

Self-Formation of Low-Frictional Nanointerface of Carbon Nitride Coatings

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論文内容要約

Chapter 1 Introduction

A carbon nitride (CN_x) is a promising coating material which shows high hardness as well as super-low friction under a nitrogen atmosphere. However, such superlubricity cannot be obtained when the atmosphere contains much humidity and oxygen. In order to solve the environmental dependency, the author discussed tribochemical reactions at the interface of CN_x and hydrogenated- CN_x ($CN_x:H$) coatings.

The aim of this thesis is to clarify the mechanism of self-formation of the low-frictional interface concerning tribochemical reactions. Furthermore, the durability of nanointerface is discussed with an effort to achieve semipermanent super-low friction system.

The importance of tribology and the demands for CN_x and $CN_x:H$ coatings are described in terms of super-low friction and durability in this chapter. The author summarized the previous reports of super-low friction with such carbon-based coatings, and the possible mechanisms of super-low friction, and the essential problems of the coatings. Besides, the author suggested the possibility of super-low friction by controlling the tribochemical reactions. Finally, the objectives and the structure of this thesis was described.

Chapter 2 Effect of relative humidity and oxygen concentration on friction properties of carbon nitride coating sliding against Si_3N_4 under a nitrogen atmosphere

In this chapter, the friction properties of CN_x against Si_3N_4 were investigated under a nitrogen atmosphere with wide range of relative humidity (RH) and oxygen concentration in order to obtain a guideline for the conditions required to achieve low friction. The results indicated that the friction properties were classified into three modes according to the average friction coefficient and the stability of friction (Mode I-I; $\mu_a < 0.05$ and stable friction, Mode I-II; partially $\mu < 0.05$ and unstable friction, Mode II; $0.05 < \mu_a$). Besides, all of wear scars after friction tests were classified into two types according to the amount of transferred-film inside the contact area (Type I; the wear scar without transferred-film, Type II; the wear scar with transferred-film). Fig. 1 indicated the distribution of friction modes for Si_3N_4/CN_x and type of wear scar as functions of RH oxygen concentration under a nitrogen atmosphere. There were optimum RH and oxygen concentration to obtain low friction of CN_x

coating under a nitrogen atmosphere. Moreover, the existence of water and oxygen in nitrogen atmosphere were necessary for obtaining low friction of CN_x coating. At high RH and oxygen concentration values ($>1.0\%RH, >10000\text{ ppm}$), the carbon in the CN_x coating was not transferred and oxidation products were generated on the surface of the Si_3N_4 ball. This resulted in a high friction coefficient of >0.05 .

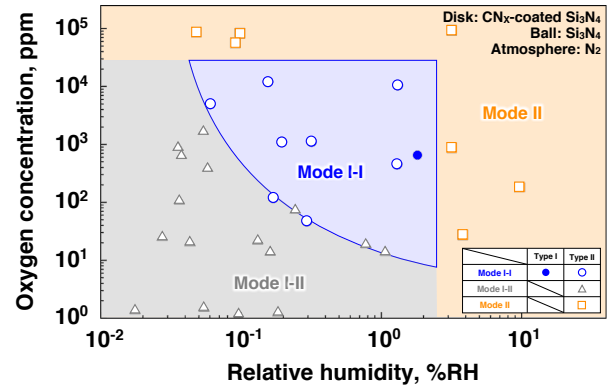


Fig. 1 Distribution of the friction modes for Si_3N_4/CN_x under a nitrogen atmosphere.

