

# Characterization and tribological evaluation of duplex treatment by depositing carbon nitride films on plasma nitrided Ti-6Al-4V

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Carbon nitride (CN<sub>x</sub>) films (with N/C ratio of 0.5) were deposited on both untreated and plasma nitrided Ti-6Al-4V substrates by D.C. magnetron sputtering using a graphite target in nitrogen plasma. TEM and XPS analysis revealed the formation of both amorphous CN<sub>x</sub> structure and crystalline  $\beta$ -C<sub>3</sub>N<sub>4</sub> phases in the deposited coatings. Nano-indentation tests showed that the film hardness was about 18.36 GPa. Both the scratch tests and indentation tests showed that compared with CN<sub>x</sub> film deposited directly on Ti-6Al-4V, the load bearing capacity of CN<sub>x</sub> film deposited on plasma nitrided Ti-6Al-4V was improved dramatically. Ball-on-disk wear tests under both dry sliding and lubricated conditions (with simulated body fluids) were performed to evaluate the friction and wear characteristics of the deposited coatings. Results showed that under both dry and lubricated conditions, the duplex treated system (i.e., with CN<sub>x</sub> film deposited on plasma nitrided Ti-6Al-4V substrate) was more effective in maintaining a favorable low and stable coefficient of friction and improving wear resistance than both individual plasma nitriding and CN<sub>x</sub> films on Ti-6Al-4V substrate. Under dry sliding conditions, the generated wear debris of spalled films were accumulated on the wear track, mechanically alloyed and graphitized, thus significantly reducing the coefficient of friction and preventing wear of the substrate. However, under lubricated conditions, due to the flowing of the fluids, the lubricating wear debris was taken away by the fluids, and therefore, the direct contact of two original surfaces resulted in high coefficient of friction and extensive abrasive wear of the substrate for CN<sub>x</sub> films deposited on Ti-6Al-4V substrate. Also when there was some small-area spallation of CN<sub>x</sub> films, the fluids could seep into the interface between the film and substrate, thus degrading the interfacial adhesion and resulting in a large area spallation.

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## 1. Introduction

Titanium alloys are widely used in aerospace and biomedical applications due to their good combination of mechanical properties and corrosion resistance [1]. However, they are notorious for poor tribological properties [2]. Surface engineering methods are widely used to improve the wear and corrosion resistance of titanium alloys [3–6]. Among them, the applications of adherent diamond, diamond-like carbon (DLC) and CN<sub>x</sub> films have been realized as promising methods [7–10]. However, soft Ti alloys may not be able to provide adequate support and adhesion strength for thin and hard CN<sub>x</sub> films. An approach to solve this problem is to design and develop duplex diffusion/coating treatments by com-

ination of hard films with plasma nitriding [11–13]. Plasma nitriding of Ti-6Al-4V produces a graded hardened case which serves as an excellent supporting layer for the hard CN<sub>x</sub> films. The hard and smooth CN<sub>x</sub> films deposited at low temperature can produce a wear resistant, low-friction coating without impairing the beneficial effects of the plasma nitriding treatment.

Duplex surface engineering involves the sequential application of two (or more) established surface technologies to produce a surface composite with combined properties, which are unobtainable through any individual surface technology [14]. Current studies on duplex treatments concentrate on combining plasma nitriding with TiN, CrN or DLC coating on steel substrates

[15–17]. There were also reports on combining  $CN_X$  films with PVD TiN films [18, 19]. However, so far, there are no reports on the duplex treatment combining plasma nitriding with  $CN_X$  films on Ti alloy substrate.

The successful application of  $CN_X$  films for tribological protection requires an extensive understanding of their friction and wear behavior and their dependence on the operating environment, such as lubricants, gases, etc. [20, 21]. However, there are few studies on the tribological behavior of carbon nitride films under different environmental conditions. The purposes of this research work are to study (1) the potentiality of combination of plasma nitriding and  $CN_X$  films on Ti-6Al-4V substrate and (2) their friction and wear behavior under both dry and lubricated conditions with simulated body fluids.

## 2. Experimental

Ti-6Al-4V plates with a diameter of 50 mm and a thickness of 3 mm were mechanically ground and polished, then ultrasonically rinsed in acetone. The surface roughness of Ti-6Al-4V sample after polishing was  $0.20 \pm 0.02 \mu\text{m}$ . Plasma nitriding was carried out with a total power of 2 kW and a voltage of 1500 V. The deposition temperature was  $800^\circ\text{C}$  and the nitriding duration was 9 hours.  $CN_X$  films with a thickness of  $2 \mu\text{m}$  were deposited on both untreated and plasma nitrided Ti-6Al-4V plates by an unbalanced magnetron sputtering system under a base pressure of  $6.68 \times 10^{-7}$  Pa. A high purity (99.99%) planar graphite target was used in a pure (99.999%) nitrogen discharge, at a gas pressure of 5 Pa and a constant gas flow rate of 40 sccm.

The discharge current on the cathode was held at 1 A, the substrate temperature was below  $200^\circ\text{C}$ , and the negative substrate bias voltage was  $-300$  V.

The surface topography of the plasma nitrided samples and the deposited  $CN_X$  films was investigated using a NanoScope-IIIa atomic force microscope (AFM). Transmission Electron Microscope (TEM), JEOL JEM-2010 F, were used to analyze the coating structure [22]. The C-N bonds were determined using an X-ray photoelectron spectroscopy (XPS), VG ESCALAB 220 XL system with Al  $K\alpha$  monochromatic X-ray source and a hemispherical analyzer at energy of 20 eV.

Film hardness and elastic recovery were evaluated using a nano-indentation tester with a penetrating depth of 150 nm. The average values were calculated from four readings on different areas of the films. The load bearing capacity of  $CN_X$  films deposited on untreated and plasma nitrided Ti-6Al-4V was assessed using a scratch tester and a Rockwell hardness tester under the normal loads of 60 Kgf. Load capacity of a film was judged from the radial and lateral cracks and spallation observed after indentation with the Rockwell hardness tester by a HITACHI S-3500N scanning electron microscope (SEM).

Tribological behaviors of Ti-6Al-4V substrate, plasma nitrided samples,  $CN_X$  films deposited on untreated and plasma nitrided Ti-6Al-4V were evaluated using a ball-on-disk tribometer under both dry and lubricated conditions (with simulated body fluid). The lubricants used in the wear tests were the synovial fluids, which contain albumin (11.3 g/L),  $\alpha$ -globulin (1.26 g/L),  $\gamma$ -globulin (3.06 g/L), hyaluronic acid

