Effect of nitrogen atoms included in CNx coatings on friction sliding against Si_3N_4 ball in nitrogen gas

Takayuki TOKOROYAMA and Noritsugu UMEHARA
Nagoya University, Department of Mechanical Science and Engineering,
Furo-cho, Chikusa-ku, Nagoya 464-8603
Japan

Abstract:

Carbon nitride (CNx) coatings are thought to have good tribological properties because of low friction and high wear resistance. This material shows a friction coefficient lower than 0.01 when slid against a Si_3N_4 ball in dry N_2 gas. The mechanism of superlow friction was believed to be due to the change in the topmost layer of the CNx surface in the wear track to a low-shear-strength layer by forming a graphite-like structure. However, the effects of nitrogen atoms in the CNx coating and the ambient N_2 gas on the transformation of the surface layers of CNx remain unclear.

In this work, we investigated the relationship between the friction coefficient and the nitrogen concentration in the wear track on the CNx coating. We measured the intensity of C KLL and N KLL on the wear track of CNx by Auger electron spectroscopy (AES), and conducted Raman analysis. We compared the N KLL/C KLL ratios of wear tracks from sliding in ambient N_2, Ar, and O_2. Only in the case of the wear track from material slid in N_2, did the N KLL/C KLL ratio decrease to almost zero and the friction coefficient became lower than 0.01. On the other hand, in the Ar environment, the N KLL/C KLL ratio in the wear track was comparable to the as-deposited CNx coating, the friction coefficient became 0.03, and the I_G position of Raman shift increased at most 3 cm^{-1}. The N KLL/C KLL intensity of the wear track after friction tests in Ar and then in N_2 was approximately 0.2 times as low as the as-deposited CNx. The friction coefficient in N_2 gas was 0.03 when incorporated nitrogen remained in the CNx surface. On the other hand, the friction coefficient was lower than 0.03 when incorporated nitrogen was desorbed.

1. INTRODUCTION

Carbon nitride is a material considered to be harder than diamond and was reported about 20 years ago [1, 2]. There is no perfect crystal of bulk β-C_3N_4, however, some researchers investigated the relationship between the coating method and the CNx structure [3-5], the optical properties [6-9], and the hardness or proof of wear [10-13].

Umehara et al. reported a superlow friction coefficient lower than 0.01 without a lubricant which had been obtained when amorphous CNx coating slid against a Si_3N_4 ball after several 10-10^3 cycles in dry nitrogen gas (the so-called "running-in" period). The mechanism of the low friction coefficient was considered to be the sliding surface of CNx changing to a graphite-like structure [14, 15]. Furthermore, AES (Auger Electron Spectroscopy) analysis revealed that nitrogen atoms were desorbed from the CNx wear surface [16], and the shearing strength and ploughing strength values became lower than as-deposited CNx [17]. As mentioned above, we suggested that nitrogen atoms incorporated in the CNx coating generate a friction force between this surface and a mating material.

First, we carried out AES depth analysis for the distribution of nitrogen concentration in order to clarify the deposition procedure which would produce superlow friction surface during the running-in period. Second, in order to clarify the effect of nitrogen gas on desorption from the CNx coating, we carried out AES and Raman analysis to compare the nitrogen concentration of each of the wear tracks from sliding in N_2, Ar, and O_2 gas. Finally, we analyzed the CNx wear track from sliding in Ar gas until the friction coefficient reached about 0.03, after which that the same wear track was used for sliding in N_2 gas. We concluded that nitrogen atoms did not desorb from the CNx coating when a friction test was performed in Ar gas. Thus, we clarified the effect of nitrogen atom incorporation in the CNx coating surface on the coefficient of friction.

