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Improvement of boundary lubrication properties of diamond-like carbon (DLC) films due to metal addition

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Abstract

The effects of added materials such as metals like titanium (Ti), molybdenum (Mo) and iron (Fe) diamond-like carbon (DLC) films on boundary lubrication and microtribological properties were investigated. The nanoindentation hardness and microwear resistance can be improved by adding the proper metal to DLC films, as evaluated by atomic force microscopy (AFM). Boundary lubrication properties of DLC films with metals are improved as comparing with DLC films without metal under lubricant with both MoDTC and ZDDP additives. Moreover, lower friction coefficient of $\mu = 0.03$ than carburized steel is exhibited with the appropriate quantity of Ti added. The tribochemical reactant was formed on the sliding surface of the Ti-containing DLC film like as carburized steel. Higher mechanical damping materials containing elements, such as Mo, Zn, P and S, formed tribochemical reactors as observed by X-ray photoemission spectroscopy (XPS) and AFM force modulation methods.

1. Introduction

Recently, with the progress of science and technology, the environments in which mechanical parts are used are rapidly expanding. Therefore, ensuring the reliability of mechanical parts, which are used under extreme conditions of high speed, high load, extreme temperature and radioactive and reactive atmospheres is becoming as important issue [1].

As surface films, diamond-like carbon (DLC) films are expected to withstand the above-mentioned severe environments [2,3]. For instance, after coating DLC films on hard brittle materials, the occurrence of cracks on the surface in the friction test can be controlled, i.e., DLC films protect the surfaces from cracking [4]. Moreover, by coating a DLC film on metals and other materials, it is also possible to lower the wear of opposing surfaces due to the low friction of DLC films. There is also some effect of preventing adhesion of surfaces caused of friction [5]. DLC films show extremely low friction due to the tribochemical reactor [6,7]. Even though DLC films have displayed many such excellent tribological properties depending on their application fields, there are many insufficiency points such as their film strength, lubrication property and adhesion to substrates. The addition of other elements to DLC films is considered to make up for the deficiencies of DLC films [8]. It has been proposed to fabricate DLC films containing silicon and other elements at on the interface between substrates and films. The tribological properties of these DLC films will be investigated [9–11].

As additive materials in DLC films, metals such as titanium, zirconium, hafnium, and tungsten, which can form high-strength carbides in DLC films, are considered. It is expected to improve tribological properties such as film strength if high-strength carbide can be formed in the defective parts of the carbon network [5].

Furthermore, it is also expected to be able to improve the boundary lubrication properties of DLC films by incorporative some metals. For instance, in an attempt at fuel-efficiency minimization of automobile

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engines by decreasing friction, coating DLC films on the shim of follower series has been investigated [12,13]. However, in engine oil, the effect of friction decrease has not yet been found on shims coated with DLC films, and compared with lubrication properties of titanium nitride films, no advantage of coating with DLC films was obtained.

In contrast, oil-soluble organomolybdenum compounds, such as molybdenum dialkyldithiocarbamate (MoTDC), are capable of providing a significant reduction of friction for engine oils, through the improvement of lubrication under boundary conditions. These friction modifiers represent important additives in many energy-conserving lubricants [14–17]. MoDTC and zinc dialkyl-dithiophosphate (ZDDP) additives in engine oil are known to form an MoDTC/ZDDP tribofilm on slid steel surface that realize lower friction. Chemical properties and structures of these tribofilms were investigated by X-ray photoemission spectroscopy (XPS) and Auger electron spectroscopy (AES). The reduction in mainly due to MoS_2 derived from the MoDTC additive plays a role in enhancing wear resistance and promoting the formation of MoS_2 [14–16]. If we can form the similar friction reactor on the DLC films, lower friction coefficient than that of steel would be obtained.

In this study, DLC films with additive metals, such as titanium (Ti), molybdenum (Mo), and iron (Fe) which are expected to react with MoDTC/ZDDP additives in lubricant, were deposited. Microtribological properties such as hardness and wear resistance of those thin films itself. And then boundary lubrication properties of these metal-containing DLC films were investigated, to clarify the effect of metal addition to DLC films.

2. Experimental methods

2.1. Deposition of metal-containing DLC films

DLC films containing metal were deposited by radio frequency (RF) magnetron sputtering with argon gas and a graphite target. The substrate was subjected to high-frequency (13.56 MHz) voltage for film deposition. To coat DLC films containing metal, a fan-shaped target of titanium (Ti), molybdenum (Mo), or ferrous (Fe) is set up on a graphite target. The size of the fan-shaped target is varied at an area ratio under 1/8, 1/16, or 1/32, to control the additive quantity of metals. The conditions for depositing films containing metal are RF power of 0.8 W on the substrate, 200 W on the target, vacuum pressure of 8 Pa and deposition time of 60 min. The substrate material is Si (100) that has been polished to a mirror finish to avoid the influence of surface roughness. In the case of coating DLC films without metal, the deposition time is 120 min because the sputtering rate is lower than those of DLC films with metal. The above-mentioned conditions result in a film thickness of about 200 nm. All conditions are listed in Table 1. To evaluate the composition of metal-containing DLC films. Auger electron spectrum (AES) analysis was performed and all the depth profiles were recorded in same conditions so that the composition of film could be compared. The atomic ratios were estimated from the saturated value of these depth profiles. Carburized chromium molybdenum steel (SCM 415, JIS), hardness Hv 690 and roughness 0.01 μm Ra were used for comparison.

2.2. Evaluation method

The thickness of DLC films containing metal, deposited with the RF magnetron sputtering device, is thin, about 200 nm. The nanoindentation hardness of the film has been estimated using an atomic force microscope (AFM) with a Berkovich-type diamond indenter under a load of 500 μN at an indentation time of 10 s, as shown in Fig. 1(b). Here, the hardness is evaluated based on the plastic deformation depth. Plastic deformation depth was evaluated from the point of intersection of the straight line fitted from the appropriate unloading curve, with the x-axis.

