COMPARISON OF FRICTIONAL CHARACTERISTICS OF TITANIUM NITRIDE FILMS PRODUCED BY ECR-DC SPUTTERING AND PVD

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ABSTRACT

The hardness of the TiN films prepared by magnetron sputtering, arc ion plating, and chemical vapor deposition has been reported to be in the range of 20 to 32 GPa and the coefficient of friction in the range of 1.1 – 0.2. The aim of the present work is to try to improve hardness as well as tribological properties of TiN films by the modification of an electron cyclotron resonance (ECR) sputtering system and to compare them with those of the films obtained by physical vapor deposition (PVD) method. Tribological properties of the films were measured in dry conditions with a CSEM ball-on-disc tribometer as well as by an “in house” developed tribometer. Physical and morphological properties of the films were analyzed by nano and micro-indentation, scratch test and X-ray diffraction.

KEYWORDS: TiN, ECR sputtering, PVD, super-hard coatings, dry sliding.

1. INTRODUCTION

TiN coatings are well known for their excellent properties such as high mechanical resistance (very hard), chemical stability (high melting point and inert in many atmospheres), electrochemical nobility (higher corrosion potential values), reasonable ductility and fracture toughness and very good tribological properties. Such excellent properties and possible combinations of them potentially render these materials to be applicable in a variety of hostile situations, such as high load and high friction, corrosive media, or elevated temperatures [1, 2]. The good wear properties are usually associated with the high hardness and resistance to plastic deformation or ploughing in abrasive wear [3]. Layers of oxides, tribo-chemically generated, could be responsible also for their good tribological behavior [4].

Hard TiN coatings have been prepared by reactive magnetron sputtering [5], electron beam sustained Ti arc plating [6] or CVD technique. The hardness of the TiN films was reported to be in the range of 20 to 32GPa [7]. In the present work we report on a new method to form superhard TiN and TiN/MoS₂ films on stainless steel substrates and bearing steel having hardness of 33 to 50 GPa using a hybrid electron cyclotron resonance – direct current (ECR-DC) hybrid sputtering and to compare them with those of the films obtained by physical vapor deposition (PVD) method. These methods are characterized by low processing pressure (10⁻² - 10⁻¹Pa) and are known to affect the properties of surfaces in terms of cleanliness and adhesion. There are many advantages of both methods e.g. very high hardness, no macroparticles are produced in such processes and deposition rate is increased (especially by using the PVD method), keeping constant the tribological and mechanical properties. The film growth and the effect of surface morphology and film composition on the hardness and the coefficient of friction are also investigated for the thin layers obtained by both methods.

2. EXPERIMENTAL PROCEDURES

2.1 Film preparation

Deposition of TiN and TiN/MoS₂ films by ECR-DC sputtering was performed in an Anelva ECR 300 S sputtering system. The microwave power with 2.45GHz frequency was introduced in a cylindrical plasma chamber of 30cm in diameter and 30cm in height through a quartz window. The Ar and N₂ gases were introduced into the plasma chamber via mass flow controllers nearby a quartz window. A magnetic coil surrounding the plasma chamber produced the magnetic field with 0.0875 T in strength, necessary to fulfill the ECR condition. The electrons having high
energy in circular motion produced the positive Ar and N2 ions. A static electric field was self-generated in the plasma stream between the plasma chamber and the substrate holder because they were electrically isolated from each other.

The static electric field and the pressure gradient as well as the supplementary negative potential applied to the target transported and accelerated the ions toward the target. The target atoms were sputtered and directed to the substrate. On the substrate surface heated at 400°C a reactive formation of TiN occurred [3]. The deposition chamber of 28cm x 32cm x 30cm in dimensions was evacuated by an oil diffusion pump and a mechanical rotary pump. The target was of cylindrical form (internal diameter: 80mm, external diameter: 90 mm, length: 60mm) and consisted of a stack of 5mm length Ti rings in the case of TiN deposition and 9 Ti rings and 1 MoS2 ring in the case of co-sputtering of Ti and MoS2. Figure 1 shows the arrangements of Ti rings and MoS2 ring in the target. In order to find optimum processing parameters, the plasma stream was diagnosed optically and electrically. Typical operation conditions are listed in Table 1. Films with thickness of 1-3µm were formed in the conditions given in the table.

PVD deposition of TiN films was performed in a system presented schematically in figure 2. The main part of the PVD deposition device are the cylindrical hollow cathode, the deposition chamber having water cooled walls, the nitrogen gas feeder, the Ti target, the copper crucible and the substrate holder.

The argon gas was admitted into the reaction chamber by the upper part of the PVD device. The argon atoms were ionized inside the cylindrical hollow cathode (item 1 shown in figure 2). The electrons were directed toward the Ti target settled on the copper crucible. Before deposition, the substrates were cleaned and activated by a glow discharge in argon at about 10Pa. Deposition parameters are shown in Table 2: pressure (P), evaporation rate (ER), N2 gas flow rate (GFR), substrate voltage (SV), substrate temperature (ST), deposition time (DT).