2. MATERIALS AND EXPERIMENTAL

CNx coatings were deposited 100 nm thick on Si(100) substrates by the Ion Beam assisted Mixing method [18, 19]. The CNx coating deposition conditions were summarized in Table Ⅰ [20]. Umehara et al. reported that consistent values of 398.5 and 399.5 eV for N1s were observed from XPS; the I_G peak position was 1549 cm^{-1}, and the I_D/I_G ratio was 1.0 [15]. Therefore, we concluded this CNx coating had 0-20 % sp^3 carbon bonds [21]. The mating part in the friction test was a Si_3N_4 ball with a diameter of 8 mm. The hardness and Young's modulus of CNx and a Si_3N_4 ball were summarized in Table Ⅱ.

A friction test apparatus was placed inside a vacuum chamber [22]. Before the friction tests, we evacuated this chamber by rotary pump to 0.1 Pa or lower. The chamber was filled for different tests with N_2 (99.998% purity), Ar (99.998% purity), and O_2 (99.998% purity) gas at atmospheric pressure. We started the friction test after the O_2 concentration in the chamber became less than 100 ppm when measuring friction in N_2 and in Ar. For tests in O_2, we

Table Ⅰ CNx coating deposition conditions

Substrate	Si(100)
Background pressure (Pa)	1.0×10^{-4}
Sputter-cleaning (min)	5.0
Sputter-cleaning acc. voltage (kV)	1.0
Sputter-cleaming acc.curent (mA)	0.1
Deposition conditions	
Carbon target (99.999% purity)	
Sputtering ion beam (99.99998% purity)	Ar
Acc. voltage (kV)	1.0
Acc. current (mA)	100
Nitrogen mixing conditions	
Sputtering ion beam (99.99998% purity)	
Acc. voltage (kV)	0.5
Acc. current (mA/cm^2)	0.03

started it after the O_2 concentration was more than 99.99%. Friction force and normal load were measured by strain gauges posted on leaf springs. The sensitivities were 0.0265 mN/mV for the friction force and 0.047 mN/mV for the normal load.

Friction tests were carried out under 0.1 N of normal load with a sliding velocity of 0.01 m/s. For the first section, we carried out 3 friction tests each using N_2, Ar, and O_2 gases until the number of sliding cycles reached 16000 cycles. For the second section, we carried out a friction test in Ar until the friction coefficient became 0.03, the chamber was then evacuated to 0.1 Pa or lower and filled with N_2 gas, after which we continued friction tests in the same wear track.

We analyzed each wear track by AES (ULVAC PHI-650). In the normal load condition, the calculated Hertzian contact diameter was approx. 20 μm, which was much larger than the AES beam diameter (at most 1 μm). Depth analysis revealed that the acceleration voltage of the Ar^+ beam of the sputter ion gun was 3.0 kV [raster size (about 3 × 3 mm^2) and the Ar pressure in the ionization chamber was adjusted for 14.4 nm/min on the reference CNx (100 nm)]. We normalized the obtained spectra of C KLL peak-to-background intensity as 1.0.

The Raman spectra were obtained using a Jasco Laser Raman spectrophotometer NRS-1000 equipped with second harmonic of a Nd:YAG laser (532 nm). We obtained the I_D and I_G position, and I_D/I_G ratio after the deconvolution of Raman spectra.

3. Experimental results

3.1 Friction test in N_2, Ar, and O_2 and AES analysis for wear track

Figures 1(a)-(c) show the friction behavior with the number of sliding cycles in N_2, Ar, and O_2 gas. Friction coefficient increased to about 0.4 at the initial stage in the case of friction in N_2 and in Ar. Then, in N_2 condition, the friction coefficient decreased to 0.01 at the end of the givin number of sliding cycles, and it reached the steady state. In the friction test in Ar, the friction coefficient decreased to approx. 0.05 rapidly, then gradually decreased to 0.03 with the number of sliding cycles. On the other hand, the friction test with O_2 showed a friction coefficient with an unsteady state. The values varied from 0.1 to 0.8.