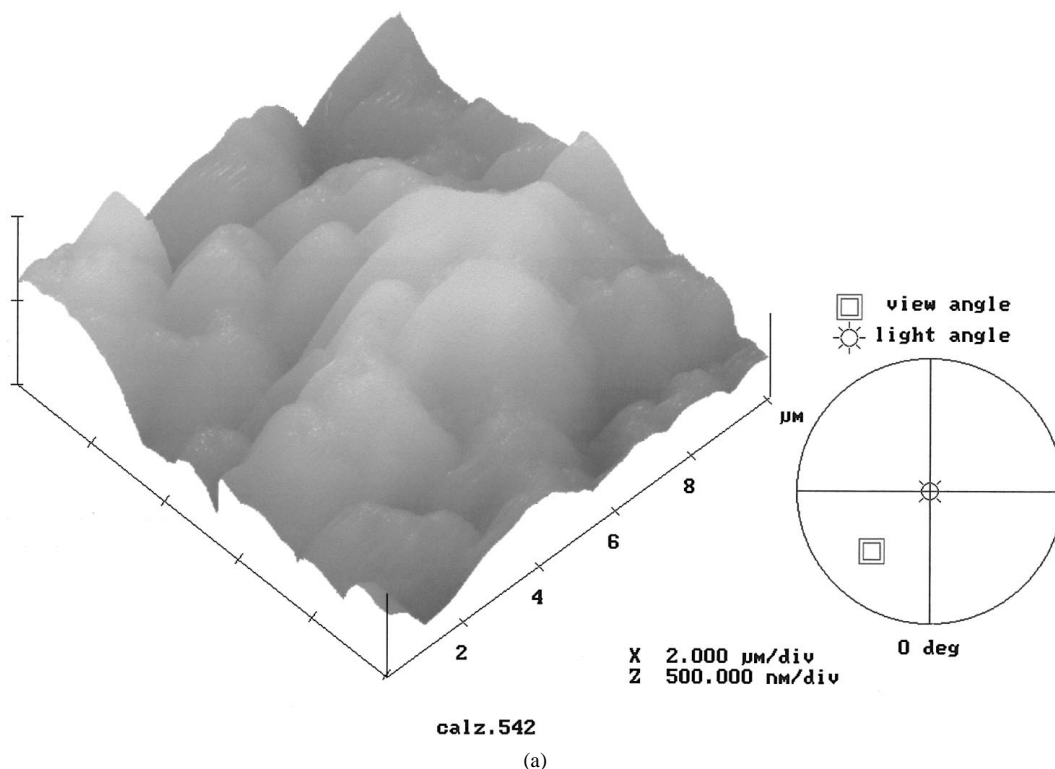
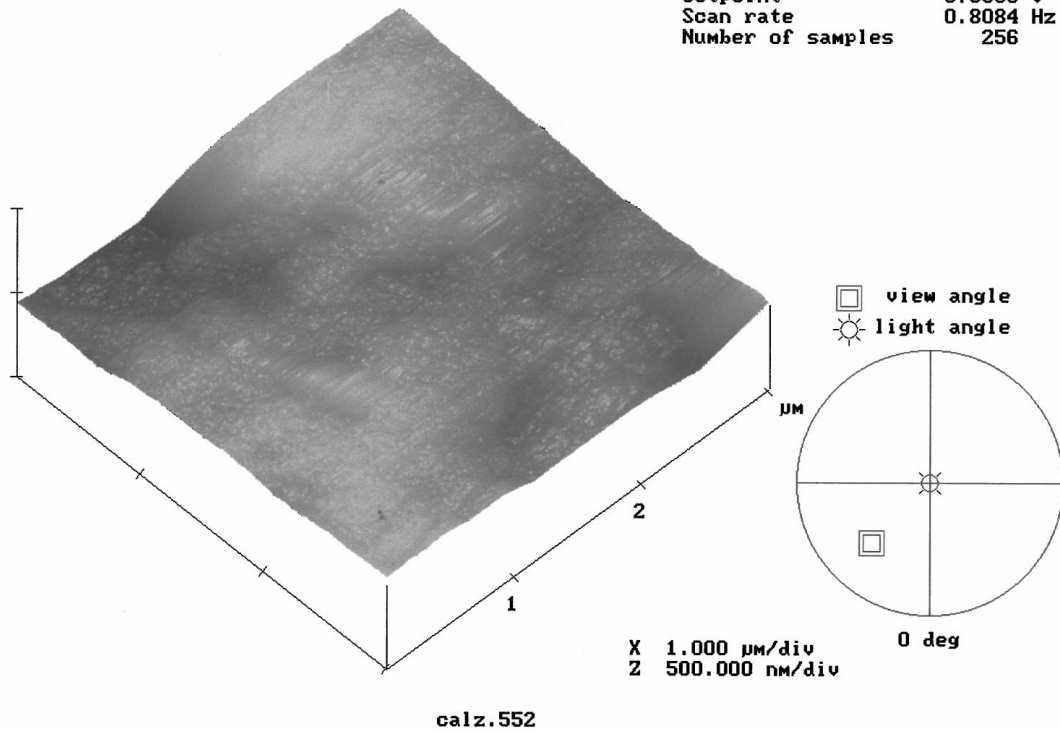
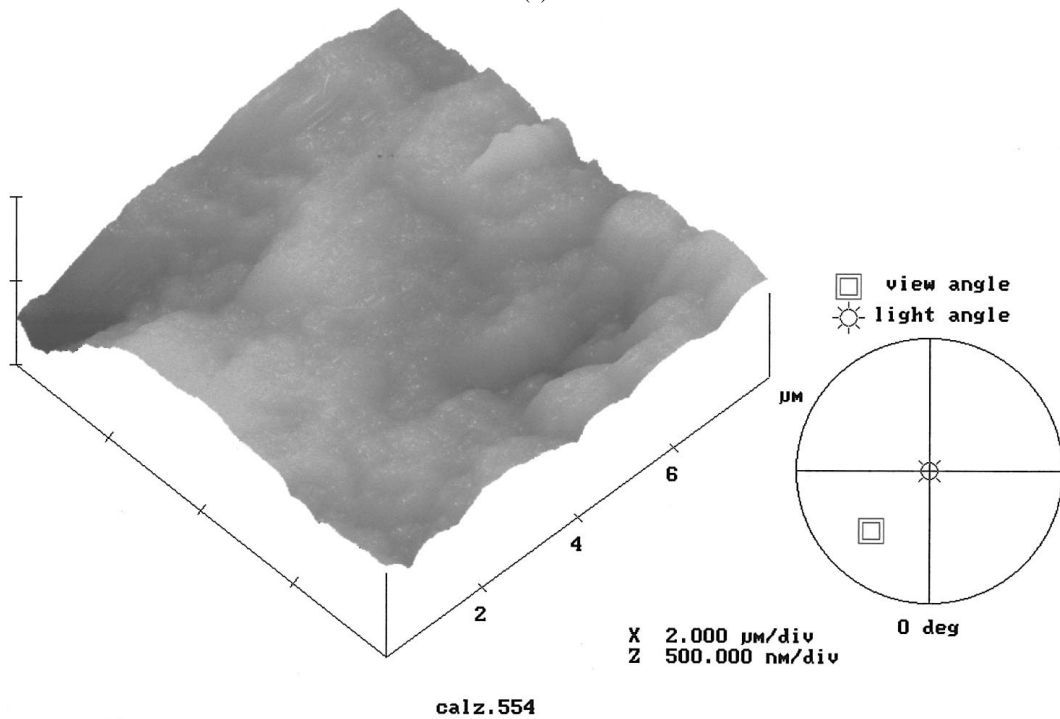


Figure 1 AFM surface morphologies of different treated samples; (a) plasma nitrided Ti alloys ( $800^\circ\text{C}$ , 9 hours), (b) carbon nitride film deposited on untreated Ti-6Al-4V substrate; (c)  $CN_X$  film deposited on plasma nitrided specimen. (Continued)

NanoScope	Tapping AFM
Scan size	3.000 $\mu\text{m}$
Setpoint	0.9808 V
Scan rate	0.8084 Hz
Number of samples	256



(b)



(c)

Figure 1 (Continued.)

(2 g/L) and distilled water [23]. Alumina balls (with a diameter of 9.5 mm and a surface roughness better than  $R_a = 0.02 \mu\text{m}$ ) were used as the counterface materials. The normal loads were 5, 10 and 20 N (with the corresponding Hertzian contact stress on Ti-6Al-4V substrate about 507, 639 and 805 MPa, respectively). All the tests were run in laboratory air (25°C and relatively humidity of 65%  $\pm$  3%) with a sliding distance of 300 m and a sliding speed of 0.2 m/s. The coefficient of friction

was continuously recorded during each test. The wear tracks on the worn specimen were examined by SEM. Wear volumes of the worn specimens were measured by a Talysurf 5 laser profilometer and wear rates were calculated according to the formula  $W = V/(D \times L)$ , where  $W$  is the wear rate,  $V$  is the wear volume,  $D$  is the sliding distance and  $L$  is the normal load. The surfaces of  $\text{CN}_x$  films before and after wear tests were evaluated by a micro-Raman spectroscopy.

### 3. Results

#### 3.1. Characterization of $CN_x$ and duplex treated coating

The deposited  $CN_x$  films were opaque, dark-brown in color, smooth with good adhesion to the substrate. Fig. 1a to c show the AFM surface morphologies of plasma nitrided Ti alloys (800°C and 9 hours), carbon nitride films deposited on both Ti-6Al-4V substrate and plasma nitrided specimen. The plasma nitrided surface was relatively rough, probably due to plasma ion bombardment and irregular growth of nitride on surface (see Fig. 1a). The roughness of plasma nitrided surface obtained from AFM was about 235 to 256 nm. The surface of  $CN_x$  films deposited on Ti-6Al-4V substrate was smooth with a roughness of 80 to 100 nm, obtained from AFM (see Fig. 1b). AFM analysis revealed that the deposition of a thin layer of  $CN_x$  film could improve the rough nature of plasma nitrided surface as shown from Fig. 1c.