Chapter 3 Effect of relative humidity and oxygen

concentration on friction properties of carbon nitride coating sliding against itself

New testing methods of 2-step friction test and re-coating were introduced in order to discuss the possibilities of CN_x coatings to obtain low friction regardless of the RH and oxygen concentration in this chapter. When the CN_x -coated Si_3N_4 ball was slid against CN_x -coated Si_3N_4 disk at an applied load below 0.7 N after pre-sliding in ambient air (250-10000 cycles), low friction coefficient below 0.05 was obtained under a nitrogen atmosphere ($<1000\text{ ppmO}_2$) with wide range of relative humidity (0.5-40 %RH). Furthermore, due to introduction of the re-coating, the CN_x/CN_x gave low friction coefficients (<0.05) under an ultra-dry nitrogen atmosphere in the RH range of 0.01-9.30 %RH and oxygen concentration range of 1-100000 ppm. When the CN_x/CN_x with re-coating showed relatively low friction coefficient about 0.028 under a nitrogen atmosphere with 0.01 %RH, a smooth surface (several nm in Ra) was formed on the wear scar. Besides, Raman analysis provided evidences that the carbonaceous structure on the top surface of wear scar was changed from the deposited CN_x as shown in Fig. 2. The low and stable friction was obtained under humid or ultra-dry nitrogen atmosphere when the structural-changed carbon was formed at the sliding interface. The structural-change of carbons as well as the atomic transformation of carbons at the sliding interface played a critical role in the formation of the low-frictional interface.

Chapter 4 Role of water and oxygen molecules in low friction of carbon nitride coatings

In this chapter, the worn surfaces were analyzed after friction tests in order to clarify the role of oxygen atoms and water molecules in the low friction of CN_x coating. When the CN_x coating showed a friction coefficient below 0.05 under a nitrogen atmosphere with optimum oxygen concentration, the structure of carbon on the worn surface of Si_3N_4 ball was different from that of the deposited CN_x coating. Besides, the deuterated-water vapor was introduced into nitrogen atmosphere. When the CN_x coating showed a friction coefficient of 0.015 under a nitrogen

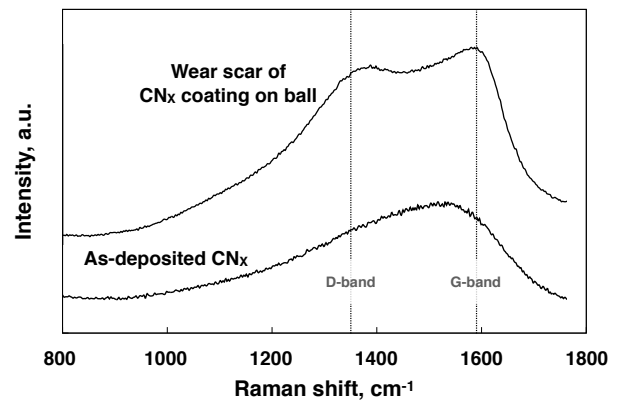


Fig. 2 Raman spectra of the worn surface on CN_x coating on Si_3N_4 ball, which showed low friction coefficient (<0.05) under an ultra-dry nitrogen atmosphere.

atmosphere (<5 %RH (D₂O), 500 ppmO₂), deuterium (D⁺) and deuterated-hydroxyl (OD⁺) radicals derived from water molecules (D₂O) in the nitrogen gas chemisorbed onto the worn surfaces (Fig. 3). The results clearly indicated that the reactions with oxygen atoms and water molecules promoted the structural-change as well as smoothing of carbons at the interface and termination of carbon dangling bonds by hydrogen as well as hydroxyl, respectively. The formation of such surface was necessary for super-low friction of CN_X coatings.

Chapter 5 Self-formation of nanointerface for super-low friction of carbon nitride coatings

In this chapter, the friction and wear tests of CN_X and CN_X:H coatings were performed under a nitrogen atmosphere with wide range of oxygen concentration in order to discuss the effect of oxygen on the self-formation of low-frictional interface. When the CN_X/CN_X showed relatively high friction, the wear depth of CN_X coating on ball increased to more than 800 nm. On the other hand, the wear depth of CN_X coating on ball also increased to more than 280 nm although the CN_X/CN_X:H provided super-low friction (Fig. 4). This meant that the wear of CN_X coating increased even if the super-low friction was obtained, which indicated that low-frictional nanointerface was continuously self-formed. Besides, the specific wear rate of CN_X coating on ball slid against CN_X:H coating remained low value below 2.0×10⁻⁸ mm³/Nm regardless of oxygen concentration (100-21×10⁴ ppm%) of a nitrogen atmosphere (3.4-3.9 %RH). As shown in Fig. 5, the specific wear rate of CN_X coating was below 2.0×10⁻⁸ mm³/Nm when the CN_X showed low friction coefficient (<0.05) against CN_X or CN_X:H. The results mentioned that the inclusion of hydrogen inside the CN_X (CN_X:H) improved the friction and wear properties regardless of oxygen concentration. Moreover, there was a critical specific wear rate of CN_X for the continuous self-formation of low-frictional nanointerface. The atomic-scale continuous transformation of carbons and hydrogens at the sliding interface (Fig. 7) played a critical role in the self-formation of