Figure 2 shows the AFM images of wear tracks on CNx coating in each of the N_2, Ar, and O_2 environments. Particularly, CNx coating evidenced little wear in the N_2 and Ar environment. On the other hand, the CNx coating wore to approx. 30 nm depth in the O_2 environment. Figure 3 shows the results of AES analysis of each wear track. The N KLL intensity of as-deposit CNx was approx. 0.2. The N KLL intensity of friction in N_2 was below the detection level, then became almost 0. In the friction test in Ar, the N KLL intensity was approx. 0.2, which was comparable to the as-deposit CNx. On the other hand, the N KLL intensity of friction in O_2 became approx. 0.29, which was 1.5 times larger than as-deposit CNx. Furthermore, it was suggested that the O_2 molecules were adsorbed on the wear track during transport to the AES analysis chamber [20].

The depth distribution of N1s peak-background intensities is shown in Fig. 4. The N KLL intensity of wear track in N_2 gradually increased so as to be comparable to the as-deposit CNx, becoming constant at 10 nm in the depth direction. However, Ar and O_2 results showed that the N KLL intensity distribution was almost constant in the depth direction of coating as it was comparable to the as-deposit CNx without the topmost layer of wear track in O_2.

To clarify the structural change of CNx surface in Ar and N_2 environment, we analyzed its surfaces with Raman as shown in Fig. 5 (a)-(c). The I_G peak, and the I_D/I_G ratio of the CNx surface slid in N_2 increased from 1556 to 1566 cm^{-1}, and from 1.10 to 1.13. However, in the friction test in Ar, the I_G peak increased from 1556 to 1559 cm^{-1}, which

3.2 Effect of incorporation of nitrogen atoms on friction coefficient

Table Ⅱ Indentation hardness and Young's modulus of as-deposit CNx and a Si_3N_4 ball

Nanoindentation hardenss	**Indentation depth (nm)**	**Indentation hardness**		**Young's modulas (GPa)**	
		CNx	**Si_3N_4 ball**	**CNx**	**Si_3N_4 ball**
ENT-1100a	**20.0**	**25.2**	**15.0**	**467.6**	**315.0**