To clarify the deformation mechanism of metal-containing DLC films, energy analysis of nanoindentation was performed [18]. Total deformation energy was calculated by taking the integral of the loading curve. Storage energy was calculated by integrating the unloading curve. Dissipated energy was evaluated as the difference of total energy minus storage energy. The modulus of dissipation was calculated as dissipated energy divided by total energy, as shown in Fig. 1(b).

To evaluate the microwear properties, we used AFM with a very sharp diamond tip of nearly 0.1 μm radius, as shown in Fig. 1(c). The tip was supported by a par-

Table 1
Deposition conditions of metal-containing DLC films and DLC films without metal films

	Metal-containing DLC films	DLC film without metal
Ar gas pressure (Pa)	8	
Frequency (MHz)	13.56	
RF power (substrate) (W)	80	
RF power (target) (W)	200	
Substrate rotation (rpm)	10	
Substrate	Si (100)	
Metal elements	Ti, Mo, Fe	–
Metal target area ratio (metal/graphite)	1/8, 1/16, 1/32	
Deposition time (min)	60	120

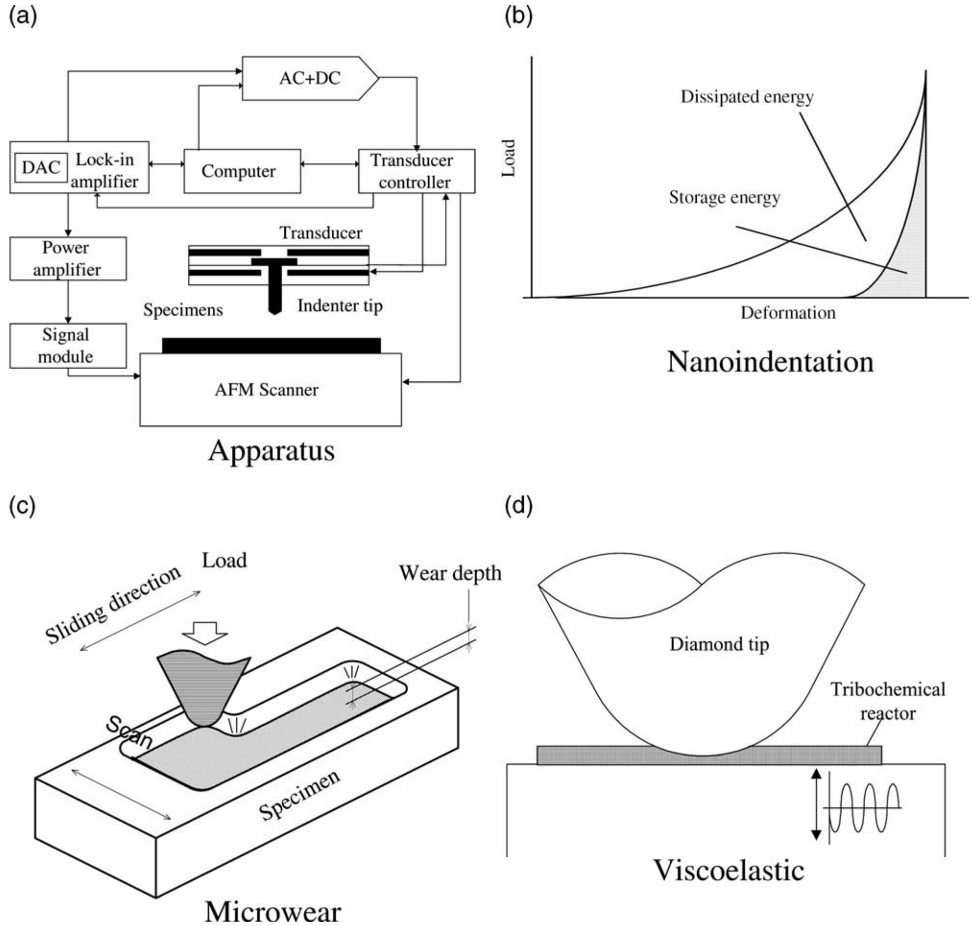

Fig. 1. Schematic illustration of micro-viscoelasticity evaluation systems. (a) Apparatus, (b) nanoindentation, (c) microwear and (d) viscoelastic.

allel leaf-spring unit. A PZT scanner moved the sample for contact, loading and scanning. A rectangular specimen coated with various metal-containing DLC and DLC films were scanned by the PZT scanner with sliding of the diamond tip. The wear profiles were measured by detecting spring displacement under one-tenth of the wear-test load.

A ball-on-disk tribometer was used to investigate friction characteristics and lubrication properties, as shown in Fig. 2. By rotating the sample with the application of a certain load on a SUS440C ball indenter, we measured friction force using a friction sensor, and the friction coefficient was calculated on a computer. The friction test was performed first in an atmosphere environment without lubricant. The friction tests were performed under 50–60% humidity condition atmosphere. Moreover, the boundary lubrication properties of DLC films containing metal were investigated. Lubricant oil is 5W-20 (SAE grade) containing both ZDDP anti-wear additive and MoDTC friction modifier additive supplied by Nissan motors. The dependence of frictional properties on reciprocation cycles was evaluated under the conditions of a load of 5.0 N, rotating speed of 100 rpm, rotating radius of 3 mm and 6000 total reciprocation cycles. The velocity was about 31.4 mm/s. After the friction test, the wear traces of the sample were observed by AFM and using an optical microscope and three-dimensional profile meter.

