

# Properties and Tribological Behavior of Ti(C,N) Coatings Deposited by Reactive Ion Plating

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Ti(C,N) films have been deposited by reactive ion plating and their tribological behavior against steel in air and in argon atmosphere was characterized. It was very effective to decrease wear rate of steel to coat Ti(C,N). The influence of atmosphere on wear of the Ti(C,N) coatings was studied in the dry sliding of steel pin using a pin-on-disk configuration. The wear rate in air was lower than that in argon atmosphere. The decrease of the sliding wear of the steel disk by applying the Ti(C,N) coating was due to formation and growth of iron-oxide particles on the surface of the coating and high shear strength of the coating. A lot of fine and thin iron-oxides were observed at the sliding surface of the Ti(C,N) coating in air and they were identified as magnetite ( $\text{Fe}_3\text{O}_4$ ). It is suggested that small iron debris is derived from pin and oxidized by the reaction with oxygen in air and a protective oxide particle can be formed by growth of oxide debris. These oxides are considered to insulate steel substrate from steel pin, resulting in decreasing adhesive force between pin and disk. Wear behavior of the Ti(C,N) coatings by changing atmosphere is discussed in comparison with a case of steel pair.

KEY WORDS: Ti(C,N) coatings; ion plating; wear; pin-on-disk; iron oxides; atmosphere.

## 1. Introduction

In recent decades a variety of surface treatment techniques such as physical vapor deposition (PVD), chemical vapor deposition (CVD) and ion implantation techniques have been used in many tribological fields. Physical-vapor-deposited titanium carbonitride (Ti(C,N)) coatings have recently become popular because they are reported to have better tribological properties than titanium nitride (TiN) coatings in certain applications.<sup>1-3)</sup> Although TiN coating is still the most widely used coating in the cutting tools and other wear-resistance applications, Ti(C,N) coating is intended for use in high-performance applications. The selection of an appropriate surface treatment or coating for a given application is becoming more difficult as the number and type of different treatment available commercially expands. In order to enable the selection of the optimum surface coating, knowledge is required, not only of the physical and mechanical properties and the process characteristics of the various coatings available, but also of their tribological performances under the conditions appropriate to the application. The tribological performances could be well understood with their tribological mechanism by changing the factors such as the loading conditions, velocity, lubrication, temperature and atmosphere. Unfortunately, very little of the published data on the tribological behavior of the Ti(C,N) coatings can be reliably compared and discussed by changing

above factors.

It is widely known that friction and wear of materials against steels are affected by atmosphere. However, the effect of atmospheric gas on the phenomenon of wear is not simple. Pepper reported that the atmospheric oxygen increased the coefficient of friction between sapphire ( $\text{Al}_2\text{O}_3$ ) and iron (Fe),<sup>4,5)</sup> interpreted as due to strong interfacial bonds established by reaction of metal oxide with  $\text{Al}_2\text{O}_3$  to form the complex oxide (spinel). Similarly, Shotter has found that iron oxides are formed at the tip of steel pivots in sapphire cup bearings and act as an abrasive to increase the wear of sapphire.<sup>6)</sup> The wear of other ceramic materials such as silicon nitride ( $\text{Si}_3\text{N}_4$ ) and zirconia ( $\text{ZrO}_2$ ) against steel is also increased by increasing the oxygen concentration of the atmosphere.<sup>7-8)</sup>

However, a reverse effect of oxygen on friction and wear is observed for  $\text{SiO}_2$ -glass/Fe and Fe/Fe systems. Hiratsuka indicates that the friction and wear are determined by the oxidation activity (the standard heat of oxide formation) of iron and the relative shear strength of the contact materials.<sup>8)</sup> The sliding behavior between steels has received much attention in recent decades. The importance of oxide films formed in air in the dry sliding of steels has been recognized<sup>9-15)</sup> with respect to decreasing wear. There is general recognition that mild and severe wear regimes exist as pointed out by Welsh<sup>9-10)</sup> and others.<sup>11-17)</sup> Mild and severe wear rates in air differed by about two orders of magnitude.<sup>7)</sup> Many

researchers have associated mild wear with oxide films and severe wear with the absence or destruction of these films. For mild wear, the specific wear rate is less than about  $10^{-8} \text{ mm}^3 \text{ mm}^{-1} \text{ N}^{-1}$ ; for severe wear, the specific wear rate is greater than about  $10^{-6} \text{ mm}^3 \text{ mm}^{-1} \text{ N}^{-1}$ . Lim and Ashby have reviewed published results on the wear of steels from tests done in air with pin-on-disk testing equipment.<sup>13-15)</sup> They have then gathered the data and displayed them on a map in which load and sliding speed are the principal variables. Despite differences in materials, surface condition and equipment used by different investigators, the wear map shows broad patterns of behavior including regimes of mild and severe wear.

Although ceramic hard coatings are intended for use in many tribological fields, their tribological performances are not reliably known as Fe/Fe or ceramics/Fe pairs shown above. The better wear resistance of ceramic hard coatings is believed to relate only to their high hardness. However, other important factors such as formation of oxide films or formation of wear debris can also be associated with wear and friction. In this paper, the effect of Ti(C,N) coatings on the wear of the steel is examined and the influence of atmosphere on the dry sliding of the coatings against steels will be discussed.