![Fig. 2 PVD deposition device principle.](image)


![Table 2: PVD deposition parameters.](table)

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<thead>
<tr>
<th>P (Pa)</th>
<th>ER (g/min)</th>
<th>GFR (cm³/min)</th>
<th>SV (V)</th>
<th>ST (°C)</th>
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2.2. Characterisation

Surface morphology was measured by an atomic force microscope (AFM) in contact mode. Scratch tests and the coefficients of friction of the films were measured with CSEM (Switzerland) micro-scratch tester and ball-on-disk tribometer at room temperature in dry conditions. Figure 3 shows the disk and the spherical ended pin of the pin-on-disk, “in house” tribometer.

Scratch testing was performed by introducing stresses at the interface between the coating and the...
substrate. This was achieved by pressing a diamond stylus on the sample surface with a normal load \( F_N \). As the sample is displaced at constant speed, the resulting stresses at the interface cause flaking or chipping of the coating. In that moment the tangential force \( F_T \) abruptly increases. The smallest load, at which the specific event, is recorded is called the Critical Load \( L_c \).

Fig. 3 Detail photograph of the spherical ended pin and the disk of the “in house” tribometer.

The coefficients of friction of the films were monitored during sliding with a speed of 0.1 m/s at 20°C and 35% relative humidity air. The used ball was alumina of 6 mm in diameter and applied loads were 1 N and 5 N.

A special care was taken to measure the hardness and the elastic modulus of the films. They were determined from force-displacements curves obtained using an ultra-low load micro-hardness indenter system (UMIS-2000) developed by CSIRO-Australia. For the determination of displacements based on depth measurements at small depths, a diamond indenter with an equilateral base (Bercovich indenter) is preferred to the four-sided Vickers of Knoop indenter, because it is easier to obtain a sharp tip. The Bercovich indenter has face angles of 65.3 degree, which makes projected areas same as that for a Vickers indenter at the same depth and gives a degree of equivalence in results. Maximum force applied was 3 mN with a resolution of 0.2 mN. The surface hardness was calculated as the applied force required inducing plastic penetration divided by the projected area of contact between the indenter and the specimen. The Young’s modulus, \( E = \frac{E_{\text{specimen}} + E_{\text{indenter}}}{2} \) was determined as the slope of the unloading force-displacement curve.

TiN films prepared by PVD method were tested with a microhardness tester using a load of 0.245 N and 15 s loading time.

3. RESULTS AND DISCUSSION

3.1. Film composition

XRD analysis of the films showed that the composition ratio (Ti/N) was influenced by the \((\text{Ar/N}_2)\) flow ratio. Samples prepared at 400W microwave power, 800V sputtering potential, 20 sccm flow of the Ar gas and 1.2 sccm flow of the \( \text{N}_2 \) gas were identified as TiN compounds having a cubic crystallographic structure and yellow color. Changing the \( \text{Ar/N}_2 \) gas flow ratio to 20/0.8 keeping other parameters constant resulted in the formation of Ti\text{N}_0.3 film having hexagonal structure and white color. We prepared TiN/MoS\text{2} films in conditions where the stoichiometric TiN films were obtained: 20 sccm Ar and 1.2 sccm \( \text{N}_2 \) flow rates. Figures 4 and 5 show the patterns of TiN and TiN/MoS\text{2} films prepared using these parameters. The crystallographic phase of TiN appeared in both films. In the TiN film the peak corresponding to TiN (200) diffraction plane was predominant. An enhancement of the TiN (111) peak relative to the TiN (200) peak can be observed in the TiN/MoS\text{2} film.

Fig. 4 XRD pattern of the TiN film prepared by ECR-DC sputtering.

Fig. 5 XRD pattern of the TiN/MoS\text{2} film prepared by ECR-DC sputtering.

The experimental results inferred that the main factor in determining the TiN coating properties prepared by PVD method was the ratio between the partial pressure of the reactive gas (\( \text{N}_2 \)) and Ti vapors, the ratio being determined by the ER and the GFR. An optimal set of parameters are shown in Table 3.

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Table 3 Optimal PVD deposition parameters.
XRD analysis of the TiN<sub>x</sub> PVD coatings using CuKα radiation (λ=1,5402Å) revealed preferred orientations of (111) and (200) for TiN phases and (111) for Ti<sub>2</sub>N phases. Figure 6 shows typical XRD pattern of the TiN film prepared by PVD.

### 3.2. Hardness

Figures 7 and 8 show typical force-displacement curves for the TiN and TiN/MoS<sub>2</sub> films, respectively, describing the range of response to the applied force.

Three indentations were made for each specimen. Continuously recording indentation tests revealed high fracture toughness due to the lack of steps during loading curves.