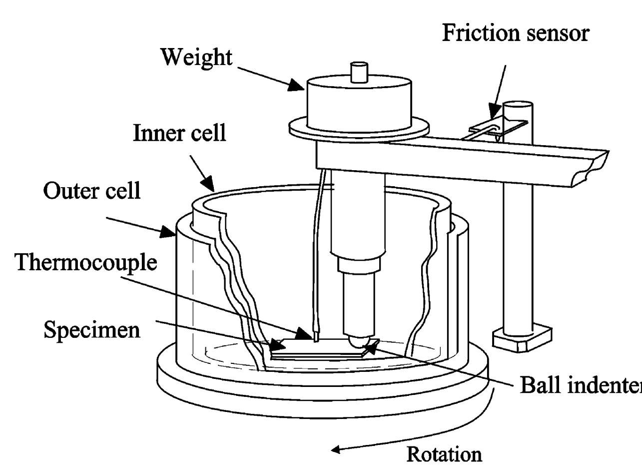

Fig. 2. Schematic illustration of ball-on-disk tribometer.

The friction tests were preformed more than three times, and the mean and typical data are discussed. The variation of saturated friction value is less than 15%.

To investigate the friction reactor, the sliding and no-sliding areas of Ti-containing DLC film, DLC film and Cr–Mo steel after tribological tests with MoDTC and ZDDP containing lubricant were analyzed by X-ray photoemission spectroscopy (XPS). Survey spectra were acquired using an X-ray spot size Φ 50 μm. The spectra were calibrated using binding energy of 284.6 eV of C1s photo peak. Residual oils were removed from the substrates before the analysis by cleaning in a detergent.

Then, to clarify the dynamic deformation properties of reactant on the sliding surface using AFM (Digital Instruments Nanoscope III) together with a dynamic stiffness measurement (DSM) system (Hysitron Inc.), [19] as shown in Fig. 1(d), viscoelastic properties of sliding and no-sliding surfaces were evaluated. With a 200-nm radius equilateral-triangle pyramidal diamond indenter, tests were performed under the conditions of frequency in the range of 10–300 Hz, a load of 20 μN and load amplitude of 5 μN.

For force modulation, a small sinusoidal a.c. force is superimposed on the d.c. and a.c. voltages, which is applied to the drive plates. The resultant oscillation in displacement monitored using the two channel lock-in amplifier. To clarify the dynamic deformation properties such as storage modulus, loss modulus, damping stiffness, amplitude and tan δ as followed presented in ref. [19]. If we determine the start point accurately and test under good controlled humidity less than 45%, we can obtain reproductive data.

3. Experimental results and discussion

3.1. Film composition and mechanical properties

The AES analysis results of metal-containing DLC films are shown in Fig. 3. As shown in Fig. 3(a), the peak intensity of titanium decreases with decreasing area ratio of titanium. By AES analysis, the relationship between the area ratio of various metal targets and the metal addition ratio was elucidated and is shown in Fig. 3(b). The quantity of metal added to DLC films increased with increasing area ratio of the metal target. The quantity of metal added is related to the sputter ratio. The addition ratio of titanium, at which the sputter ratio is low, [20], is relatively small as compared with molybdenum (Mo) and iron (Fe).

The nanoindentation curves of DLC films containing various metals, such as titanium, molybdenum and iron, are shown in Fig. 4(a). Average value of hardness and three times of standard deviation (3σ) in this study is summarized in Fig. 4(b). The estimated average indentation hardness in this study is summarized in Fig. 4(b). DLC films containing titanium and molybdenum have higher nanoindentation hardness than DLC film without metal. In particular, titanium is an effective additive for obtaining high hardness. On the other hand, Fe-containing DLC film shows lower hardness. In this study, Vickers and nanoindentation hardness values of the silicon substrate were 1500 and 13 GPa, respectively. An average hardness value as high as 30 GPa at 500 μN can be obtained with a Ti-containing DLC film, in this measurement.

Deformation energies evaluated in the nanoindentation test are shown in Fig. 5. Total energies, which equal the sum of dissipated and storage energies, of Ti- and Mo-containing DLC films are smaller than that of

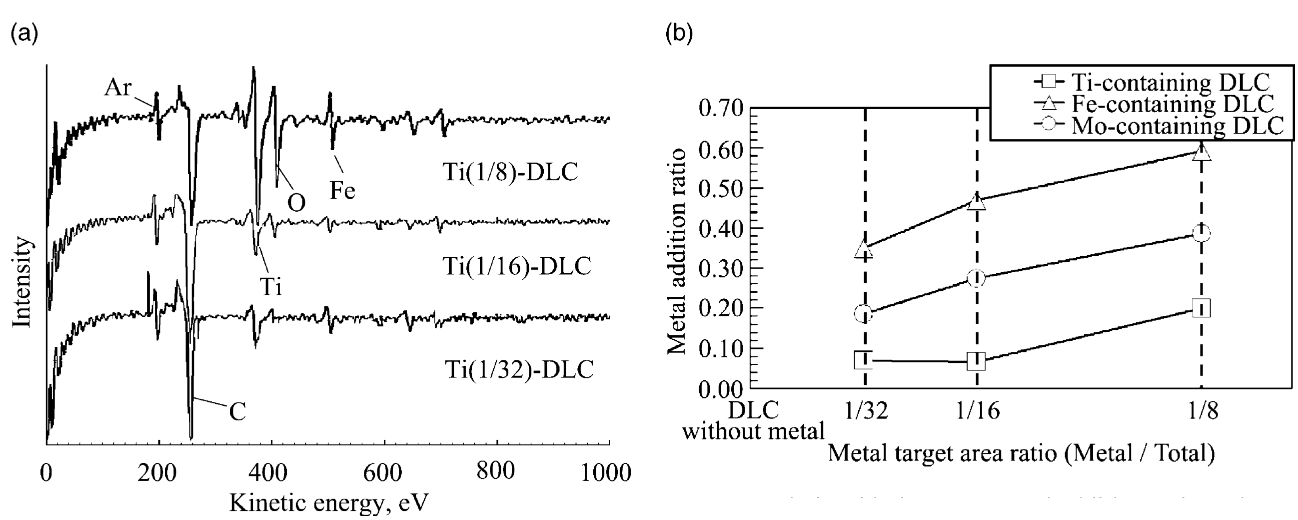

Fig. 3. Analysis of the metal-containing DLC films by AES. (a) AES spectra of Ti-containing DLC films and (b) relationship between metal addition ratio and metal target area ratio.

