Atomic composition of Diamond-Like Carbon Film coated at over 100 μm/h by using Microwave-excited high-density near plasma

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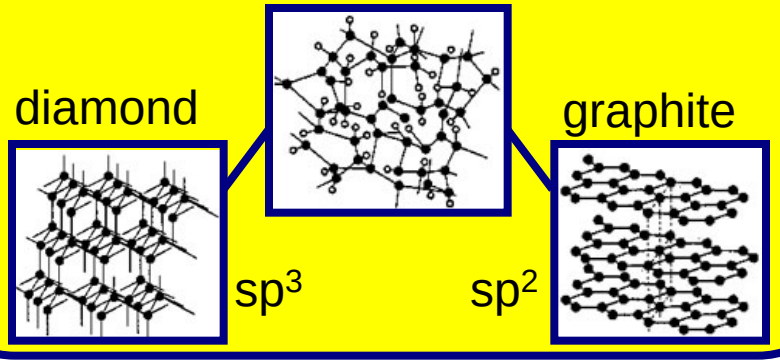
Recent progress of DLC

high hardness

high wear resistance

Diamond-like carbon (DLC)

~ amorphous carbon ~



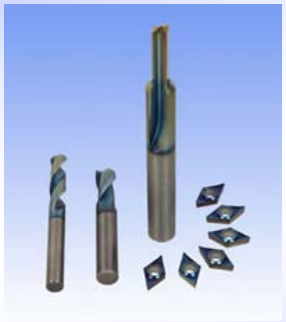
low friction coefficient

high corrosion resistance

DLC has excellent material properties

DLC has gathered wider and wider attention in industry

automobile parts



cutting tool

http://www.nippon-itf.co.jp

valve

watch

http://casio.jp/wat/

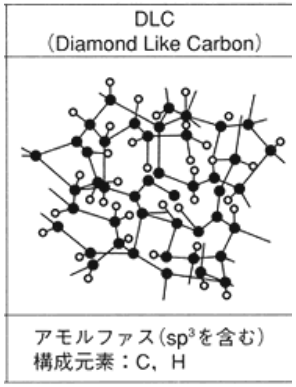
Background

- Further saving of fuel and electric power consumed by machines is required.

⇒Requrement to tribology：Decrease of energy loss due to friction

⇒Key technology：A low friction carbon film: DLC (Diamond-Like Carbon）

⇒Problem：high cost of coating→limited application

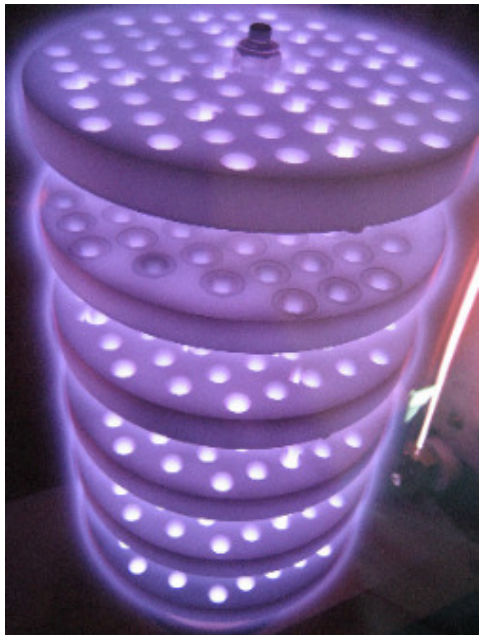


Lofwfriction

⇒Cost reduction→Application to wider variety of machince parts → <u>Expand the merit of energy saving by DLC</u>

Industrial demand : One-piece flow process

Conventional



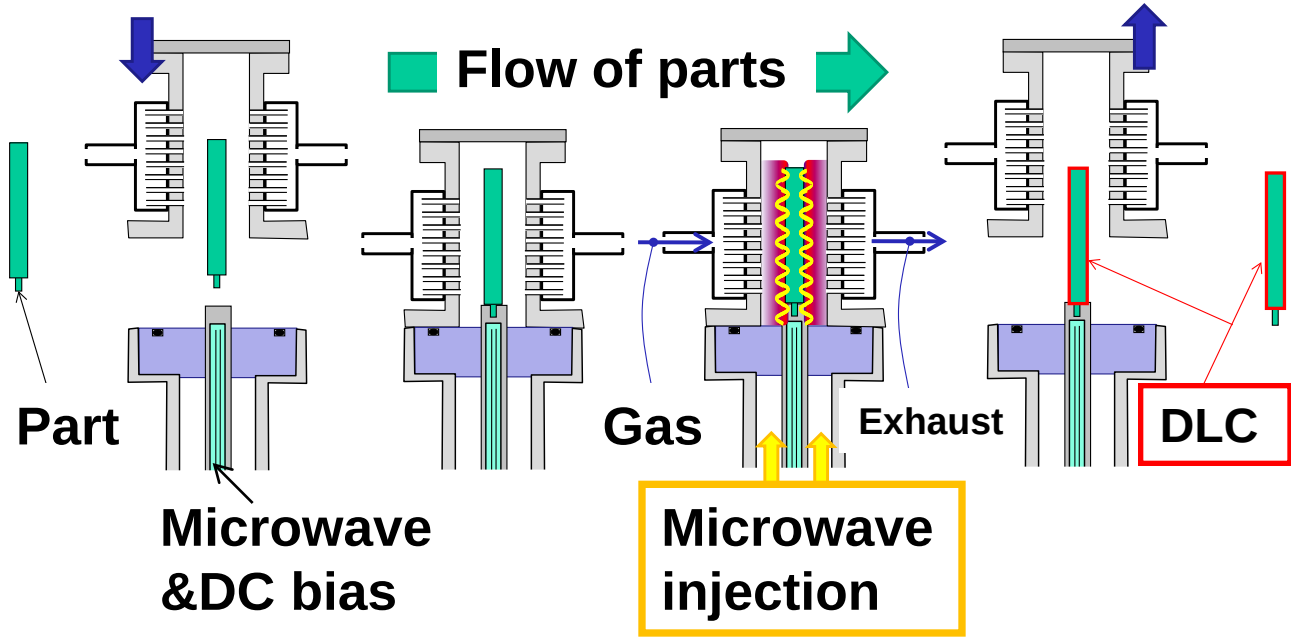
1000 parts in 1 batch

Deposition rate:1 μm/h

Batch process

- Huge cost of large equipment
- Not just in time

Our proposal (new method)



