Ultra-high-speed coating of DLC at over 100 µm/h without softening of low-temperature tempered steel substrate

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1. Introduction

Recently, application of DLC (Diamond-Like Carbon) to the sliding surfaces of mechanical elelments 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 promissing 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~10^8–10^{10} 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~10^{11}–10^{13} cm^{-3}), which is sustained by microwave propagation along plasma-sheath interface adjacent to metal surface [1,2]. 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 [3].

In this work, in order to understand the characteristics of DLC deposited at over 100 µm/h, DLCs obtaiend by using DC plasma and mircowave-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 mircowave-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 temperatue during ultra-high-speed DLC coating with micorwaves 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 staineless-teel 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

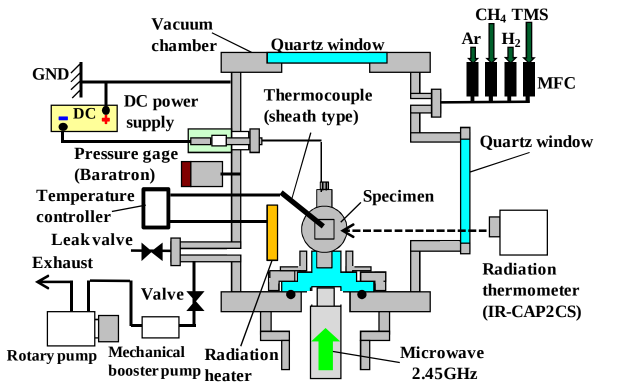

Fig. 1 Schematic of DLC coating apparatus with a novel plasma CVD employing high-density near plasma.

Table.1 Coating conditions

		DC	DC+Heater	DC+MW
Gas flow, sccm	Ar	40		
	CH_4	200		
	TMS	20		
Total gas flow Q_{total}, 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

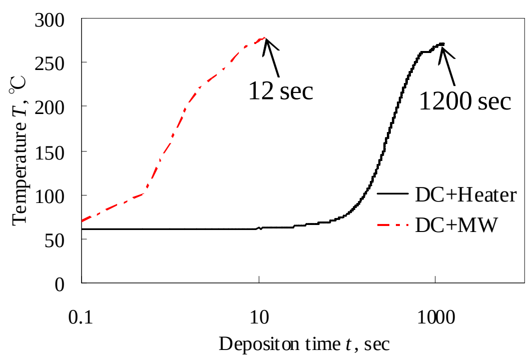

Fig. 2 Time-dependent changes of substrate temperature during deposition, by DC plasma with heater and micro-wave-excited high-density near plasma.

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.

DLC films were deposited by different 3 methods: DC plasma, DC plasma with additional heating, and mircowave-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. Depostion rate was calculated as the average value of deposition rate at upper and lower steps. Substrate hardness before and after deposition was 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.Comparison of coated DLC films

In Fig. 2, the substrate temperature during DLC deposition by mircowave-excited high-density near plasma is shown. The substrate temperature rapidly increased from 60 to 270 °C in 12 sec after microwave injection. Konishi et al. have reported the considerable change of the hydrogen content and hardness of DLC film with substrate temperature [4]. In order to correctly evaluate the differece between the two DLCs deposited by DC plasma and mircowave-excited high-density near plasma, it is prefarable to separate the effects of substrate temperature increase and coating method difference. For this puopose, DLC film was deposited by DC plasma with additional heating, so that the maximum substrate temperature during coating 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 and 4 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 adding 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 reulsted 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 mircowave-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 under the same condition.

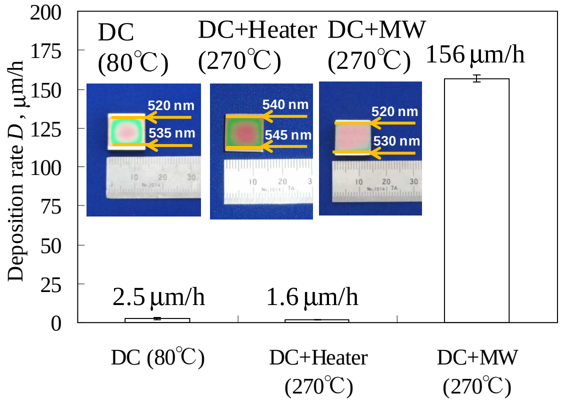

Fig. 3 Deposition rate of DLC film deposited by DC plasma, DC plasma with additional heating, and microwave-excited high-density near plasma.