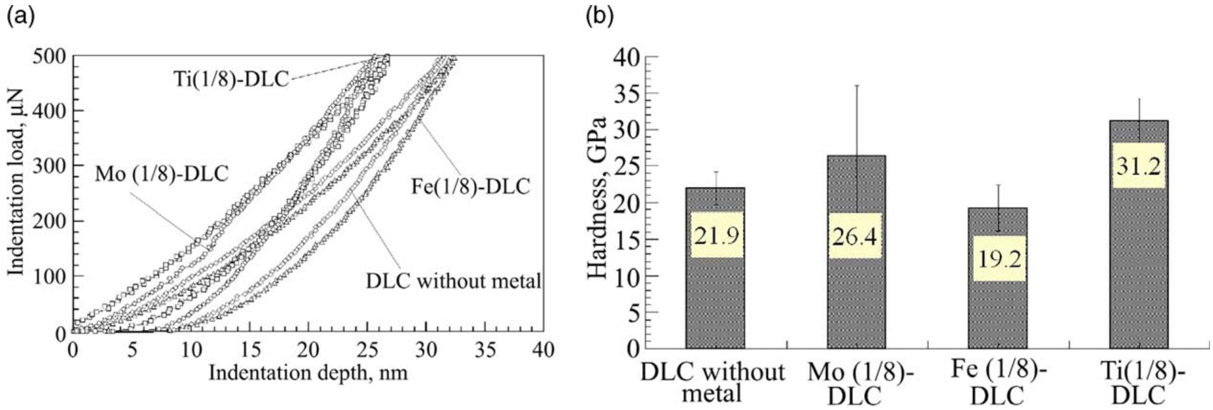

Fig. 4. Nanoindentation curves and hardness. (a) Nanoindentation curves of various metal-containing DLC films and (b) nanoindentation hardness.

DLC film without metal. The dissipated energy of these DLC films change with the total energy, however, the difference in storage energy is small with metal addition.

The relationship between the modulus of dissipation and nanoindentation hardness is shown in Fig. 5(b). The modulus of dissipation decreases as nanoindentation hardness increases. The hardest Ti-containing DLC film shows the lowest modulus of dissipation, therefore, fewer dissipated permanent deformations such as cracks or dislocations were caused by nanoindentation.

The microwear profiles of 3×3 μm square metal-containing DLC films compared with DLC film are shown in Fig. 6(a). The DLC film shows a 13-nm-deep wear scar at 30 μN load. The depth of wear grooves on Ti-containing DLC film is less than that on DLC film. Fig. 6(b) shows the wear depth dependence on the load for various metal-containing DLC and DLC films. The wear depth of these films increases with load. The wear depth of DLC film reached 13 nm at 30 μN, and then the rate of wear increase of DLC film decreases with increasing load. Microwear of metal-containing DLC films was decreased by metal addition. Both Ti- and Mo-containing DLC films show excellent microwear resistance.

3.2. Friction properties under dry conditions

For a friction test without lubrication, the friction coefficient dependence on the sliding cycle is shown in Fig. 7. For both SCM415 and Si (100), friction coefficients are as large as 0.5–0.7. The friction coefficient of DLC film without metal gradually increases from 0.3 to 0.7. Friction coefficients of these sputtered DLC films were higher than those of CVD-DLC films as nearly 0.1 [4] and ionplated DLC films as nearly 0.15 [11] evaluated by similar friction test. High friction of these sputtered DLC films is due to the properties such as lower sliding endurance and hardness. The friction coefficient of Ti-containing DLC film is about 0.2 and is stable. Similar to Cr–Mo steel and Si (100), the friction coefficients of Mo- and Fe-containing DLC films are higher than that of DLC film without metal. On observing the shapes of wear traces with respect to the exfoliation and damage of DLC films, the damage on titanium containing DLC films is less than that on DLC film without metal. In the case of Mo-containing

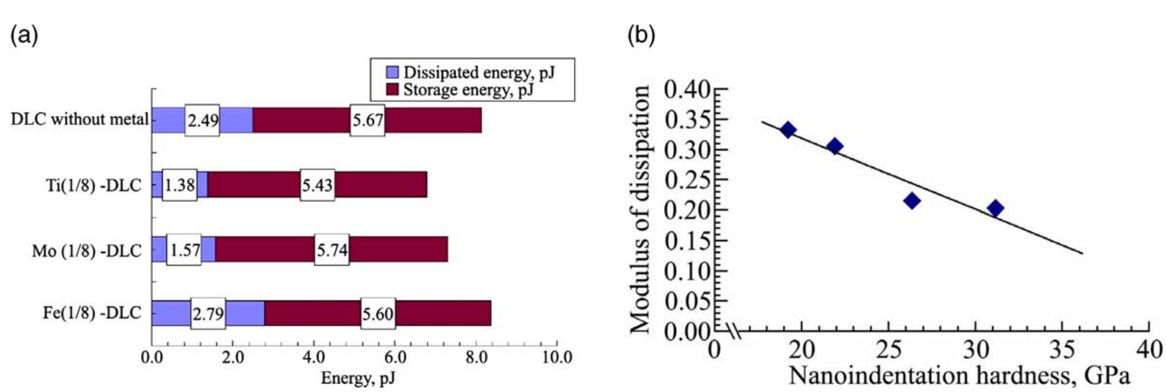

Fig. 5. Deformation energy and modulus of dissipation. (a) Energy of nanoindentation and (b) modulus of dissipation vs nanoindentation hardness.

