



# Low frictions of self-mated CN<sub>x</sub> coatings in dry and humid inert gas environments



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## ABSTRACT

The friction behavior of CN<sub>x</sub> coated Si<sub>3</sub>N<sub>4</sub> disk sliding against CN<sub>x</sub> coated Si<sub>3</sub>N<sub>4</sub> ball (denoted as CN<sub>x</sub>/CN<sub>x</sub>) in dry and humid inert gas environments (i.e. nitrogen, argon, and helium) is investigated in this study. The sliding contact of self-mated CN<sub>x</sub> coatings has been realized thanks to the promising two-step ball-on-disk friction test, where the rubbed Si<sub>3</sub>N<sub>4</sub> ball in the running-in stage (step 1) is replaced by a new CN<sub>x</sub> coated Si<sub>3</sub>N<sub>4</sub> ball in the subsequent stage (step 2). As a result, friction coefficients of less than 0.05 are obtained for self-mated CN<sub>x</sub> coatings in all three dry inert gas environments with relative humidity under 5%RH. Moreover, friction coefficients of less than 0.10 are obtained for the sliding contact of CN<sub>x</sub>/CN<sub>x</sub> in inert gas environments with relative humidity of larger than 35%RH. Especially, the lowest friction coefficient of 0.020 is achieved in the nitrogen gas environment with relative humidity of 37%RH. Furthermore, the sliding contact of self-mated CN<sub>x</sub> coatings survives after friction tests in humid nitrogen and argon gas environments. The low frictional performance and low sensitivity of friction to water vapor for the self-mated CN<sub>x</sub> coatings in inert gas environments are mainly attributed to the formation of a *sp*<sup>2</sup> rich carbon tribo-layer on the mating surface. The pronounced frictional performance of self-mated CN<sub>x</sub> coatings has made them good candidates for the demanding industrial applications.

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## 1. Introduction

Excellent tribological performances of diamond-like carbon (DLC) and amorphous carbon nitride (CN<sub>x</sub>) coatings, such as super-low frictions (e.g.  $\mu < 0.01$  in a dry nitrogen gas environment with relative humidity of less than 5%RH) and high wear resistance in inert gas environments (i.e. nitrogen, argon, and helium), have aroused enormous research interest in the last two decades, and thus have been considered as good candidates in the development of low friction technology for reducing the friction and wear of sliding elements in the cutting-edge industrial applications [1–5]. However, the low friction mechanisms of those coatings in inert gas environments are still not yet thoroughly understood. Furthermore, the super-low frictions of those coatings in inert gas environments are susceptible to the oxidizing gas species (water vapor and molecular oxygen) [6–11], and therefore the super-low frictions cannot sustain in an ambient environment, which severely limits the extended utilization of those coatings in the practical industrial applications.

According to our recent study on the low friction mechanisms of CN<sub>x</sub> coatings in inert gas environments [12], a thin amorphous carbon layer

(thereafter referred to as the carbon tribo-layer) with a thickness of approximately 10 nm has been found as a sub-surface of the wear scar on the ball surface where the transfer film (thereafter referred to as the tribo-film) can hardly be observed using the naked eye as well as confocal microscopy. It has been strongly argued that this carbon tribo-layer rather than the tribo-film is beneficial for achieving stable and low friction coefficients ( $\mu \leq 0.05$ ) of CN<sub>x</sub> coatings in inert gas environments. Moreover, the high friction coefficients ( $\mu > 0.05$ ) in oxygen-containing (>1 vol.% O<sub>2</sub>) inert gas environments have been attributed to the formation of an oxidized tribo-film (e.g. SiO<sub>2</sub> tribo-film) on the mating ball surface by the tribochemical reactions between Si<sub>3</sub>N<sub>4</sub> ball and molecular oxygen. Therefore, it is assumed that the low friction coefficients in inert gas environments could sustain in reactive gas environments when Si<sub>3</sub>N<sub>4</sub> substrate is prevented and the carbon tribo-layer is preserved on the contact interface as well.

On the other hand, to get friction coefficients in the order of 0.01 for DLC and CN<sub>x</sub> coatings in ambient environments, one effective strategy is incorporating metal or non-metal elements (e.g. Ag, Ti, Al, Ir, and Si) into those coatings [13–19]. Friction coefficients of less than 0.10 or even 0.01 have been observed in ambient air with Ag-DLC [13], Ti-DLC [14], Al-DLC [15], TiSi–C:H [16], and a-C:Si:Al coatings [17]. Particularly, the low friction coefficient (about 0.06) of Al-DLC coating (Al of 2.3 at.%) in ambient air (relative humidity of  $35 \pm 5\%$  RH) is due to the formation of a continuous and compact carbon tribo-film other than a metallic tribo-film on the mating ball surface [17].