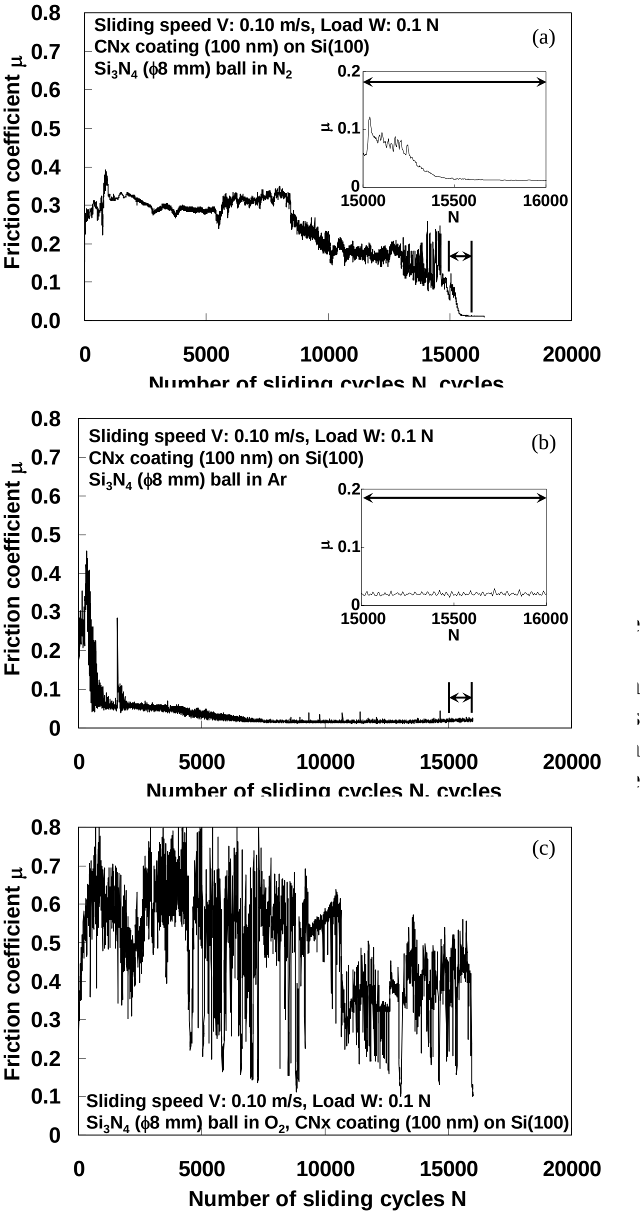


Figure 1 The friction coefficient behavior of each environmental gas (a) in N_2, (b) in Ar, and (c) in O_2.

Figure 6 (a) shows the friction coefficient behavior of CNx coating sliding against a Si_3N_4 ball in N_2 gas after the friction coefficient became 0.03 in Ar. At the initial stage of the sliding in Ar, the friction test was run until the friction coefficient became approx. 0.03. After that, in the middle stage, the friction test was stopped while the vacuum chamber was evacuated and filled with N_2 gas at atmospheric pressure. At the end stage, we restarted the friction test at the same wear track in N_2 gas. The friction coefficient increased to 0.13 just after the replacement of Ar gas with N_2 gas. Then the friction coefficient decreased to

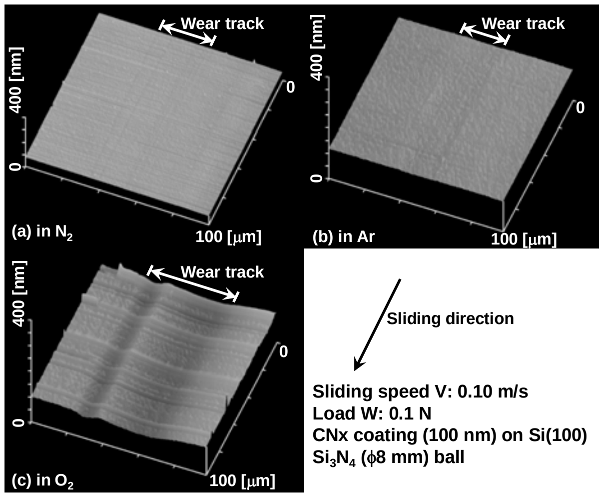


Figure 2 AFM images of wear track on CNx coating, (a) in N_2, (b) in Ar, and (c) in O_2

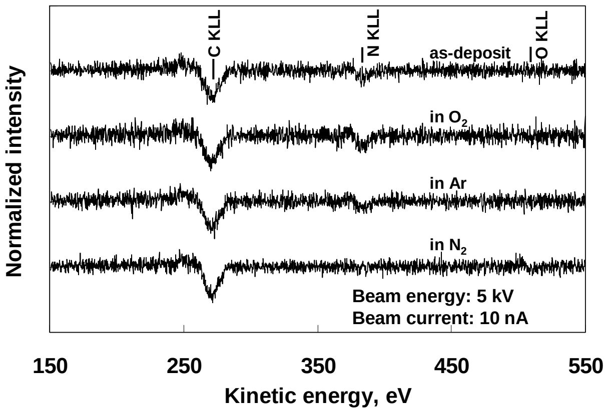


Figure 3 AES analysis for wear track of each environmental gas after 16000 cycles.

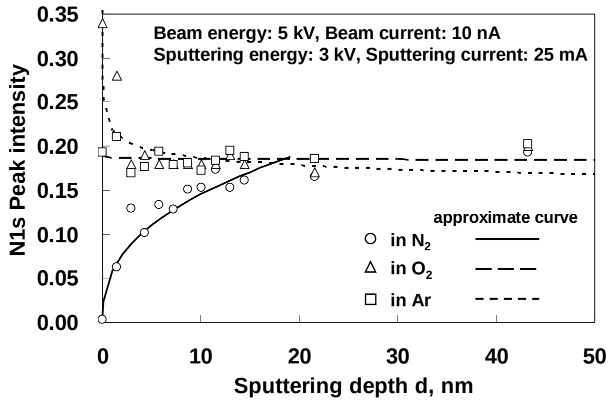


Figure 4 N KLL depth distribution in CNx coating after friction test in each environmental gas.