## 2. Experimental Details

### 2.1. Substrates and Deposition Process

Alloy tool steel (JIS SKD11; AISI D2) was used for the substrates as the disk material. This was hardened by heating, quenching and annealing in air. The hardness of the substrate was 610–650 HV (loading 1.96 N). A carbon steel (JIS S45C; AISI 1045) was selected as the pin material. Compositions are given in **Table 1**. Prior to coating, the substrates were mechanically polished to an average roughness ( $Ra$ ) less than  $0.1 \mu\text{m}$ .

For the deposition of the Ti(C,N) coatings, reactive ion plating with an electron beam evaporator was used. All substrates were ultrasonically cleaned with ethanol and acetone for 15 min each before coating. The substrate was sputter etched before deposition using an argon pressure of 25 Pa, a current of 0.2 A and a voltage of 500 V for a period of 30 min. Titanium of 99.9% purity was evaporated by using electron beam of the power of 10 kW. The titanium gas was activated and ionized by an ionization electrode. The Ti(C,N) film was deposited on the negatively-biased substrate in a  $\text{C}_2\text{H}_2\text{-N}_2$  gas mixture. Content of carbon in the Ti(C,N) film was controlled by changing the composition of  $\text{C}_2\text{H}_2$  in the reaction gas.<sup>3)</sup> The total pressure was 0.05 Pa, the substrate temperature was held at  $500^\circ\text{C}$ , the deposition time was 60 min. The deposition rate was  $0.1 \mu\text{m}$  per minute, giving a total film thickness of  $6 \mu\text{m}$ .

**Table 1.** Composition of specimen steels. (wt%)

	C	Si	Mn	Cr	Mo	V	Fe
SKD11	1.50	<0.40	<0.60	12.0	1.0	0.3	Bal.
S45C	0.46	0.25	0.75	<0.20	—	—	Bal.

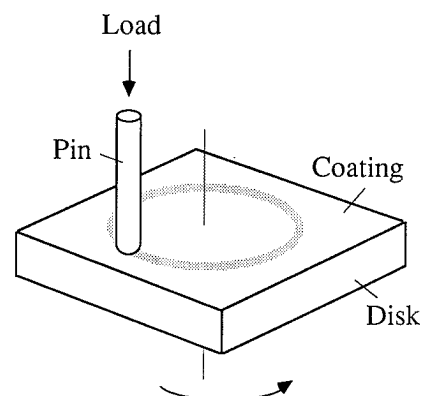
### 2.2. Pin-on-disk Wear Test

The test was carried out on a pin-on-disk type friction test rig using a rounded pin. The schematic of the experimental setup is shown in **Fig. 1**. The pin diameter was 4 mm. The wear track diameter was 20 mm. The test rig was contained in a vacuum chamber. The chamber was evacuated to about 1 Pa by a rotary pump and then argon or dried air was introduced through the leak valve. The test pressure was  $10^5 \text{ Pa}$  (1 atm). The size of the substrate (disk) was  $25 \text{ mm} \times 25 \text{ mm} \times 5 \text{ mm}$ . The disks were coated with TiN, Ti(C,N) and TiC coatings and run against uncoated steel pin. The disk and the pin were degreased by an ultrasonic cleaner prior to the tests. The normal force on the disk was 29 N and the sliding speed was 100 mm/s over a sliding distance of 500 and 1 000 m. The wear was measured from the weight loss and the change of surface roughness of the specimen. Our initial investigation shows that there is a good correlation between the weight loss of the disk or the change of surface roughness and the weight loss of the pin. In this paper, the weight loss of the pin was mainly used to characterize the wear because the weight loss of the pin was much larger and accurate than that of the disk.

### 2.3. Characterization of the Coatings and Wear Surfaces

Fundamental properties of the coatings were characterized by X-ray diffraction analysis (XRD), glow discharge spectroscopy (GDS), electron-probe-microanalysis (EPMA), and scanning electron microscopy (SEM). XRD was performed to analyse phases of the coatings. GDS was used to study the chemical composition depth profile of both the Ti(C,N) coatings and the substrate. EPMA was carried out to analyze the chemical composition of the coatings with a calibration using TiC and TiN standard ceramics. The Vickers Hardness method was used to determine the hardness of the coatings with 0.49 N (50 g) load. The structure of the coatings was studied using SEM and transmission electron microscopy (TEM).

Wear surface was examined by optical microscopy, SEM, Auger electron spectroscopy (AES) and profilometry. Surface microanalysis of wear tracks was carried out using AES. Auger electron spectra were obtained using a 5 keV electron beam with a 100 nA current. Depth-composition profiling was done with 3 kV  $\text{Ar}^+$ .



**Fig. 1.** Schematic diagram of the pin-on-disk wear test apparatus.

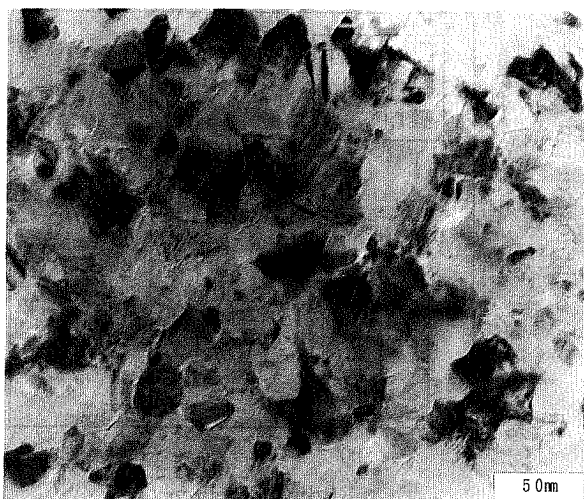


Fig. 2. TEM image of TiN deposited by reactive ion plating.