1 parts in 1 batch

Deposition rate (requirement: 100-1000 μm/h

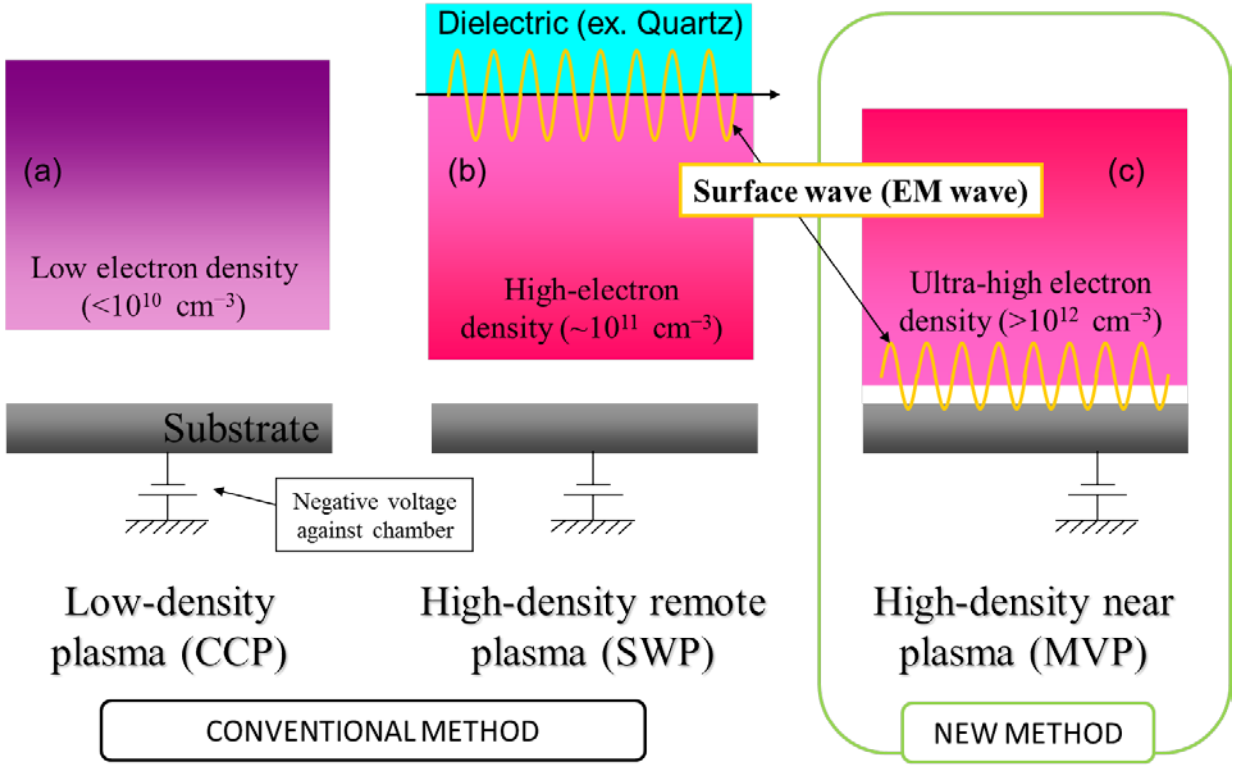
Inline (One-piece flow) process by ultra-high speed coating

- Cheaper cost of smaller equipment
- JUST in time

suitable for low cost mass production such as automobile parts

MVP Microwave-sheath Voltage combination Plasma

MVP is sustained by microwave propagation along plasma-sheath interface, where the metal is negatively biased for expansion of sheath layer.



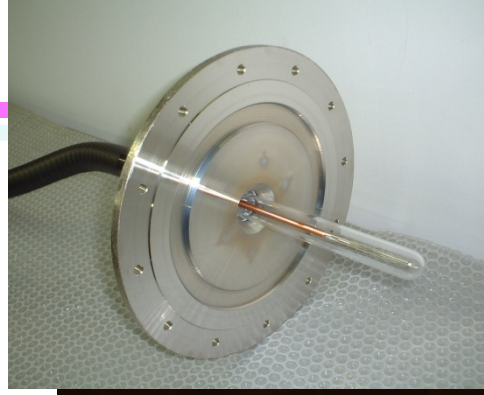
H. Kousaka, et. al., *Jpn. J. Appl. Phys.* **44** (2005) L1154–L1157.

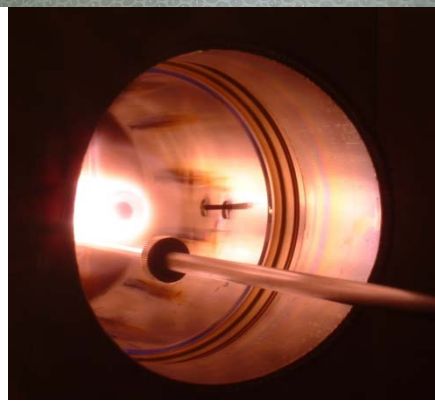
Previous results of DLC coating by MVP

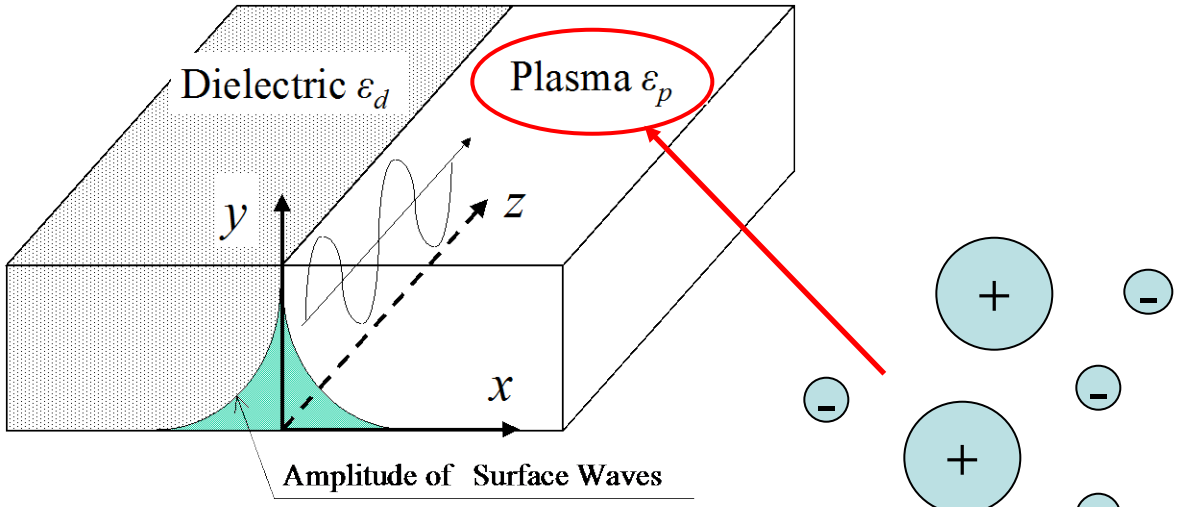
Such a high density plasma(>10^{12} cm^{-3}) gave a considerably high deposition rate of **188 μm/h,** hardness of **12.9 GPa .**

T. Okamoto, et. al., *Proc. International Tribology Conference HIROSHIMA 2011, D2-14 (CD-ROM).*

Surface Wave-excited Plasma (SWP)