Fig. 2 shows the high-resolution TEM micrograph and corresponding electron diffraction pattern of  $CN_x$

film. Relatively sharp electron diffraction ring patterns were observed indicating the film consisted of polycrystalline clusters of carbon nitride. The electron diffraction patterns could be indexed to the reflections expected for the theoretical  $\beta-C_3N_4$  structure [8]. The lattice spacings were measured directly from the diffraction rings, and the d-spacings are 2.77, 2.44, 1.93, 1.53, 1.33, 1.21, 1.11 and 1.07 Å, respectively, which were in good agreement with the calculated data and empirical results [24, 25]. The peaks could be consistently indexed as the (200), (101), (111), (310), (221), (002), (202) and (411) planes. The high resolution TEM image clearly shows the formation of crystalline structure. The maximum size of some single carbon nitride crystals was about 200 nm but the film mainly consists of tiny crystallites (grain size <20 nm) and clusters of grains [22].

Fig. 3a and b show the typical carbon (1s) and nitrogen (1s) core level spectra for the carbon nitride film from XPS analysis. The peaks were fitted using the peak deconvolution approach proposed

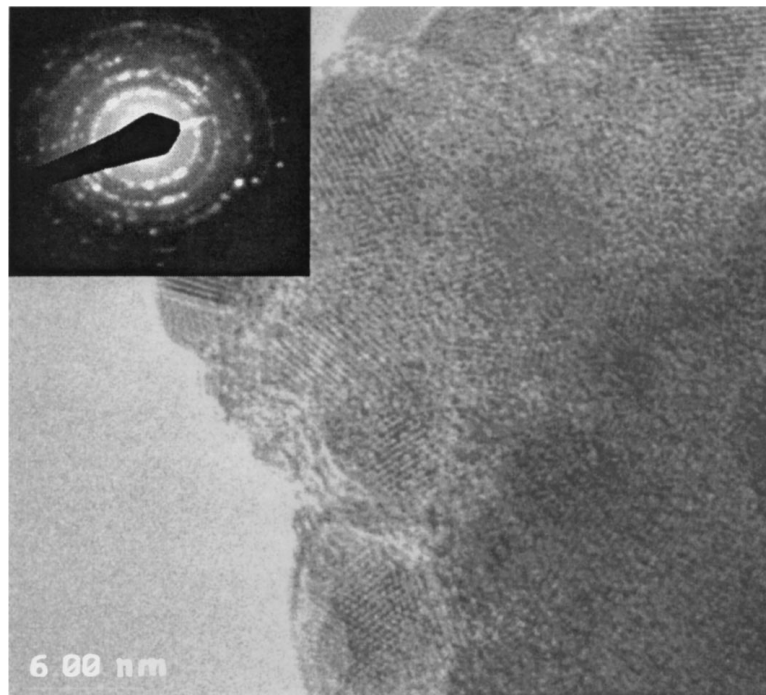


Figure 2 TEM and corresponding selected area electron diffraction pattern of  $CN_x$  film.

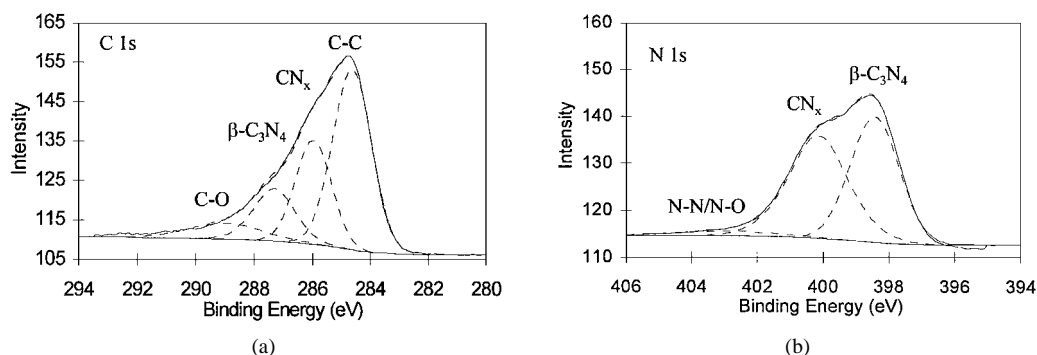


Figure 3 The carbon and nitrogen 1s spectra for carbon nitride film (with N/C ratio of 0.5) from XPS analysis; (a) carbon 1s spectra; (b) nitrogen 1s spectra.

by Marton *et al.* [26, 27]. The fitted peaks corresponded to four types of phases (i.e., C-C;  $CN_X$ ;  $\beta-C_3N_4$  and C-O) in C 1s spectrum and three types of phases (i.e.,  $\beta-C_3N_4$ ;  $CN_X$ ; N-N (or N-O)) in the N 1s spectrum. The C peak at 284.64 eV was considered to represent the adventitious carbon. The two central peaks at 285.96 and 287.32 eV corresponded to  $sp^2$  and  $sp^3$  bonding of  $CN_X$  and  $\beta-C_3N_4$ , respectively. The peak at 289 eV could be identified as superficial C-O species. The area ratio under these peaks was C-O :  $\beta-C_3N_4$  :  $CN_X$  : C-C = 1 : 1.9 : 3.3 : 6.1. In Fig. 3b, the peak at 398.46 eV was probably the  $sp^3$  bonding of  $\beta-C_3N_4$ , and the peak at 400.17 eV was  $sp^2$  bonding of  $CN_X$  by analogy to pyridine [28] and HMTA [29]. The peak at 402.88 eV could be identified as superficial N-O/N-N species. The ratio of area under these peaks is N-O/N-N :  $CN_X$  :  $\beta-C_3N_4$  = 1 : 13.5 : 13, indicating that the incorporated nitrogen combines mainly with carbon to form  $CN_X$  and  $\beta-C_3N_4$ . The ratio of N/C in the films obtained from XPS was about 0.5 which was far below the desired value of  $\beta-C_3N_4$  (1.33). The above XPS results confirmed the formation of amorphous  $CN_X$  as well as the crystalline structure of  $\beta-C_3N_4$  phase in the deposited carbon nitride films.

Nano-indentation studies showed that the intrinsic hardness of  $CN_X$  film was about  $18.36 \pm 2$  GPa and elastic modulus was about  $132.4 \pm 12$  GPa. This hardness value was far from that of the predicted value of  $\beta-C_3N_4$  [30], but was quite comparable with that of DLC coatings [31]. The carbon nitride film showed a significant elastic relaxation during the removal of the load (see Fig. 4).

Fig. 5 shows the typical friction-load curves of the scratch tests for  $CN_X$  films deposited on untreated and plasma nitrided Ti-6Al-4V. Compared with that of carbon nitride film deposited directly on Ti-6Al-4V, the load bearing capacity was improved dramatically with the application of plasma nitrided layer between Ti-6Al-4V and  $CN_X$  film. This conclusion can also be derived from the indentation tests. Fig. 6 shows SEM micrographs of the indentation impressions on  $CN_X$  films deposited on untreated and plasma nitrided Ti-6Al-4V. For the  $CN_X$  films deposited directly on Ti-6Al-4V, there is large-area cracking and spallation occurring

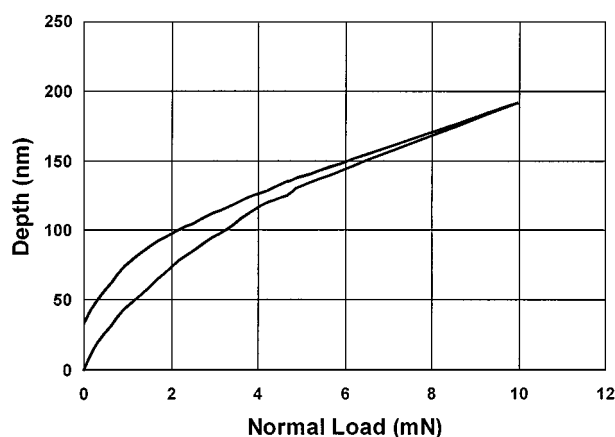


Figure 4 Nano-indentation results on carbon nitride film with an indentation depth of 150 nm.

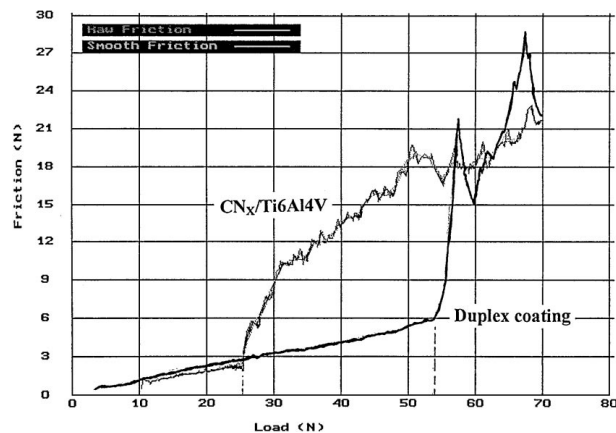


Figure 5 The typical friction-load curves of the scratch tests for  $CN_X$  film deposited on untreated and plasma nitrided Ti-6Al-4V.