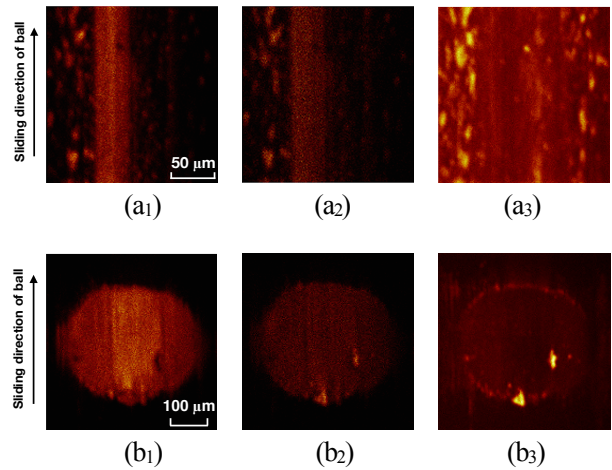


Fig. 3 (a₁) and (b₁) D⁺, (a₂) and (b₂) OD⁺, (a₃) and (b₃) O⁻ TOF-SIMS mapping images of the worn surfaces on (a) CN_X-coated Si₃N₄ disk and (b) CN_X-coated Si₃N₄ ball.

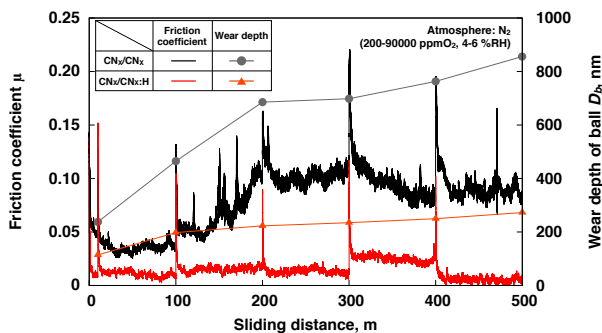


Fig. 4 Friction properties and wear depth changes of CN_X-coated Si₃N₄ ball slid against CN_X or CN_X:H coatings under a nitrogen atmosphere.

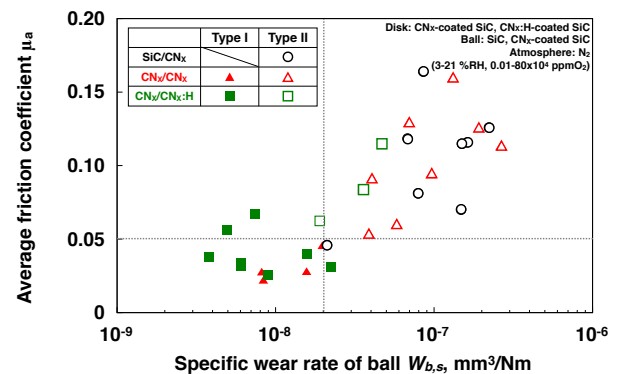


Fig. 5 Correlation between the specific wear rate of CN_X-coated ball and the average friction coefficient of SiC/CN_X, CN_X/CN_X and CN_X/CN_X:H, and the distribution of wear scar type.

low-frictional nanointerface.