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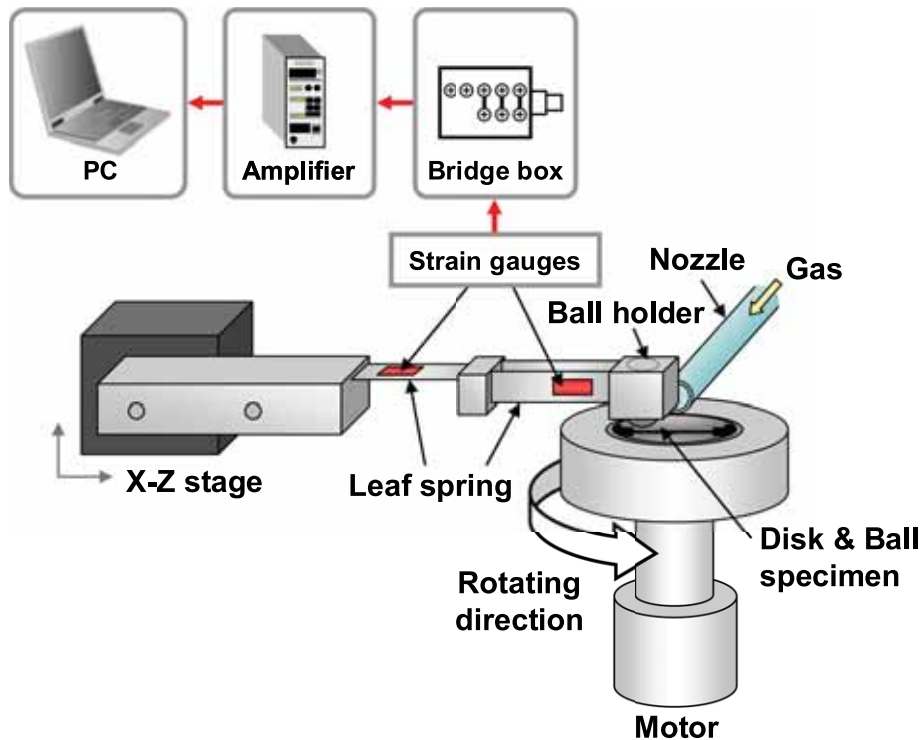


Fig. 1. Schematic illustration of the ball-on-disk tribometer with a gas nozzle.

In summary, it is argued that the formation of a carbon layer on the mating surface is effective for reducing the sensitivity of friction to water vapor and/or molecular oxygen for CN<sub>x</sub> coatings in inert gas environments. According to our recent research, the formation of a carbon layer and prevention of an oxidized tribo-film on the contact interface can be realized in the sliding contact of self-mated CN<sub>x</sub> coatings [12]. The two-step friction test, where the rubbed Si<sub>3</sub>N<sub>4</sub> ball in the running-in stage (step 1) is replaced by a new CN<sub>x</sub> coated Si<sub>3</sub>N<sub>4</sub> ball in the subsequent stage (step 2), has been successfully applied to acquire the sliding contact of self-mated CN<sub>x</sub> coatings [20]. Therefore, with the objective to clarify the potential outstanding frictional performance of self-mated CN<sub>x</sub> coatings, the friction behavior of self-mated CN<sub>x</sub> coatings is investigated in both dry and humid inert gas environments. Finally, the low friction mechanisms of self-mated CN<sub>x</sub> coatings are discussed from the viewpoint of structural change on the contact interface.

## 2. Experimental details

### 2.1. Deposition of CN<sub>x</sub> coatings

An ion beam assisted deposition system (IX-30-30, Hitachi Ltd., Japan) was employed for coating fabrication and the schematic illustration of this system can be found in Ref. [21]. CN<sub>x</sub> coating was grown on the substrate by the deposition of carbon from a carbon target (99.999% pure) together with the bombardment and mixing of carbon with the nitrogen ions generated simultaneously from an ion beam gun. The substrate materials were Si<sub>3</sub>N<sub>4</sub> disks (φ30 mm × 4 mm) and 8-mm-diameter Si<sub>3</sub>N<sub>4</sub> balls. The surface roughness (*R<sub>a</sub>*) of the Si<sub>3</sub>N<sub>4</sub> disk was 20–80 nm and its hardness was 16 GPa. The surface roughness (*R<sub>a</sub>*) of the Si<sub>3</sub>N<sub>4</sub> ball was 4–6 nm and its hardness was 15 GPa. These substrates were sequentially cleaned in an ultrasonic bath with acetone, ethanol, and deionized water for 20 min each before loading into the deposition

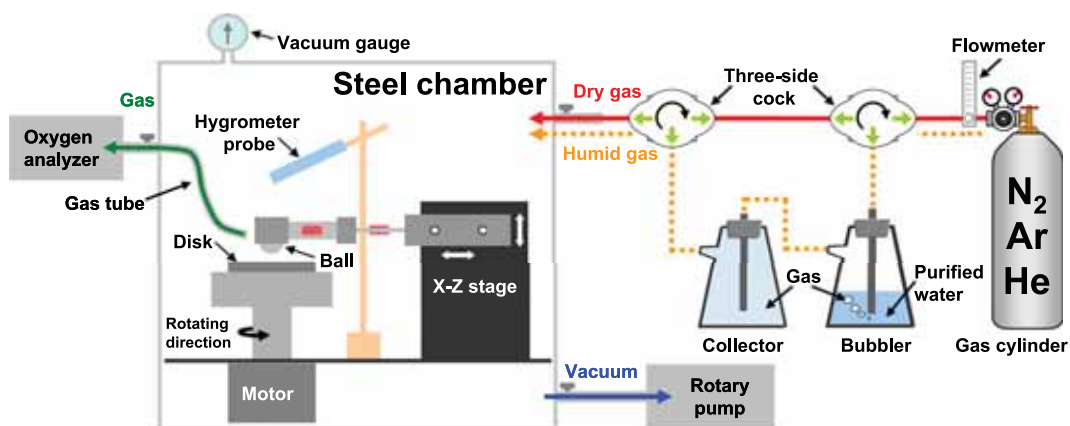


Fig. 2. Schematic illustration of the ball-on-disk tribometer situated inside a steel chamber with the gas supply system for controlling the relative humidity.