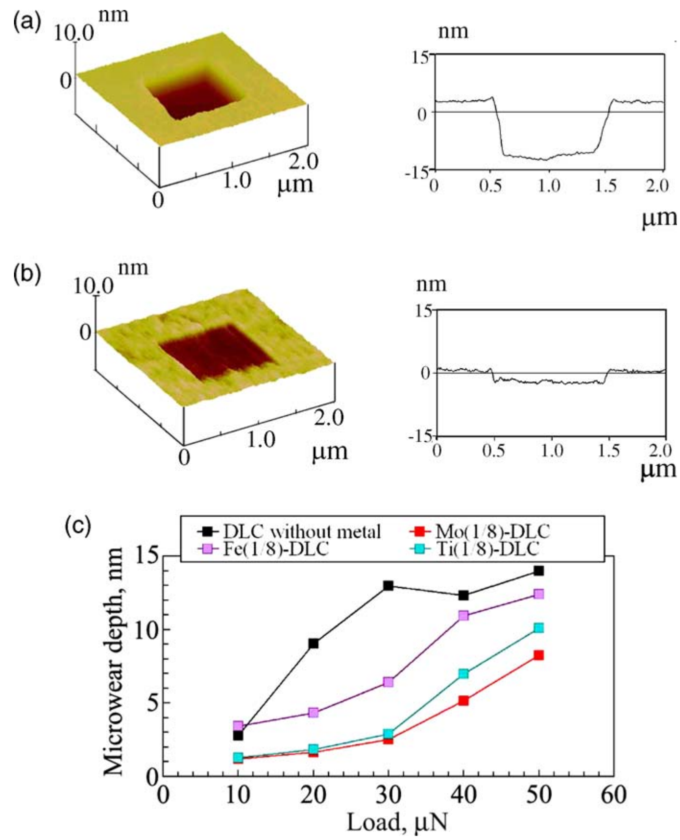

Fig. 6. (a) DLC film without metal (wear depth: 13.0 nm), (b) Ti-containing DLC film (wear depth: 2.9 nm) and (c) microwear dependence on load.

DLC films, the damage on their frictional surface is large, and exfoliation occurs on the films. The wear of Fe-containing DLC films increases greatly compared with DLC films. Mo inclusion in DLC film increases the friction and wear damage in spite of the higher hardness and microwear resistance. It can be seen that friction and wear rate can be reduced by adding Ti to DLC films under dry conditions.

Fig. 8 shows average friction coefficients for DLC films deposited with different metal additives. On comparing DLC films deposited with a target area ratio of 1/32 with those deposited under target area ratios of 1/16 and 1/8, the friction of Mo-containing DLC films and that of Fe-containing DLC films decreased, as shown in Fig. 8. It is considered that adhesion between the metal in the DLC films and SUS 440C declined and friction decreased as the quantity of metal added decreased. In particular, the friction coefficient of Ti-containing DLC films deposited with a Ti target area ratio of 1/32 is low, about 0.2. There is a certain addition quantity at which friction can be decreased to a minimum.

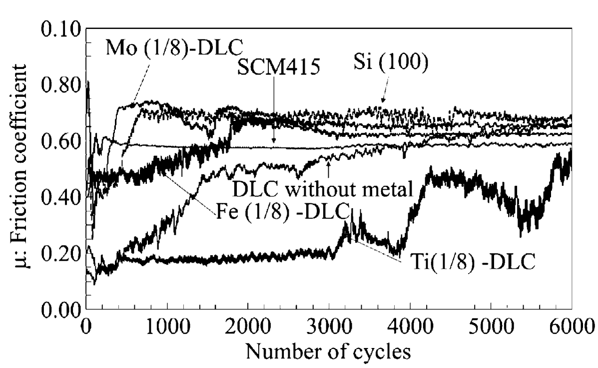

Fig. 7. Friction coefficient of various metal-containing DLC films under dry condition.

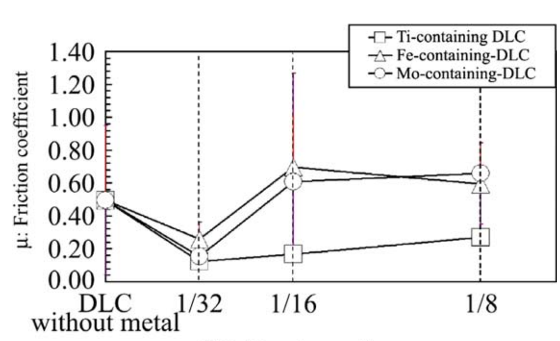

Fig. 8. Friction coefficient dependence on metal target area under dry condition.

3.3. Boundary lubrication properties with lubricant containing MoDTC and ZDDP

Fig. 9 shows the boundary lubrication properties of various metal-containing DLC films with lubricant containing Mo-DTC. Although the friction coefficient of DLC films without metal can be decreased to $\mu = 0.2$ and becomes stable due to the supply of lubricant, it is higher than those of Si (100) and SCM415. In this case, the lubrication effect of MoDTC-containing oil is negligible in DLC films without metal. In comparison, the friction coefficient of all metal-containing DLC films was very low. In particular, the friction coefficient of Fe-containing DLC films is actually high initially, but it diminishes to 0.07 with boundary lubrication. Under the same conditions, it is shown that Ti-containing DLC film has the lowest friction coefficient, $\mu = 0.03$.

The friction coefficients of DLC films without metal and of the silicon substrate reach saturation values, as the number of sliding cycle increases. In contrast, under the same conditions, the friction coefficients of metal-containing DLC films tend to decrease slowly even though their values are initially high. Such a tendency is marked, particularly in Fe- and Ti-containing DLC films. These results are considered to be due to the metal-containing DLC films having active sites that react with extreme-pressure additives under friction. Consequently, a reactor of low shear strength is produced. Therefore, friction coefficients of metal-containing DLC films become low, though the effect of extreme-pressure additives is small in DLC films without metal.

Fig. 10 shows the dependence of friction coefficients in the case of boundary lubrication of various metal-containing DLC films on metal target size. All friction coefficients become lower than those of DLC films without metal. In Ti-containing DLC film, the friction coefficient becomes markedly low, $\mu = 0.03$, when Ti target area ratio is $1/32$. Therefore, the mechanism of the low friction coefficient of Ti-containing DLC film is deduced to be the lower friction coefficient in a dry environment and the existence of a low friction reactant with the addition of an appropriate metal.