Wave number in the *z* direction

$$k_z = \varepsilon_d^{1/2}\frac{\omega}{c}\left[\frac{\omega_{pe}^2-\omega^2}{\omega_{pe}^2-(1+\varepsilon_d)\omega^2}\right]^{1/2} \qquad \omega_{pe}=\left(\frac{e^2 n_e}{\varepsilon_0 m_e}\right)^{\frac{1}{2}}$$

(m_e: electron mass, e: electron charge, c: speed of light, ω: excitation frequency, n_e: electron density, ε_0: permittivity of vacuum, ε_d: relative permittivity of quartz)

Required condition for SWP generation

$$\omega_{pe}^2-(1+\varepsilon_d)\omega^2>0 \Rightarrow$$

2.45 GHz, ε_d=3.7 ----→ n_e>3.0×10^{11}cm^{-3}

2.45 GHz, ε_d=1.0 ----→ n_e>1.7×10^{11}cm^{-3}

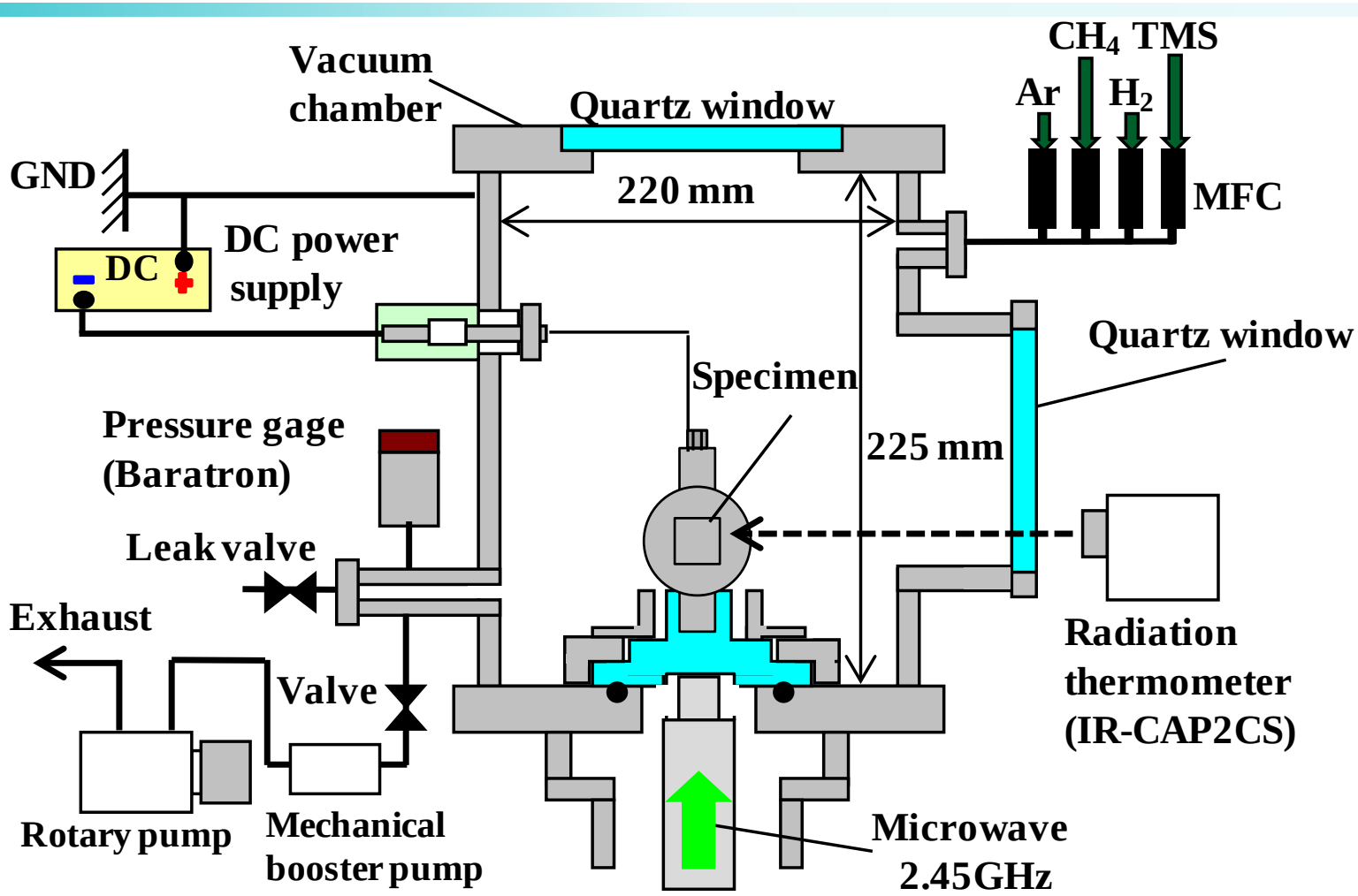
Motivation of this work

1. Film properties of DLC film coated at such high rate are unknown.
2. Substrate temperature often increases above 200℃, which is the tempering temperature of many steels typically used for mechanical elements.

Purpose

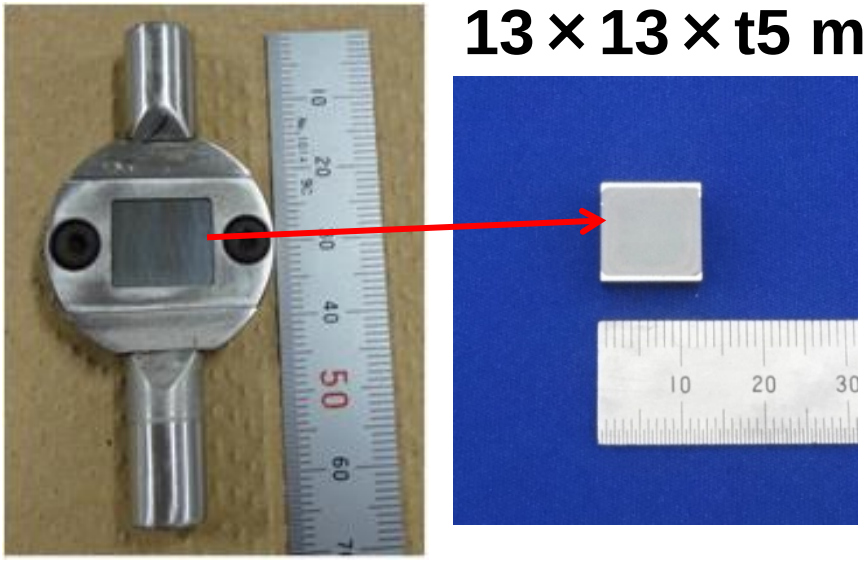
1. Compare atomic composition of DC and MVP deposition at same environment in order to understand the characteristics of DLC film coated at over 100 μm/h.
2. Confirm whether the substrates was softened or not during DLC coating at temperatures higher than 200 ℃.

Experimental apparatus



2.45 GHz microwaves can be introduced via coaxial waveguide and quartz plate. The top of the substrate is connected to a high voltage DC power supply to apply a negative voltage.