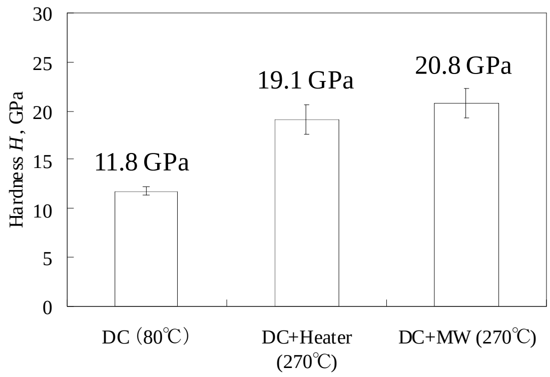

Fig. 4 Hardness of DLC films deposited by DC plasma, DC plasma with additional heating, and microwave-excited high-density near plasma

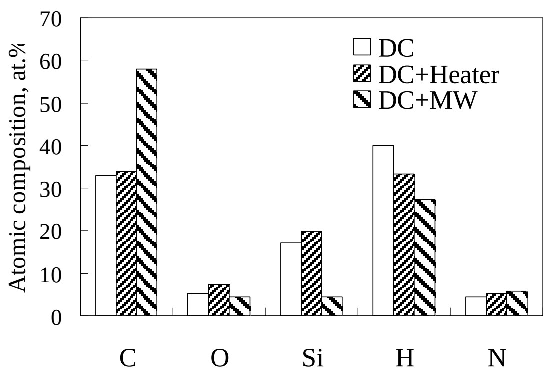

Fig. 5 Atomic composition of DLC films deposited by DC plasma, DC plasma with additional heating, and microwave-excited high-density near plasma.

Figure 5 shows 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 terminates 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 increaes with increasing Si content due to the increase in total sp^3 content in the film. Therefore, it is considered that the increase of hardness by additional heating was caused by the decreace of hydrogen content and increase of silicon content. On the other hand, comparing the DC plasma and mircowave-excited high-density near plasma cases, 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 aditional heating was considerably different from that by mircowave-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.

3.2.Substrate hardness after DLC coaing

As can be seen in the preceding subsection 3.1, substrate temperature was increased to more than 200 ℃, which is the tempering temperature of low-temperature tempered steels such as the alloy steel substrate (SCM415, JIS) employed. Therefore, we should confirm whether the substrates were softened or not during DLC coating. Figure 6 shows the hardness of the DLC-coated substrates together with the hardness of a substrate before coating. Hardness test showed that the decrease of substrate hardness did not occur in the coating by mircowave-excited high-density near plasma even though the maximum substrate temperature exceeded 200 ℃ during coating. In contrast, substrate hardness decreased after the coating by DC plasma with additional heating. It was considered that higher temperature than 200 ℃ does not nescessarily induce substrate softening. Considering the time of high temperature than 200 ℃ is much shorter in the microwae-assisted case than in the DC plasma, it is expected that substrate softening can be avoided if high-temperature period is enough short.

Hardness of quenched steel is changed by tempering, due to the decomposition of martensite, precipitation and coalescence of carbide and rearrangement and disappearance of dislocation. The mechanical properties such as hardness, strength and toughness, are changed with advancing these metallurgical reactions during tempering. Arrehenius' assumption gives a qualitative estimation for the effect of tempering. According to his assumption, the rate of reaction, r can be written in the form $r = A\exp(-Q/RT)$, where Q is activation energy, T is temperature in kelvin, R is gas constant and A is a constant for an interested reaction. The amount of the reaction can be considered as the product of r and the reaction period. Based on these assumptions, tempering parameters were proposed by Hollomon and Jaffe. They have reported the tempered hardnesses obtained from various time-temperature cycles were found to be correlated through a parameter of the form $P = T(C + \log_{10} t)$,

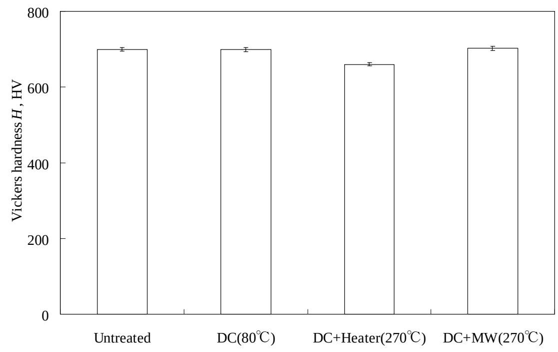

Fig. 6 Hardness of low temperature tempered steel substrate after coating of DLCs deposited by DC plasma and microwave-excited high-density near plasma.

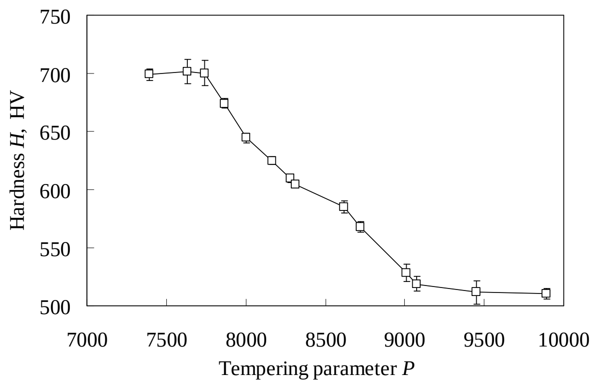

Fig. 7 Tempering data of SCM415 alloy steel substrate from various fixed temperature tempering by electric furnace