lower than 0.01. After the friction test, AES analysis for the wear track was carried out (see Fig. 6 (b)). As mentioned above, the N KLL/C KLL intensity of friction only in Ar gas was comparable to as-deposit CNx. However, the

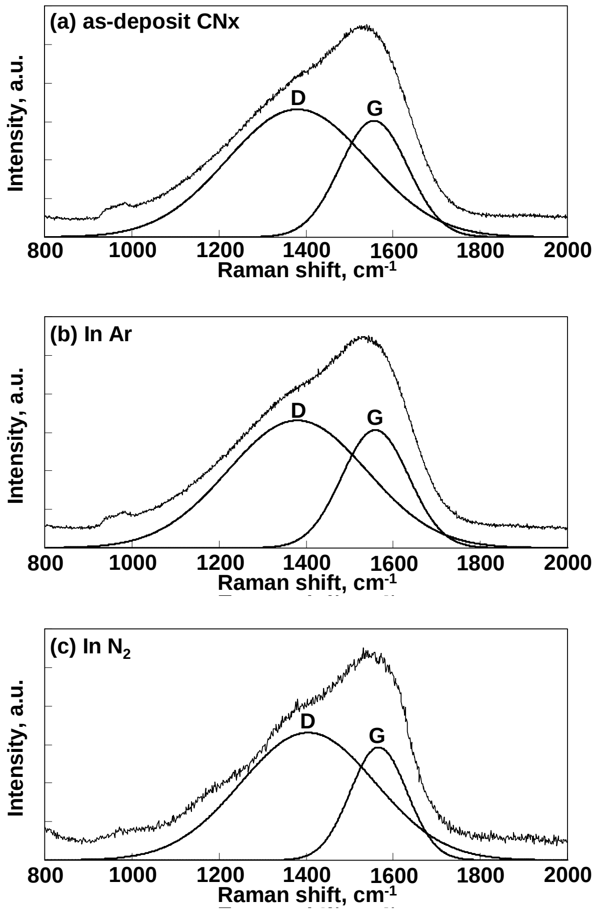


Figure 5 Raman spectra of (a) as-deposit CNx, (b) friction test in Ar, and (c) friction test in N_2.

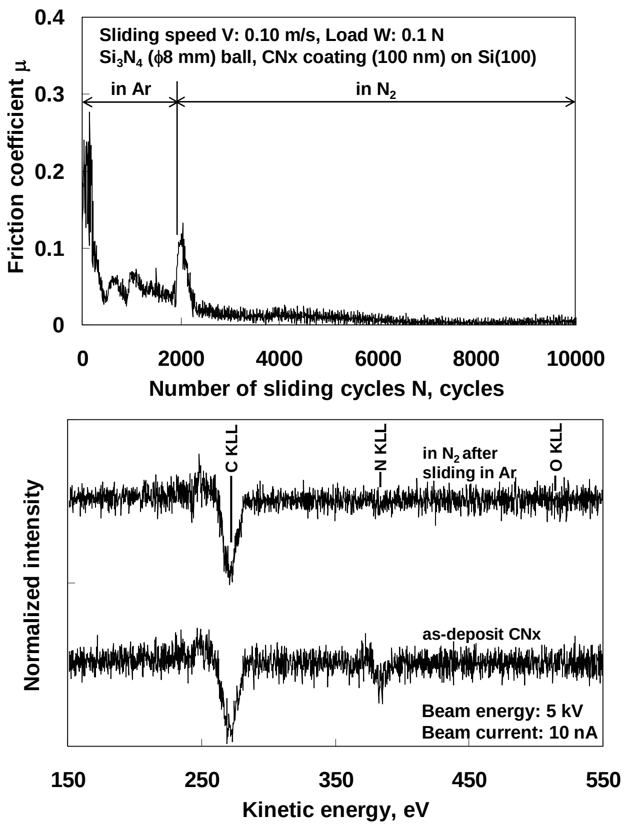


Figure 6 (a) Friction test in N_2 gas from sliding after in Ar, and (b) AES analysis of wear track in N_2 through Ar.

