Improvement of Friction and Wear Performance of Titanium Nitride Films by Chlorine Ion Implantation

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TiN films were prepared on high speed tool steel substrates by means of hollow cathode discharge ion plating, and were implanted with chlorine ions at doses from 1×10^{20} to $1 \times 10^{21} \text{ m}^{-2}$ to improve tribological properties. Friction and wear tests were carried out on a pin-on-disk tribometer with type 304 stainless steel ball as the counter material.

The structure of the surface layers modified by ion implantation was characterized by X-ray diffraction analysis (XRD). X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical bonding states and the depth distribution of elements in surface layers of TiN films. Surface observation and chemical composition analysis of the wear track were also carried out by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX), respectively.

The chlorine ion implantation significantly reduced the friction coefficient of the TiN films against the stainless steel balls. The wear mode has drastically changed from adhesive wear to abrasive wear by this Cl-implantation to the TiN film. With increasing Cl dose, not only the friction coefficient but also the wear volume of the stainless steel balls were reduced. This implies that the implanted chlorine prevents the adhesion of the counter material, resulting in the significant reduction of the friction coefficient.

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I. Introduction

TiN film coating has been successfully applied to industrial tools as the wear-resistant layer on cutting tools and die tools. In the recent trend, TiN films are to be also used for tribological parts and members in the automobiles: piston-rings⁽¹⁾ and cam followers⁽²⁾. The problem to be noticed there is that the friction coefficient of TiN against commercial steels is not always low. Sometime TiN coatings suffer from severe adhesion of counter part materials. As the first method to improve these tribological properties, or, to reduce the weight of loss by wear and friction, addition of carbon into TiN, to form (TiCN) film, was made by the ion plating⁽³⁾: resulting in better performance in wear compared to them as-deposited TiN film. For further improvement of tribological properties, it is necessary to find a new additive element adaptive to TiN.

Authors have proposed the active use of an ion implantation technique to simulate the surface-modification effect on the tribological behavior of thin and thick coating materials. In the literature⁽⁴⁾⁻⁽⁸⁾, it was found that (1) Al addition by the ion implantation should reduce the oxidation rate of TiN films at the initial stage of oxidation, and, (2) oxidation behavior of that surface-modified TiN films should be closely resembling to that of the TiAlN films. With respect to the tribological properties of these thin and thick films, there are relatively many studies in the literature: (1) Ion implantation

by nitrogen⁽⁹⁾⁻⁽¹²⁾, (2) Carbon implantation into TiN films⁽¹³⁾⁻⁽¹⁵⁾, and (3) Metallic element implantation into TiN films⁽¹²⁾. The common features to those implantation techniques are: (1) Precipitation of the hard compounds into the surface layer, and (2) Implantation-induced residual stresses in compression.

In order to satisfy the requirement of more advanced tribological properties for the automobile part or turbines, however, new alternative concept must be introduced in the ion implantation. Authors have proposed new implantation methodology of light element (D) and halide elements (F, Cl, ...) aiming for structure material control to attain low friction state in the reduced abrasive wearing mode.

In the present paper, the chlorine ion implantation is employed as the first antidote processing to investigate the effect of surface material control on the tribological behavior. At first in this study, ion-plating technique was utilized to yield the TiN films deposited on the steel substrate as the targeting sample. Then, the ion-implantation was performed by varying the implanted chlorine dose. For comparison to Cl-implantation, argon was also implanted into the same TiN film. In order to quantitatively describe the tribological behaviors of unimplanted and implanted TiN film deposited, the pin-on-disk tribometer was used. Through direct comparison of the kinematic friction coefficient and the wear volume of the counter material, the preference to the chlorine implantation was verified with reference to Ar-implanted and the unimplanted TiN films.

II. Experimental

The experimental procedure in the present study was summarized in **Fig. 1**. The sintered high speed tool steel, after hardening and mirror-polishing by diamond powder, was used as a substrate, the dimensions of which are: 25 mm in diameter and 4 mm in thickness. The substrate was cleaned by Ar ion bombardment for preparation of TiN film coating. TiN film was physically deposited by using a manufacturing-type hollow cathode discharge ion plating in thickness of approximately 2 μm at temperatures of 673–723 K.