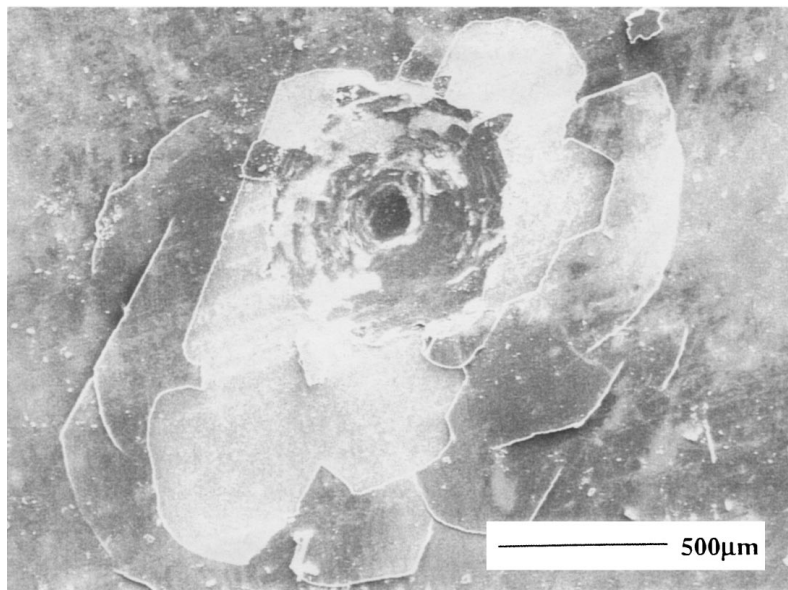
after indentation (see Fig. 6a) due to the brittle nature of  $CN_X$  film and the poor load bearing capacity of film-substrate system. For  $CN_X$  films deposited on plasma nitrided Ti-6Al-4V substrate, some radial and ring cracks but no spallation were observed indicating a good load bearing capacity (see Fig. 6b).

### 3.2. Tribological behavior under dry sliding conditions

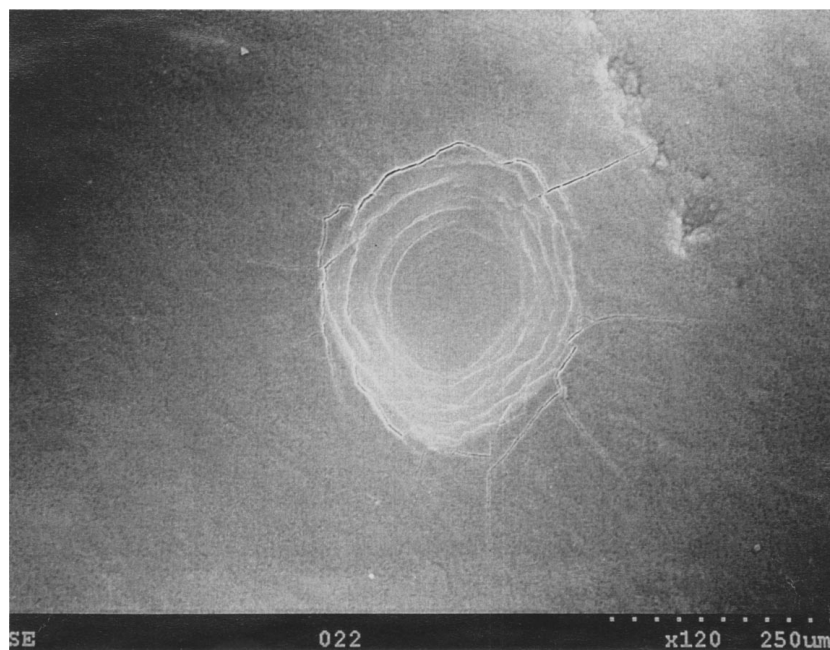
Figs 7 and 8 show the comparison of coefficient of friction and wear rates for four types of specimens with different normal loads and dry sliding conditions. For untreated Ti-6Al-4V, the long-term coefficient of friction remained a high value of about 0.4 to 0.5 and was almost independent upon the applied normal load as shown in Fig. 7a. Wear rate was quite high for untreated Ti-6Al-4V (see Fig. 8a). Under dry sliding conditions, the dominant wear mechanism for untreated Ti-6Al-4V was adhesive wear, abrasive wear and delamination as shown in Fig. 9a [32].

For plasma nitrided Ti-6Al-4V under dry sliding condition, there was a critical load at which the wear mechanism was probably changed. Under a relatively low normal load of 5 N, both the coefficient of friction and wear rate remained low as shown in Fig. 7b and 8b. With the normal load increased to 10 N and 20 N, the coefficient of friction increased abruptly to a high value of 0.4 to 0.5 after 150–200 m sliding and the wear rates showed high values (see Figs 7b and 8b). The dominant wear mechanisms changed from mild wear to spallation (or crushing) of nitrided layer as shown in Fig. 9b. The above results indicated that plasma nitriding was not effective in improving the friction property and wear resistance under high normal loads.

$CN_X$  films deposited on Ti-6Al-4V substrate maintained a low value of coefficient of friction and a low wear rate under a normal load of 5 N as shown in Figs 7c and 8c. However, under a normal load of 10 N, due to the poor load bearing capacity and the resulted large-area spallation of  $CN_X$  films shown in Fig. 9c, there was a significant increase and variation in coefficient of friction. However, the coefficient of friction remained low (less than 0.2) even after the coating spallation. Some of the coating fragments might be entrapped within



(a)



(b)

Figure 6 SEM micrographs of the Rockwell indentation impressions of  $CN_x$  films deposited on (a) Ti-6Al-4V and (b) plasma nitrided Ti-6Al-4V.

the wear track, comminuted into fine particles, finally mixed up with the substrate materials to form a mechanically alloyed, lubricating debris layer. The low coefficient of friction after coating spallation was probably due to the formation of this debris layer, which will be discussed later.

Fig. 7d shows the variation of coefficient of friction for duplex treated specimen under different normal loads sliding with  $Al_2O_3$  ball. The long-term coefficient of friction for duplex treated coating remained at a low and stable value (less than 0.2). The wear rates of the duplex treated specimen were rather low, as shown in Fig. 8d. Wear rates of  $CN_x$  films on nitrided layer were much smaller than those of untreated Ti-6Al-4V, plasma nitrided samples and  $CN_x$  coated Ti-6Al-4V. Fig. 9d shows the surface morphology of the wear track under a normal load of 20 N. There

is only minor spallation of the film occurring on the wear track, because the coating at original asperities were fractured and fragmented. These coating fragments and wear debris were comminuted and mechanically mixed, thus forming a mechanically alloyed wear-resistant and lubricating layer on the wear track. In order to prove this conclusion, Raman tests have been carried out on the coating surfaces before and after sliding wear, the results are shown in Fig. 10.  $CN_x$  films, like diamond-like-carbon (DLC), are metastable films with small clusters of microcrystalline  $sp^3$  and  $sp^2$  C-C bonding and C-N bonding coexisting in an amorphous matrix. Compared with that of as-deposited films, the D band ( $1335\text{ cm}^{-1}$ ) and G band ( $1595\text{ cm}^{-1}$ ) of the worn coatings becomes sharp in the spectrum as a result of the graphitization [33–35]. This phenomenon clearly shows that the graphitization and degradation of  $CN_x$