To indicate the effect of lubricant containing ZDDP and MoDTC additives, the dependence on the metal target area ratio is shown in Fig. 11. The effect of decreasing the friction coefficient of boundary lubrication is evaluated by dividing the friction coefficient of DLC films under the boundary lubrication condition

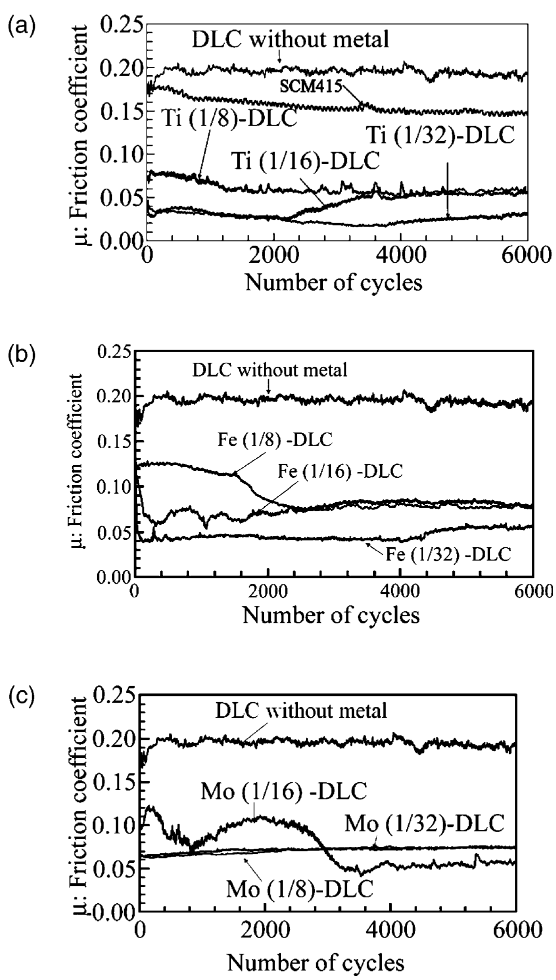

Fig. 9. Boundary lubrication properties of various metal-containing DLC films. (a) Ti-DLC, (b) Fe-DLC and (c) Mo-DLC.

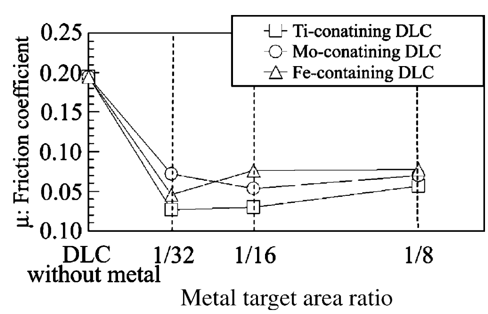

Fig. 10. Friction coefficient dependence on metal target area with boundary lubrication.

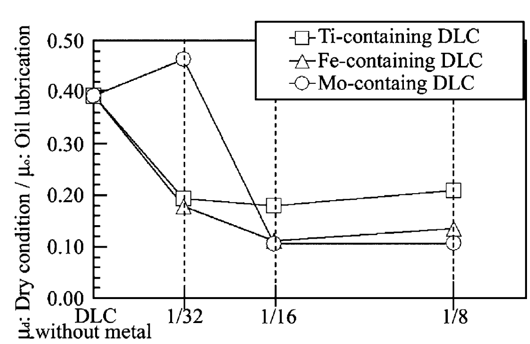

Fig. 11. Effect of boundary lubrication with Mo-DTC-containing oil.

Table 2
Atomic concentrations in sliding area evaluated by XPS. N.D., Not Detected

Specimen	C(ls)	O(ls)	Ti(2p)	Fe(2p)	Mo(3d)	Zn(2p)	P(2p)	S(2p)	Na(ls)	Ca(2p)	Si(2p)	N(ls)
Ti-DLC(1/8)	54	28	2.7	0.38	0.09	0.92	N.D.	N.D.	N.D.	1.31	11.3	1.19
Ti-DLC(1/16)	37	38	N.D.	N.D.	N.D.	1.75	2.9	0.51	0.61	6.5	11.8	N.D.
Ti-DLC(1/32)	61	25	0.7	1.26	0.29	0.79	0.62	N.D.	N.D.	3.2	6.1	1.73
DLC-IP	42	26	N.D.	N.D.	N.D.	0.29	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
SCM415	39	41	N.D.	7.6	0.86	0.57	2.5	1.36	N.D.	7.2	0.58	N.D.

by that under dry condition. The value less than 1.0 is obtained in all cases. In particular, the effect of friction reduction in metal-containing DLC films is conspicuous. The same effect of slowly declining friction can also be found in DLC films which contain a metal, such as Ti, Fe and Mo, with increasing number of sliding cycles, as shown in Fig. 9. In this case, the effect of the ZDDP and MoDTC additives appears gradually. If the reaction process of the surface due to sliding is considered, it is easy to comprehend this point.

3.4. Surface analysis and viscoelastic properties

To clarify the reason for the low friction coefficient with boundary lubrication of metal-containing DLC films, XPS analysis of the sliding track was performed, as shown in Table 2. Carbon, oxygen, and zinc were detected. Other tribochemical reactor formations due to sliding were not found in sliding tracks in DLC films. On the other hand, the constituent elements of additive, such as Mo, Zn, P, S, and Ca, are observed in Ti-containing DLC films.

Therefore, the main reason why the Ti-containing DLC films deposited had a low friction coefficient with boundary lubrication in lubricants with ZDDP and MoDTC additives is considered to be that the friction reactant, as indicated by the low shear strength like on the steel. It is thought that a friction reactant was formed from MoDTC/ZDDP additives on the sliding track of Ti-containing DLC films. Titanium plays a part in assisting the formation of such compounds and the reactor remains on the surface. The friction reactant on carburized Cr–Mo steel has more Mo and P than those of Ti-containing DLC films as shown in Table 2. Therefore, the friction decreased with sliding cycle at early stage and reached to 0.08 due to the formation of MoDTC/ZDDP friction reactor film.