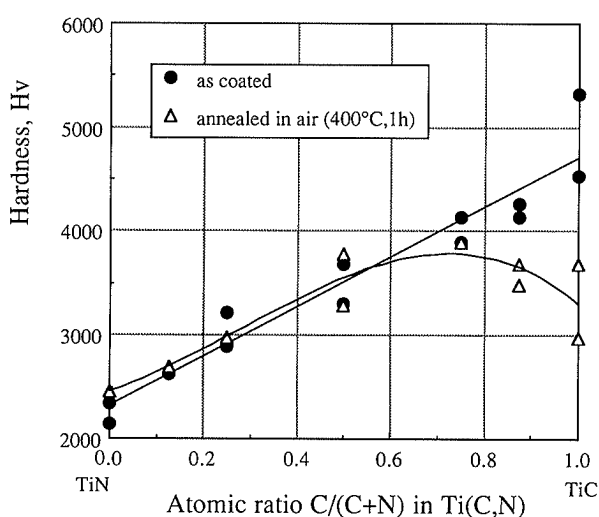


Fig. 3. Vickers hardness values of Ti(C,N) coatings.

The sputter rate of the surface is estimated to be  $10 \text{ nm min}^{-1}$ . In order to reveal the heterogeneity of the oxide composition, particular points of the wear surface were analysed. The selected area ( $0.25 \mu\text{m}^2$ ) was very small compared to the size of many oxide grains. The peak-to-peak amplitudes of the Auger signals of iron (962 eV) and oxygen (505 eV) were used for identification of iron oxides.

### 3. Results and Discussion

#### 3.1. Hardness of the Coatings and Property Correlations

Plots of Vickers Hardness as a function of the composition are shown in Fig. 3. The hardness values between 2100 and 5300 were obtained. The hardness of the Ti(C,N) coatings shows an increase in value with an increase in the carbon content going from pure TiN to pure TiC. TiC exhibited the highest hardness (5300) which was much higher than reported value (2800 HV) of bulk TiC.<sup>18)</sup> PVD-processed TiC and TiN sometimes show such extremely high hardness.<sup>19)</sup> The reasons of high values in hardness could be stoichiometric phase composition, compressive residual stresses, strong growth orientation, and dense and fine microstructure

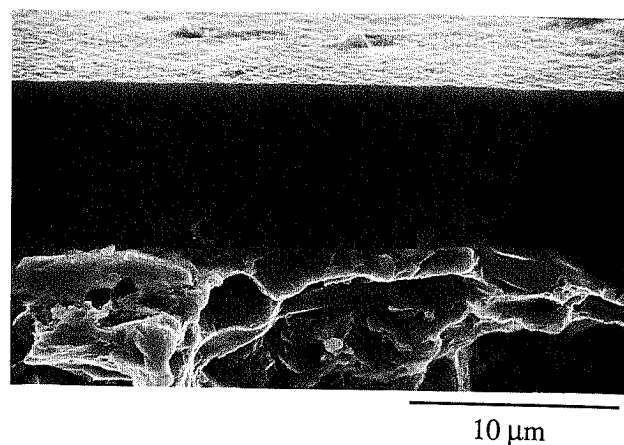


Fig. 4. SEM micrograph of fracture cross-section of the  $\text{TiC}_{0.7}\text{N}_{0.3}$  coatings.

in the Ti(C,N) coatings. Each contribution to the hardness is shown below.

Data of EMPA indicated that the atomic percent of titanium of the Ti(C,N) coatings ranged between 50.1 and 51.1. This showed that the composition of the Ti(C,N) coatings was close to stoichiometric. It has been reported that stoichiometric Ti-N coatings have high hardness.<sup>18)</sup>

The residual compressive stress can increase the coating hardness.<sup>3,20,23)</sup> However, very high residual stresses in a PVD coating can lead to both plastic deformation and microcracking, thus affecting the tribological performance of the coated component detrimentally. In low-temperature PVD coatings like this study, intrinsic growth stresses predominate rather than thermal shrinkage mismatch between the coating and substrate upon cooling from the deposition temperature. The simplest analogy to explain compressive residual stress in PVD is that of "shot peening" which proceeds on an atomic scale by energetic particle bombardment during the growth of the PVD coatings. Compressive residual stresses were detected in the Ti(C,N) coatings and the values were estimated between 4 and 10 GPa by the  $\sin^2 \psi$  method. The values are not extremely high but similar to reported values of TiN.<sup>20)</sup> In the previous study,<sup>3)</sup> the compressive residual stress in the Ti(C,N) coatings could be released by annealing at  $900^\circ\text{C}$  and the hardness values showed 25% decrease.

PVD coatings exhibit a relatively high degree of preferred orientation which may be controlled to a certain extent by process parameters. A direct correlation between the growth orientation and the large variations in hardness of Ti(C,N) has not been shown clearly. However, a (111) texture or a (200) texture in the coatings showed high hardness.<sup>18,24)</sup> X-ray diffraction analysis showed that the Ti(C,N) film had a strong (111)-type texture. Wide  $d$ -values were observed between TiN and TiC, corresponding to Vegard's law. A broadening of the peaks of the Ti(C,N) coatings reported by Hedenqvist *et al.*<sup>20)</sup> was not detected, indicating a small defect density, homogeneous composition or good crystallinity.

