 is given in Table 2. The results from the wear test at high temperatures for pure MoS_2, which was carried out by Kubart et al.,[18] shows that both the friction coefficient and wear rate at the temperature of 100°C are lower compared to that of the room temperature. Then, they increase with the increase of the temperature. Although a similar behavior has been observed in our study, a much lower friction coefficient and wear rate for Nb-doped MoS_2 were determined compared to that of pure MoS_2.

Conclusions

The high-temperature tribological behavior of MoS_2/Nb solid lubricant coatings was studied to optimize the limited use of MoS_2 solid lubricant coatings in

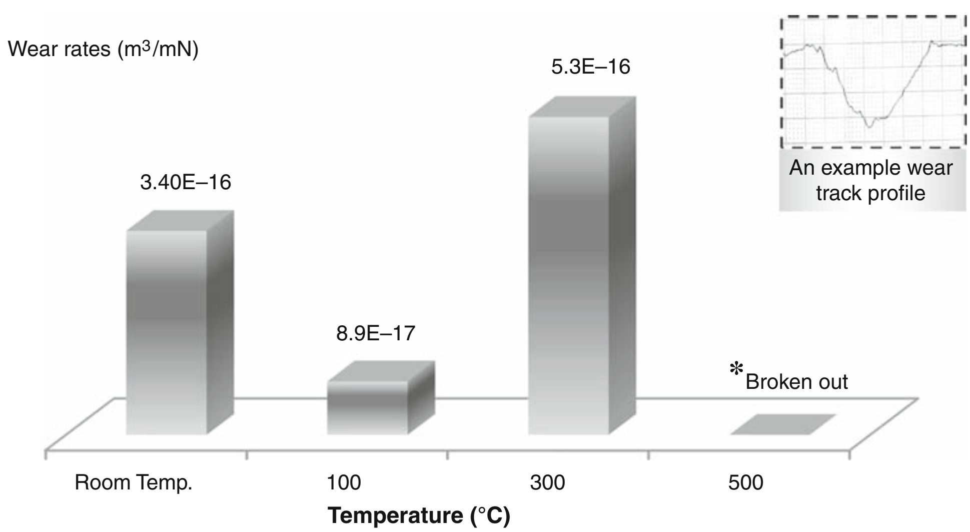

Fig. 9: The wear rates of the MoS_2/Nb composite solid lubricant coatings and a sample wear track profile

Table 2: The friction coefficient and wear rate of pure MoS_2[18] and MoS_2/Nb at different wear test temperatures

Wear test temperatures (°C)	Pure MoS_2[18]		MoS_2/Nb	
	Friction coefficient (μ)	Wear rate (m^3/mN)	Friction coefficient (μ)	Wear rate (m^3/mN)
Room temperature	0.14	2.25E−11	0.072	3.4E−16
100	0.05	1.0E−11	0.014	8.9E−17
300	0.1	1.5E−11	0.035	5.3E−16
>300	Broken out			

atmospheric conditions and higher temperatures, and the results obtained were summarized. Noncolumnar, dense, and compact coatings were obtained as a result of pulsed-dc magnetron sputtering technique.

From in situ XRD studies, the (002) plane of MoS_2 to which the low friction coefficient was attributed did not change relative to the increase of the temperature. It was observed, however, that with the increase of the temperature, extra $Nb_{1-x}S$ phases formed from the combination of sulfur with Nb. This phase that formed at 500°C was crystalline.

Considering the tribological behavior without the failure of the film, the optimum temperature was determined as 100°C from the high temperature tribo tests performed at room and different temperatures. The friction coefficient was measured at about $\mu = 0.014$ at this temperature. At the temperatures of 300 and 500°C, rapid oxidation of the coatings with the temperature and formation of an $Nb_{1-x}S$ phase with a high-friction coefficient compared to MoS_2 resulted in the increase of the friction coefficient. The abrasive particulars observed from the wear tracks and Al_2O_3 ball images at 500°C and nonuniform transfer film increased the friction coefficient. In addition, while the lowest wear rate was determined from the wear test at 100°C, it was determined that this rate increased for the other temperatures.

As a result, it was determined that MoS_2/Nb composite solid lubricant coatings present a quite low friction coefficient at 100°C, and are appropriate for industrial applications at this temperature in atmospheric conditions.

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