Friction and Electrical Contact Resistance of Iridium-Containing DLC Coatings for Electrically Conductive Tribo-Elements

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Electrically conductive tribo-coatings (i.e. Ir-DLCs) were developed using a hybrid deposition process, combining RF-PECVD with DC magnetron sputtering of Ir. Pin-on-plate tribotests in reciprocating motion were performed in air on Ir, DLC and Ir-DLC coated plates against bearing steel pins under 0.5 N load. The electrical contact resistance was measured during the tribotests, and for Ir-DLC it was below 30 Ω. Neither the pure DLC layer nor the pure Ir layer reached friction coefficients lower than 0.2, while the Ir-DLC went down to 0.05. For Ir-DLCs, however, relatively high and unstable friction was occasionally observed. Possible causes of the instability are discussed by focusing on the characteristics of the tribofilm and the formation of wear debris.

Keywords: friction, electrical resistance, metal-containing DLC, iridium, tribofilm

1. Introduction

Diamond-like carbon (DLC) coatings have unique properties such as low friction, high wear resistance, chemical inertness, a relatively high optical band gap, and high electrical resistivity. The nature and properties of the DLC can be further modified by doping with elements such as Si, F, N, and various metals. Even electrical conductivity can be obtained by adding metals, which allow the use of DLCs as materials for sensors. The application of DLCs could be extended for use in electrical motors, slip-rings, etc., if sufficient tribological properties and electrical conductivity can be achieved at the same time.

The authors previously obtained electrical conductive tribo-materials by adding metals to DLC (hereafter, Me-DLC) using a hybrid deposition process. Fundamental studies on tribological properties of the Me-DLCs are underway. In this paper, results are reported for Iridium (Ir) as additional element. The friction coefficient and electrical contact resistance during the tribotest of Ir-DLC are presented and compared with those of a pure DLC and a sputtered Ir coating. Evolution of the tribofilm and the behavior of wear debris with number of sliding cycles are discussed.

2. Test Procedure

Ir-DLC films were deposited onto either JIS SUS316L stainless steel or onto the (111) surface of single crystal silicon. Prior to the deposition, the stainless steel substrates were mirror finished to have a surface roughness parameter Ra below 0.05 μm. After polishing, the substrates were cleaned in heptane using an ultrasonic bath.

The hybrid deposition process used here was a combination of radio-frequency plasma enhanced chemical vapor deposition (RF-PECVD) and DC magnetron co-sputtering of the metal (i.e. iridium or Ir) target. Ir target was supplied by Furuya Metal Co. Ltd. According to the supplier, the purity of the target is 99.99%.

In the deposition chamber, the sputtering target is located face down at the upper side, while the substrate holder is face up at the bottom. RF power is applied to
more Ir was included in the Ir-DLC matrix at those all the tribotests reported in this paper. The plates were power. resulted in Ir-DLCs of different Ir contents. Qualitatively, of sliding was 3 steel (equivalent to JIS SUJ2 or AISI 52100). The stroke balls of 6 DC magnetron sputtering of the metal target for 30 min. The substrate using RF-generated methane plasma and DC magnetron sputtering of the metal target and the holder is 100 mm. The deposition chamber was evacuated to less than 4.0×10⁻⁶ Pa for all depositions. The substrate was then cleaned by RF-generated Ar plasma for 10 min. The pressure and the Ar flow rate used for the cleaning were 1.3 Pa and 10 sccm respectively. After that, Ir-DLC was deposited onto the substrate using RF-generated methane plasma and DC magnetron sputtering of the metal target for 30 min. Deposition parameters and deposition IDs are summarized in Table 1. Note that the sample prepared without metal sputtering (i.e. DLC/Si) yielded pure DLC, while the other sample without methane (i.e. Ir-Sputtered(80)/SUS) produced a sputtered Ir coating. The flow rate of CH4 was identical (3.0 sccm) for all depositions except for the Ir-Sputtered (80)/SUS. DC power for the Ir sputtering ranged from 0 to 80 W, which resulted in Ir-DLCs of different Ir contents. Qualitatively, more Ir was included in the Ir-DLC matrix at higher DC power.

A pin-on-flat reciprocating tribometer was used for all the tribotests reported in this paper. The plates were those prepared by the process described above. Pins were balls of 6 mm in diameter made of NF 100C6 bearing steel (equivalent to JIS SUJ2 or AISI 52100). The stroke of sliding was 3 mm and the sliding velocity was 2 mm/s.

A normal load of 0.5 N was applied using a dead weight. This load yielded an initial Hertzian contact diameter and maximum pressure of about 43 µm and 520 MPa, respectively (neglecting the coatings which were all thinner than 1 µm). Tests were performed in ambient air (i.e. temperature of 23 to 25°C and relative humidity of 50 to 60%). The number of oscillating cycles was 2000 unless noted. For further understanding of running-in processes, additional tests with shorter cycles were performed. The actual number of cycles in each test is specified in graphs.