SEM examination of a fracture cross-section of the Ti(C,N) coatings revealed a fine, dense fibrous crystal structure within the film and good bonding of the film

to the substrate. This is shown in Fig. 4. At low substrate temperatures such as 500°C, PVD ceramic coatings exhibit a zone I morphology, according to the terminology of Movchan and Demchishin.<sup>21)</sup> This morphology consists of clusters containing a very large number of ultrafine grains that exhibit a tapered crystallite morphology in the growth direction with micro-porosity between the tapered crystallites. Films with such a structure have inferior mechanical properties. In contrast, for substrate temperatures higher than a certain value (520°C for TiC<sup>22)</sup>, the films show fine fibrous structures with relatively superior mechanical properties (Zone II structure). In this study, the Ti(C,N) coatings showing zone II structure could be deposited by the reactive ion plating which enhanced activation and ionization of reaction gases. The grain size is of overwhelming importance in affecting the strength of polycrystalline materials, and hard coatings are no exception. A Hall-Petch relationship should describe the increase in microhardness with the inverse square root of the grain size,  $\Delta H = Kd^{-1/2}$ , where  $d$  is the grain size and  $K$  is a constant. This relationship has been confirmed in PVD metal films.<sup>25)</sup> From TEM micrographs of the Ti(C,N) films, it can be seen that the film is dense with a very fine grain size ranging from 20 to 200 nm (Fig. 2), which is much finer, in two orders of magnitude, than grains of CVD coatings.<sup>23,25)</sup> The PVD methods such as reactive ion plating at lower deposition temperature and high deposition rates impose kinetic limitations on grain growth, thus yielding finer grain size. This causes small change of surface roughness between substrate and coatings. The surface roughness ( $R_a$ ) of the Ti(C,N) coatings was less than 0.1  $\mu\text{m}$  and was independent of composition of the coatings.

It is important to know the temperature dependence of the hardness of coated systems as part of a comprehensive study of the tribological properties of hard ceramic coatings. The temperature of some coated tips is often 1000°C which is sustained for a few minutes during continuous turning, or it may fluctuate between 200 and 700°C within microseconds in interrupted cutting such as milling.<sup>23)</sup> Effect of annealing in air on the hardness of the Ti(C,N) coatings is shown in Fig. 3. The Ti(C,N) coating whose composition was near TiN maintained its room temperature hardness. The samples were annealed in air at 400°C for 30 min after the deposition. However, decrease of the hardness of the Ti(C,N) coating whose composition was close to TiC was significant. This softening of the coatings depended upon the chemical composition and annealing temperature. XRD and GDS analysis showed that TiO<sub>2</sub> (anatase) was formed at the surface of the annealed sample whose hardness is under 1000<sup>35)</sup>HV. The rapid decrease of the hardness of the Ti(C,N) coatings is due to the formation of soft reaction products (TiO<sub>2</sub>) at the surface of the coatings when the annealing temperature is about 400°C. The oxidation should be concerned first for the detrimental annealing during service. The changes in the coating microstructure and the relaxation of residual stresses in the Ti(C,N) coatings with increasing annealing temperature are followed by the oxidation.

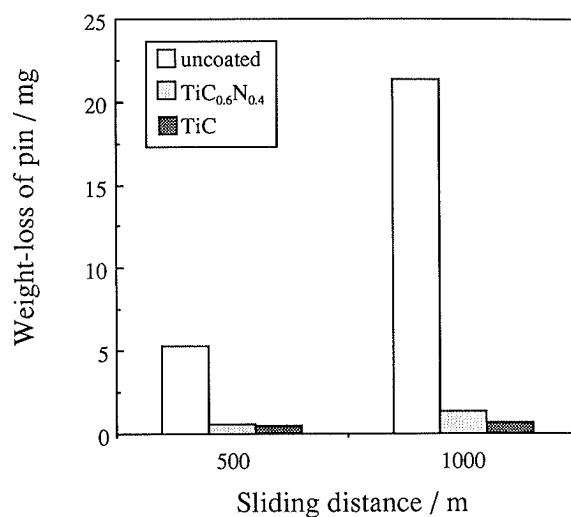
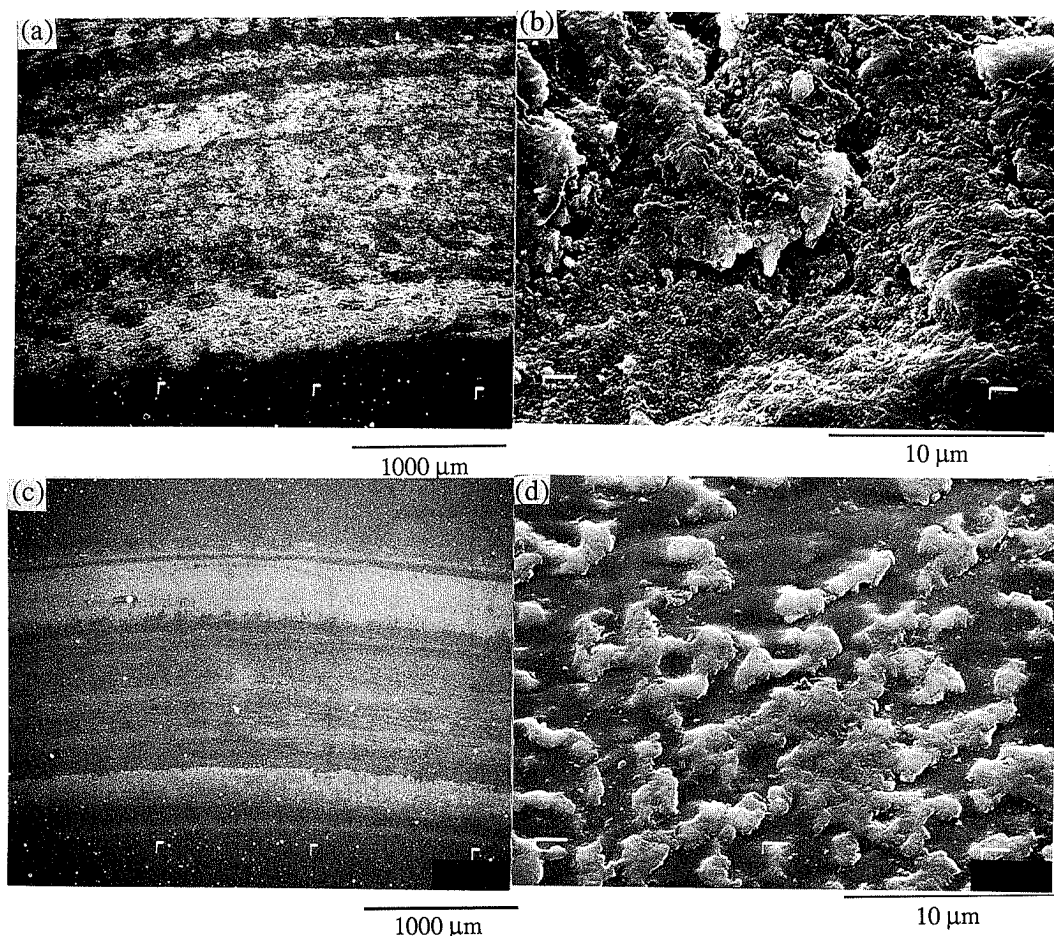


