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**Macro-Manufacturing**

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### Self-Lubrication of Machining Tools in Dry via In-situ Formed Tribofilms

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#### ABSTRACT

Green manufacturing technology has become a significant innovative keyword to reduce the environmental burden and CO<sub>2</sub> emission at the stage of manufacturing and production. In daily operations by machining, huge amount of lubricating oils and cleansing agents is wasted so that dry machining technology provides us a way to completely reduce these wastes. Among several candidates, self-lubrication via in-situ formation of lubricious oxide films is accommodated to protective coatings in order to attain low friction and wear state even at higher cutting speed range. Materials science of in-situ formed lubricious oxide tribofilms is stated with consideration of accommodation mechanism via the chlorine implantation. Mechanical characterization is made for evaluation on elasto-plastic deformation of lubricious oxides. Turning test is employed to evaluate dry machinability of various tools for wide range of cutting speed. Self-lubrication in dry machining is described both for bare WC and TiCN-coated WC tools with and without chlorine implantation. Precise microstructure analyses are made by using the laser microscope, EDS and XPS. In-situ formation of lubricous oxides proves that self-lubrication process takes place even in dry machining to reduce the flank wear and friction coefficient.

#### INTRODUCTION

Green manufacturing has become a key technology toward significant reduction of environmental burden and CO<sub>2</sub> emission in industrial production [1]. In daily operation by machining and forming, huge amount of lubricating oils and cleansing agents are wasted so that dry machining and dry forming are an important goal in the green manufacturing. At the absence of lubricants, tool/die – work material system suffers from high flash temperature on the solid-solid contact surfaces. Increase of flash temperature, leads to severe adhesive wear, where adhesive metallic constituents from work materials are oxidized and these oxides cause high friction and high wearing state [2]. Dry machining and dry forming cannot be accommodated to practical operation without self-lubrication by tribocoating between tools and work materials.

There are three tribocoating methods for self-lubrication to be working in dry as listed in Table 1. Hard coatings like DLC (Diamond-Like Carbon), c-BN or CVD-diamonds are effective to preserve low friction and wear state until the flash temperature is less than the critical value [3]. In-situ solid lubrication works well in the dry wear condition by embedded MoS<sub>2</sub> and WS<sub>2</sub> until the protective coating is completely diminished [4]. Under severe wearing conditions, these two tribocoatings have a risk to break away or to significantly increase the specific wear rate. As before-mentioned, normal oxide films made from metallic adhesives have little or no capacity of self-lubrication. As surveyed

in Refs. [5,6], chromium oxides or chromium-ferrous oxide films, in-situ formed in dry deep drawing of stainless steel sheets by alumina die, significantly reduce the friction coefficient to attain nearly the same deep-drawability as observed by using the lubricated die. In the literature [7-9], low friction and low wear volume was reported in the wearing tests for titanium bearing ceramics and composites. Most of these studies reported or predicted that low friction and wearing comes from in-situ formation of intermediate titanium oxides or Magneli-phase oxides. These findings point out the third way of self-lubrication by in-situ formation of lubricous oxides.

Table 1: Three types of tribo-coating methods for dry forming and dry machining.

Self-Lubrication via Hard Protective Coating	Self-Lubrication via Solid Lubricants	Self-Lubrication via Lubricious Oxide Films
Deposition of DLC or diamond thin films	Co-deposition of MoS <sub>2</sub> /WS <sub>2</sub> with metallic matrix	Halogen implantation or PIII into Ti-bearing protective coating films (TiN/TiC/TiCN)
1) High covalency is favored for little abrasive wearing, 2) Softened a-C:W films can deform to relax high stresses, or, in-situ polymerization takes place for a-C:Si films, 3) They have little wear resistance against Ti/Fe base work materials.	1) Wearing mode is controlled to be in solid-lubrication mode with low wear rate and friction coefficient, 2) Life of protective coating is strongly dependent on break-away of embedded solid lubricants.	1) Wearing mode is controlled to be in solid-lubrication or boundary lubrication modes by suppressing severe oxidation, 2) Lubricous oxides are formed to reduce friction and wear. 3) Self-lubrication continues to be working until original coating breaks away.