Several researchers demonstrated that the friction reduction mechanisms are closely related to the transfer of MoS_2 [14–16]. Iron is necessary for the tribochemical reaction of MoDTC to form MoS_2 material [21]. However, in this experiment, carburized Cr–Mo steel and Fe-containing DLC films show higher friction coefficient than that of Ti-containing DLC films. This result is speculated that carburized Cr–Mo steel and Fe containing DLC films are lower hardness and higher dry friction coefficient than Ti-containing DLC films.

In these boundary lubrication processes, the friction reactant films are formed. The friction behavior could be depended on the shearing strength, surface stiffness and the distribution of films. Therefore, it is available for investigating surface properties of friction reactant films in viscoelastic and plastic region using force modulation measurement.

The viscoelastic characteristics of sliding areas were evaluated by AFM force modulation, as shown in Fig. 1(d). To confirm the formation of the reactor, the micro-viscoelastic characteristics of the points on both the sliding area and the no-sliding area were evaluated. The measurement points and their section profiles are shown in Fig. 12, as observed by AFM. The viscoelastic characteristics of points (*A–D*) of the sliding area were evaluated, compared with that of no-sliding point *F*. The friction scars of several nanometers depth are observed on the sliding surface, although the no-sliding area is not damaged. The viscoelasticity characteristics of sliding tracks *A–E* and no-sliding area *F* are shown in Figs. 13–15. The storage modulus [E] and loss modulus [E'] dependences on frequency are different between the sliding area and no-sliding area, as shown in Fig. 13. (a). Rates of change of E and E' in the sliding area are larger than those of no-sliding area. Comparing sliding track points *A–E* in the sliding area, these E and E' values are found to depend on the depth of measured points. Moduli E and E' of shallow points *A* and *B* are lower than those of deep grooves *D* and *C*. Loss modulus E' reaches the maximum at a frequency of 40 Hz in sliding track and 70 Hz in the no-sliding area, as shown in Fig. 13(b).

There are large differences in damping between sliding tracks *A–E* and no-sliding area *F*, as shown in Fig. 14(a). Damping was 0.05 kg/s in sliding tracks *A–E* and 0.02 kg/s in the no-sliding area *F*, when frequency was 40 Hz. The damping of sliding tracks is greater than that of no-sliding area *F*. Stiffness of the no-sliding area is lower than that of sliding tracks, as shown in Fig. 14(b). Both amplitude and the tan δ of the no-sliding area are lower than those of sliding tracks, as shown in Fig. 15(a), (b). Therefore, the higher mechanical damping and tan δ reactant was

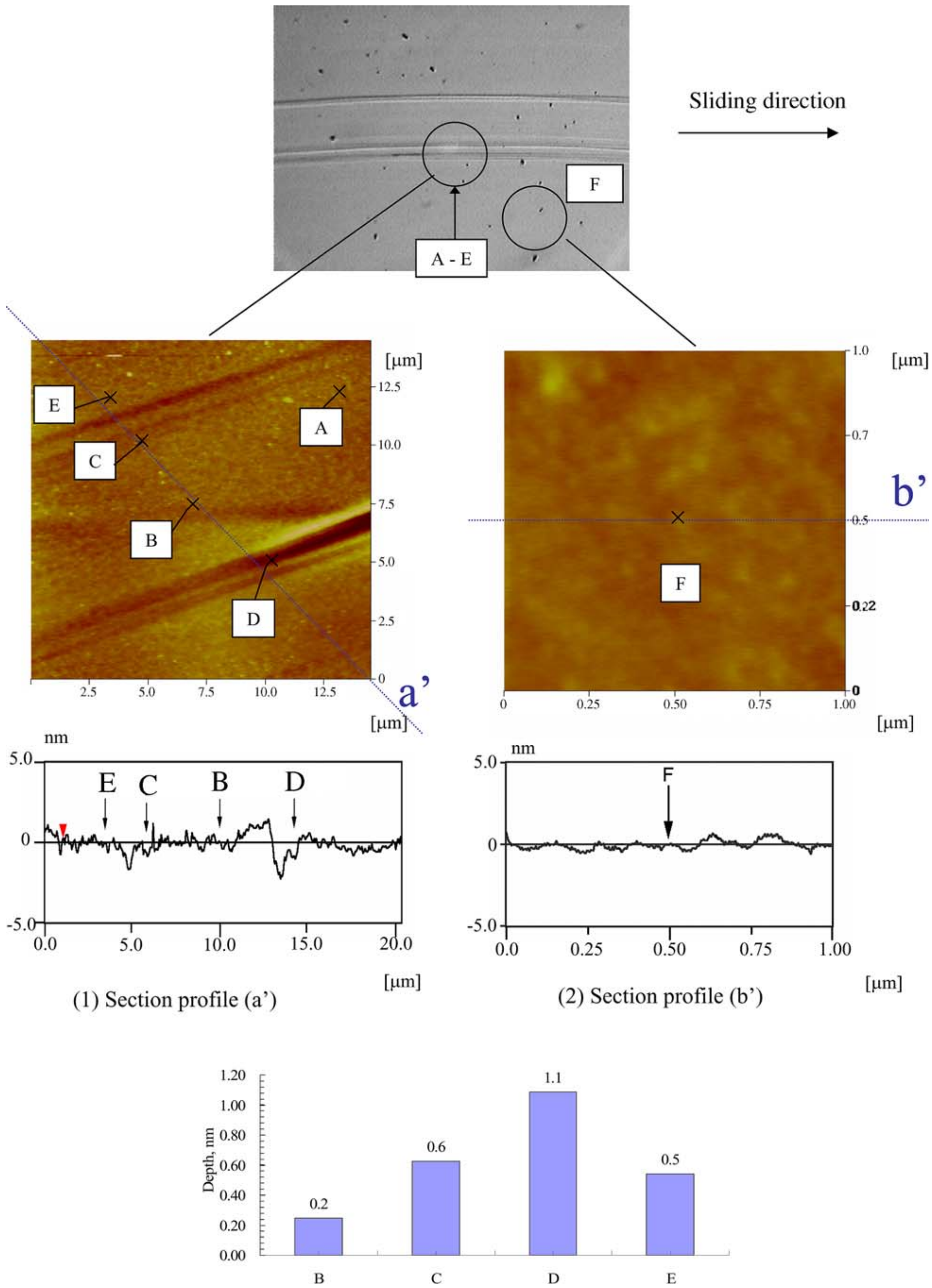

Fig. 12. Profiles and viscoelasticity of measured points of sliding area with boundary lubrication. (a) Image of sliding track and test points, (b) image of no-sliding area and test points and (c) depth of evaluation points.