Fig. 5. Results of wear tests in air.

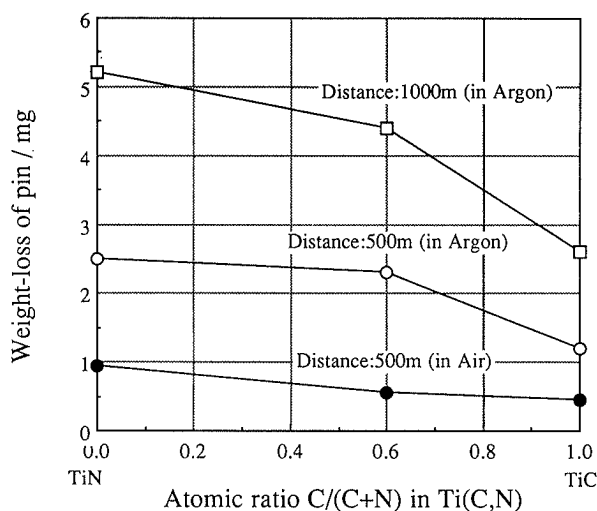
### 3.2. Effect of the Coatings on Wear of Steels

Results of wear tests in air are plotted in Fig. 5. It should be noticed that in these tests the pin was made of carbon steel without any coating and the disk was protected by the Ti(C,N) coatings or the uncoated alloy tool steel. In air at a sliding distance of 500 m, the wear rate of the pin against uncoated steel disk was of the order of  $10^{-8} \text{ mm}^3 \text{ mm}^{-1} \text{ N}^{-1}$ , which corresponds to the mild wear regime. The wear increased with sliding distance. And the Ti(C,N) coatings can effectively decrease the wear of substrate against steel pin. The wear of the coated disk is only 1/10 to 1/5 of the wear of steel couples. Figure 6 shows the wear track of the disks tested in air over a sliding distance of 500 m. Inner side of the wear tracks of (a) and (c) are shown in (b) and (d) in high magnification, respectively. The roughness of the surface of uncoated disk increased from  $R_a = 0.1$  to 0.9  $\mu\text{m}$  whereas the change of the surface roughness of the coated disk was smaller than 0.1  $\mu\text{m}$ . A lot of transfer particles are observed in SEM micrograph in Fig. 6 and the original smooth surface of steel disks was hardly found on the wear track of the uncoated steel disk. AES analysis shows that a lot of iron oxides are detected on the wear track of the coated disk. The Ti(C,N) coatings remained at the wear track on the disk after the wear tests. This indicates that the coatings successfully insulate the steel substrate from the pin. It is noted from the AES analysis that the transfer materials on the wear track came from pin materials (Fe). Chromium and molybdenum, included only in the disk substrate, were not detected in the transfer materials. Effect of composition of the Ti(C,N) coatings on sliding wear against steel pin is shown in Fig. 7. The wear of the Ti(C,N) coatings shows a decrease in value with an increase in the carbon content.

In general, the wear of metals is determined by two factors; one is the adhesive force between two materials, and the other is the relative shear strength of the two materials.<sup>8)</sup> The adhesive force tends to be high between the same metals. And there is a rough correlation between the shear strength and the hardness. Therefore, it can be said that the lower-adhesive and harder substrates are



**Fig. 6.** Wear track of disks tested in air over a sliding distance of 500 m. (a) and (b) are uncoated disks, (c) and (d) are  $\text{TiC}_{0.6}\text{N}_{0.4}$  coated disks. (b) and (d) show inner side of the wear tracks of (a) and (c), respectively.



