Ultra-high-speed coating of Si-containing a-C:H film at over 100 μm/h

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Abstract

Diamond-like carbon (DLC) coating with a microwave-excited high-density near plasma gave a considerably high deposition rate over 100 μm/h, which is 100 times larger than the conventional method (~1 μm/h), together with a hardness over 10 GPa. In this work, in order to understand the characteristics of DLC film deposited at over 100 μm/h with microwave assistance, DLC films obtained by using DC plasma and microwave-excited high-density near plasma were compared from the viewpoints of deposition rate, hardness, atomic composition and friction properties. It was shown that the hardness of low-temperature (210 °C) tempered steel (SCM415, JIS) did not decrease after the DLC coating of 520 nm for 12 seconds by microwave-excited high-density near plasma even though the substrate temperature was increased up to 270 °C during coating. On the other hand, the hardness of the same substrate decreased from 700 Hv to 660 Hv after the DLC coating of 540 nm for 1200 seconds by DC plasma with the same maximum temperature of 270 °C.

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1. Introduction

Recently, application of DLC (Diamond-Like Carbon) to the sliding surfaces of mechanical elements is spreading gradually and steadily with increasing demands for energy saving by friction reduction and lifetime extension by wear reduction. In this field, higher-speed coating method with applicability to 3-dimensional shapes is strongly desired. Plasma CVD (Chemical Vapor Deposition) employing DC or RF discharge is a promising candidate for such demands because plasma can be generated along the 3-dimensional surface of a mechanical element; however, typical coating speed of DLC is not so high, ~1 μm/h with such a conventional plasma CVD; in addition, further drastic increase in the coating speed is not expected due to relatively low electron density \(n_e \sim 10^{10} \text{cm}^{-3}\) in DC or RF discharge plasma employed. The use of higher-density plasma is considered to be essential for increasing the coating speed. Thus, we have proposed a high-speed coating method of DLC with a novel plasma CVD employing much higher-density plasma \(n_e \sim 10^{13} \text{cm}^{-3}\), which is sustained by microwave propagation along plasma-sheath interface adjacent to metal surface [1-3]. In our previous work, such a microwave-excited high-density near
plasma gave a considerably high deposition rate of 188 μm/h, which is about 180 times larger than that of conventional method, together with a hardness of 12 GPa in DLC coating [1].

In this work, in order to understand the characteristics of DLC deposited at over 100 μm/h, DLCs obtained by using DC plasma and microwave-excited high-density near plasma were compared. It should be noted that substrate temperature often increases above 200 °C, which is the tempering temperature of many steels typically used for mechanical elements, during high-rate coating with microwave-excited high-density near plasmas. If such a high temperature induces softening of low-temperature tempered steels, our new proposal, or microwave-assisted ultra-high-speed coating cannot be applied to a lot of mechanical elements. Thus, we further investigated the effect of increased temperature during ultra-high-speed DLC coating with microwaves on the hardness of substrate.

2. Experimental Setup

Figure 1 shows our experimental apparatus. Internal diameter and height of the chamber are 220 and 225 mm, respectively. A rotary pump and mechanical booster pump are connected to the stainless-steel chamber in order to decrease the gas pressure down to 1 Pa before deposition. 2.45-GHz microwaves are injected from a coaxial waveguide connected to the lower flange, propagating into the chamber through a quartz window. A specimen is installed so that the one end contacts the quartz window. In addition, tungsten wiring is connected to the specimen so that negative voltage provided from the pulsed DC power supply is applied to the specimen against the grounded chamber. Substrate is alloy steel substrate (SCM415, JIS), which had been tempered 2 hours at 210 °C to get a Vickers hardness of 700 Hv.