Authors [10-13] have first found that titanium intermediate oxides including Magneli phase, Ti<sub>n</sub>O<sub>2n-1</sub>, are in-situ formed during wearing in the halogen implanted TiN coating. These lubricious oxide layers are thought to work as a tribofilm to significantly improve the tribological performance. Through precise surface analyses [14,15], significant penetration of oxygen atoms into TiN coating is observed in the wear track at the presence of chlorine in TiN. Titanium mono-oxide, TiO, is first formed in a series of oxidation reaction in wearing the chlorine-implanted TiN. Furthermore, it is found that low temperature oxidation of titanium and TiN takes place by chlorine implantation to Ti and TiN thin films. In addition, dry machinability and formability is improved by using the in-situ formed lubricious oxide films [16-18]. In the present paper, the self-lubrication process by formation of lubricious tribofilms is described from fundamental point of view in tribology and materials science. Turning test is utilized to evaluate self-lubrication behavior in dry machining for various cutting speeds. Formation of lubricous oxide films on the flank surface of tools is precisely analyzed and discussed with comparison to self-lubrication in dry sliding tests.

LUBRICIOUS OXIDE TRIBOFILMS FOR SELF-LUBRICATION

Friction and wear behavior in dry conditions is determined by materials selection for die and work as well as oxidation mode. After Refs. [5-6, 19], friction coefficient reduces itself with selecting the

covalent bonding material for die materials rather than ionic- or metallic-bonding ones. Metallic work materials with lower elastic modulus are easier to be adhesive to die materials. TiN-coated tools or dies often suffer from severe adhesive wear with high specific wear volume ( $W_s$ ): e.g.  $W_s$  is in the order of  $10^{-3}$  to  $10^{-4}$   $\text{mm}^3\text{N}^{-1}\text{m}^{-1}$ . Reduction of specific wear volume corresponds to change from severe oxidation to mild oxidation. When  $W_s$  reduces down to  $10^{-7}$   $\text{mm}^3\text{N}^{-1}\text{m}^{-1}$ , wearing mode turns to be abrasive with mild oxidation. Even in the abrasive wearing mode, its severity is described by the abrasive coefficient ( $k=W_s \times H$  for hardness,  $H$ ): e.g.  $k = 10^{-2}$  to  $10^{-3}$  for dry abrasive wearing between the same metallic solids,  $k = 10^{-3}$  to  $10^{-4}$  between two different metallic solids,  $k = 10^{-4}$  to  $10^{-7}$  between metallic and non-metallic solids, and,  $k = 10^{-8}$  for boundary lubrication. Reduction of the specific wear volume by two to three orders is required to change the severe adhesion wearing to the solid-lubrication mode. The abrasive coefficient must be also reduced to mild abrasive wearing with metallic to non-metallic contact or to be less than  $k = 10^{-5}$ . Table 2 summarizes the dry pin-on-ball testing results by this self-lubrication via Cl-implantation to TiN with comparison to cases without self-lubrication. Wear volume of counter material was measured after the sliding distance ( $L$ ) is 600 m. Low friction and wear comes from a tribofilm which is in-situ formed during dry sliding test.

Table 2: Comparison of wearing mode, friction coefficient, wear volume and specific wear volume among TiN coating on SKD11 discs with and without ion implantations.