**Fig. 7.** Influence of atmosphere and composition of the coatings on wear of steel pin.

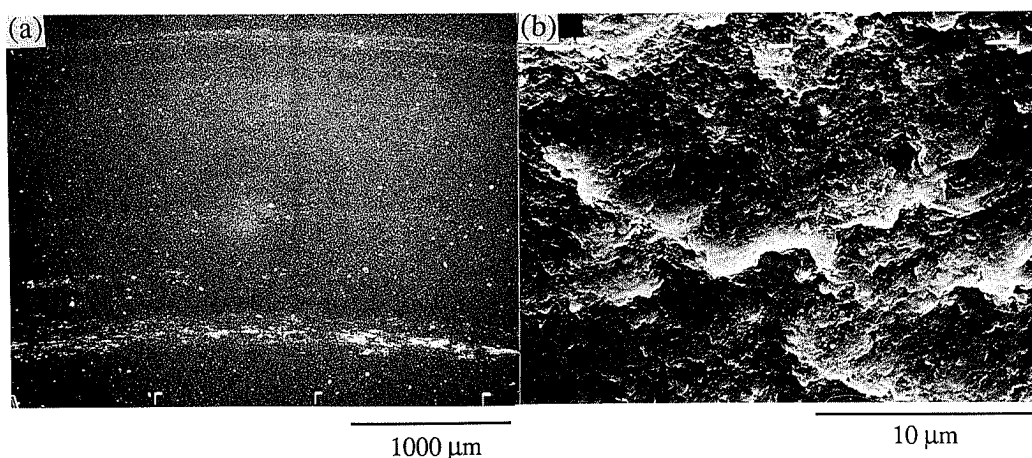
more wear resistant. On the hard surface, deformation of the surface during sliding friction can be limited and oxide particles can grow effectively. It should be noted on wear characteristics of hard  $\text{Ti(C,N)}$  coatings from a view point of oxide formation and growth of the oxide particles at the sliding surface. The importance of oxide films formed in air in the dry sliding of steels has been recognized<sup>9-15</sup> with respect to decreasing wear. Initially, oxides seem to form both on the  $\text{Ti(C,N)}$  coatings and on the steel substrate at the dry friction in air. However, it is thought that harder surface can sustain the fracture

of oxides more firmly. When the oxide films form on the soft steel substrate, the film is pressed to initiate cracks first because the substrate can deform more flexible, then broke up into pieces of oxide and removed from the surface. In this case, the oxides will not successfully insulate the substrate from steel pin, resulting in large friction and wear caused by the strong adhesive force between steel substrate and steel pin.

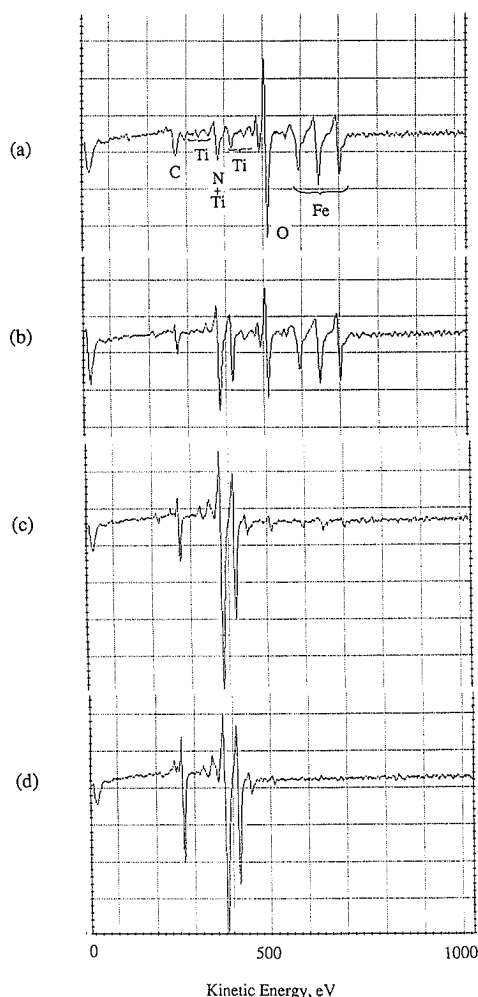
From the results of wear tests and analysis of the wear track by SEM and AES, it is recognized that the wear characteristic was changed by coating the  $\text{Ti(C,N)}$  films, e.g. the wear of the uncoated disk could be characterized by adhesive transfer of pin material and this could be effectively decreased by the hard  $\text{Ti(C,N)}$  coatings with formation of oxides at the sliding surface. The mechanism of the wear and the importance of the oxide-formation to decrease the wear will be discussed next.

### 3.3. Influence of Atmosphere on Wear of the Coatings

Sasada<sup>26)</sup> has proposed that chemisorption of oxygen plays an important role in mild wear of transition metals. This emphasis is consistent with the approach taken in other papers.<sup>27)</sup> The change of wear mode or the difference of wear volume was explained by the effects of atmospheric gas on each metal surface. Sliding tests in air and in argon atmosphere were conducted to study the effects of oxygen on the wear of the coatings. **Figure 7** shows that the sliding wear in air is lower than that in argon atmosphere. Iron oxides formed on the wear track in air (Fig. 6(d)) were seldom found on the surface of the coatings tested in argon atmosphere. And a lot of transfer

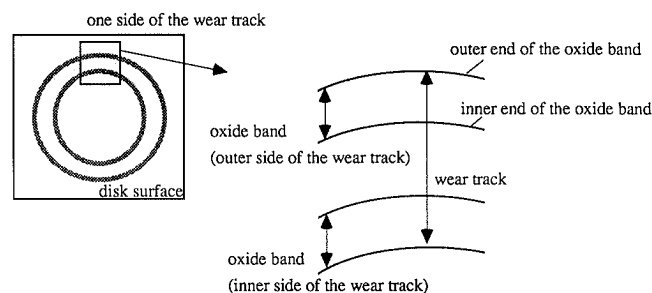


**Fig. 8.** Wear track of the  $\text{TiC}_{0.6}\text{N}_{0.4}$  coated disks tested in argon atmosphere. (a) one side of the wear track, (b) inner side of the wear track showing in high magnification.