intensity of the wear track from sliding in N_2 gas after the friction coefficient became 0.03 in Ar gas decreased to approx.0.2 times smaller than as-deposit CNx. Therefore, the nitrogen incorporated into the CNx coating surface generated friction force, however, it was effective at a superlow friction coefficient region ($\mu < 0.03$).

4. DISCUSSION

The possibility of nitrogen atom desorption from the CNx coating was considered from the viewpoint of the flash temperature generated by the friction between the CNx coating and the Si_3N_4 ball. To clarify the effect of the flash temperature on nitrogen desorption, we carried out a 10-min. annealing test for CNx coating at 500℃ in N_2, 1.0×10^{-3} Pa vacuum (HV), and in air. After that, each surface was analyzed by AES as shown in Fig. 7. It was clear that the N KLL/C KLL ratio of annealing in N_2 and in HV decreased from as-deposit CNx. However, the flash temperature was estimated at about 1.4℃ [23] at the contact area between the CNx coating and the Si_3N_4 ball when we assumed that the CNx coating thermal conductivity was 1000-2000 W/m·K [24]. This result indicated that flash temperature generation did not explain the nitrogen non-desorption from CNx slid in Ar because the friction coefficient in Ar gas always has a consistently higher value than in N_2. Therefore, the flash temperature generated in Ar was higher than in N_2. On the other hand, in a normal air environment, CNx coating gradually disappeared during annealing. After that it completely disappeared from the Si wafer.

The nitrogen gases were thought to directly affect the nitrogen atom desorption from CNx coating. However, nitrogen molecules are known to be inert in general. Therefore, generation of energy is necessary to break the incorporation between C-N bonds from the friction area in the N_2 environment. Thus, we concluded that it is possible that such energy was generated by tribomicroplasma [25, 26].

The mechanism of nitrogen desorption from the CNx wear track after sliding in N_2 was thought to be the generation of tribomicroplasma. Nakayama et al. reported that tribomicroplasma was generated at the rear port of the sliding contact when a diamond pin was slid against a

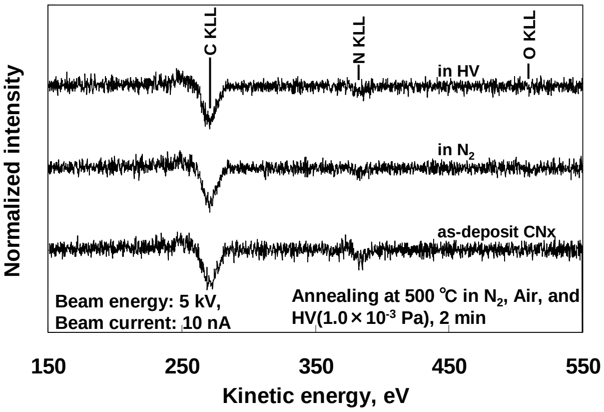


Figure 7 AES analysis for annealing at 500 in HV and in N_2, and as-deposit CNx.

sapphire disk in several environments [25, 26]. Since electrons, ions, and photons were generated from this tribomicroplasma area, several wavelength ultra violet (UV) rays were derived from photons whose generation was related to the surrounding environmental gas. Table Ⅲ shows several wavelengths of UV generated by tribomicroplasma, the energies calculated from this wavelength, and the relative bonding energies [27]. In N_2 environment, 295-778 nm wavelength-rays were generated. On the other hand, only 696 and 778 nm wavelength-rays were generated in the O_2 environment. Therefore, we concluded that decomposition of C-C and C-N incorporated in CNx was more when it was slid in N_2 gas. Then, the decomposed nitrogen atoms were considered to readily become dimmer and desorb from the CNx surface [28, 29].