Substrate



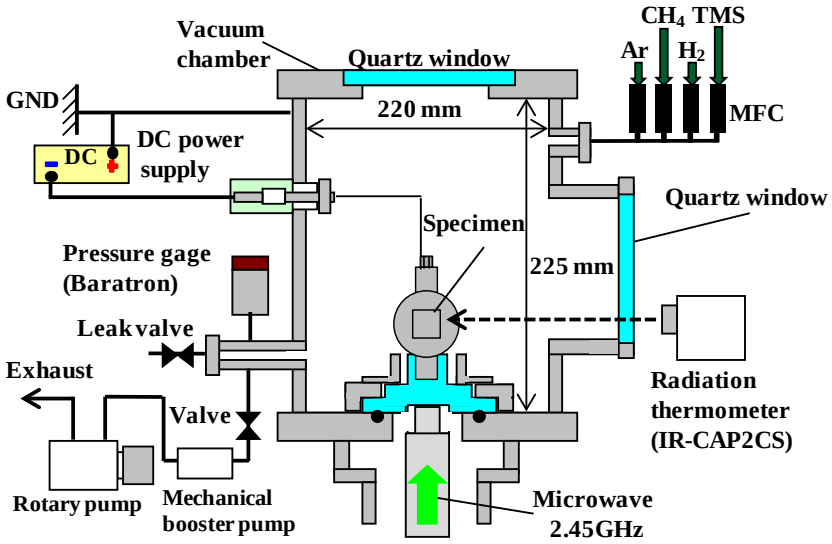
Typically used for sliding parts of automobiles

Substrate:

SCM415 (Cr,Mo containing alloy steel block)
Tempered at 200 ℃ to get Vickers hardness 700 HV

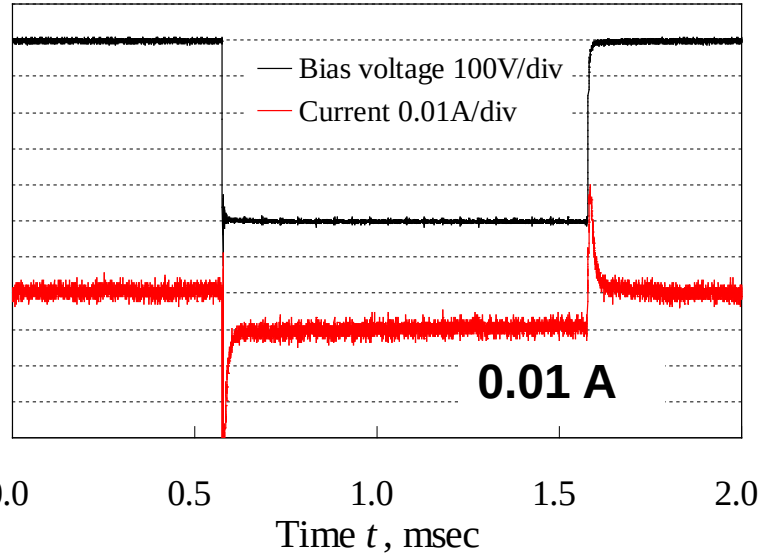
This substrate could have been softened if the substrate temperature exceed 200 ℃.

Comparison of DC, MVP(DC+MW)

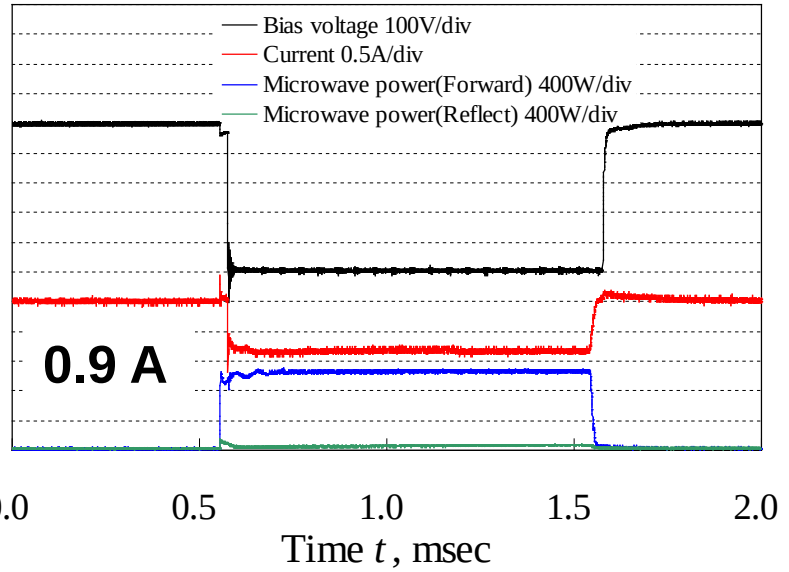


By injecting microwave, pulse current became 90 times larger than DC plasma because plasma density increased.

DC Frequency 500 Hz, Duty ratio 50 %



MVP(DC+MW) Frequency 500 Hz, Duty ratio 50 %



Comparison of DC, MVP(DC+MW)

Movies : Ar plasma generation by 2 methods.

DC DC -500 V

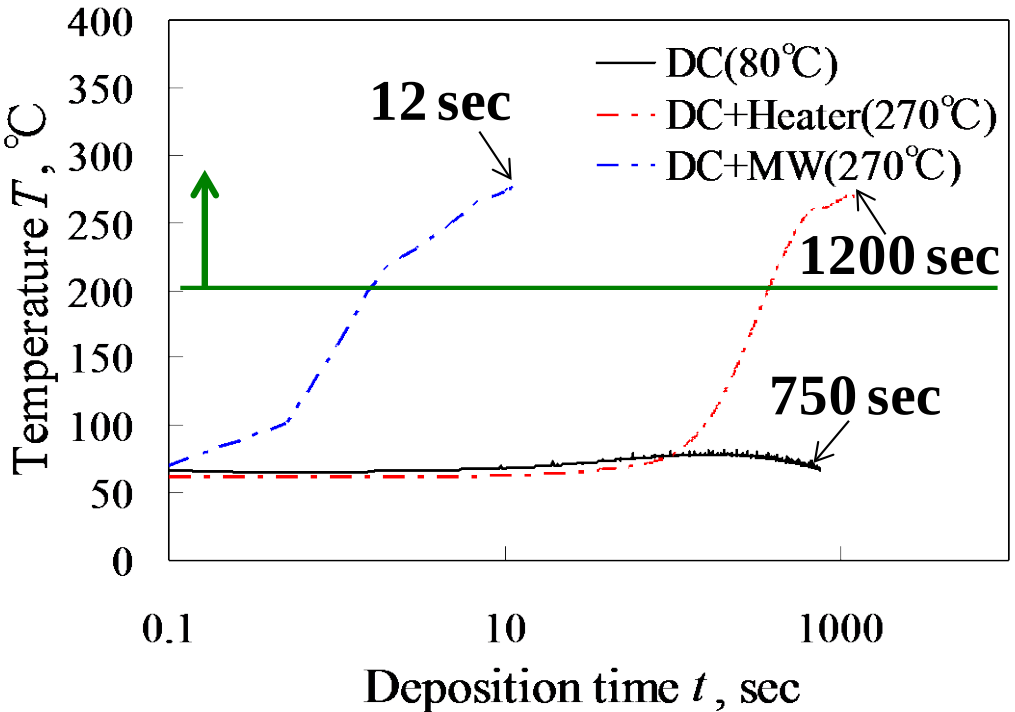
MVP(DC+MW) DC -500 V, MW 500 W

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
	Duty ratio			50%
Bias	Voltage	-500 V		
	Pulse frequency	500 Hz		
	Duty ratio	50%		
Temperature T, ℃		80	270	270