**Fig. 9.** AES analysis of the  $\text{TiC}_{0.6}\text{N}_{0.4}$  coated disks tested in air. (a) as coated, (b) sputtered for 3 min, (c) sputtered for 10 min, (d) sputtered for 30 min.

materials were found on the surface from the SEM image as shown in **Fig. 8**. It is suggested that formation of oxides in air can decrease the wear of the coatings. However, in the wear of ceramics such as silicon nitride<sup>7)</sup> and alumina<sup>4,5)</sup> against steel, oxygen is shown to be a detrimental factor. Pepper<sup>4,5)</sup> reported that the generation of metal oxide by oxygen exposures resulted in an increase in friction, interpreted as due to strong interfacial bonds established by reaction of metal oxide with  $\text{Al}_2\text{O}_3$  to form complex oxide ( $\text{FeAl}_2\text{O}_4$ ). Effect of



**Fig. 10.** Schematic of the wear track of the coated disk tested in air.

oxygen on wear should depend on physical and chemical characteristic of oxides formed at the sliding interface.

Oxides found on the wear track tested in air were identified as  $\text{Fe}_3\text{O}_4$ . The importance of oxide has been emphasized in the dry sliding of steels.<sup>9-15)</sup>  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$  (magnetite) were reported to be beneficial and  $\text{Fe}_2\text{O}_3$  (hematite) was detrimental.<sup>16)</sup> This difference may be due to shear strength or hardness of each oxide. The Vickers hardness of polycrystalline  $\text{Fe}_3\text{O}_4$  is about 560 and that of  $\text{Fe}_2\text{O}_3$  is about 755. Quinn<sup>12)</sup> and many others have assumed that particular oxide present is the one which would be present at thermodynamic equilibrium, *i.e.*  $\text{Fe}_2\text{O}_3$  at lower temperatures,  $\text{Fe}_3\text{O}_4$  at intermediate temperatures and  $\text{FeO}$  at higher temperatures, depending upon pressure of oxygen. Oxides could insulate steel substrate from steel pin or flow plastically, resulting in decreasing adhesive force between contact materials. The mechanism of decreasing the wear of the  $\text{Ti}(\text{C}, \text{N})$  coatings in air could be similar to the case of steel pair with formation of  $\text{Fe}_3\text{O}_4$ .  $\text{FeTiO}_3$  and  $\text{TiO}_2$  were reported<sup>30,31)</sup> as wear particles in the sliding of steels on  $\text{TiN}$  coated disks. However, these could be derived from metallic titanium which deposited during  $\text{TiN}$  deposition in the case of unstable arc-evaporated process.<sup>32)</sup> It is reasonable to assume that, in the case of low quality surface finish, the formation of titanium oxide was a result of excessive oxidation of the surface of the metallic titanium due to the combined effects of frictional heating and the shearing action within the contact area.

AES analysis indicated that the oxides were not complex oxides including titanium, carbon and nitrogen, but almost pure  $\text{Fe}_3\text{O}_4$ . Therefore, it is concluded that the iron oxides form at the sliding surface by the chemical

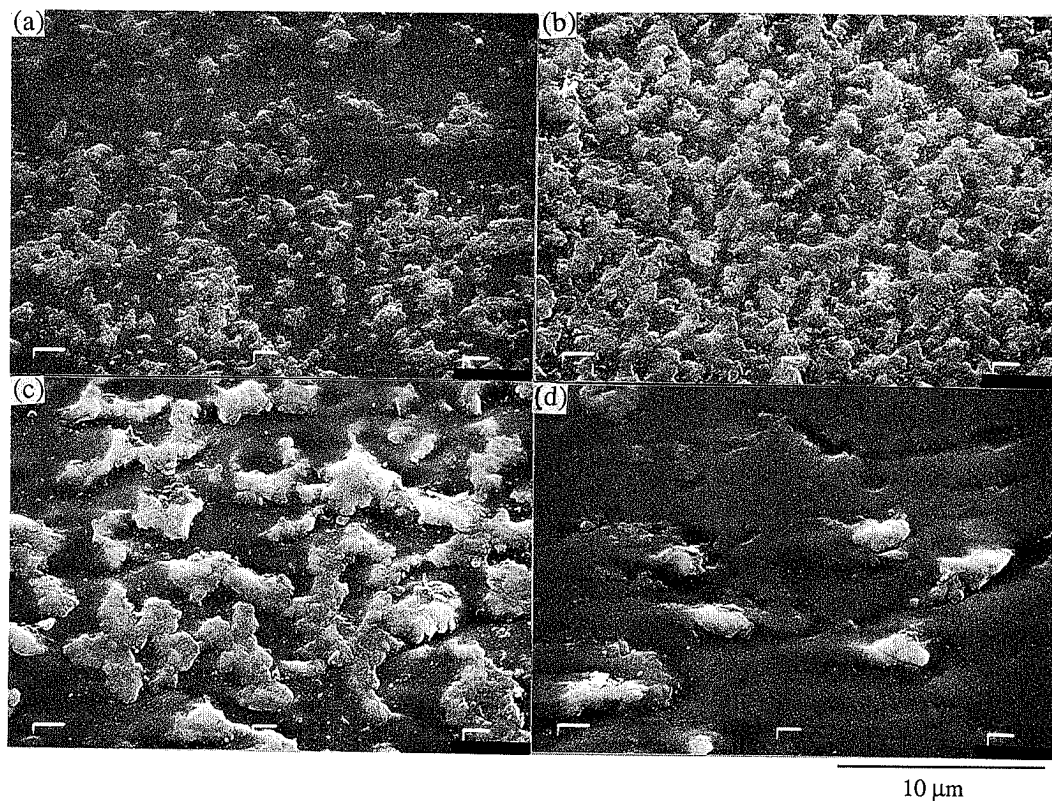


Fig. 11. SEM image of the oxide band in the wear track of the coated disks tested in air. (a) outer end, (b) outer side, (c) inner side, (d) inner end of the oxide band.