The chlorine ions were implanted into the surface region of the films subsequent to the above TiN film preparation, using a manufacturing-type implanter. **Table 1** summarized the standard capability of the present Cl-ion implanter. In the Cl-ion implantation, the Cl-doses were varied by 1×10^{20} , 2×10^{20} , 5×10^{20} and $1 \times 10^{21} \text{ m}^{-2}$ for a constant implantation energy of $1.6 \times 10^{-14} \text{ J}$ (100 keV). For generation of Cl ion beams, AlCl_3 was utilized as an ion source. The vaporized molecular gas was mass analyzed and selected to yield the single-charged Cl ions for implantation. As for a reference to Cl-ion implantation, Ar was also implanted into the TiN film with the dose of 5×10^{20} and $1 \times 10^{21} \text{ m}^{-2}$ by an energy of $1.6 \times 10^{-14} \text{ J}$ (100 keV). The sample temperature was not controlled; the temperature in the sample holder did not exceed 450 K during implantation by the typical ion beam current density, ranging from

3×10^{-10} to $4 \times 10^{-10} \text{ A/m}^2$.

The friction and wear testings were performed by a pin-on-disk tribometer for the ion-implanted samples. The austenitic stainless steel balls of type 304 with the diameter of 6 mm were used as a counter material. The normal load was controlled to be constant by 2 or 5 N, and relative sliding speed to be 0.01 m/s. No lubricants were added onto the ball-substrate interface at the room temperature in air. The friction coefficient was defined by the following equation:

$$\mu = Ft/L, \quad (1)$$

where μ is the friction coefficient, Ft the tangential traction and L the normal load.

X-ray diffraction analysis (XRD) was used to identify the structure of the Cl-implanted films. For the wear track evaluation, scanning electron microscope (SEM) observation and energy dispersive X-ray spectroscopy (EDX) analysis were carried out. X-ray photoelectron spectroscopy (XPS) with the $\text{MgK}\alpha$ for the excitation X-ray source was used to analyze the chemical bonding state and the depth distribution of elements in the surface layers of the TiN films, with the Ar ion sputtering at an energy of $3.2 \times 10^{-16} \text{ J}$ (2 keV).

III. Results

Figure 2 compares the XRD profiles between the Cl-implanted and the unimplanted TiN films. The profile from the Ar-implanted TiN film is also included in this figure for reference. Just as the as-deposited TiN film, no peaks other than TiN single phase can be seen in the XRD profile for the Cl implanted TiN film; no alloyments, no compounds nor precipitations were synthesized by this Cl-implantation. Although TiN peak intensity was reduced with increasing the Cl-ion dose, little or no peak shift was recognized with comparison to the XRD profile for the unimplanted TiN film. To be noted, the same XRD profile was also obtained for the TiN film implanted with $1 \times 10^{21} \text{ m}^{-2}$. Hence, the implanted Cl atom might be present as an interstitial solute atom into TiN structure without any significant change of TiN lattices.

The depth profiles of the Cl-implanted TiN film by $1 \times 10^{21} \text{ m}^{-2}$, were measured by XPS together with Ar ion sputtering of the samples. As shown in **Fig. 3**, the implanted chlorine atoms distribute in a Gaussian-like profile in the surface of the TiN film. The chlorine concentration becomes maximum at the inside of the TiN film; it reaches 4 to 5 mol% at the sputtering time of 240 s. As had been explained in Ref. (16), it is rather difficult to quantitatively determine the penetration depth of implanted ions from the material surface since the sputter rates depend on the surface material and its chemical states. The Monte-Calro simulation something helps us to estimate the average projection range of the implanted element. As depicted in **Fig. 4**, using TRIM code⁽¹⁷⁾, the average projection range ($\bar{R}_p$) and the maximum penetration depth (R_{max}) were estimated by $\bar{R}_p = 60 \text{ nm}$

Fig. 1 A flow of the present experimental procedure.

Table 1 Capabilities of the Cl-ion implanter.

Ion source	Freeman type
Ion species	Gas or metal
Vaporize temperature	Up to 873 K
Mass separation	Static magnetic field
Accelerating voltage	Up to $2.88 \times 10^{-14} \text{ J}$ (180 keV)
Ion beam current	Up to 300 μA
Irradiation size	50 mm square
Target chamber pressure	1 to $1.5 \times 10^{-5} \text{ Pa}$

Fig. 2 X-ray diffraction patterns of TiN films implanted with and without Cl.

Fig. 4 Calculated depth profile of Cl implanted into TiN at energy of 100 keV.

Fig. 3 XPS depth profiles of constituent elements (Ti, N and Cl) with O and C for Cl-implantation into TiN film by 1×10^{21} Cl/m².

and $R_{\max} = 130$ nm, respectively. To be noticed, it is assumed that TiN coating has bulk density and no surface damages were introduced in this calculation; further fundamental studies are still necessary for quantitative estimation of $\bar{R}_p$ and $R_{\max}$.