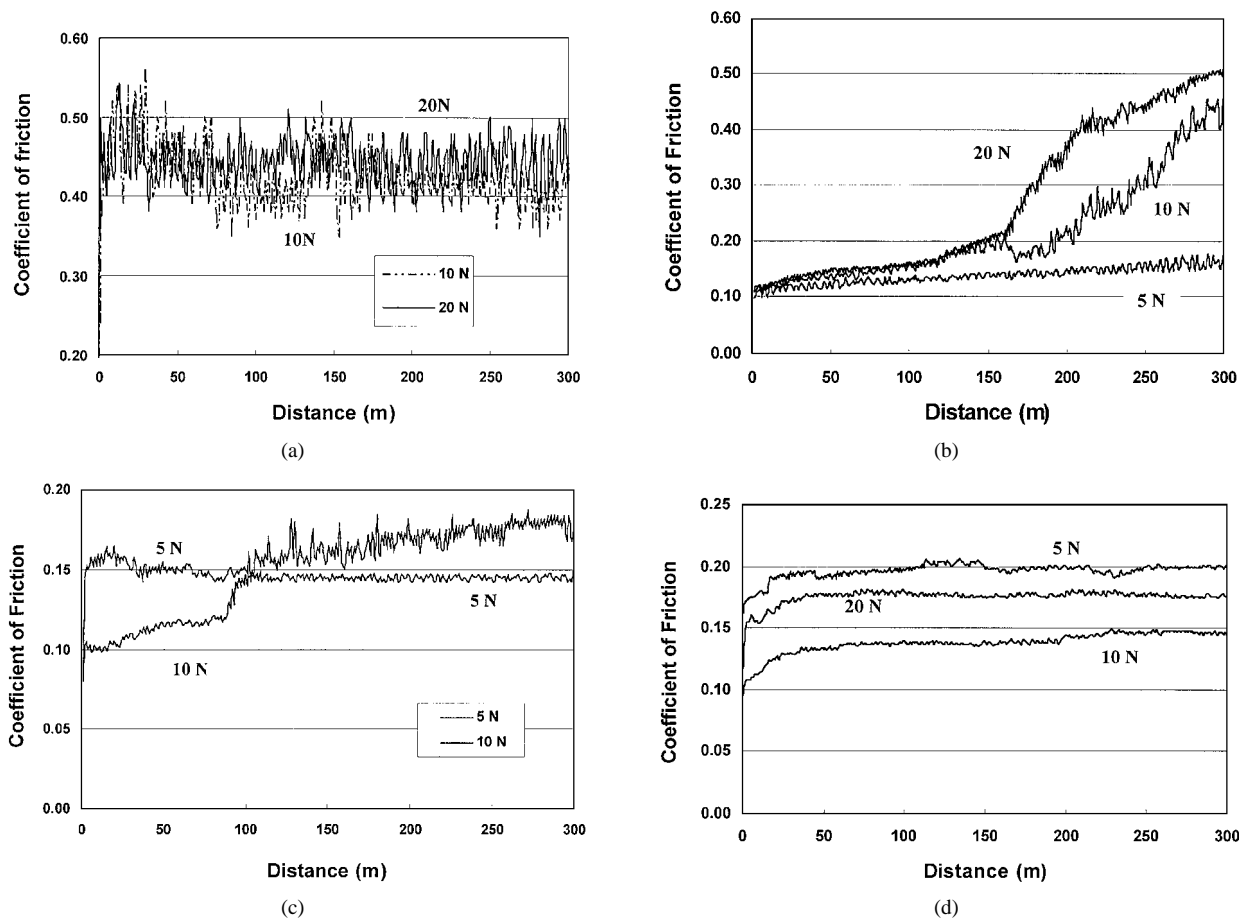


Figure 7 The coefficient of friction of different samples under dry sliding condition and different normal loads. (a) Untreated Ti-6Al-4V; (b) plasma nitrided Ti-6Al-4V; (c) CN<sub>x</sub> film deposited on untreated Ti-6Al-4V; (d) CN<sub>x</sub> film deposited on plasma nitrided Ti-6Al-4V.

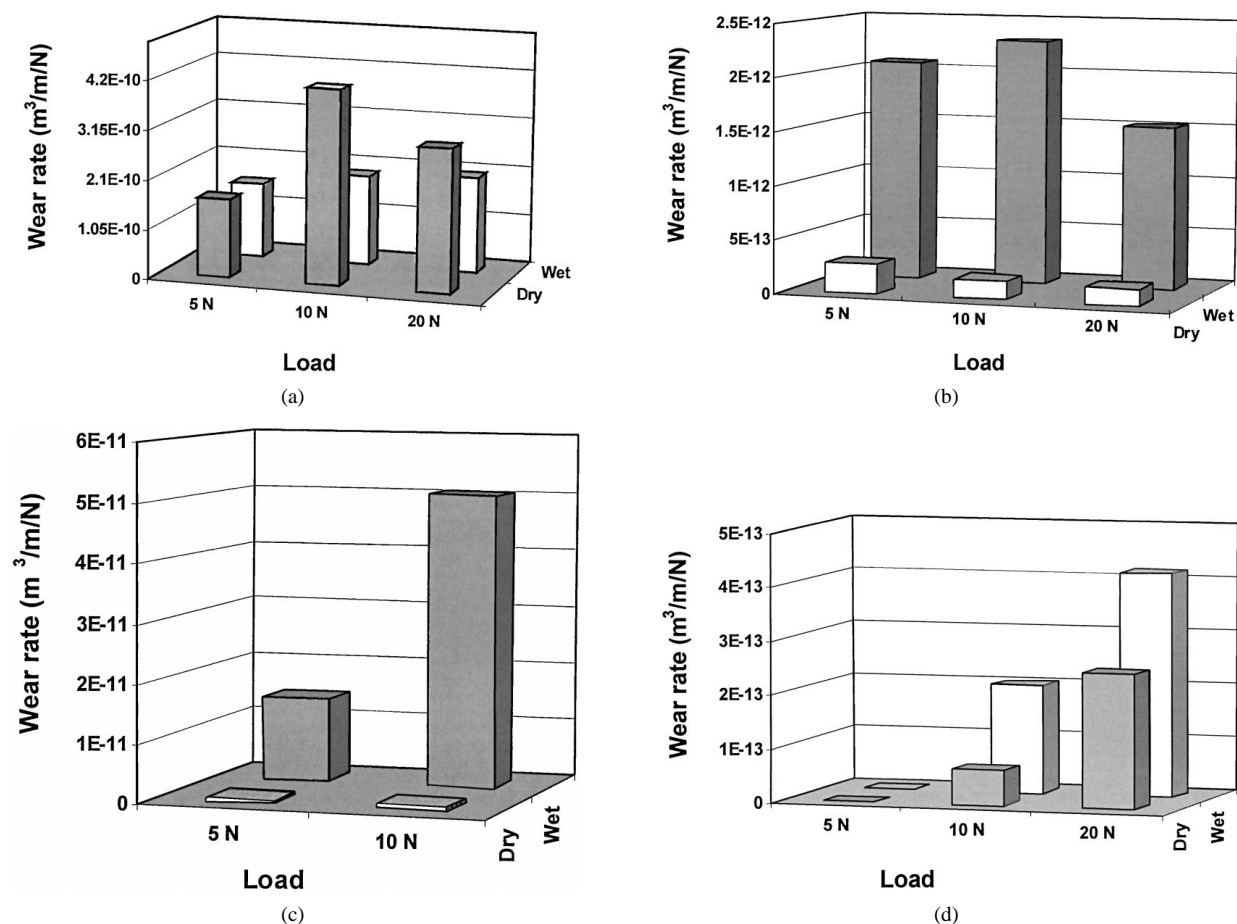


Figure 8 The wear rates of different samples under both dry sliding and lubricated conditions with simulated body fluids. (a) Untreated Ti-6Al-4V; (b) plasma nitrided samples; (c) CN<sub>x</sub> film deposited on untreated Ti-6Al-4V; (d) CN<sub>x</sub> film deposited on plasma nitrided Ti-6Al-4V.

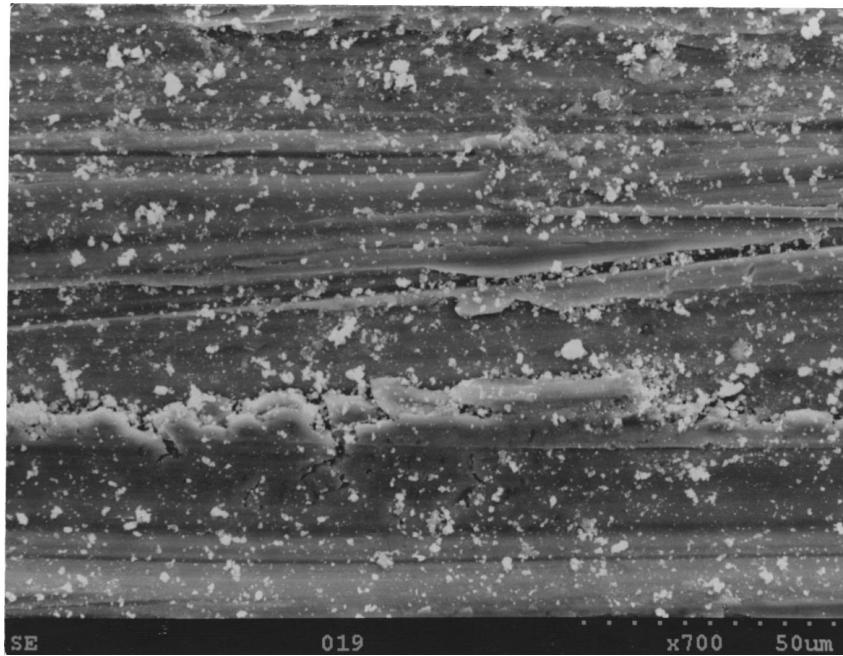
films occurs and it has a significant lubricating effect on the wear and friction properties of  $CN_x$  films during sliding.