The tribometer was equipped with an electrical contact resistance (ECR) measurement system, allowing data recording during sliding. The system measures ECR in the range of ~1 to 10⁷ Ω, and results are plotted on a logarithmic scale. Electrical connection to the pin was made with silver paint, which may cause some scattering of data from one pin to another for low ECR, below 10 Ω. More details on the ECR measurement system can be found elsewhere.

Following the tribotests, all the wear tracks on both plate and pin were observed with an optical microscope. Selected wear tracks were observed using an optical microscope. Energy dispersive X-ray microanalysis (EDX) at 15 kV was performed to identify elements in the near-surface region of the samples.

### 3. Test Results

The friction coefficient and electrical contact resistance of Ir-DLCs deposited with a DC power of 60 W (Ir-DLC(60)/SUS) are plotted in Fig. 1. The minimum friction coefficient was about 0.05. In addition, a large variation in the friction behavior was observed when a test was repeated under the same conditions on an untested area of the same plate against a new pin. Despite these variations in friction, the electrical contact resistance was small (< 30 Ω) and relatively stable except for the two large peaks that appeared after 1000 cycles for one of the experiments, which exhibited high friction.

Optical microscope photographs of the Ir-DLC(60)/SUS and mated pins after the 2000 cycles test, which resulted in low and stable friction (µ ~ 0.05) as well as high and unstable friction (µ ~ 0.1-0.4), are

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### Table 1  List of Deposition Parameters

<table>
<thead>
<tr>
<th>Deposition ID</th>
<th>Ir-DLC (60)/SUS</th>
<th>Ir-DLC (80)/SUS</th>
<th>Ir-Sputtered (80)/SUS</th>
<th>DLC/Si</th>
</tr>
</thead>
<tbody>
<tr>
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<td>SUS316L</td>
<td>SUS316L</td>
<td>Si</td>
</tr>
<tr>
<td>Source Gas and Flow Rate</td>
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<td>CH₄ 3 sccm</td>
<td>None 0 sccm</td>
<td>CH₄ 3 sccm</td>
</tr>
<tr>
<td>Metal</td>
<td>Ir</td>
<td>Ir</td>
<td>Ir</td>
<td>None</td>
</tr>
<tr>
<td>DC Power for Metal Sputtering</td>
<td>60 W</td>
<td>80 W</td>
<td>80 W</td>
<td>0 W</td>
</tr>
<tr>
<td>Thickness</td>
<td>0.5 µm</td>
<td>0.8 µm</td>
<td>0.7 µm</td>
<td>0.3 µm*</td>
</tr>
</tbody>
</table>

* The thickness of DLC/Si was estimated from other samples deposited under the same condition.
Fig. 4  EDX analysis results, showing distributions of Ir, Fe, O, and C, on the steel pin, after sliding against Ir-DLC(60)/SUS under low and stable friction conditions ($\mu \sim 0.05$) as in Fig. 1 (after 2000 cycles)

shown in Figs. 2 and 3, respectively. When the friction remained low and stable throughout the 2000 cycles test, the width of the wear track on the plate was small (50 $\mu$m) and only a small amount of wear debris was generated. On the other hand, when the friction was high and unstable, the width of the wear track on the plate was large (250 $\mu$m) and a large amount of wear debris was generated. In addition, a patchy tribofilm such as the one seen in Fig. 2(b) was observed on the wear track of pins and prevented the pins from being worn in most cases including tests with smaller number of cycles. Only in the case of the high and unstable friction in Fig. 1, a significant wear of the pin was observed as shown in Fig. 3(b).

Distributions of iridium (Ir), iron (Fe), oxygen (O), and carbon (C) on the wear tracks of pins were analyzed by EDX. Results are shown in Fig. 4 (for low and stable friction) and Fig. 5 (for high and unstable friction), respectively. SEM photographs of the analyzed regions are shown in Fig. 5.

A significant amount of Ir was detected from the tribofilm (compare Fig. 2(b) with Fig. 4). It appears that more C co-exists with Ir although it is not very clear from Fig. 4 because of the low sensitivity of EDX for light elements such as carbon. The wear track of the pin shown in Fig. 3(b) can be divided into three regions: light-, gray-, and dark-colored regions. From optical microscope and SEM observations of higher magnifications (not shown), the dark-colored region was identified as an agglomeration of wear debris. The light-colored region includes a significant amount of Fe, no Ir, and little O and C. The gray-colored region includes Ir and C. The dark-colored region (i.e. wear debris) includes O, C and Fe. Because Ir is not easily oxidized at room temperature, O in the dark-colored region probably originated from the wear debris of the pin in the form of iron oxide.