Chapter 6 Tribochemistry for continuous self-formation of low-frictional nanointerface in sliding of carbon nitride coatings

The friction tests of CN_x against a deuterated- CN_x ($CN_x:D$) and the characterization of gaseous products were simultaneously conducted in high vacuum in order to discuss the role of tribochemistry in the continuous self-formation of low-frictional nanointerface in this chapter. When the CN_x showed super-low friction coefficient (<0.01) against deuterated- CN_x ($CN_x:D$) in high vacuum, the fragment ions of $m/e=4$ (deuterium), 16 (deuterated-methane), 30 (deuterated-ethylene) and 32 (deuterated-ethane) increased (Fig. 7), which indicated that the hydrogen and hydrocarbons evolved from the sliding interface. Furthermore, the deuterated-ethylene (or ethane) continued to evolve when such super-low friction was observed. The evolution of ethylene assisted the continuous self-formation of nanointerface, which provided super-low friction of CN_x coatings.

Chapter 7 General conclusions

In this chapter, the general conclusions were described.

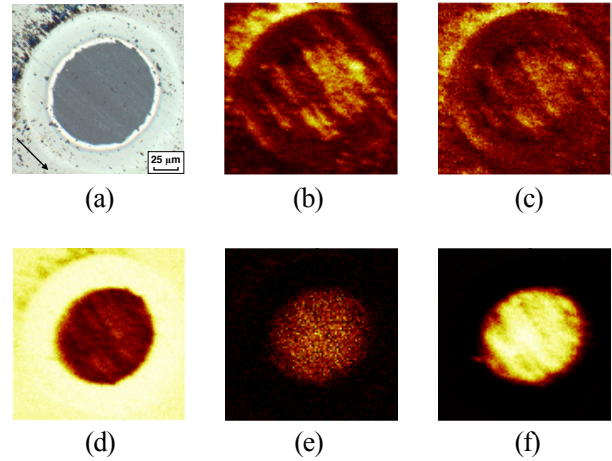


Fig. 6 (a) Confocal optical image and (b) $^{13}C^+$, (c) H^+ , (d) C^+ , (e) SiC^+ and (f) SiN^+ TOF-SIMS mapping images on the wear scar of CN_x -coated Si_3N_4 ball slid against $^{13}CN_x:H$ coating.

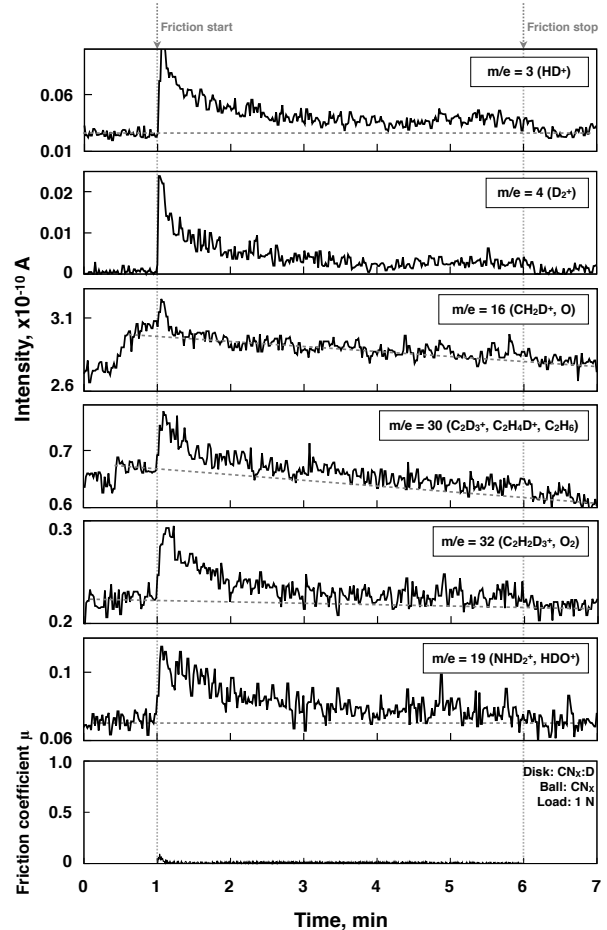


Fig. 7 Variations in intensities of the fragment ions and friction properties of $CN_x/CN_x:D$ in vacuum.