The binding energy of Cl was estimated to be approximately 3.2×10^{-17} J (200 eV) from the Cl_{2p} spectrum. This value is close to the binding energy for inorganic chlorides rather than that for metal chlorides. Being compared with the standard spectra⁽¹⁸⁾, the binding energy of Cl is 3.198×10^{-17} J (199.9 eV) from the Cl_{2p} spectrum for the poly-vinyl-chloride.

The oxygen content in TiN film decreases rapidly and becomes a constant concentration of approximately 10 mol% at the inner region. High concentrations of O near the film surfaces are probably caused by the natural oxidation of TiN with atmosphere at room temperature. The oxygen concentration at the inner regions are considered to be in the contaminate level during the film deposition since 10 to 15 mol% of O is also included in the unimplanted films prepared by the ion plating. Car-

bon was detected only at the top of the TiN film surface. Although the formation of carbon layer was reported for the C-implanted TiN film⁽¹¹⁾⁻⁽¹³⁾, the measured carbon distribution is typical to the surface contaminant.

The kinematic frictional behavior, or, the variation of the friction coefficient (μ) against the threading stroke is a very important relation to determine the quality of surface structure. Figure 5 depicts the effect of Cl-implantation on this kinematic friction behavior of TiN film against the stainless steel ball with the reference to both unimplanted and Ar-implanted TiN films. The unimplanted TiN film shows high friction coefficient from the beginning to the end of the measurement, having nothing to do with the applied normal load. On the other hand, Cl-implantation has drastically changed this kinematic friction behavior. When the Cl-implantation dose is 1×10^{20} m⁻², although the friction coefficient is high at the initial stage, μ gradually decreases from 1.2 to 0.1–0.2 with the threading stroke. With increasing the Cl dose, this transition duration is reduced, and, diminished on the TiN film implanted by 1×10^{21} m⁻². In the case of Cl-implanted TiN film by 1×10^{21} m⁻², the wearing mode becomes stationary from the beginning, and the friction coefficients is nearly constant by 0.1–0.2. This value of the kinematic friction coefficient is thought to be corresponding to the typical stationary wearing of TiN film in dry circumstance. Even at the same dose, when Ar was implanted into TiN film, its kinematic friction behavior becomes in great contrast to that in the case of Cl-implantation. No reduction of friction was seen although the threading distance, and, its value was the same as the unimplanted case. This reveals that Cl ions are preferable species to drastic reduction of frictions.

The above noticeable change of frictional behavior is thought to reflect on the wearing mode on the surface of metals. Figure 6 shows the microscopic view of the wear track after kinematic friction with the stainless steel ball on the unimplanted and the Cl-implanted TiN film by 1×10^{21} m⁻², respectively. The dark regions were ob-

Fig. 5 Friction coefficient of TiN films against stainless steel ball implanted with (a) (b) Cl and (c) Ar. Normal load is (a) 2N and (b) (c) 5N. Relative sliding speed is $v=0.01$ m/s.

served in the wear track of the unimplanted TiN film; Fe and Cr were detected from those regions, being accompanied with a small amount of O by the EDX measurement. This suggests that the adhesion of the counter material (stainless steel) occurred, and, its constituent elements were printed onto the surface of the target materials. The same adhesion behavior was observed on the TiN film implanted with Ar. Then, the implanted Cl into the surface of TiN film should have a significant influence on the reduction of friction coefficient.

The wear mode of the unimplanted and Ar-implanted TiN films against the stainless steel balls is considered to be in adhesive wearing. On the other hand, only small amount of wear particles is observed in the wear track of the Cl-implanted TiN film by $1 \times 10^{21} \text{ m}^{-2}$. From this wear track, Ti, N and Cl were detected. Hence, the wear mode of the Cl implanted TiN film is considered to be in abrasive wearing.

This drastic change of the wear mode accompanies with large reduction of friction coefficient. Due to this effective Cl-implantation, the adhesive wear mode might change itself to the stationary abrasive wear of the Cl-implanted TiN, where the loss of weight must be suppressed to the minimum level.