reaction between iron originated from pin material and oxygen in atmosphere. The large wear of pin could be due to the big difference of shear strength between the coatings and steel pin in this wear test. Such difference of shear strength of contact materials may be more practical for industrial applications.

Outside of the wear track of the samples tested in air was different from inside of the wear track. Oxide band was found at the outer side and at the inner side of the wear track as schematically shown in Fig. 10. Gradual changes in grain size of the oxides were observed in this band. Figure 11 shows that the fine oxides smaller than  $0.5\ \mu\text{m}$  in lateral diameter around the outer end of the oxide band (Fig. 11(a)) and oxide particles of larger grain size of  $2\ \mu\text{m}$  at the inner side of the band (Fig. 11(c)). Around the inner end of the oxide band (Fig. 11(d)), small scratches were observed at the surface of the coatings. It is suggested from above observation that iron debris particles are derived from pin and these are oxidized and a protective oxide particle can be formed by growth of oxide debris, not by derivation of oxide films grown at the wear surface. The grain growth of the oxide particles could be limited around the center of the sliding track by the break and removal of oxide particles, which reach a critical size.

Temperature should be an important factor to promote the oxidation at the sliding surface. When two surfaces slide together, most of the work done against friction is turned into heat. The resulting rise in temperature may modify the mechanical and metallurgical properties of the sliding surfaces, and it may cause oxidation. The frictional heat could be generated at the tiny contact areas. The instantaneous temperature ("flash temperature") of these contact points is obviously higher than the average temperature ("bulk temperature") of the

surface.<sup>13-15</sup> As already shown oxides were found on the Ti(C,N) film whose composition was close to TiC at  $400^\circ\text{C}$ . At  $100\ \text{mm/s}$  the flash temperature is calculated near  $150^\circ\text{C}$  for steel surfaces. This temperature is not high enough to oxidize the Ti(C,N) coatings or to oxidize steel substrate, but may be enough to oxidize sub-micron iron particles. It should be noted that the oxides were forming not film but very thin particles in each sliding distance. The thickness of the thin particle ranged from  $100$  to  $200\ \text{nm}$  which was estimated based on the sputtering time to get no oxygen peaks in AES analysis as shown in Fig. 9. Figure 9 also indicates that iron oxides form on the surface of the coatings and the coatings successfully insulate the steel substrate from the pin during sliding friction.

The grain growth of the oxide particles could be limited around the center of the sliding track by the break and removal of oxide particles, which reach a critical size. Oxidation could occur very rapidly for sub-micron particles.<sup>16,28</sup> Small wear particles about  $100\ \text{nm}$  were not unusual in mild wear.<sup>29</sup>  $\text{Fe}_3\text{O}_4$  depends on grain boundary diffusion for continued growth, therefore it grows faster if the oxide is fine-grained. Of course, sliding can modify the oxidation kinetics in a number of ways. It can be stated that local oxidation kinetics of wear debris plays more important role in formation of oxides at the contact surfaces than average thermochemical equilibrium.

The flush temperature depends strongly on sliding velocity and thermal conductivity of the surface, but hardly at all on load. The presence of the Ti(C,N) coatings increases the flush temperature by increasing the resistance to heat flow. Thermal conductivity of TiN is  $19\ \text{W}/(\text{m}\cdot\text{K})$ ,<sup>33</sup> which is much lower than that of Fe ( $80.4\ \text{W}/(\text{m}\cdot\text{K})$ <sup>34</sup>). The high flush temperature promotes

the oxidation reaction. This could be another reason that oxide formation was observed more abundantly on the surface of the Ti(C,N) coatings than on the steel substrate.

#### 4. Conclusion

The hardness of the Ti(C,N) coatings has shown an increase in value with an increase in the carbon content going from pure TiN to pure TiC. The reasons of high values in hardness could be stoichiometric phase composition, compressive residual stresses, strong growth orientation, and dense and fine microstructure in the Ti(C,N) coatings. The coatings obtained by reactive ion plating have shown a fine, dense fibrous crystal structure and good bonding of the coatings to the substrate.

The wear of the uncoated disk could be characterized by adhesive transfer of pin material and this could be effectively decreased by the hard Ti(C,N) coatings. The decrease of the sliding wear of the steel disk by applying the Ti(C,N) coating was due to formation and growth of iron-oxide particles on the surface of the coatings and high shear strength of the coating. Oxides found on the wear track were identified as Fe<sub>3</sub>O<sub>4</sub>. It is suggested that small iron debris is derived from pin and oxidized by the reaction with oxygen in air and a protective oxide particle can be formed by growth of oxide debris. These oxide particles are considered to insulate steel substrate from steel pin, resulting in decreasing adhesive force between pin and disk.

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