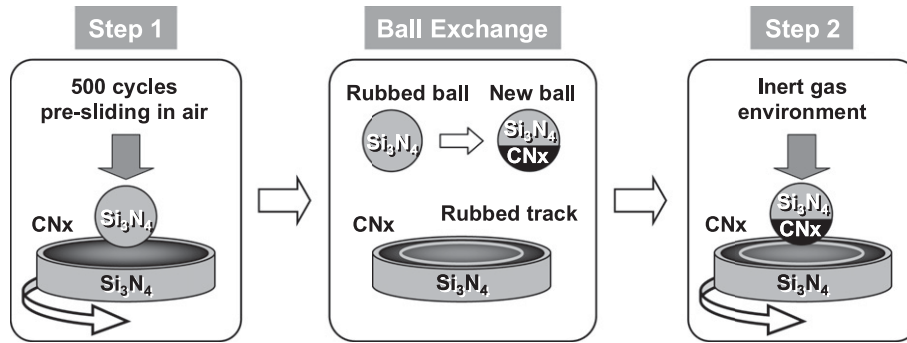


Fig. 3. Schematic illustration of the two-step ball-on-disk friction test.

chamber. Prior to deposition, they were further sputter-cleaned by 5 min bombardment with nitrogen ions to remove the native oxides and other adsorbed species from their surfaces. The deposition rate of carbon was maintained about 2.0 nm/s and monitored via a calibrated quartz crystal oscillator. The total coating thickness on both  $\text{Si}_3\text{N}_4$  disk and  $\text{Si}_3\text{N}_4$  ball is about 400 nm. Detailed deposition parameters have been described previously in Refs [12,21].

## 2.2. Friction tests

Friction tests in inert gas environments with constant relative humidity of less than 5%RH (thereafter referred to as dry inert gas environments) were conducted by using a customized ball-on-disk tribometer equipped with a gas blow unit, as schematically shown in Fig. 1. The gas environment around the contact interface was controlled by directly blowing the gas into the contact point using a gas nozzle. The gas nozzle (4.5 mm in inner diameter) was placed perpendicular to the ball holder, with a vertical angle of  $15^\circ$  and a distance of 10 mm from the contact point between the ball and the disk. The gas flow rate was fixed at 2.0 L/min. Three types of high purity commercial inert gases such as nitrogen (>99.9995 vol.%), argon (>99.999 vol.%), and helium (>99.99995 vol.%) were used for friction tests.

Friction tests in three inert gas environments with a progressive increase of the relative humidity from less than 5%RH to more than 35%RH (thereafter referred to as humid inert gas environments) were carried out by using a customized ball-on-disk tribometer which was mounted inside an environmental controllable steel chamber, as schematically shown in Fig. 2. A hygrometer (Hygroclip S, Rotronic AG, Switzerland) and an oxygen analyzer (LC-300, Toray Engineering Corporation, Japan) with resolutions of less than 1.0%RH and 0.1 vol.%  $\text{O}_2$  were applied to measure the relative humidity and oxygen concentration in the steel chamber, respectively. A gas tube was used for a precise detection of oxygen concentration near the contact point between the ball and the disk. Prior to the friction test, the steel chamber was evacuated to 5 kPa or lower and then purged with dry gases at a relatively high flow rate (e.g. 4.0 L/min) for three to five cycles to achieve a stable condition with relative humidity of less than 5%RH and an oxygen concentration of less than 0.1 vol.%. After that, the gas flow rate into the chamber was decreased to 2.0 L/min to maintain a slight positive pressure inside the chamber, hence avoiding the backfilling of the outside air. This kind of environmental control method has been adopted by several researchers to carry out the friction test in a nominal dry gas environment [22–25]. The gas supply system for adjusting the relative humidity, as shown in Fig. 2, consisted of a flowmeter, two three-side cocks, and two glass bottles (denoted as bubbler and collector).

To establish a sliding contact of self-mated  $\text{CN}_x$  coatings, a two-step ball-on-disk friction test was employed [20], as schematically shown in Fig. 3. In step 1, a new  $\text{Si}_3\text{N}_4$  ball was employed for 500 cycles pre-sliding in air (an optimum pre-sliding condition based on a systematical study in Ref. [20]). And then it was replaced by a new  $\text{CN}_x$  coated  $\text{Si}_3\text{N}_4$

ball, thereafter, the  $\text{CN}_x$  coated  $\text{Si}_3\text{N}_4$  ball ran against the rubbed  $\text{CN}_x$  coating on the disk in different gas environments in step 2.

$\text{CN}_x$  coated  $\text{Si}_3\text{N}_4$  disks were made to rub against the  $\text{Si}_3\text{N}_4$  balls (denoted as  $\text{Si}_3\text{N}_4/\text{CN}_x$ ) or  $\text{CN}_x$  coated  $\text{Si}_3\text{N}_4$  balls (denoted as  $\text{CN}_x/\text{CN}_x$ ) with a normal load of 0.40 N, creating an initial peak Hertzian contact pressure of 517 MPa for the contact material combination of  $\text{CN}_x/\text{CN}_x$ . The wear track diameter on the disk varied between 12–27 mm, which corresponded to 0.16–0.35 m/s sliding velocity at a fixed rotation speed of 250 rpm. The friction test ran for a maximum sliding duration of 48 min. Two sets of strain gauges were attached on the leaf springs to measure the normal load and the friction force. The signals of the normal load and friction force were continuously recorded and then the friction coefficient was calculated.