DLC film thickness: 500nm

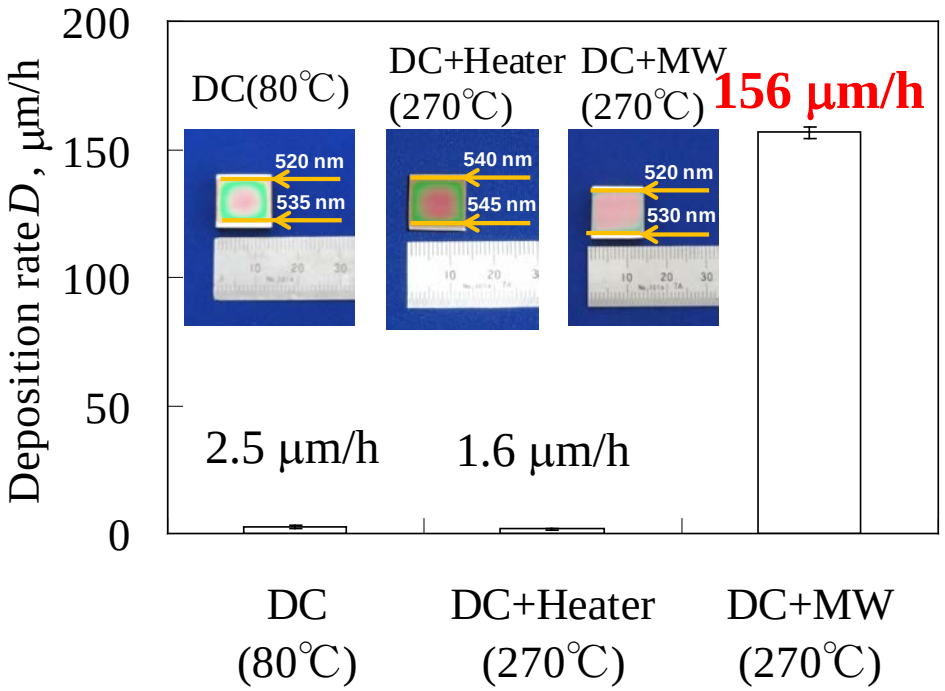
In the coating of DC plasma with additional heating, maximum substrate temperature during coating becomes the same as 270 ℃ of the microwave-enhanced case.

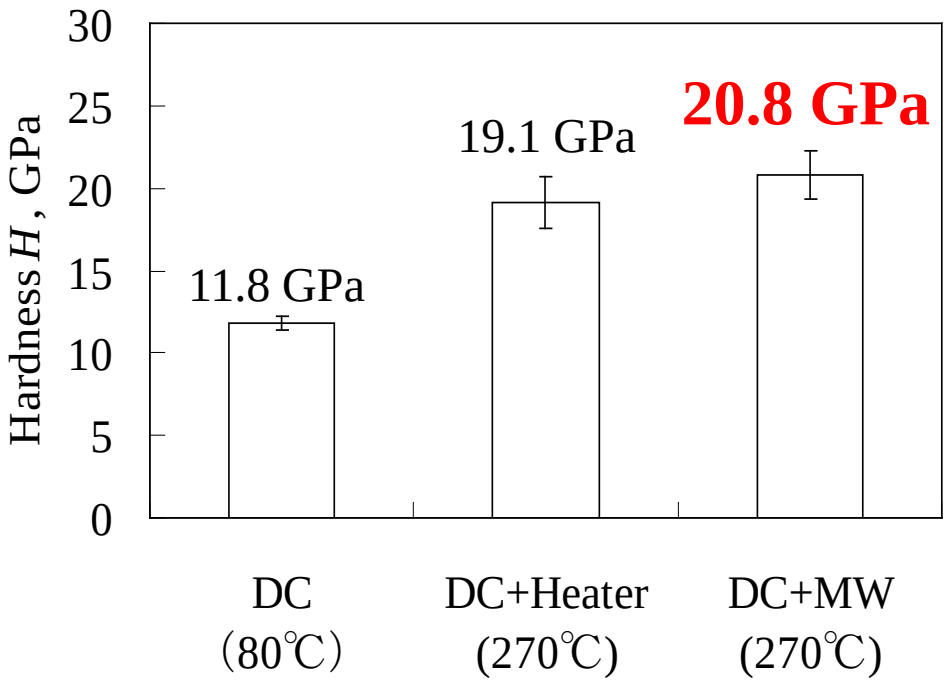


Tempering temperature

Substrate could have been softened.

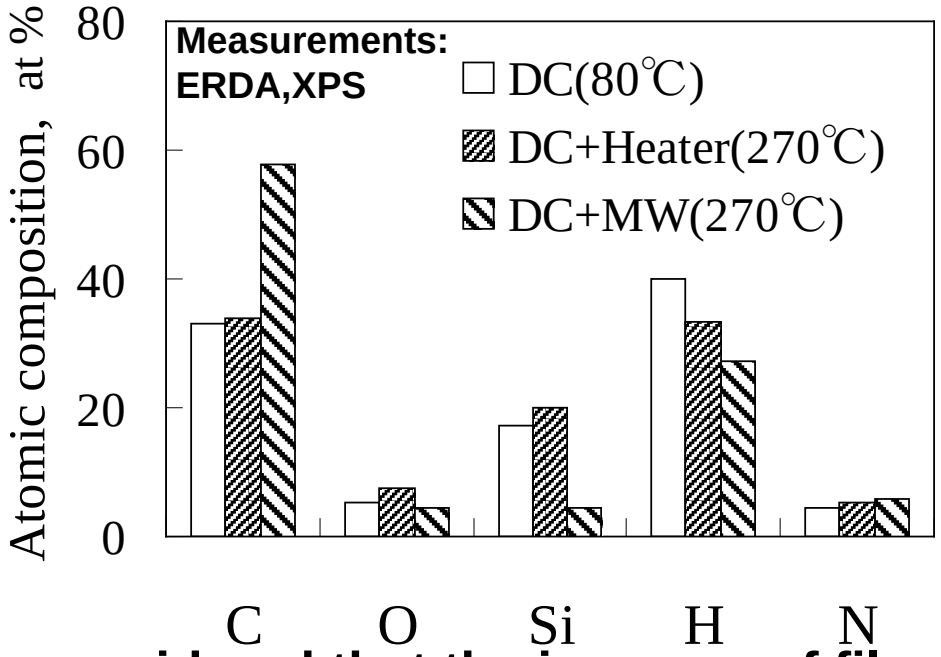
Results ~Comparison of deposition methods~