Fig. 5  SEM micrographs and EDX analysis results, showing distributions of Ir, Fe, O, and C, on the steel pin after sliding against Ir-DLC(60)/SUS plate under high and unstable friction ($\mu \sim 0.1-0.4$) conditions as shown in Fig. 1 (after 2000 cycles)
The friction coefficient and electrical contact resistance of Ir-DLC(80)/SUS are shown in Fig. 6. The evolution of friction and electrical contact resistance are roughly similar to those in Fig. 1. The minimum friction coefficient is similar for all the Ir-DLCs tested. It appears to be unaffected significantly by the DC power (i.e. Ir content). Optical microscope photographs of the pins that slid against the Ir-DLC(80)/SUS for 2000 cycles are shown in Fig. 7. A protective tribofilm with a small amount of wear debris was formed when the friction coefficient remained low and stable throughout the test (i.e. Fig. 7(a)). The tribofilm was also observed on the pin after the 12 cycles test, suggesting that the tribofilm formation started at the onset of sliding. On the other hand, when the friction coefficient was unstable, a large amount of wear debris was formed (i.e. Fig. 7(b)). Although the tribofilm was formed and the pin itself was not worn as observed by optical microscope, a deep groove was formed on the Ir-DLC plate.

The friction coefficient and electrical contact resistance of pure DLC and sputtered Ir coatings are compared with those of the Ir-DLC(80)/SUS and is shown in Fig. 8. (Note that the pure DLC is deposited on Si wafer because it was very difficult to obtain sufficient adherence of the coating to the stainless steel substrate without forming interlayer.)

The pure DLC resulted in a relatively high friction coefficient ($\mu \sim 0.3$) with very high resistance ($\sim 10^7 \Omega$). It has been verified in separated experiments (not shown) that the friction coefficient of the pure DLC for this study didn’t reach below 0.1 under light load conditions (i.e. up to 1.0 N) although it did so under higher load conditions (i.e. 2.0 to 10.0 N). After 2000 cycles, almost no evidence of wear was found on the DLC plate by optical microscope. The mated pin had a wear scar of about 60 µm in diameter (not shown). The surface of the wear track, as observed by optical microscope, was slightly discolored to grayish and appeared very smooth and flat with several light scratches. Thin flake-like wear debris surrounded the wear track, which appeared to be squeezed-out from the contact area.

The sputtered Ir coating resulted in a high friction coefficient ($\mu \sim 0.3$-$0.4$). Stick slip sound was generated throughout the test. Its electrical contact resistance was initially low ($< 10 \Omega$) and was comparable to the Ir-DLC. It then gradually increased to 10 kΩ or higher before 2000 cycles. After 2000 cycles, almost no evidence of wear was found on the sputtered Ir coating plate by optical microscope. The optical microscope photograph of the mated pin is shown in Fig. 9. It has a large wear track (> 150 µm in diameter). The surface of the wear...
Fig. 9 Optical micrograph of the pin after sliding against Ir-Sputtered(80)/SUS for 2000 cycles

Fig. 10 Optical micrograph of the pin after the 58 cycles test against Ir-DLC(60)/SUS in Fig. 1

track looks similar to that in Fig. 3(b) in the sense that it is not covered by a protective tribofilm and has many scratches. The wear track was surrounded by brownish wear debris. Separated short-cycle tests confirmed that these wear tracks on the pin already started to form after only 10 cycles.

4. Discussion

It is necessary for electrically conductive tribo-elements to maintain a stable connection with conductive substrates. Iridium has good electrical conductivity and a good anti-oxidation property with a high hardness. The Mohs hardness of pure Ir is 6.5-7.5, which is harder than iron oxides (5.5-6.5). The mated steel pin also has sufficient electrical conductivity and hardness. However, when the steel pin slid against the sputtered Ir plate in air, the electrical contact resistance increased right after the onset of sliding as seen in Fig. 8(b). This is probably because of the formation of non-conductive wear debris originated from the steel pin (i.e. iron oxide) because there was no significant damage to the sputtered Ir plate. Even if there was damage, the wear debris of Ir should hardly be oxidized.

It is interesting to note that the sputtered Ir coating and even pure DLC resulted in a much higher friction coefficient than Ir-DLCs. Neither the pure DLC layer nor the pure Ir layer sliding against steel reached a friction coefficient below 0.2, while the Ir-DLC sliding against the steel went down to 0.05. For Ir-DLCs, however, relatively high and unstable friction was occasionally observed for an unknown reason. In the following discussion, the results are considered by focusing on the characteristics of the tribofilm and the formation of wear debris with possible causes of the instability.