## 2.3. Characterization of worn surfaces on the balls

Worn surfaces on the balls were observed with an optical microscope (ECLIPSE LV150 and Digital Slight DS-L1, Nikon Corporation, Japan). The carbon bonding structure of worn surfaces on the balls was characterized by a laser micro-Raman spectroscopy (NRS-3100, JASCO Corporation, Japan) operating with a 532 nm green laser as the excitation source.

## 3. Results and discussion

### 3.1. Friction behavior of $\text{CN}_x/\text{CN}_x$ in dry inert gas environments

Friction curves of  $\text{CN}_x/\text{CN}_x$  under three dry inert gas environments without pre-sliding are shown in Fig. 4. As is clear, friction coefficients of less than 0.04 were reached after an initial running-in process, but spikes appeared randomly in the subsequent steady stage. Especially, a relatively high and unstable friction coefficient was recorded at the

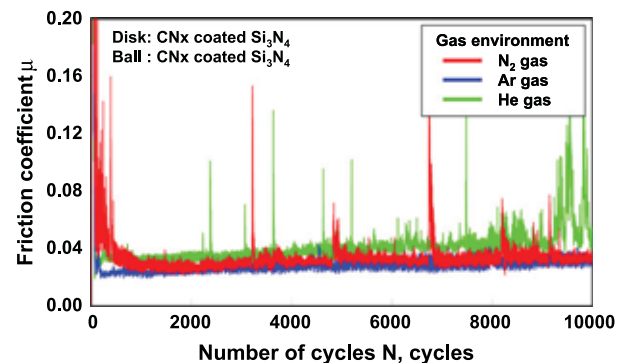


Fig. 4. Friction curves of  $\text{CN}_x/\text{CN}_x$  under three dry inert gas environments without pre-sliding.

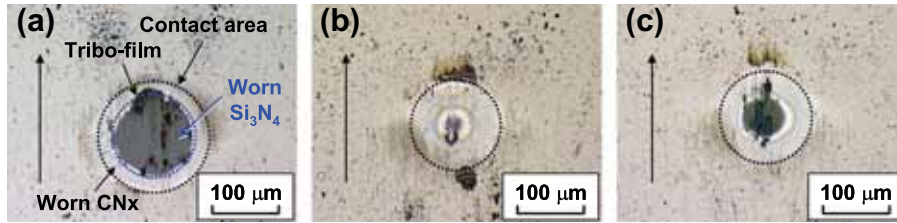


Fig. 5. Optical images of the wear scars on the CNx coated  $\text{Si}_3\text{N}_4$  balls of CNx/CNx after friction tests in (a) nitrogen, (b) argon, and (c) helium gas environments without pre-sliding. The black arrows indicate the sliding direction of the ball. The dotted circles represent the contact area on the wear scar.

final stage of the test in the helium gas environment. Optical images of the corresponding worn surfaces on the CNx coated  $\text{Si}_3\text{N}_4$  balls, as shown in Fig. 5, obviously revealed that the CNx coatings inside the contact area delaminated from the ball surfaces (thereafter referred to as CNx coating worn out on the ball surface) after the friction tests in dry inert gas environments. This phenomenon generally occurred at the initial sliding process (e.g. 100 cycles), as described in our previous research [5]. Thus, the contact material combination developed from CNx/CNx to  $\text{Si}_3\text{N}_4$ /CNx. Besides, the tribo-film was observed on the  $\text{Si}_3\text{N}_4$  substrate inside the contact area on the worn surface of CNx coated  $\text{Si}_3\text{N}_4$  ball. The tribo-film generated inside the contact area varied with the gas species, especially, larger amount of tribo-film was observed in the helium gas environment, corresponded to the higher fluctuation of the friction coefficient at the final stage.

On the other hand, in the two-step ball-on-disk friction test, with the introduction of 500 cycles pre-sliding in air by  $\text{Si}_3\text{N}_4$  ball, CNx/CNx demonstrated a more stable friction coefficient after a short running-in process, though the friction coefficient in the helium gas environment was larger than that in nitrogen and argon gas environments, as shown in Fig. 6. Additionally, the corresponding optical images of worn surfaces on the CNx coated  $\text{Si}_3\text{N}_4$  balls, as presented in Fig. 7, obviously indicated that the CNx coatings still covered the whole contact area of the ball surfaces (thereafter referred to as CNx coating remained on the ball surface) after friction tests in all three inert gas environments. Thus, a sliding contact of self-mated CNx coatings was successfully realized even after the friction test. And the tribo-film can hardly be observed inside the contact area on the worn surface of CNx coated  $\text{Si}_3\text{N}_4$  ball as well.

The effect of pre-sliding on the average friction coefficient (final 5000 cycles) of CNx/CNx in three dry inert gas environments is summarized in Fig. 8. The corresponding error bar represented the standard deviation of the friction coefficient within each test. The average friction coefficient as well as the corresponding standard deviation of CNx/

CNx decreased greatly after pre-sliding. Self-mated CNx coatings gave lower and more stable friction coefficients in all three dry inert gas environments. Especially, the lowest friction coefficient of 0.019 was observed in the argon gas environment after pre-sliding. Therefore, it was found that self-mated CNx coatings can exhibit low friction coefficients of less than 0.05 not only in the dry nitrogen gas environment [20] but also in dry argon and helium gas environments. The promising frictional performance of self-mated CNx coatings in dry inert gas environments was clarified.