### 3.3. Tribological behavior under lubricated conditions with body fluids

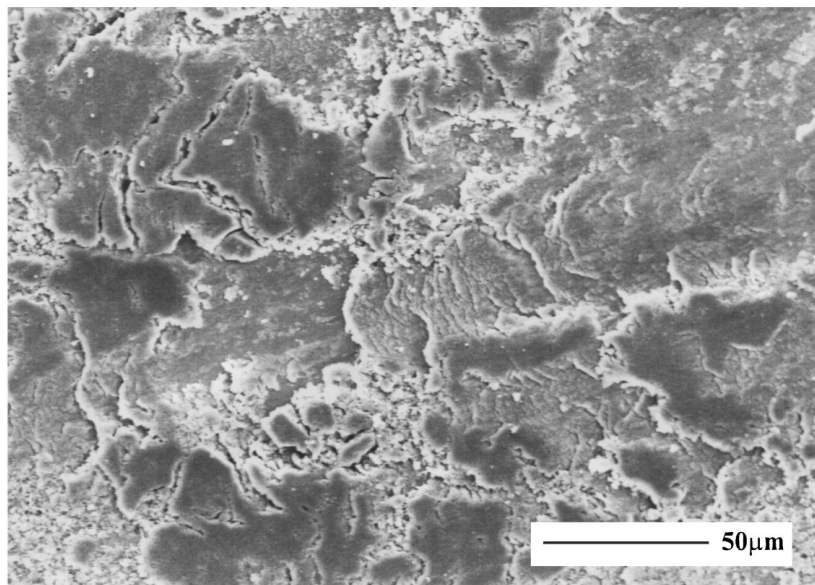
Figs 10a and 8a show the coefficient of friction curves and wear rates for untreated Ti-6Al-4V samples under lubricated condition and different normal loads. The long-term coefficient of friction remained stable at about 0.25–0.35 and was much lower than that of Ti-6Al-4V under dry sliding conditions. The wear rates

of untreated Ti-6Al-4V under lubricated conditions are lower than that under dry sliding conditions. Under the lubricated wear conditions, the dominant wear mechanism for untreated Ti-6Al-4V substrate was abrasive wear (see Fig. 12a).

Fig. 11b shows the coefficient of friction of plasma nitrided samples under different normal loads lubricated with body fluids. The initial coefficient of friction was quite low, but after a short time sliding, the coefficient of friction increased rapidly to a high value of about 0.4. The higher the normal load, the earlier this sudden increase occurring. During the long term running, the coefficient of friction decreased gradually



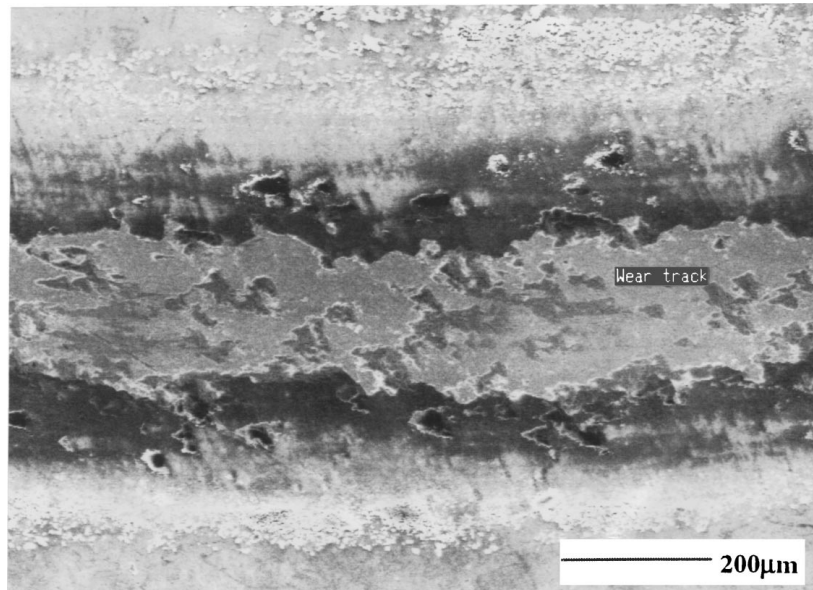
(a)



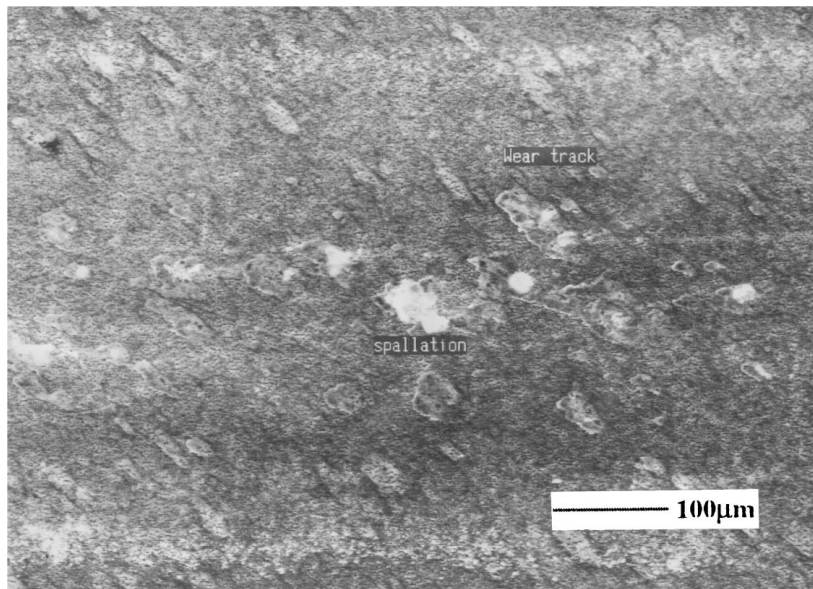
(b)

Figure 9 (a) Extensive adhesive and abrasive wear on worn Ti-6Al-4V under dry sliding conditions; (b) The spallation (or crushing) of plasma nitrided layer under a normal load of 10 N and dry sliding condition; (c) Large-area spallation of  $CN_x$  films deposited on Ti-6Al-4V substrate under dry sliding condition; (d) Surface morphology of wear track of  $CN_x$  films deposited on plasma nitrided layer showing the small spallation of the films occurring on wear track. (Continued)





(c)



(d)

Figure 9 (Continued).

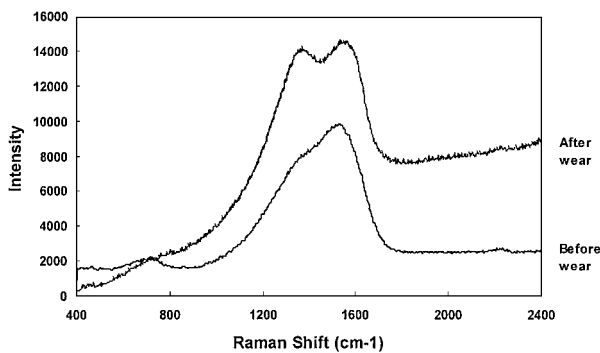


Figure 10 Raman analysis result on the wear tracks showing the micrographitization of this debris layer.

to a low value of 0.2. The significant increase in coefficient of friction was probably due to the abrasive wear (see Fig. 12b) which was caused by the rough nature of plasma nitrided surface (which needs further inves-

tigation). The wear rates for plasma nitrided surface under lubricated conditions were quite large compared with dry sliding conditions, indicating significant abrasive wear due to the flowing away of lubricating wear debris with the body fluids.

Fig. 11c shows the coefficient of friction of  $CN_X$  films deposited directly on Ti-6Al-4V substrate under lubricated condition with body fluids. The initial coefficient of friction was usually rather low (less than 0.1). However, after a long term sliding, the coefficient of friction suddenly jumped to a high value of 0.25–0.3, identical to that of Ti-6Al-4V substrate under lubricated conditions. Observation on the wear tracks revealed a large-area spallation of  $CN_X$  films and severe wear on Ti-6Al-4V substrate (see Fig. 12c). The corresponding wear rates were much higher than those of  $CN_X$  film under dry sliding conditions due to this large area spallation of films and abrasive wear of the substrate (see Fig. 8c).