	As-deposited TiN	Ar-implanted TiN	Cl-implanted TiN
Wearing Mode	Adhesive Wear	Adhesive Wear with Sticking Mode	Abrasive Wear
Friction Coefficient ( $\mu$ )	0.8 – 1.2	1.0	0.1 – 0.2
Specific wear volume ( $W_s$ , $\text{mm}^3\text{N}^{-1}\text{m}^{-1}$ )	$10^{-5}$ – $10^{-4}$	$10^{-4}$	$10^{-7}$ – $10^{-6}$
Wear Volume ( $W_v$ , $\text{m}^3$ )	$10^{-11}$	$10^{-11}$	$10^{-13}$

Literature [7-9] reported many experiences in serendipity that low friction and wear might come from formation of intermediate titanium oxides or Magneli phase of  $\text{Ti}_n\text{O}_{2n-1}$ . As theoretically proven by Ref. [20], these oxides in series for  $n > 3$  have crystallographic slipping planes in their unit cell so that this type of intermediate oxides has a capacity of plastic deformation in wearing. These empirical and theoretical estimates predict that large population of Magneli phase in the in-situ formed oxides other than  $\text{TiO}_2$  leads to reduction of wear and friction by plastic deformation of tribofilms. Precise analysis of Cl-implanted TiN coating before and after dry sliding test demonstrates the formation of intermediate titanium oxides, their plastic deformability during dry wear and the loading capacity of tribofilms.

As pointed by Table 2, argon implantation into TiN coating has nothing to do with self-lubrication or formation of tribofilms. That is, physical modification via ion implantation has little contribution to self-lubrication. Direct comparison of chemical compounds in the wear track between bare TiN coated and Cl-implanted, TiN coated tools, provides a proof that there exit lubricous oxides formed in the wear track. Figure 1 compared XPS profiles in the wear track by narrow scanning between two samples after  $L = 600$  m. In the case of bare TiN-coated sample, since the whole surface is mainly covered by Fe-base oxides, the counts of titanium were much reduced by adhesive wearing on the original TiN coating. Most of TiN was fully oxidized to  $\text{TiO}_2$ ; no intermediate oxides were left after dry sliding test. This implies that no lubricous oxide films could be synthesized by severe

tribo-oxidation reaction in the wear track. On the other hand, intermediate oxide peaks as well as TiN peak are detected in Fig. 1, telling that mild oxidation takes place with such sluggish rate that main of oxidation reaction stream to  $\text{TiO}_2$  terminates intermediately during the sliding test.

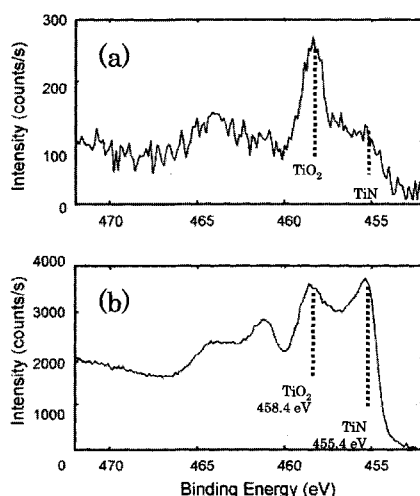


Fig. 1: Comparison of XPS profiles in depth between un-implanted (upper profile a)) and Cl-implanted titanium films (lower profile b)) after dry oxidation test.

These intermediate oxides were left in the wear track in the form of residual films or debris particles. In order to precisely analyze the phase and microstructure of these residuals, the wear debris particles were collected from the wear track without chemical treatment to prepare for TEM observation. To be discussed later, about 40 % of oxides are titanium mono-oxide; its microstructure was traced in the TEM micrograph. Figure 2 (a) shows a typical TEM micrograph of cubic-structured TiO crystals. Among its crystallographic structures, some skewed microstructure was detected. Its magnified image was shown in Fig. 2 (b). This skewed image proves that original cubic structure of TiO plastically deforms in twinning mode by the applied normal pressure during dry sliding test. That is, titanium mono-oxide with TiO is a lubricious oxide to reduce the applied shear stresses during dry sliding. This implies that TiO as well as Magneli phase oxides are responsible for self-lubrication as a tribofilm. As had been discussed in Refs. [12-15], low temperature tribo-oxidation process, is preserved on the whole life to sustain sluggish oxidation reaction rate, and, to promote the population of intermediate oxides in dry wearing condition. Implanted chlorine makes catalytic contribution to deeper oxygen penetration into TiN coating. Figure 3 compares oxygen atom profiles in the wear track at the beginning of dry sliding test between TiN coatings with and without Cl-implantation. Figure 3 proves that oxygen penetration is much promoted at the presence of chlorine atoms in TiN films with comparison to oxygen profile in the contaminant level without chlorine implantation. This implies that Cl-implantation assists TiN to have much oxygen concentration at the vicinity of its surface even in low flash temperature.