The surface roughness ( $R_a$ ) of the CNx coated  $\text{Si}_3\text{N}_4$  disk changed from  $0.034 \mu\text{m}$  to  $0.037 \mu\text{m}$  after 500 cycles pre-sliding in ambient air. Thus, the geometrical parameter of the worn surface on the CNx coated  $\text{Si}_3\text{N}_4$  disk could not be considered as the key point for obtaining low frictions of self-mated CNx coatings in inert gas environments. Besides, the atomic concentration of nitrogen slightly decreased from 9.8 at.% in the initial CNx coating to 8.2 at.% in the worn CNx coating on the disk surface after pre-sliding according to the X-ray photoelectron spectroscopy (XPS) analysis. Therefore, stable and low friction coefficients of self-mated CNx coatings in the dry nitrogen gas environment have been attributed to the formation of a thin lubricious top layer on the CNx coated  $\text{Si}_3\text{N}_4$  disk surface during the pre-sliding in Ref. [20]. To gain more insights into the low friction mechanisms, the structural change of CNx coating on the ball surface after the friction test was analyzed by Raman spectroscopy and typical result is presented in Fig. 9. It can be seen that the intensity of D band together with the intensity ratio of D band to G band ( $I(D)/I(G)$ ) of the worn CNx coating decreased gradually in the following order: Initial surface > Point 1 > Point 2 > Point 3. The lowest value of  $I(D)/I(G)$  was obtained at the center of the contact area. It was strongly suggested that a graphite-like or graphite-domain structure is formed on the top surface of the ball [26–28], which has also been detected on the worn CNx coating on the disk surface after the friction test in the nitrogen gas environment [11,20,29,30]. As CNx coating still covered the whole ball surface, it

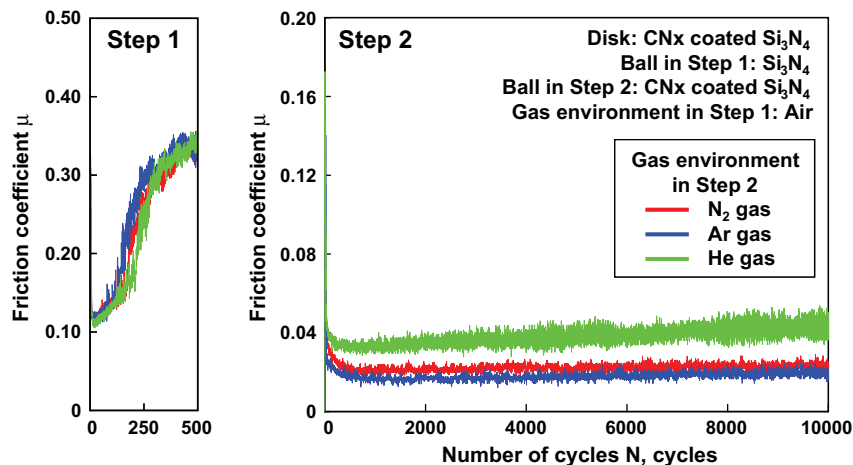
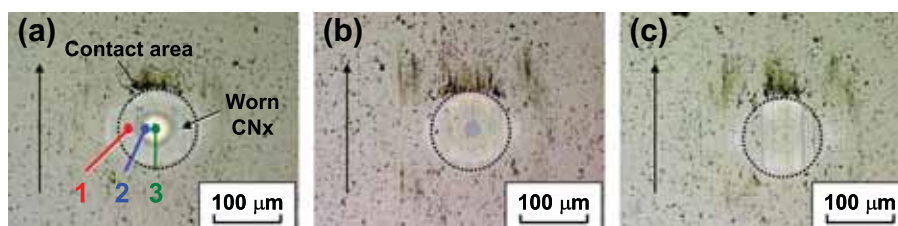


Fig. 6. Friction curves of CNx/CNx under different inert gas environments after pre-sliding in air by  $\text{Si}_3\text{N}_4$ /CNx.





**Fig. 7.** Optical images of the wear scars on the balls of CNx/CNx after friction tests in (a) nitrogen, (b) argon, and (c) helium gas environments with pre-sliding in air by Si<sub>3</sub>N<sub>4</sub>/CNx. The black arrows indicate the sliding direction of the ball. The dotted circles represent the contact area on the wear scar.

was assumed that a graphitic layer is generated on the top surface of CNx coating. Consistent with our recent work [12], this graphitic layer is defined as the carbon tribo-layer.

With the introduction of the two-step ball-on-disk friction test, it was found that oxidized tribo-film and corresponding tribochemical reactions are avoided on the contact interface, whereas the carbon tribo-layer is generated on the top surface of CNx coating. Thus, it was claimed that the formation of this carbon tribo-layer is beneficial for obtaining stable and low friction coefficients of self-mated CNx coatings in inert gas environments. Furthermore, it has been assumed in Ref. [12] that the prevention of tribochemical reactions from oxidizing gas species could decrease the sensitivity of friction to water vapor and/or molecular oxygen for self-mated CNx coatings in inert gas environments, which is promising for the achievement of low friction coefficient in an ambient environment. Therefore, friction tests were conducted in inert gas environments with a progressive increase of the relative humidity and results will be presented in the subsequent section.