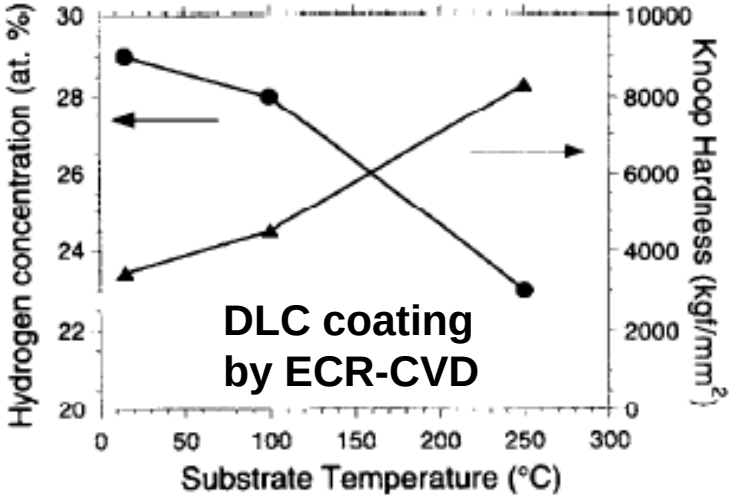




Deposition rate and film hardness considerably increased by injecting microwave.
Comparing the two DC plasma cases, hardness was increased with the increase of substrate temperature.

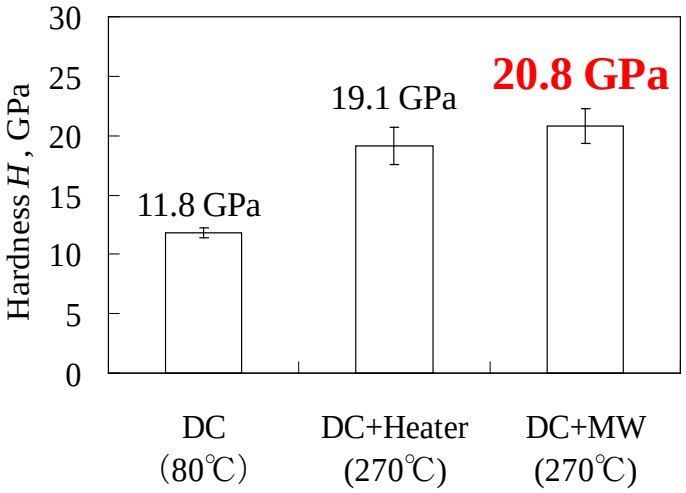
Results & Discussion ~Atomic composition~





Y. Konishi, et. al., *Nuclear Instruments and Methods in Physics*, Research B 118 (1996) 312-317

It is considered that the increase of film hardness by additional heating was caused by the decrease of hydrogen content.

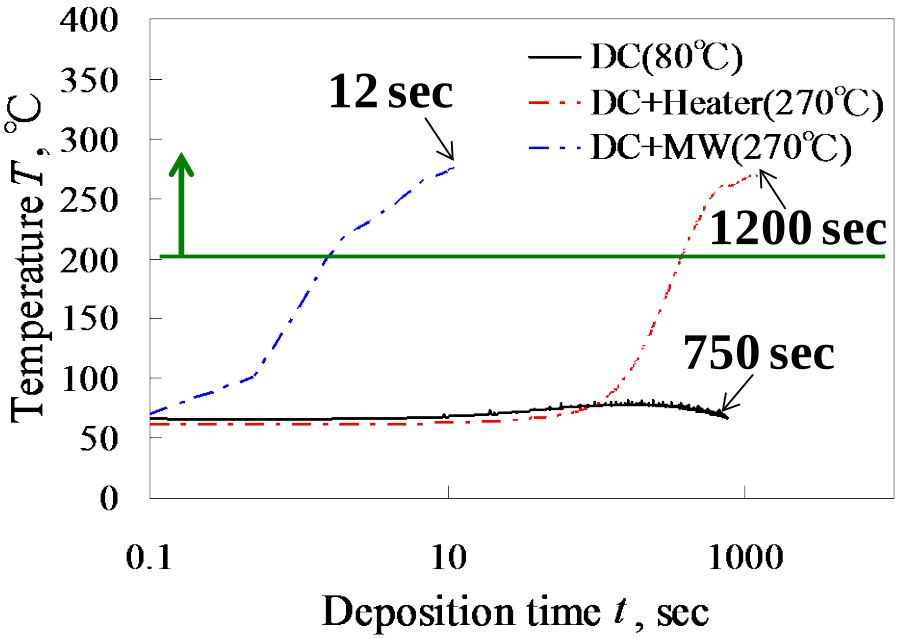


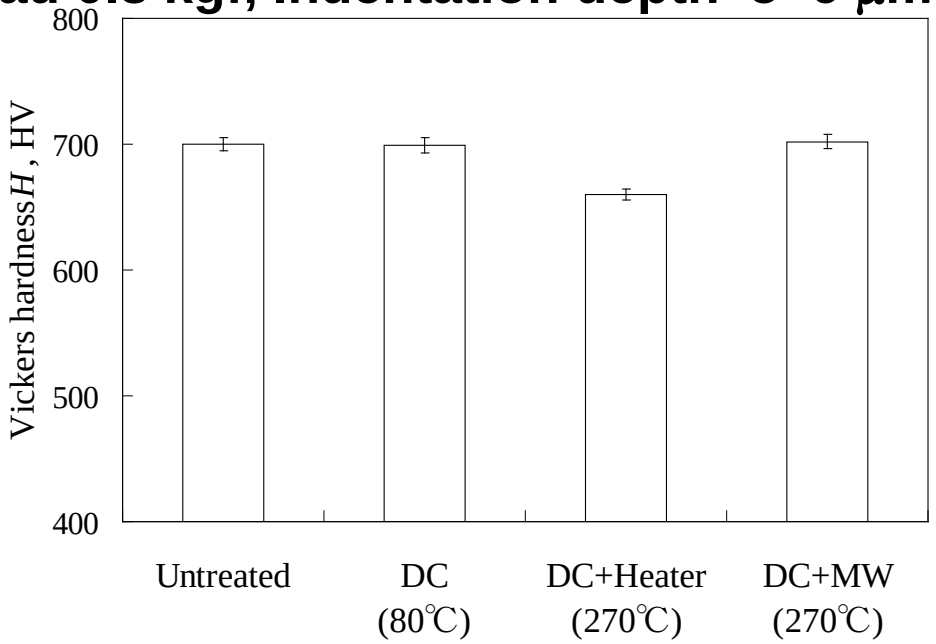
Comparing the 2 cases: DC plasma and DC with microwave plasma, hardness value were almost the same.