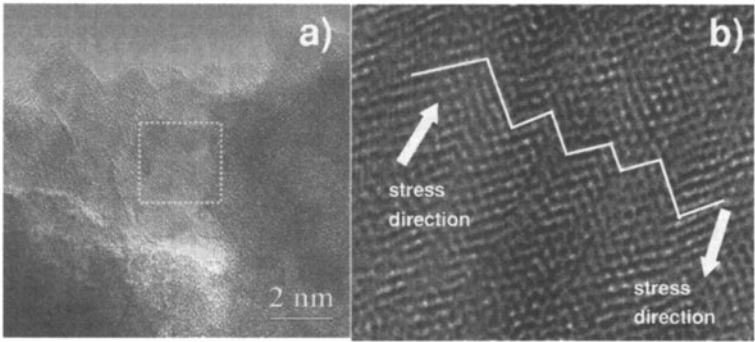


Fig. 2: Twinning deformation of TiO during the dry sliding test: a) High resolution TEM micrograph of debris particles in wear track, and, b) Magnified image of dotted zone in a).

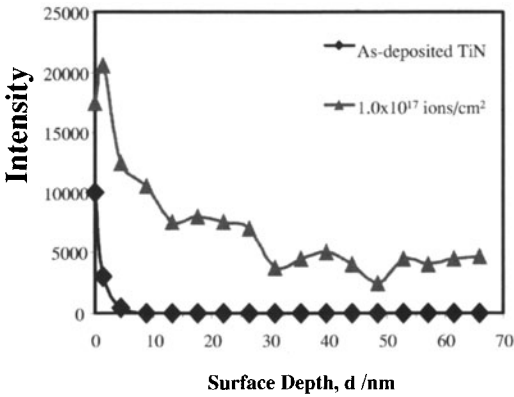


Fig. 3: Comparison of oxygen atom profiles in the wear track along the depth of TiN coating at the beginning of dry sliding tests.

Figure 3 also implies that Cl-implanted TiN coating has an oxygen-enriched surface layer even at the beginning of wear testing in dry. This formation of surface layer reflects on the mechanical response of TiN coating. Nano-indentation was used to investigate the change of surface hardness with increasing the dose and implantation energy of chlorine for Cl-implanted TiN coating films. Figure 4 compared the measured load-displacement curves. Loading sequence was limited by 1.1 mN in every case. More plastic displacements are detected with increasing the chlorine doses and energies for implantation. That is, the oxygen-enriched layer or titanium mono-oxide layer has higher capacity of elasto-plastic deformation than an original TiN film.

Self-lubrication process of Cl-implanted TiN coating stands on the in-situ formation of lubricous, plastically deforming intermediate titanium oxide layers. Since abrasive wearing takes place with low abrasive coefficient, solid-lubrication process is sustained even in dry conditions. For feasibility test of this process in practice, dry machinability is experimentally evaluated in what follows.