Table Ⅲ The UV ray frequency generated at tribomicroprasma and several bonding energies

Wave length, nm	energy kJ/mol	Species	Binding energy, kJ/mol
		H-O	460
		H-C	410
295	406.11		
		H-N	390
316	379.12		
		C-O	360
337	355.50		
		C-C	350
358	334.64		
381	314.44		
392	305.62		
		C-N	305
400	299.51		
		N-O	220
696	172.13		
		N-N	160
778	153.99		
		O-O	146

5. CONCLUSION

In this paper, we first carried out friction tests between CNx coating and a Si_3N_4 ball in N_2, Ar, and O_2. We conducted an AES analysis for each wear track to obtain the depth distribution of N KLL intensity. Second, in order to determine the effects of nitrogen atoms incorporated in CNx coating on the friction coefficient, we conducted friction tests between CNx and a Si_3N_4 ball in Ar gas until the friction coefficient became 0.03, and then with continued friction tests in N_2 gas after Ar gas was replaced in the friction test chamber. AES analysis was performed on the same wear track in each case. The following results were obtained.

(1) The N KLL/C KLL intensity of the wear track from sliding in N_2 showed almost 0 at the topmost layer, and N KLL intensity gradually increased to a value comparable to the as-deposit CNx. at approx. 10 nm depth.

(2) There was no nitrogen desorption from CNx coating from sliding in Ar gas. The N KLL/C KLL intensity was constant and comparable to the as-deposit CNx from the surface to the substrate. Furthermore, the CNx coating wore little in Ar.

(3) The N KLL/C KLL intensity of the wear track was approximately 0.2 times the as-deposit CNx whose track was friction-tested in Ar, and then in N_2 after the friction coefficient reached a steady-state value (μ < 0.03) in Ar. The friction coefficient in N_2 gas was 0.03 when the incorporated nitrogen remained in the CNx surface. On the other hand, the friction coefficient was lower than 0.03 when the incorporated nitrogen desorbed.

Acknowledgement

The authors thank Professor Koji Kato of Tohoku University for the use of the IBAD equipment.

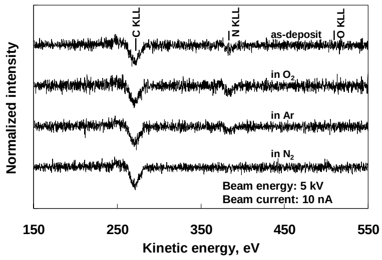
REFERENCES

[1] A.Y. Liu and M.L. Cohen, Science, (1989) 841.
[2] M.L. Cohen, Science, 261 (1993) 307.
[3] J.F. Palacio, S.J. Bull, J. Neidhardt, L. Hultman, Thin Solid Films, 494 (2006) 63.
[4] J. Neidhardt, L. Hultman, E. Broitman, T.W. Scharf and I.L. Singer, Diamond Relat. Mater., 13 (2004) 1882.
[5] J. Takadoum, J.Y. Rauch, J.M. Cattenot and N. Martin, Surf. Coat. Technol., 174-175 (2003) 427.
[6] I. Bertoti, M. Mohai, A. Toth and B. Zelei, Nucl. Instr. and Meth. in Phys. Res. B, 148 (1999) 645.
[7] L. Jiang, A.G. Fitzgerald, M.J. Rose, A.M. Gundlach and R. Cheung, Surf. Interface Anal., 34 (2002) 728.
[8] R. Ohta, T. Yokota, V. Anita, N. Saito and O. Takai, Vacuum, 80 (2006) 752.