IV. Discussion

Although the mass of Ar and Cl is close to each other in the periodic table of elements, the friction and wear properties were quite different between Ar- and Cl-implanted TiN films. This change in the wear mode of TiN films should never be attributed to radiation defects by amorphalization or formation of vacancies induced through the ion implantation. Wear reduction was reported on the Cl ion implantation into the cemented carbide cutting tools for machining the titanium alloy⁽¹⁹⁾, but the wear mechanism was not discussed. In order to make quantitative discussion on the kinematic friction

Fig. 6 Scanning electron micrograph of wear track after friction with stainless steel ball: (a) unimplanted TiN film and (b) $1 \times 10^{21} \text{ Cl/m}^2$ implanted TiN film.

behavior in wearing, let us here calculate the wear volume of stainless steel ball and evaluate its change with the Cl dose. The wear volume of stainless steel ball was calculated by the following equation:

$$v = \pi d^4 / 64r, \quad (2)$$

where v is the wear volume of stainless steel ball, d the diameter of wear flat and r the radius of a stainless steel ball.

Figure 7 shows the wear volume change of stainless steel ball taken after 50 m sliding in the friction tests with the normal load of 5N and the relative sliding speed of 0.01 m/s. The wear volume of stainless steel ball for the Cl-ion implanted TiN films reduces significantly with increasing the Cl dose. On the other hand, the lower dose Cl-implantation and the Ar implantation have nothing to do with the reduction of wear volume. These results agree with the changes of the friction coefficient in the friction tests.

Let us here make comments in the chlorine-effect on the tribological behavior. Empirically, adhesion of Cl in the chemical compound was found to be effective in reduction of the friction coefficient. In fact, Cl was an effective additive agent of the extreme pressure lubricant in the form of $C_nH_{(2n+2-m)}Cl_m$; under the presence of this type of lubricant, the friction coefficient is always reduced to 0.05–0.1⁽²⁰⁾. Remember from XPS analysis that the implanted Cl is present as an agent in the molecular compound.

Then, the implanted Cl is thought to behave as an extreme pressure agent on the interface between TiN film and stainless steel ball in friction. As illustrated in Fig. 8, since the surfactant agent in chiding Cl ions plays as a lubrication buffer material to unburden the direct contact of the counter material on the TiN film, no adhesion takes place and loss of weight in wearing is minimized.

In case when the above mechanism really works to reduce severe wearing, their agents must be included in the wear particles. In fact, Cl-ions were detected by EDX

Fig. 7 Wear volume of stainless steel ball after friction tests.

Fig. 8 A schematic drawing of the Cl-implanted TiN film surface.

(a) Scanning electron micrograph

(b) Elements detected from wear particle

Fig. 9 Result of analysis by SEM and EDX for wear particle on stainless steel ball tested against with $1 \times 10^{21} \text{ Cl/m}^2$ implanted TiN film. (a) SEM image around contact point and (b) EDX spectrum obtained from arrow indicated in micrograph.

analysis of wear particles in the friction test of the Cl-implanted TiN films, as shown in Fig. 9. Furthermore, since TiN film might be in the indirect contact with the counter material, the wear mode of the TiN films changes from the adhesive wear to the abrasive wear by the Cl ion implantation, resulting in high improvement of the friction and wear properties. The topographic measurements were performed for the wear track of the Cl-implanted TiN films by a Talysurf profilometer. The depth (D) of wear tracks was 300–400 nm after the friction tests. Since D is deeper than the average projection range ($\bar{R}_p$ 60 nm) and the maximum penetration depth ($R_{\max}$ 130 nm) of the Cl ions into TiN calculated by TRIM code. Hence, low friction coefficient might be attained even when the implanted layer diminished in wear; at the presence of Cl agents in the worn powders, the friction coefficient would be sufficiently low. Further studies are necessary to prove the above possibility in the wear mechanism. This tribological mechanism is of great importance to make surface material design effective to reduction of friction coefficient and loss of weight in abrasive wearing.

V. Conclusion

The tribological properties of the TiN films implanted with Cl are investigated. The results obtained through the experimental works, were summarized in what follows:

(1) The Cl implantation into TiN films does not cause any precipitation of new phase such as a hard compound or change of TiN phase.

(2) The depth profile of the TiN film is shaped by a Gaussian-like distribution of Cl, and, the maximum Cl concentration is 4 to 5 mol%. The binding energy of Cl_{2p} is approximately equal to 3.2×10^{-17} J (200 eV).

(3) With increasing the Cl dose, the friction coefficient and the wear volume of stainless steel ball are drastically reduced.

(4) The wear mode changes itself from the adhesive wear for unimplanted TiN film to the abrasive wear for the Cl implanted TiN film.

(5) The implanted Cl is thought to play a role as an extreme pressure agent at the interface between TiN film and stainless steel ball; resulting in that where Cl is detected in the wear particles induced in the friction test on the Cl implanted TiN films.

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