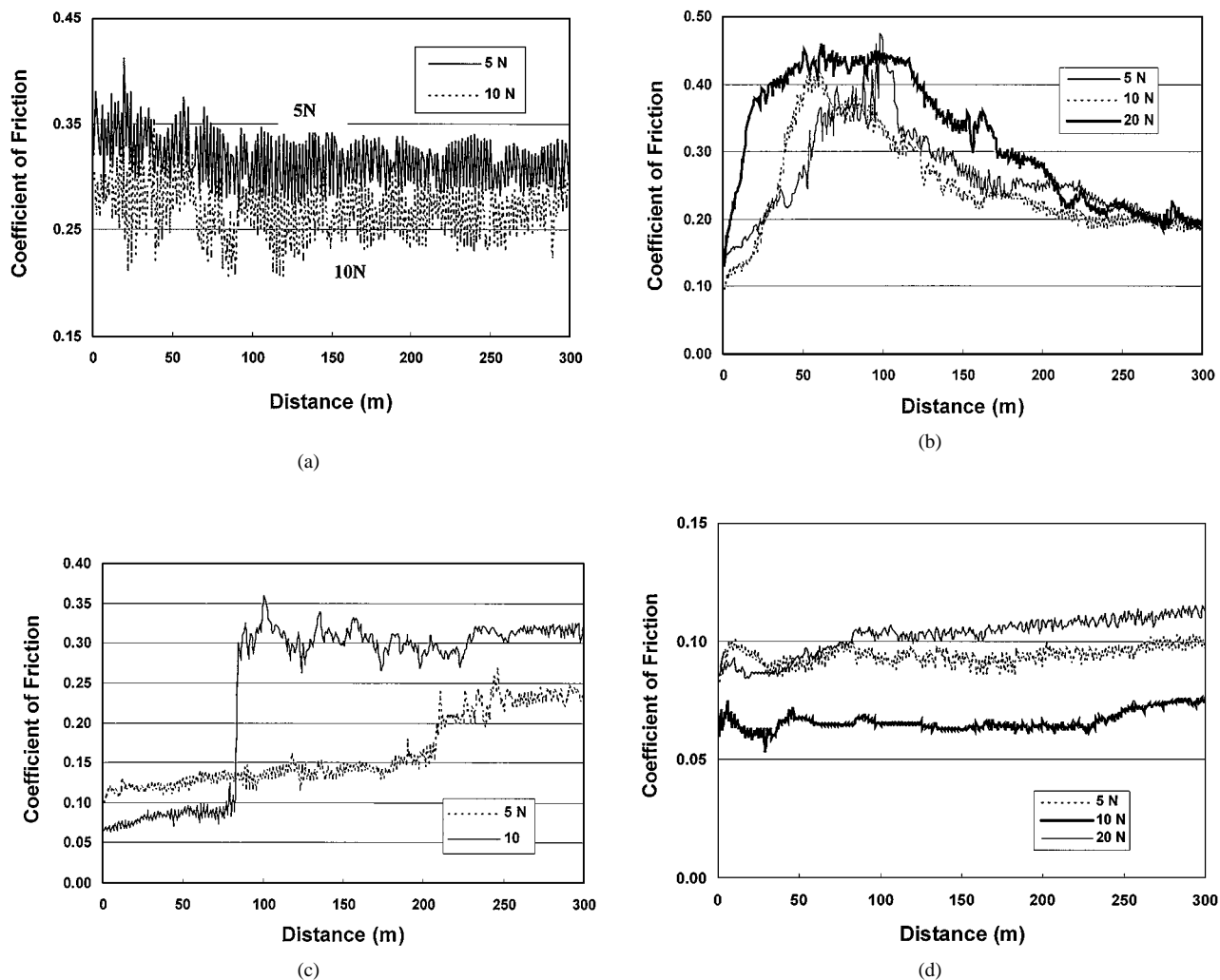


Figure 11 The coefficient of friction of different samples under lubricated sliding condition and different normal loads. (a) Untreated Ti-6Al-4V; (b) plasma nitrided samples; (c)  $CN_X$  film deposited on untreated Ti-6Al-4V; (d)  $CN_X$  film deposited on plasma nitrided Ti-6Al-4V.

Fig. 11d shows the variation of coefficient of friction of duplex treated specimen under different normal loads and lubricated conditions with body fluids. The coefficient of friction of duplex treated coatings was rather low and stable (less or near to 0.1). The wear rates of duplex treated specimen under lubricated conditions were much higher than that of duplex treated coating under dry sliding conditions (see Fig. 8d). The reason is probably due to the flowing of the lubricant, which can carry away the lubricating wear debris and cause the wear of two counterfaces. Fig. 12d shows the surface morphology of the wear track under a normal load of 20 N revealing wear on duplex treated coating.

#### 4. Discussions

From the above results, it can be concluded that the duplex treated system is more effective in maintaining a favorable low and stable coefficient of friction and improving wear resistance than both individual plasma nitriding and individual  $CN_X$  film under dry sliding and lubricated conditions. The excellent tribological performance of duplex treated system could be explained by the following reasons:

(1) Plasma nitriding of Ti-6Al-4V produces a graded hardened case which serves as an excellent supporting layer for the hard  $CN_X$  films.

(2) The  $CN_X$  films deposited at low temperature can produce a wear resistant and low-friction surface without impairing the beneficial effects of plasma nitriding treatment. The decrease in coefficient of friction with the application of  $CN_X$  films on pre-nitrided specimen is probably one of the explanations for the improvement in wear resistance. Smooth and low friction  $CN_X$  films could effectively reduce both the interface stresses and the stresses near the surface thus providing a good tribological behavior [36];

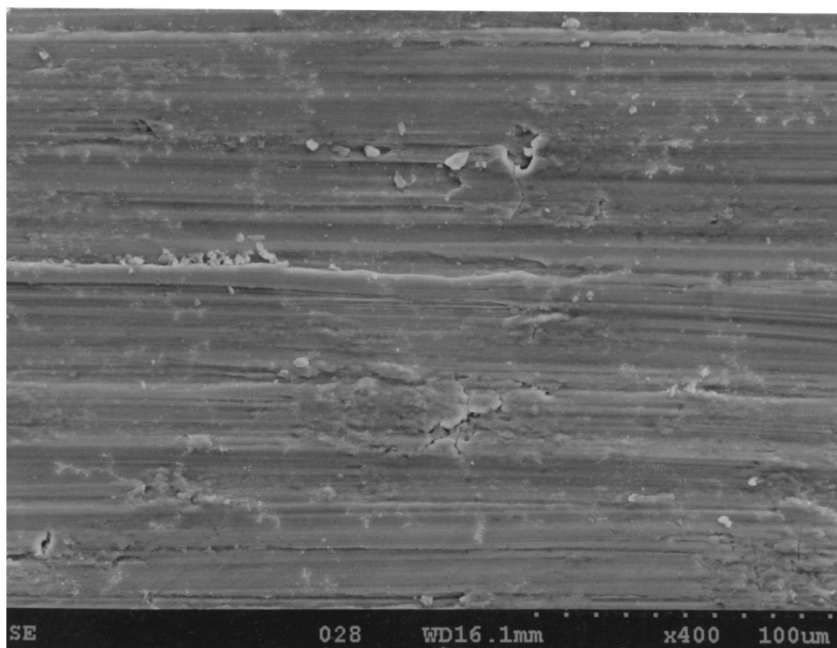
(3) For  $CN_X$  films deposited directly on Ti-6Al-4V substrate, the load bearing capacity was relatively poor thus affecting its tribological performance. With the application of  $CN_X$  films on the pre-nitrided Ti-6Al-4V substrate, the load bearing capacity increased dramatically and therefore the tribological properties could be improved significantly;

(4) For  $CN_X$  films, if small amounts of debris are generated, it can play an important role during wear processes, depending on whether it is soft (graphitic) or hard (diamond-like) and how easily it is ejected from