### 3.2. Friction behavior of CNx/CNx in humid inert gas environments

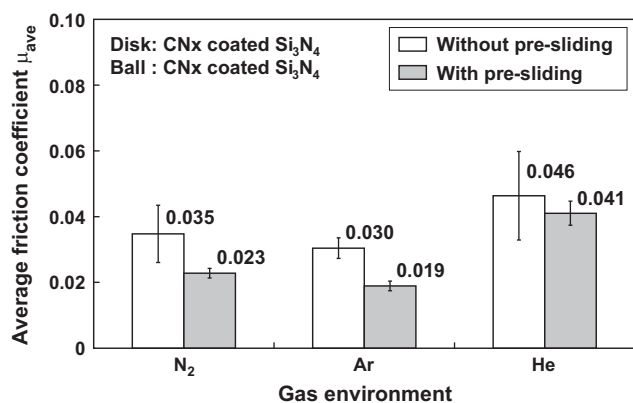
Typical friction curves of CNx/CNx in the argon gas environment with progressively increasing relative humidity without and with pre-sliding are given in Figs. 10 and 11, respectively. Optical images of worn surfaces on the CNx coated Si<sub>3</sub>N<sub>4</sub> balls are shown in Fig. 12a and b, respectively. As shown in Fig. 10, the friction coefficient of CNx/CNx without pre-sliding increased sharply with the increase of the relative humidity from 5 to 10%RH, and then it continuously increased to more than 0.40 with large fluctuation when the relative humidity was around 40%RH. As a result, CNx coating worn out on the ball surface after the friction test (Fig. 12a). On the contrary, after pre-sliding in air for 500 cycles by Si<sub>3</sub>N<sub>4</sub>/CNx, the friction coefficient of less than 0.05 of CNx/CNx in the argon gas environment was preserved with the increase of the relative humidity except a slight increase in the initial stage, as shown in Fig. 11. Furthermore, CNx coating remained on the CNx coated Si<sub>3</sub>N<sub>4</sub> ball surface after

the friction test (Fig. 12b). The effect of the relative humidity in the argon gas environment on the friction behavior of CNx/CNx without and with pre-sliding is summarized in Fig. 13. The sensitivity of friction to water vapor for the sliding contact of CNx/CNx decreased drastically when the CNx coating remained on the ball surface, and low friction coefficient of 0.025 was achieved in the argon gas environment with relative humidity up to 37%RH.

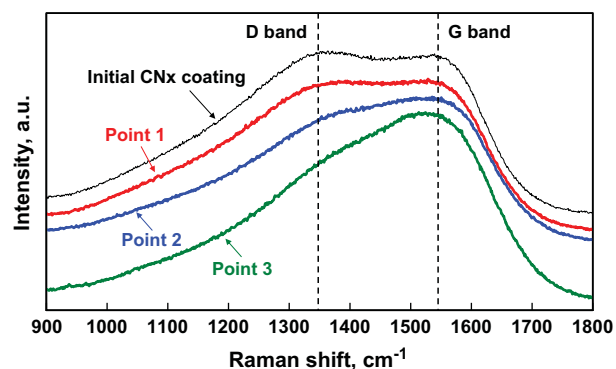
Friction behaviors of CNx/CNx without pre-sliding in nitrogen and helium gas environments with progressively increasing relative humidity were similar to that in the argon gas environment; friction coefficients of higher than 0.30 were observed when the relative humidity was up to 40%RH. The introduction of water vapor into inert gas environments generally causes tribochemical reactions or tribo-oxidation on the contact interfaces, which leads to higher adhesive force and thus increases the friction coefficient. In the case of the friction tests with pre-sliding, the friction behavior of CNx/CNx in the nitrogen gas environment was similar to that in the argon gas environment, and low friction coefficient of 0.020 was achieved in relative humidity of 35%RH (Fig. 13) when CNx coating remained on the ball surface after the friction test (Fig. 12c). However, the friction coefficient in the helium gas environment increased linearly from 0.020 to 0.080 with increasing relative humidity from 1 to 40%RH (Fig. 13). Consequently, the CNx coating delaminated at the center of the contact area on the CNx coated Si<sub>3</sub>N<sub>4</sub> ball surface (Fig. 12d), and the sliding contact of self-mated CNx coatings was not preserved in the whole sliding process.

### 3.3. Low friction mechanisms of self-mated CNx coatings

It has been concluded that one of the necessary conditions for achieving stable and low friction coefficients of CNx coatings in inert gas environments is preventing the absorption of oxidizing gas species (water vapor and molecular oxygen) on the contact interface [10,11]. The presence of oxidizing gas species into inert gas environments causes strong tribochemical reactions on the contact



**Fig. 8.** Effect of pre-sliding on the average friction coefficient of CNx/CNx under different inert gas environments.



**Fig. 9.** Raman spectra of typical locations (i.e. Points 1, 2, and 3) on the worn surface of CNx coated Si<sub>3</sub>N<sub>4</sub> ball in CNx/CNx after the friction test in the nitrogen gas environment with pre-sliding in air by Si<sub>3</sub>N<sub>4</sub>/CNx, as labeled in Fig. 7a. The Raman spectrum of the initial CNx coating is also provided for comparison.