![Fig. 1. Schematic of DLC coating apparatus with a novel plasma CVD employing high-density near plasma. (b) Photgraphs of plasma surrounding a substrate in (b) DC and (c) DC+MW cases.](image)

### Table 1. Coating conditions

|                         | DC   | DC+Heater | DC+MW |
|-------------------------|------|-----------|-------|
| **Gas flow, sccm**     | Ar   | CH₄       | TMS   |
|                         | 40   | 200       | 20    |
|                         | Total gas flow $Q_{\text{total}}, \text{sccm}$ | 260 |
| **Pressure $P$, Pa**   | 75   |           |       |
| **Deposition time $t$, sec.** | 750  | 1200      | 12    |
| **Microwave(2.45 GHz)** | Peak power | 1 kW   |       |
|                         | Pulse frequency | 500 Hz |       |
| **Bias**                | Voltage | -500 V   |       |
|                         | Pulse frequency | 500 Hz |       |
| **Duty ratio**          |       |           | 50%   |
| **Temperature $T$, °C** | 80   | 270       | 270   |
DLC films were deposited by different 3 methods: DC plasma, DC plasma with additional heating, and microwave-excited high-density near plasma, under the conditions shown in Table 1. For each method, coating time was decided so that coating thickness becomes 550 nm. The film thickness value of DLC was obtained by measuring the step height at the interface between DLC coated and uncoated surfaces on the steel substrate by using stylus type surface roughness tester. Deposition rate was calculated as the average value of deposition rate at upper and lower steps. Substrate hardness before and after deposition were measured by micro Vickers hardness tester at an indentation load of 0.3 kgf.

The atomic composition of DLC coatings was determined by a high-resolution ERDA (Elastic Recoil Detection Analysis) and XPS (X-ray Photoelectron Spectroscopy). H/C ratio was measured by ERDA, while O/C, Si/C, and N/C ratios were measured by XPS. ERDA was operated with 500 kV nitrogen ion at an angle of 67.5° with respect to the surface normal. Detection of recoil protons was performed at an angle of 22.5°. A position-sensitive multichannel plate detector was used for the ERDA measurements. Hydrogen contents of the films were calculated from the ERDA results in comparison with the result of standard sample (DLC film with 29% hydrogen contents). XPS was operated with Al Kα X-ray source (25W). Samples were sputtered cleaned prior to XPS analysis in order to assess the origin of the impurities such as oxygen. The sputtering conditions were 4 kV argon ions with raster scanning 2 mm square area for 1 min.

3. Results and discussion

3.1 DLC coating with CH₄ as a main source gas

As shown in Fig. 2, the substrate temperature during DLC deposition by microwave-excited high-density near plasma rapidly increased from 60 to 270 °C in 12 sec after microwave injection. Konishi et al. reported that the hardness of DLC film significantly decreases with decreasing substrate temperature through the increase of hydrogen content in the film [5]. Therefore, in order to correctly evaluate the difference between the two DLCs deposited by DC plasma and microwave-excited high-density near plasma, it is preferable to separate the effects of substrate temperature increase and coating method difference. For this purpose, DLC coatings were conducted by DC plasma with and without additional heating, so that the maximum substrate temperature during coating with additional heating becomes the same as 270 °C of the microwave-enhanced case. In DLC coating by DC plasma without additional heating, the maximum substrate temperature was 80 °C.
Figures 3(a) and 3(b) show the deposition rate and hardness of DLCs, respectively, obtained by 3 methods. It is clearly shown that the deposition rate and hardness considerably increased by microwave injection for plasma generation. Comparing the two DC plasma cases, deposition rate was decreased and hardness was increased by increasing substrate temperature. It is considered that the increase of DLC density resulted in the increase of hardness and the decrease of deposition rate. The hardness of the DLC by DC plasma with additional heating showed almost the same hardness as that by microwave-excited high-density near plasma. Comparing these two cases; it can be concluded that deposition rate of DLC can be increased by 100 times by microwave injection if the hardness of DLC is not changed.
Figure 4 shows the atomic composition of DLCs deposited by the 3 methods. Comparing the two cases with DC plasma, hydrogen content was decreased and silicon content increased by additional heating. Hydrogen atoms terminate the dangling bonds that increases the number of C–H bonds which relieve the internal stress and induce softer polymer like structure in DLC film [5]. In addition, T.Iseki et al. reported that the hardness of DLC film increases with increasing Si content due to the increase in total sp³ content in the film [7]. Therefore, it is considered that the increase of hardness by additional heating was caused by the decrease of hydrogen content and increase of silicon content. On the other hand, comparing the 2 DC plasma cases and microwave-excited high-density near plasma case, both of the hydrogen and silicon contents decreased, while the C content significantly increased by injecting microwave. As a result, the atomic composition of DLC deposited by DC plasma with additional heating was considerably different from that by microwave-excited high-density near plasma, while the hardness values of these DLCs were almost the same; it is implied that surface reaction mechanism in DLC formation was changed due to not only the increased substrate temperature but also the significantly increased plasma density in the microwave-assisted case.