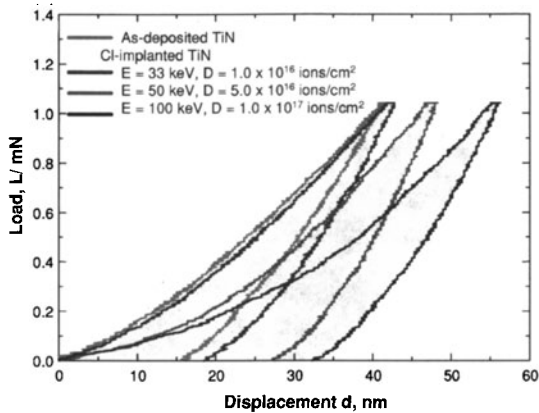


Fig. 4: Variation of the load – displacement relations in nano-indentation with increasing the dose of chlorine.

EXPERIMENTAL PROCEDURE

Preparation of Samples

The throw-away cemented carbide tool of P10 type was selected as a common specimen. They were shaped triangular without chip-breakers and their rake face. These tool materials are composed of WC (Co) as well as TiC and TaC. TiCN and TiN coatings were employed to investigate the effect of ceramic protective coatings on the improvement of machinability. TiN coating was deposited by follow-cathode ion plating. TiCN, or solid solution of TiN and TiC with Al<sub>2</sub>O<sub>3</sub> were deposited on the cemented carbide tool. The chlorine ions were implanted into both the rake and flank faces of bare and coated tools. AISI 304 and carbon steels with the type of S45 after de-oxidation by titanium or aluminum were employed as a work material. Main chemical composition of S45C was: silicon, manganese and titanium with the balance of iron. The contents of phosphorous, sulphur, copper, nickel and chromium were suppressed to be less than 0.001 mass %. In particular, the content of phosphorous is 0.002 mass % and only 0.001 mass % for sulphur.

Chlorine Implantation

Chlorine positive ions or Cl<sup>+</sup> were implanted into these testpieces, which were mounted on the target manipulator. The beam incident angle was fixed to normal to the specimen surface. The ion source chamber was evacuated by the diffusion-pump. Both the beam line and the sample holder were further evacuated by the turbo-pump. The standard operating conditions were 1.0 x 10<sup>-5</sup> Pa in vacuum, 1.0 x 10<sup>17</sup> ions/cm<sup>2</sup> for chlorine dose and 100keV for energy. AlCl<sub>3</sub> with the purity of 99.99 % was used for an ion source of the Freeman type with a vaporizer. In the implanter, after ion beam was generated, it was mass-separated to a single-charged Cl<sup>+</sup> ion beam.



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### Turning Tests

Turning tests were conducted for evaluation of dry machinability. Both the cutting depth ( $D_c$ ) and feed ( $f$ ) were fixed to be constant:  $D_c = 1.0$  mm and  $f = 0.1$  mm/rev. The cutting speed ( $V_c$ ) was varied from 10 m/min to 500 m/min for each tool. Using a lathe equipped with axial load sensors, both the reactive and feed forces were measured independently. Two types of worn surfaces were observed after the specified feed distance in this turning test by using the laser microscope.

### Analysis

X-ray Diffraction (XRD) method was used to identify the phases after Cl-implantation to TiN coatings. High resolution transmission electron microscope (HRTEM) was used to describe the change of TiN lattice structures before and after implantation. Selected area electron diffraction (SAED) was also used to make precise analysis of debris particles. X-ray photoelectron spectroscopy (XPS) was utilized to describe the chemical composition and its depth profile. Local chemical compositions in the in-situ formed tribofilms, were analyzed by Energy Dispersive X-ray Spectroscopy (EDS).

## EVALUATION OF DRY MACHINABILITY

### Dry Machinability of TiN Coated WC tools

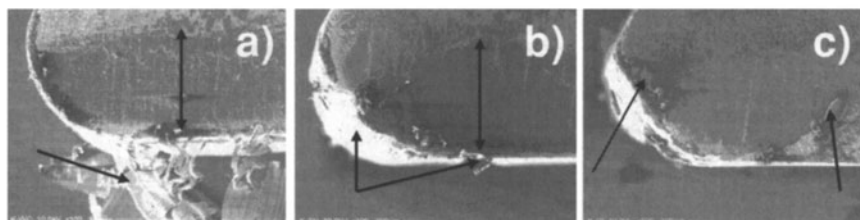


Fig. 5: Comparison of rake face wear near the cutting edge of the tools: a) Bare cemented carbide, b) TiN-coated and c) Cl-implanted, TiN-coated tools.