However, both of the hydrogen and silicon contents decreased, while the carbon content significantly increased by injecting microwave.

Results ~Substrate hardness after DLC coating~

Measurement : Micro hardness tester
Indentation load 0.3 kgf, Indentation depth 5~6 μm

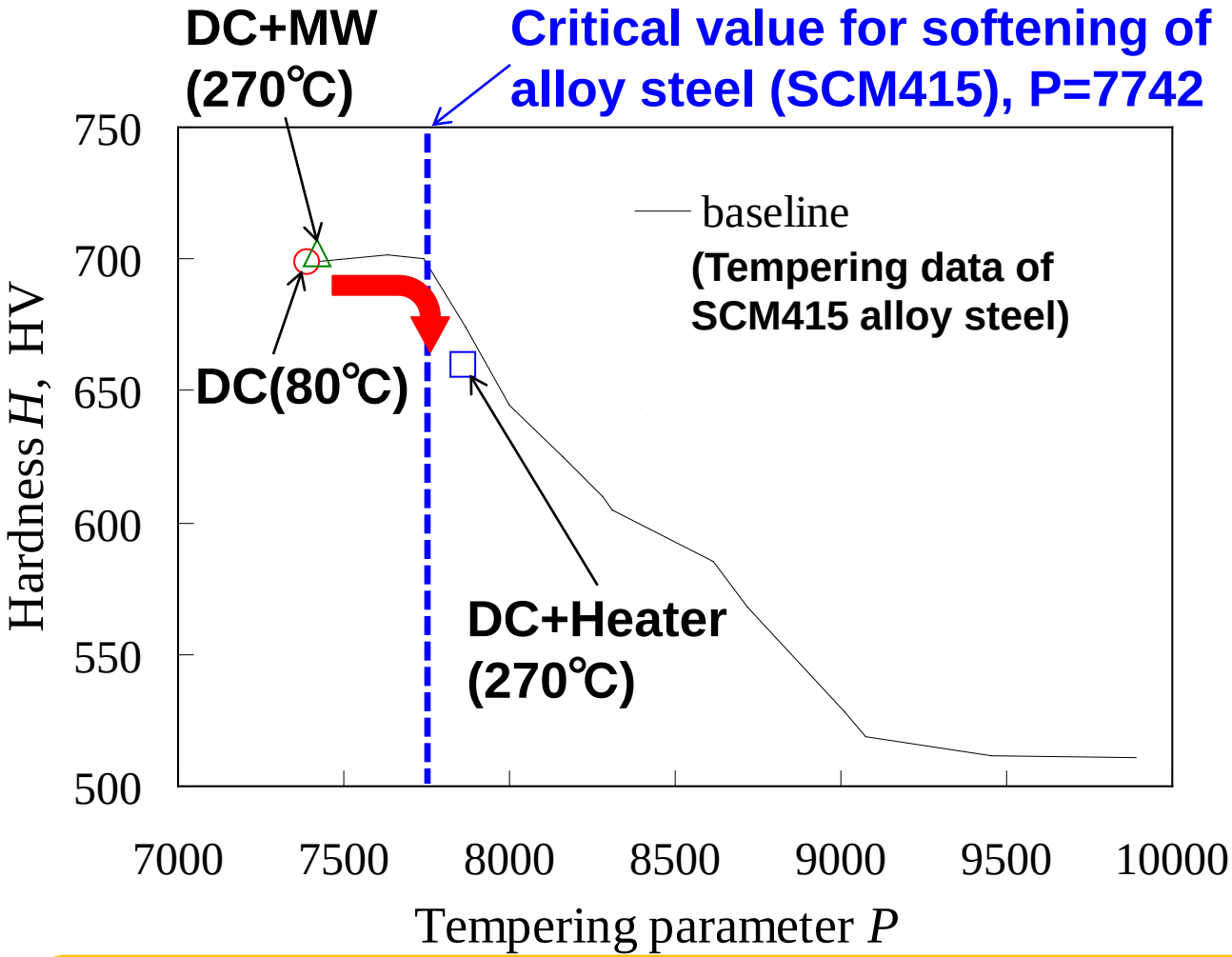




The decrease of substrate hardness did not occur in the coating by microwave-excited high-density near plasma even though the maximum substrate temperature exceeded 200 ℃ during coating.

It is expected that substrate softening can be avoided if high-temperature period is enough short.

Results ~Tempering parameter~



Tempering parameter

$$P = T(\log t + C)$$

T : Temperature [K]

t : time [hrs.]

C : Material constant

C=15 (for SCM415)

J.H. Hollomon and L. D. Jaffe, *Trans. AIME*, 1945, vol. 162, p. 223.

Tempering parameter did not exceed the critical value (P=7742) above which the alloy steel substrate softens in the coating by microwave-excited plasma.

Conclusion ~Comparison of film properties~

1. The deposition 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 deposition rate and hardness of the DLC deposited by microwave-excited high-density near plasma were 156 μm/h and 20.8 GPa, respectively.
2. Comparing the DC plasma and DC with microwave plasma cases, both of the hydrogen and sillicon contents decreased, while the carbon content significantly increased by injecting microwave.
3. The decrease of substrate hardness did not occur in the coating by microwave-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.

Friction test ~ In ambient air ~

DLC coated disk against SUJ2 ball (bearing steel)