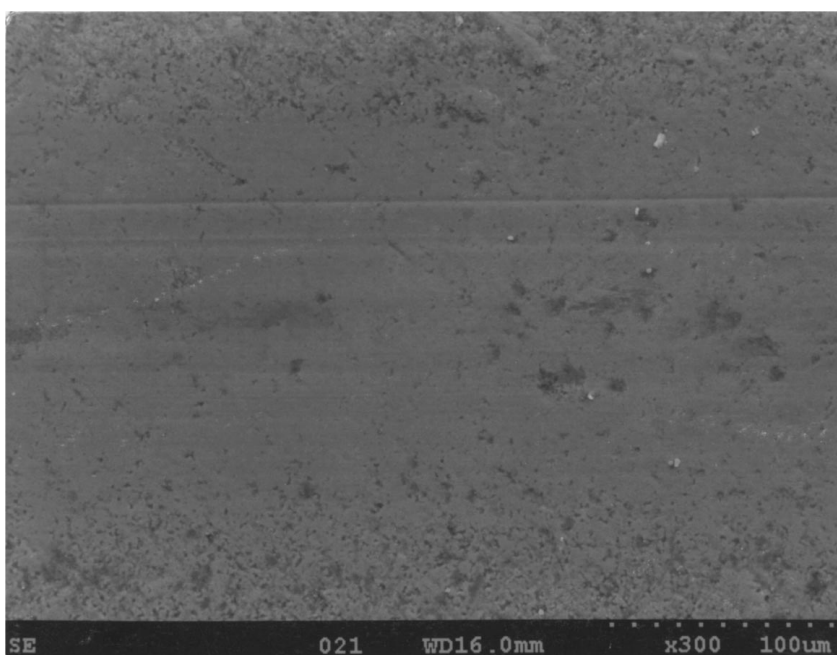
the surface [37]. Raman analysis on the worn coating surface have indicated that the mechanical-chemical interactions between the sliding conterfaces and the environment can lead to micro-graphitization and degradation of the compacted debris layer at the microcontacts. This debris layer has a significant lubricating effect, thus significantly reducing the coefficient of friction and preventing wear of the substrate.

However, under lubricated conditions, when there is small area-spallation of  $CN_X$  films (due to high internal

stresses in thin films, poor adhesion strength with substrate, or high contact stresses during sliding), the fluids could seep into the interface between the film and substrate, thus degrading the interfacial adhesion. The failure mechanism by body fluids appeared to involve the penetration of fluids through the existing small perforations, followed by penetration between  $CN_X$  films and substrate. Due to the flowing of the fluids, the lubricating wear debris was taken away by the fluids, and therefore, the direct contact of two original surfaces resulted in a large wear volume.

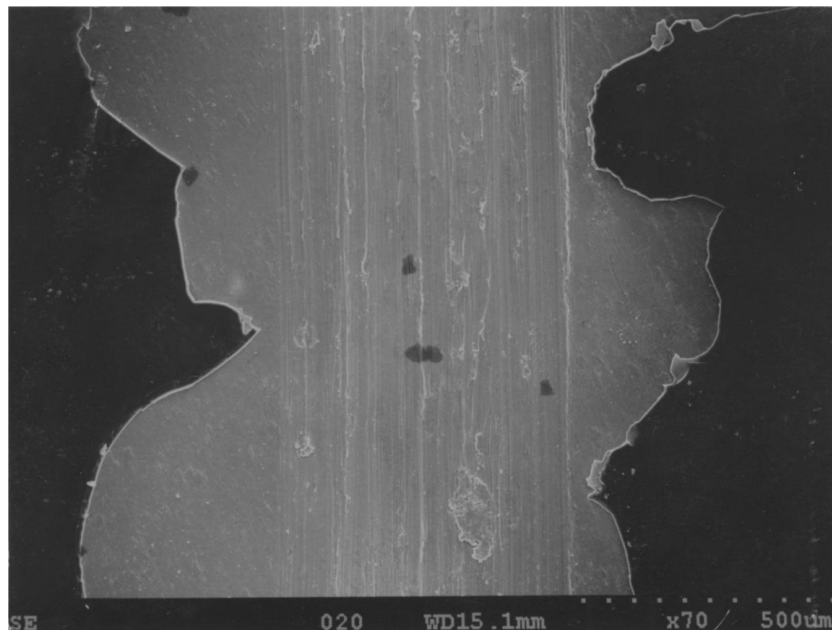


(a)

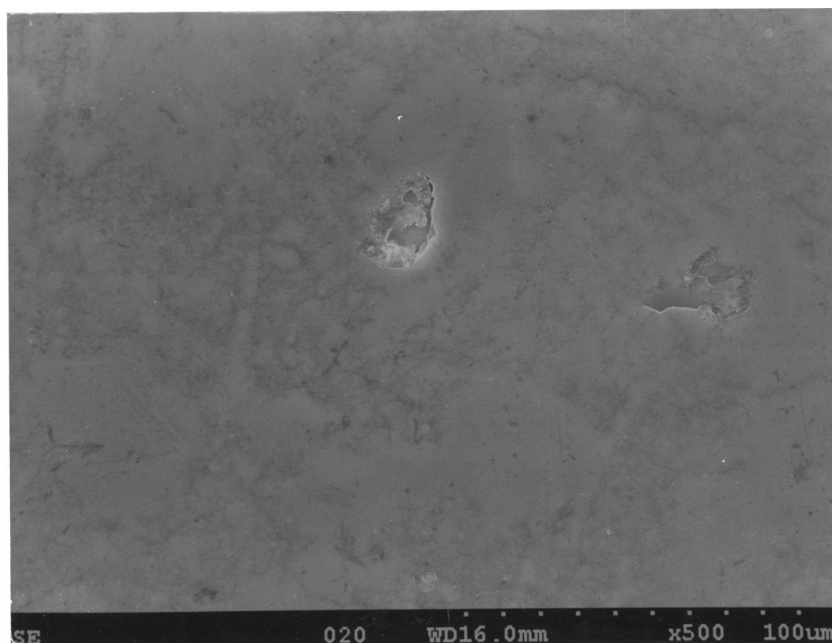


(b)

Figure 12 (a) Extensive adhesive and abrasive wear on worn Ti-6Al-4V under lubricated sliding conditions; (b) Scratching during the beginning period on worn plasma nitrided Ti-6Al-4V under lubricated sliding conditions; (c) A large-area spallation of  $CN_X$  films and severe wear on Ti-6Al-4V substrate on the wear tracks of  $CN_X$  films deposited on Ti-6Al-4V substrate under lubricated condition; (d) The worn surface morphology of the wear track under a normal load of 20 N revealing slight wear on duplex treated coating. (Continued)



(c)



(d)

Figure 12 (Continued).

## 5. Conclusions

The tribological properties of untreated Ti-6Al-4V, plasma nitrided Ti-6Al-4V, carbon nitride films deposited on untreated and plasma nitrided Ti-6Al-4V were studied under different normal loads, dry sliding and lubricated sliding conditions with body fluids. The following conclusions can be derived from the experimental results:

1. TEM and XPS analysis revealed the formation of both amorphous  $CN_X$  and crystalline  $\beta-C_3N_4$  phase in the deposited films. Nano-indentation tests showed that the film hardness was about 18.36 GPa.

2. Both the scratch and indentation tests showed that compared with the  $CN_X$  film deposited on Ti-6Al-4V, the load bearing capacity of  $CN_X$  film deposited on plasma nitrided Ti-6Al-4V was improved dramatically.

3. Ball-on-disk wear tests showed that under both dry and lubricated condition, the duplex treated system was more effective in maintaining a favorable low and stable coefficient of friction and improving wear resistance than both individual plasma nitriding and individual  $CN_X$  film on Ti-6Al-4V substrate. Under dry sliding conditions, the generated wear debris of spalled films was accumulated on the wear track, mechanically alloyed and graphitized, thus significantly reducing the coefficient of friction and preventing wear of the substrate. However, under lubricated conditions, when there is small area-spallation of  $CN_X$  films, the fluids could seep into the interface between the film and substrate, thus degrading the interfacial adhesion and resulting in the spallation of  $CN_X$  films. Due to the flowing of the fluids, the lubricating wear debris was taken away by the fluids, and therefore, the direct

contact of two original surfaces resulted in a large wear volume.

4. The reasons for this significant improvement in tribological behaviors with the application of duplex treatment can be attributed to the combined benefits from both plasma nitriding and  $CN_X$  films: (1) Plasma nitriding of Ti-6Al-4V produces a graded hardened case which serves as an excellent supporting layer for the hard  $CN_X$  films; There is a significant improvement in load bearing capacity with the application of plasma nitrided layer between  $CN_X$  films and Ti-6Al-4V substrate. (2) The  $CN_X$  films deposited at low temperature can produce a wear resistant and low-friction surface without impairing the beneficial effects of pre-plasma nitriding treatment; Smooth and low friction  $CN_X$  films could effectively reduce both the interface stresses and the stresses near the surface thus providing a good tribological behavior.

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