[9] H. Habuchi, H. Koketsu and T. Katsuno, Diamond Relat. Mater., in press.
[10] Y. Miyajima, S. Nitta, S.R.P. Silva and D.A. Zeze, Thin Solid Films, 491 (2005) 161.
[11] P. Prieto, C. Quiros, E. Elizalde and J.M. Sanz, Surf. Interface Anal., 36 (2004) 820.
[12] M. Gioti and S. Logothetidis, Diam. Relat. Mater., 12 (2003) 957.
[13] X.C. Wang, Z.Q. Li, P. Wu, E.Y. Jiang and H.L. Bai, Diamond Relat. Mater., 15 (2006) 1732.
[14] N. Umehara, K. Kato, and T. Sato, Proc. Int. Conf. Metallurgical Coat. Thin Films, (1998) 151.
[15] N. Umehara, M. Tatsuno, and K. Kato, Proc. Int. Trib. Conf. Nagasaki, (2000) 1007.
[16] T. Tokoroyama, M. Goto, N. Umehara, T. Nakamura and F. Honda, Tribol. Lett., 22 (2006) 215.
[17] T. Tokoroyama, T. Nakamura, N. Umehara, Proc. Int. Trib. Conf. Kobe, (2005) 200.
[18] L. Zhou, K. Kato, N. Umehara, Y. Miyake, Wear, 243 (2000) 133.
[19] D.F. Wang, K. Kato, N. Umehara, Surf. Coat. Technol., 123 (2000) 177.
[20] K. Kato, N. Umehara, and K. Adachi, Wear, 254 (2003) 1062.
[21] A.C. Ferrari, Surf. Coat. Technol., 180-181 (2004) 190.
[22] T. Tokoroyama, N. Umehara, H. Tomita and Y. Takenoshita, Trans. Jpn. Soc. Mech. Eng. (C), 69 (2003) 2824.
[23] M. F. Ashby, J. Abulawi, and H.S. Kong, Tribology Trans., 34 (1991) 577.
[24] S. Myhra, Thin Solid Films, 459 (2004) 90.
[25] K. Nakayama and R.A. Nevshupa, ASME J. Tribol., 125 (2003) 780.
[26] K. Nakayama and R.A. Nevchupa, Vacuum, 74 (2004) 11.
[27] T.L. Cottrell, The Strengths of Chemical Bonds (Butterworths Scientific Publications, London, 1958).
[28] S.S. Todorov, D. Marton, K.J. Boyd, A.H. Al-Bayati, and J.W. Rabalais, J. Vac. Sci. Technol. A, 12 (1994) 3192.
[29] N. Hellgren, M.P. Johansson, E. Broitman, P. Sndstrom, L. Hultman, and J.-E. Sundgren, Thin Solid Films, 382 (2001) 146.

The effect of Nitrogen atoms included in CNx coatings on friction sliding against Si_3N_4 ball in Nitrogen gas

Takayuki TOKOROYAMA, Noritsugu UMEHARA
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan



Carbon nitride (CNx) coating shows a friction coefficient lower than 0.01 if it slid against a Si_3N_4 ball in dry N_2 gas. The mechanism of superlow friction was believed to be due to the change in the topmost layer of the CNx surface in the wear track to a low-shear-strength layer by forming a graphite-like structure.

However, the effects of nitrogen atoms in the CNx coating and the ambient N_2 gas on the transformation of the surface layers of CNx remain unclear. We measured the intensity of C KLL and N KLL on the wear track of CNx by AES. The N KLL intensity of as-deposit CNx was approx. 0.2. Its intensity of friction in N_2 was lower than can be detected, then it became almost 0. In the case of the friction test in Ar, it was showed that the N KLL intensity was approx. 0.2, which was comparable to the as-deposit CNx. On the other hand, the N KLL intensity of friction in O_2 became approx. 0.29 whose value was 1.5 times larger than as-deposit CNx. Only in the case of the wear track slid in N_2, did the N KLL/C KLL ratio decrease to almost zero and the friction coefficient became lower than 0.01, the N KLL intensity gradually increased to a comparable value to the as-deposit CNx at approx. 10 nm depths.