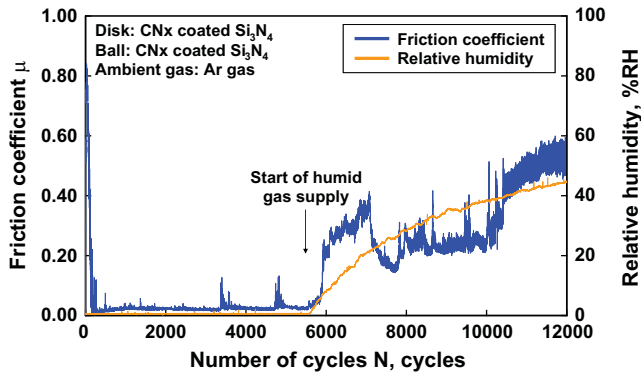


Fig. 10. Friction curve of CNx/CNx in the argon gas environment with progressively increasing relative humidity without pre-sliding.

interface, and destroys the low friction coefficients of CNx coatings. The oxidized tribo-film (e.g. SiO<sub>2</sub> tribo-film [11]) is a typical product of those tribochemical reactions. However, few amounts of tribo-films were observed inside the contact area on the CNx coated Si<sub>3</sub>N<sub>4</sub> ball when the sliding contact of self-mated CNx coatings was obtained, as obviously shown in Fig. 12b and c. In addition, the extreme low friction coefficients of self-mated CNx coatings were observed in humid inert gas environments. Therefore, it was further confirmed that the prevention of an oxidized tribo-film on the mating surface is favorable for reducing frictions of CNx coatings in humid inert gas environments.

To further understand the low friction mechanisms of self-mated CNx coatings in humid inert gas environments, the worn surface on the CNx coated Si<sub>3</sub>N<sub>4</sub> ball was analyzed by Raman spectroscopy and the result is shown in Fig. 14. It was found that the intensity ratio of D band to G band (I(D)/I(G)) decreased gradually in the following order: Initial surface > Point 1' > Point 2' > Point 3', which agrees well with the analysis result of worn CNx coating after sliding in a dry inert gas environment (Fig. 9). It was clarified that the carbon tribo-layer formed in a dry inert gas environment survives after the sliding process in a humid inert gas environment. On the contrary, in the case of the sliding contact of self-mated highly hydrogenated DLC (H-DLC) coatings, the super-low friction coefficient observed in a dry inert gas environment increased greatly when oxidizing gas species were added [24,31,32]. Therefore, it is believed that the carbon tribo-layer is the key point for

achieving low frictions of self-mated CNx coatings in humid inert gas environments.

The formation of the high performance carbon tribo-layer on the self-mated CNx coatings is strongly related to the pre-sliding process, such as ball material, cycles, and gas species [20]. Particularly, when a CNx coated Si<sub>3</sub>N<sub>4</sub> ball was employed for pre-sliding, the friction coefficient of self-mated CNx coatings in the nitrogen gas environment increased linearly from 0.010 to 0.080 with the increase of the relative humidity from less than 2 to 45%RH [9]. Low friction coefficient of less than 0.05 was not preserved in the humid nitrogen gas environment, although the sliding contact of self-mated CNx coatings was formed. Therefore, it is argued that the low friction of self-mated CNx coatings in humid inert gas environments is determined not only by the carbon tribo-layer but also by the structure of this layer. Moreover, the increase of G band area in the Raman spectra indicated that a carbon tribo-layer enriched in sp<sup>2</sup> bondings is generated on the top surface of the contact interface. A sp<sup>2</sup> dominated carbon layer has also been observed in several types of carbon-based solid lubrication coatings, such as DLC [33], ultrananocrystalline diamond [34], and amorphous carbon [35]. The formation of this carbon layer is beneficial for achieving low frictions of those coatings.

As mentioned in the Introduction section, the low friction coefficients of less than 0.10 or even 0.01 of doped DLC (e.g. Al-DLC) coatings in ambient air were systematically associated with a homogeneous carbon-rich tribo-film on the steel ball surface [15]. In addition, the insensitivity of friction to molecular oxygen has been observed in the H-DLC coating with the formation of a uniform carbon-rich tribo-film on the steel ball surface [36]. Based on the reversibility of the low friction behavior in different gas environments (e.g. progressively increasing or decreasing oxygen concentration), coupled with the absence of evidence of tribo-oxidations on the contact interface (based on AES and XPS analyses), it has been argued that the unique friction response to oxidizing gas species is due to the weakly adsorbed water vapor and molecular oxygen other than the oxidized tribo-film on the contact interface [32, 36]. Moreover, the super-low friction coefficient of fullerene-like DLC (FL-DLC) coatings in ambient air as well as the low sensitivity of friction to environments have been attributed to the feature structures of FL-DLC, such as curved, closed, and caged graphite planes, which effectively eliminate the energetic carbon dangling bonds on the contact interface, thus prevent the oxidation of the contact interface and stabilize the friction coefficients of FL-DLC coatings in different gas environments (e.g. dry nitrogen gas, air with relative humidity of 20%RH and 70%RH) [37,38]. Therefore, it is proposed