In the case of Ir-DLC, a large amount of wear debris was also generated when the friction coefficient was high and unstable. Oxygen was detected from the wear debris (i.e. the dark region in Fig. 3(b)), suggesting the formation of iron oxide. The steep increase in the electrical contact resistance seen in Fig. 1(b) was probably caused by the incorporation of such non-conductive wear debris into the contact interface. In addition, no protective tribofilm was present on the wear track of the pin (Fig. 3(b)), which is similar to that observed in Fig. 9.

On the other hand, when the friction coefficient was low and stable, a tribofilm containing Ir and C was found (e.g. Figs. 2(b) and 4). This tribofilm had a “protective” function against oxidation and wear of the pin. Although the formation of a tribofilm is a key to achieve low and stable friction, low wear, and good electrical conductivity, it was found to be insufficient. If wear debris like in Fig. 7(b) was formed, it would be incorporated into the contact interface and result in unstable friction and large wear although it wouldn’t affect the electrical conductivity due to its metallic nature.

The initiation of the wear debris formation has been confirmed as occurring in the early stage of the friction cycles. For example, Fig. 10 is an optical microscope photograph of the pin that slid against the Ir-DLC(60)/SUS for 58 cycles (see also in Fig. 1). A crack is seen on the tribofilm (indicated as the red circle in Fig. 10.) It seems about a half part of the tribofilm was delaminated and lost. These cracks and/or delamination of the tribofilm were also found in other shorter cycle tests whenever unstable friction behavior was observed. In fact, Ir is known to be exceptionally more brittle than other fcc metals although the origin of this brittleness is somehow controversial and not yet clear.

There are, however, cases where such a brittle failure of Ir-containing tribofilm did not occur and thus low and stable friction continued throughout the tests. Although the critical parameters affecting this phenomenon are not yet fully understood, several possibilities are discussed below.

The most important factors would be the composition and the structure of the tribofilm. From the past experiences with other Me-DLCs (i.e. W-5-7 and Cu-DLCs), the authors believe that Ir is dispersed in the Ir-DLC as nano-sized metal clusters that are surrounded by the DLC matrix. The structure of the tribofilm on the pin could consist of an agglomeration of nano-sized Ir clusters surrounded by amorphous carbon. Depending on how carbon supports the Ir clusters, the ductility of the tribofilm (as a nano-composite material) could be significantly higher than that of pure Ir.

The adherence of the tribofilm to the pin is also important for stable tribofilm formation, which could be affected by the native oxide layer on the steel pin. Concerning the sliding of DLC/steel in ultra-high vacuum, it has been reported that the native oxide layer on the steel largely influenced on the formation of the tribofilm on the steel pin. When the native oxide layer on the steel pin was removed by Ar etching before the tribotest, the number of cycles before reaching super-low
friction decreased significantly. This is explained by considering the affinity of C for Fe.

Similar phenomena could occur between Ir and the steel pin. According to Fe-Ir phase diagram,[12] up to about 20% Ir is soluble in Fe at room temperature, while more than 10% Fe is soluble in Ir. Another solid solution phase with (20-50%Fe):(50-80%Ir) also exists. On the other hand, Ir probably does not form an adherent tribofilm on the iron oxide because of its low reactivity with oxygen. This could explain why a stable tribofilm was occasionally formed under equivalent conditions and even on the same plate. There was no clear trend that the earlier tests resulted in the low and stable friction rather than the later tests. This is probably because native oxide film formation on the pin stabilized so quickly that the state of the native oxide was not significantly affected by the order of the tests. However, this does not mean that the effect of the native oxide layer was the same for all the tests because of other factors such as surface roughness.

Severe contacts of asperities due to very rough surfaces may help to break the native iron oxide and expose a fresh surface of metallic iron so that Ir (and C) can form adherent tribofilm. Mechanical alloying could take place because of the asperity contacts and may result in an adherent tribofilm. Although all the pins were prepared to a controlled roughness and cleanliness, these effects could not be neglected. These points will be investigated further in the future.

In addition to the fundamental aspects discussed above, it would be even more important to use robust tribo-elements that would not be affected by small changes in design and manufacturing parameters. The anti-oxidation property, sufficient hardness and ductility, affinity with the mating material, etc. would be necessary for the use of the specific metal as an electrically conductive tribo-material. Although Pt-DLC could be one of the candidates, Pt may be rather soft compared with Ir. In such a case, the authors could optimize the Me-DLC by using Pt-Ir alloys or other metals as a sputtering source. Results of these activities will be reported in future papers.

5. Conclusions

The Iridium-containing DLC / steel pair can achieve a low and stable friction coefficient (~0.05) and a low electrical contact resistance (< 30 Ω) at the same time in an oscillating sliding contact in air. The formation of a protective and electrically conductive tribofilm is necessary for achievement of stable low friction and high conductivity. The prevention of wear debris formation is also necessary to preserve a low and stable friction as well as a low wear.

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7. References