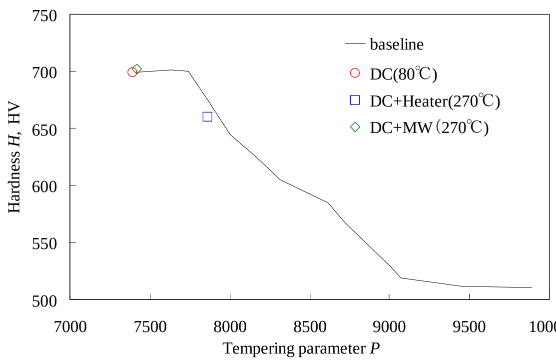

Fig. 8 Comparison of tempering data from various plasma process and those obtained by electric furnace

where T is the absolute tempering temperature in Kelvin (assumed to be fixed during the entire treatment), C is a material constant, and t is the time in seconds [7]. C is determined so that same parameter is given to the same hardness substrates which were obtaied by a short time tempering at a high temperature and a long time tempering at a low temperature. According to this formula, advancing of tempering depends on not only the tempering temperature but also on tempering time. Thus, our ultra-high-speed coating method could prevent substrate softening.

In order to derive the guideline for avoiding substrate softening, we made a comparison of tempering data from various fixed temperature tempering and those obtained by various plasma processes in the preceding subsection 3.1. Fi\rst, in order to determine the material constant C for the Alloy steel (SCM415), substrates (SCM415) were tempered at different fixed temperatures of 240, 250, 260, 270, 290, 320, 340, 370, and 400 ℃ by electric furnace for a tempering time of 30 min. In addition, alloy steel substrates (SCM415) were tempered at different fixed temperatures of 260, 270, 290, and 320 ℃ by electric furnace for a tempering time of 120 min. Substrate temperature was measured by thermocouple. In these experiments, substrate tempered at 290 ℃ for 30 min showed almost the same hardness as that tempered at 270 ℃ for 120 min. From these two results, C was determined as 15 for the alloy steel substrate (SCM415) employed. Figure 7 shows tempering data of SCM415 alloy steel substrate from various fixed temperature tempering by electric furnace. Substrate hardness after tempering at various temperatures are clearly correlated with tempering parameter. In the electric furnace trials, tempering took place for a given time at a fixed temperature. On the contrary, in our coating process, constant temperature does not appear as in Fig. 2. Semiatin et al. proposed effective tempering parameter for the treatments involved continuous heating and cooling [8]. The total continuous cycle is broken into a number of very small time increments, each of duration Δt_i and characterized by some average temperature T_i. It is assumed that the temperature for the equivalent isothermal treatment is the peak temperature of the continuous one, or T^*. Having specified the temperature of the equivalent isothermal cycle as T^*, an effective tempering time t^* for this cycle can be estimated. This is accomplished by solving for the increment in t^*, or Δt_i^* for each of the Δt_i in the continuous treatment by using the equation $T_i\,(C + \log_{10} \Delta t_i) = T^*(C + \log_{10} \Delta t_i^*)$. Summing the Δt_i^* for each portion of the continuous cycle yields the total effective tempering time t^* at temperature T^* and hence the effective tempering parameter $T^*(\mathrm{C} + \log_{10} t^*)$.

According to this formula, effective tempering parameters of substrate during coating were calculated for the deposition by microwave-excited high-density near plasma for 12 sec. and the deposition by DC plasma with additional heating for 1200 sec. For example, continuous heating and cooling process fro 1200 sec. in the latter DC plasma coating is converted into the total effective tempering time of 700 sec. at fixed-temperature of 270 ℃.

Figure 8 shows comparison of tempering data from various plasma processes and those obtained by electric furnace. Tempering data from plasma process revealed agreement with tempering data from fixed temperature process by electric furnace. Tempering parameter of the coating by DC plasma with additional heating exceed the value above which the alloy steel substrate softens. On the other hand, tempering parameter of the coating by mircowave-excited high-density near plasma did not exceed the value above which the alloy steel substrate softens due to the shortening of coating time. Futhermore, microwave excited high-density near plasma method can make DLC film at high temperature that conventional method may induce the softening of substrate.

4. Conclusions

In this work, in order to understand the characteristics of DLC film deposited at over 100 μm/h with microwave assistance, DLC films obtaiend by using DC plasma and mircowave-excited high-density near plasma were compared. The deposittion rate and hardness of the DLC deposited by DC plasma were 2.5 μm/h and 11.8 GPa, respectively; on the other hand, the deposittion rate and hardness of the DLC deposited by mircowave-excited high-density near plasma were 156 μm/h and 20.8 GPa, respectively. The deposition rate and hardness of DLC film were considerably increased by adding microwave injection for plasma generation under the same coating condition. However, in the microwave assisted case, the substrate temperature was increased to more than 200 ℃, which is the tempering temperature of low-temperature tempered steels including the alloy steel substrate (SCM415, JIS) employed. Therefore, we confimed whether the substrates was 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 mircowave-excited high-density near plasma even though the substrate temperature increase up to 270 ℃ during coating. This is because tempering parameter did not exceed the critical value (7742) above which the alloy steel substrate softens.

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