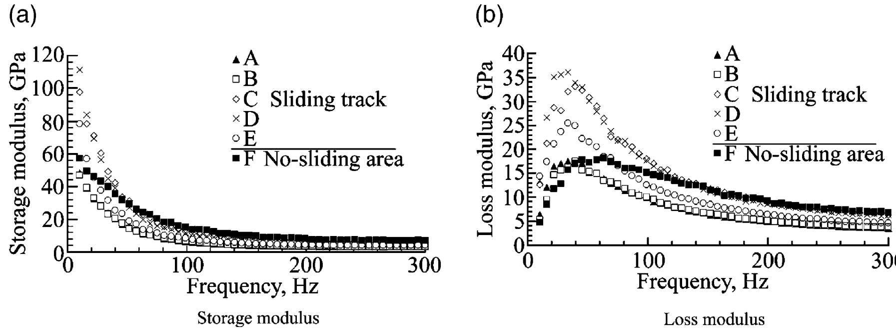

Fig. 13. Storage modulus and loss modulus. (a) Storage modulus and (b) loss modulus.

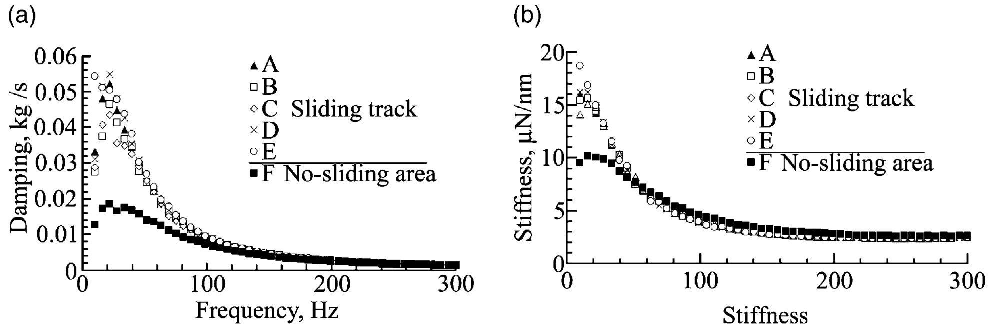

Fig. 14. Damping and stiffness.

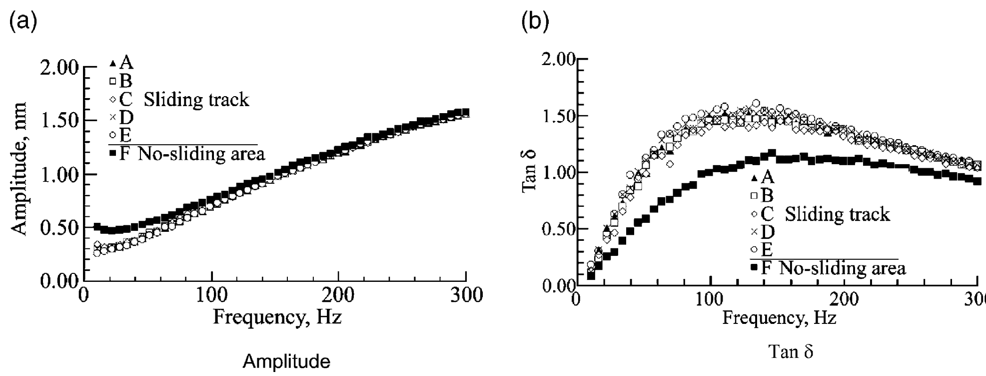

Fig. 15. Amplitude and tan δ. (a) Amplitude and (b) tan δ.

formed on the sliding track. These films show low shearing resistance.

These results indicate that the viscoelastic characteristic of a sliding track differs greatly from that of the no-sliding area. The reactant that consists of viscoelastic material with higher damping and tan δ was formed on the track by friction under boundary lubrication with MoDTC/ZDDP-containing lubricant. It is conceivable that this reactor has low shearing strength as MoS_2, which reduces the friction coefficient under boundary lubrication.

4. Conclusion

Boundary lubrication properties of lubricant with MoDTC and microtribological properties of metal-containing DLC and DLC without metal films have been evaluated. The main results are as follows:

1. Boundary lubrication properties of DLC films can be improved due to addition of metals such as Ti, Mo and Fe. Especially, Ti-containing DLC films showed the lowest friction coefficient of $\mu = 0.03$ in MoDTC-containing lubricant in spite of the high friction coefficient of DLC without metal.
2. A tribochemical reactor containing elements, such as Mo, Zn and S, were formed on sliding tracks on Ti-containing DLC films like as carburized Cr–Mo steel, as revealed by evaluations by XPS and the AFM force modulation method.
3. Viscoelastic properties such as high damping and tan δ of sliding tracks on the Ti-containing DLC film that showed a low friction coefficient, became high compared with those of the no-sliding area. Therefore, on the sliding surface, lower shearing resistant reactants were formed.
4. Nanoindentation hardness and microwear resistance can be improved by the addition of titanium and molybdenum to DLC films
5. Friction and wear can be reduced by the addition of Ti into DLC films in a dry environment.

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