It should be noted that, in the DC plasma case with additional heating and the microwave assisted case, the substrate temperature was increased to more than 200 °C, which is the tempering temperature of low-temperature tempered steels including the alloy steel substrate (SCM415, 700 Hv, JIS) employed. Therefore, we confirmed whether these substrates were softened or not during DLC coating. As a result, it was shown that the decrease of substrate hardness did not occur in the coating by microwave-excited high-density near plasma; on the other hand, the substrate hardness decreased from 700 to 660 Hv in the coating by DC plasma with additional heating. It can be considered that substrate softening did not occur due to significantly short time (12 sec.) coating in the microwave-assisted case, even though the substrate temperature increased up to 270 °C during coating.

3.2 DLC coating with C₂H₂ as a main source gas

For further increasing deposition rate, we tried to use C₂H₂ as a main source gas instead of methane, because it is generally known that C₂H₂ can increase the deposition rate of DLC compared to CH₄ [8]. Depositions was conducted at a gas flow rate of C₂H₂, 200 sccm for 7 second, where the other conditions were set to be the same as those of the MW+DC case in Table. 1. Note that the substrate temperature at the start of coating was around 300 °C, and thus final temperature increased to 435 °C. In this coating, a deposition rate of 506 um/h was obtained, while the hardness was 10.1 GPa which is much smaller than that of the MW+DC case with methane (Fig. 3(b)). Figure 5 shows the atomic composition of DLCs deposited by MW+DC with CH₄ and C₂H₂. As clearly seen, the carbon and hydrogen contents were increased and decreased, respectively, from the CH₄ to C₂H₂ cases. The substrate temperature increase in the C₂H₂ case is expected to decrease the content of hydrogen [4]; nevertheless, the hardness of the C₂H₂ case was significantly decreased. In case of using in the C₂H₂, it is considered that much larger amount

![Atomic composition of DLC films deposited by DC plasma, DC plasma with additional heating and microwave-excited high-density near plasma.](image-url)
of hydrogen is unexpectedly included in the film; it can be concluded that we should suppress the hydrogen inclusion for taking advantages of high deposition rate of \( \text{C}_2\text{H}_2 \) in coating DLC with a hardness larger than 20 GPa.

Fig. 5. Atomic composition of DLC films deposited microwave-excited high-density near plasma (MW+DC) with CH\(_4\) to C\(_2\text{H}_2\).

4. Conclusions

Diamond-like carbon (DLC) coating with a microwave-excited high-density near plasma gave a considerably high deposition rate over 100 \( \mu \text{m/h} \), which is 100 times larger than the conventional method (~1 \( \mu \text{m/h} \)), together with a hardness over 10 GPa. In this work, in order to understand the characteristics of DLC film deposited at over 100 \( \mu \text{m/h} \) with microwave assistance, DLC films obtained by using DC plasma and microwave-excited high-density near plasma were compared from the viewpoints of deposition rate, hardness, atomic composition and friction properties. It was shown that the hardness of low-temperature \( (210 \ ^\circ \text{C}) \) tempered steel (SCM415, JIS) did not decrease after the DLC coating of 520 nm for 12 seconds by microwave-excited high-density near plasma even though the substrate temperature was increased up to 270 \( ^\circ \text{C} \) during coating. On the other hand, the hardness of the same substrate decreased from 700 Hv to 660 Hv after the DLC coating of 540 nm for 1200 seconds by DC plasma with the same maximum temperature of 270 \( ^\circ \text{C} \).

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