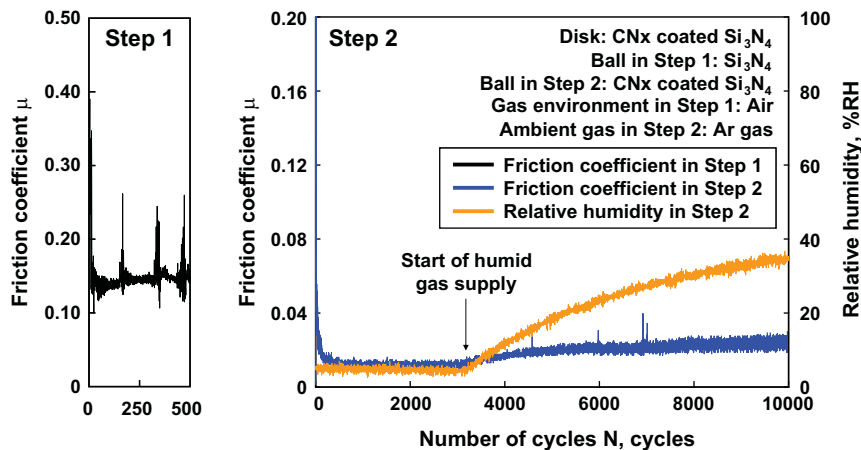
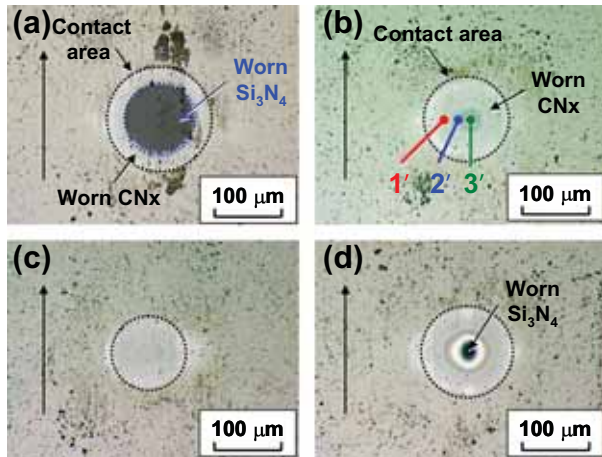


Fig. 11. Friction curve of CNx/CNx in the argon gas environment with progressively increasing relative humidity after pre-sliding in air by Si<sub>3</sub>N<sub>4</sub>/CNx.



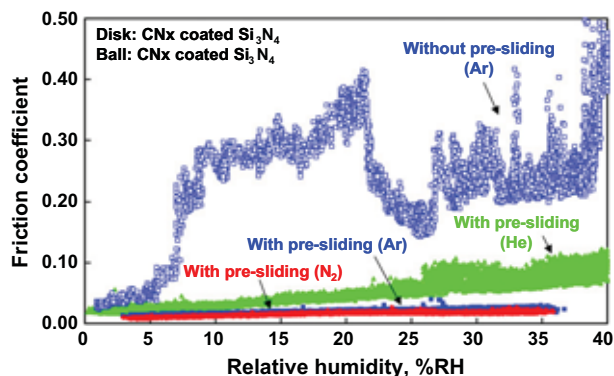
**Fig. 12.** Optical images of the wear scars on the CNx coated  $\text{Si}_3\text{N}_4$  balls of CNx/CNx after friction tests in the argon gas environment with progressively increasing relative humidity (a) without pre-sliding and (b) with pre-sliding. (c) and (d) are the similar results in nitrogen and helium gas environments. The black arrows indicate the sliding direction of the ball. The dotted circles represent the contact area on the wear scar.

that the super-low friction and low sensitivity of friction to water vapor for self-mated CNx coatings in inert gas environments can be attributed to the formation of a  $sp^2$  rich carbon tribo-layer with a special nano-structure on the top surface of the coating. Detailed analysis will be conducted to clarify the nano-structure in the carbon tribo-layer in the near future.

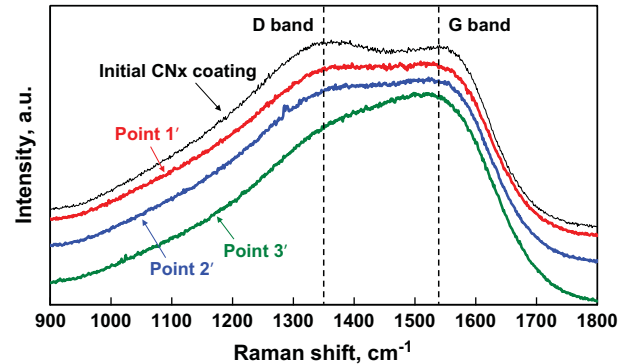
#### 4. Conclusions

The friction behavior of CNx/CNx in dry and humid inert gas environments (i.e. nitrogen, argon, and helium) is investigated in this study. The results are concluded as follows:

- (1) Sliding contact of self-mated CNx coatings has been realized thanks to the promising two-step ball-on-disk friction test. Friction coefficients of less than 0.05 are obtained for self-mated CNx coatings in all three dry inert gas environments with relative humidity under 5%RH.
- (2) Friction coefficients of less than 0.10 are obtained for the sliding contact of CNx/CNx in inert gas environments with relative humidity of larger than 35%RH. The lowest friction coefficient of 0.020 is achieved in the nitrogen gas environment with relative humidity of 37%RH. Furthermore, the sliding contact of self-mated CNx coatings sustains in humid nitrogen and argon gas environments.
- (3) Low frictional performance and low sensitivity of friction to



**Fig. 13.** Effect of the relative humidity in inert gas environments on the friction behavior of CNx/CNx without and with pre-sliding.



**Fig. 14.** Raman spectra of typical locations (i.e. Points 1', 2', and 3') on the worn surface of CNx coated  $\text{Si}_3\text{N}_4$  ball in CNx/CNx after the friction test in the argon gas environment with pre-sliding in air by  $\text{Si}_3\text{N}_4$ /CNx, as labeled in Fig. 12b. The Raman spectrum of the initial CNx coating is also provided for comparison.

water vapor for the self-mated CNx coatings in inert gas environments are mainly attributed to the formation of a  $sp^2$  rich carbon tribo-layer on the mating surface.

#### Conflict of interest

There is no conflict of interest.

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