Rake face after the cutting distance of 500 m by 300 m/min was observed in Fig. 5. In case of cemented carbide tools, severe adhesion of work materials was seen at the cutting edge and on their rake face. Similar adhesion is also detected on the rake face of TiN-coated tools; a few adhesives were seen at the cutting edge. On the contrary, little adhesions were observed both on the rake face and at the cutting edge in Fig. 5 c). This reduction of adhesive wear in dry cutting of stainless steels proves that chlorine implantation works well to improve dry machinability via self-lubrication.

### Dry machinability of TiCN coated WC tools

TiCN coated WC tools with and without Cl-implantation were used to investigate the dry machinability for two types of work materials: Ti-deoxidized S45C and Al-deoxidized S45C. Figure

6 depicts variation of the flank wear width ( $V_B$ ) after a cutting length of 500 m with increasing the cutting speed. At lower cutting speed range, there is a little difference in  $V_B$  between TiCN coated WC tools without and with Cl-implantation. For  $V_c > 300$  m/min, the flank wear increased exponentially with  $V_c$  for TiCN-coated WC tools. Severe oxidation wear of TiCN takes place in dry conditions at higher cutting speeds. In the case of Cl-implanted TiCN-coated tools, the flank wear width only increases linearly with the cutting speed.

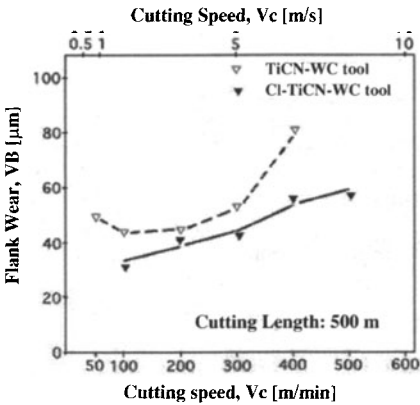


Fig. 6: Variation of frank wear width with increasing the cutting speed for TiCN-coated and Cl-implanted, TiCN-coated tools against Ti-deoxidized S45C work.

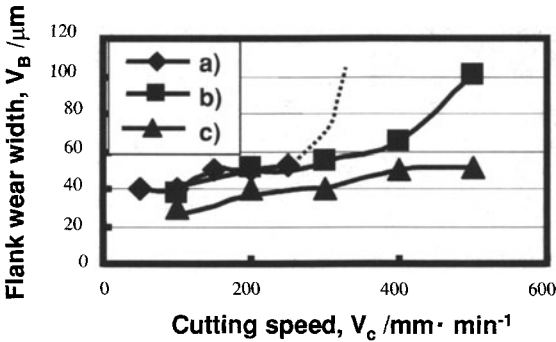


Fig. 7: Variation of flank wear width increasing the cutting speed for three dry cutting conditions: a) Cl-implanted WC tools against Ti-deoxidized S45C, b) Cl-implanted TiCN-coated WC tools against Al-deoxidized S45C and c) Cl-implanted TiCN-coated WC tools against Ti-deoxidized S45C.

Three types of dry cutting conditions were prepared to investigate the effect of Cl-implantation on the dry machinability. In case of Cl-implanted bare WC tools against Ti-deoxidized S45C work, lubricous oxides can be made from TiC in additives of cemented carbide and titanium additive in work materials. In case of Cl-implanted TiCN-coated WC tools against Al-deoxidized S45C, titanium source only comes from TiCN. On the other hand, amount of titanium resource increases in case of