Rotation radius 2.5 mm

In ambient air

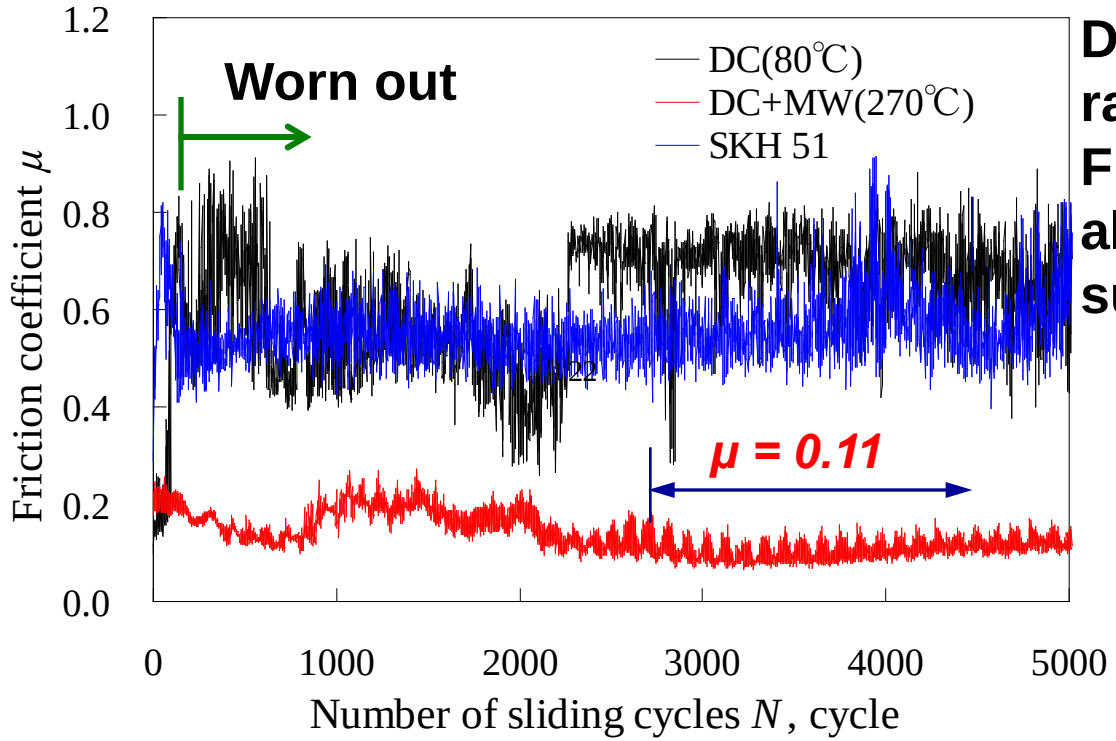
Specimen	DC(80℃)	DC+MW(270℃)	SKH51(substrate)
Ball	SUJ 2	SUJ 2	SUJ2
Disk	DLC (DC 80℃) on SKH 51 substrate	DLC (DC+MW 270℃) on SKH 51 substrate	SKH 51
Load, N	0.5	0.5	0.5
Rotation speed, rpm	100.0	100.0	100.0
Sliding speed, mm/s	26.2	26.2	26.2

Temperature : 22℃

Humidity : 53%RH

Maximum Hertzian contact pressure

P_{max} : ~ 433 MPa



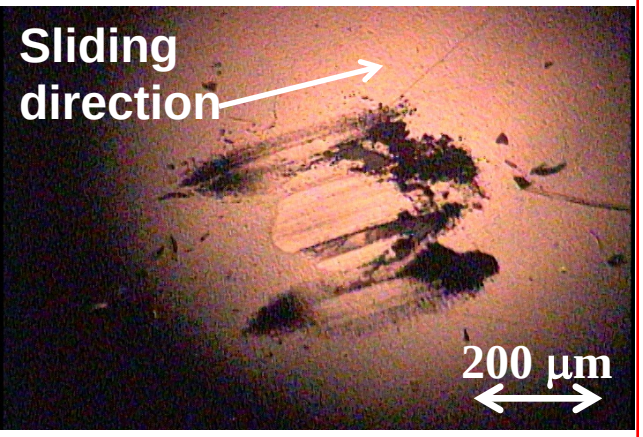
DLC film coated by DC method rapidly worn out.
Friction coefficient became almost same value with substrate.

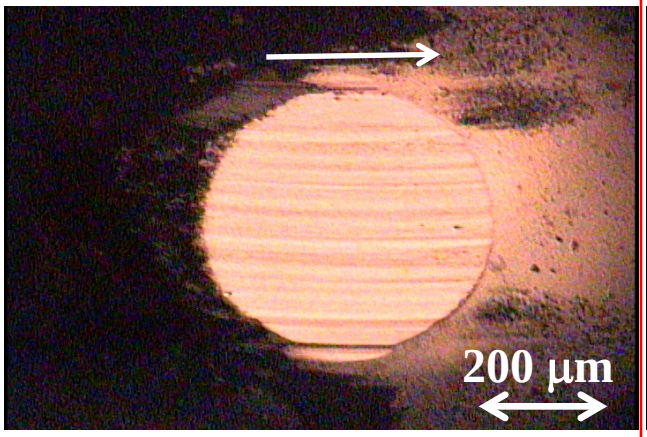
DLC film coated by DC with microwave plasma showed low friction of μ = 0.11 .

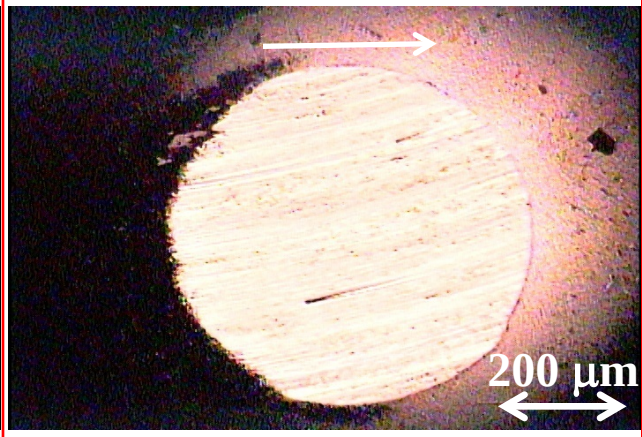
Friction test ~ In ambient air ~

OMS images for balls and DLC-coated disks

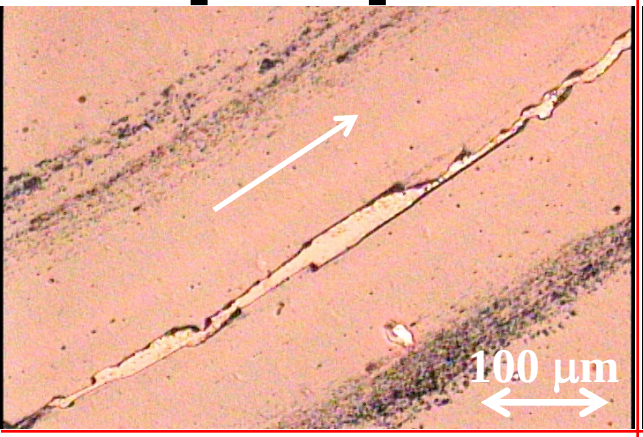
Ball(SUJ2) [x 50]

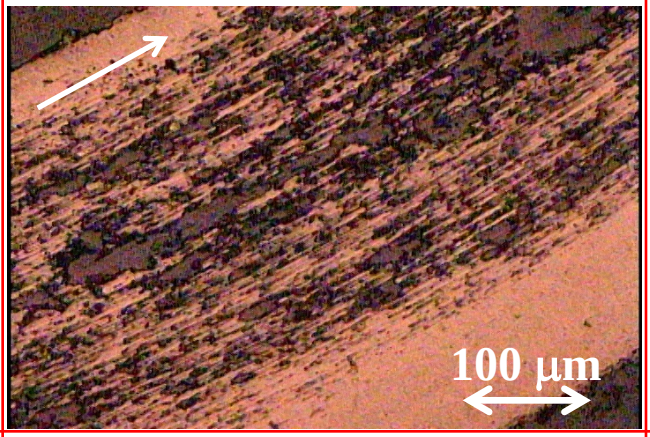






Disk [x 100]





DC+MW (270℃)	DC (80℃)	SKH 51