![Fig. 7 Load-displacement curves for the three indentation of TiN film.](image7)

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![Fig. 8 Load-displacement curves for three indentations on TiN/MoS<sub>2</sub> film.](image8)

**Fig. 8 Load-displacement curves for three indentations on TiN/MoS<sub>2</sub> film.**

The high degree of the depth indentation recovery confirmed the high elastic limit of the TiN and TiN/MoS<sub>2</sub> films. The main parameters of the indentations and calculations averaged from the three indentations are shown in Table 3. The scatter in data is due to factors such as surface roughness and crystallite size, variation in hardness with crystallographic direction and microstructural defects such as twins and stacking faults.

By averaging the three sets of measurements, the mean values of hardness and Young’s modulus were found to be 35 ± 5GPa for the TiN films and 52 ± 0.5GPa for the TiN/MoS<sub>2</sub> films. These values are higher than those of the other TiN films produced by a PVD deposition system [8]. The higher energy of the reacting particles as well as of the Ar ions bombarding directly the film during the formation may be a cause for the larger hardness of the TiN and TiN/MoS<sub>2</sub> films obtained here [9].

TiN PVD coatings prepared using the deposition parameters presented in Table 3 were found to have microhardness of about 22GPa measured using 0.245N load and 15s indentation time.

### 3.3. Adhesion strength

Transversal scratches on the film surfaces were performed with the Y-axis translation table of the CSEM micro-scratch tester. The applied perpendicular load was increased from 0 to 100N at a speed of 10N/min. The testing distance was 10 mm. The tester recorded the applied load, the displacement, the tangential force and the acoustic emissions.

Figure 7 presents a typical data of tangential force during the test. The abrupt increase in the tangential force reveals the critical load (L<sub>c</sub>) at which the film cracks under the applied load. One can observe the difference between the critical load of 4 N and 16N for the TiN and TiN/MoS<sub>2</sub> films, respectively. A critical load of 55N was measured for the TiN films prepared by PVD having thickness of 2-3µm. The deposition rate of those films was about 4,5µm/h.

![Fig. 9 Typical tangential force curves as function of scratch distance of TiN and TiN/MoS<sub>2</sub>films.](image9)

**Fig. 9 Typical tangential force curves as function of scratch distance of TiN and TiN/MoS<sub>2</sub>films.**

### 3.4. Coefficient of friction
The coefficients of friction of TiN and TiN/MoS₂ films against an alumina ball are shown in figure 8 as a function of the sliding distance and load of 5N.

The measurements were made in dry conditions: 20°C and 35% relative humidity air. At the beginning of the test the coefficient of friction increased abruptly to a value of 1.25 ± 0.5 and 1.05 ± 0.5 for the TiN film depending on the applied load. TiN/MoS₂ film exhibited also an abruptly increase of the coefficient of friction up to 0.6 ± 0.2 and 0.4 ± 0.2 and then decreased to 0.5 ± 0.01 and 0.2 ± 0.01, respectively, and then remained stable. This behavior is assigned to the strong adhesive sliding in the TiN case. On a smooth or highly polished surface the friction is largely governed by the combined effects of various adhesive interactions across the sliding interface. Lower coefficient of friction was observed for the TiN/MoS₂ films. This effect was more important in the case of 5N load. Both higher roughness and the MoS₂ included into the interstice of the TiN crystal are considered to be the main reasons for the low coefficient of friction.

There are four main parameters that are controlling tribological processes: the coating hardness, the film thickness and the type of wear debris. Relationship between these four parameters will decide the contact conditions being characterized by specific tribological contacts. After a “running in” period, the coefficient of friction became stable. After this period, when due to the wear the coating is removed, the coefficient of friction increases due to the direct contact between the TiN coated pin material and the steel disk. As an example, the frictional behavior of the TiN film prepared by PVD is shown in figure 11 (the applied load was 7.696N and sliding speed was 1 m/s).

Between the initial friction stage, which corresponds to the contact coating-steel disk and the total removing of the coating, we can identify 5 stages:

Stage I: the coefficient of friction is slowly increasing, corresponding to the “running in” phase.

Stage II: it is a “plateau” which corresponds to the wear of the columnar zone of the TiN coating.

Stage III: it is also a “plateau” which corresponds to the wear of the amorphous zone of the coating, where we can find particles of the substrate. The coefficient of friction is higher during this stage.

Stage IV: corresponds to an abrupt increase of the coefficient of friction that may be explained by removing completely the coating.

Stage V: it is a plateau which corresponds to the friction coefficient between the uncoated pin and the steel disk.

When the load was only 1.84N, the coating resisted longer time, tested at the same sliding speed of 1 m/s.

The coefficient of friction variation on the any plateau can be attributed to: the abrasive wear when the pin asperities produce wear debris on the steel disk; the pin or spherical shaped wear debris can be inserted into some interstitial places, changing the sliding friction into the rolling one with a direct decrease of the coefficient of friction. After the removal of the debris the sliding abrasive wear becomes important and the coefficient of friction increases. The process can be restarted again.

Another cause may be the development of a material transfer zone from the pin to the disk or from the disk to the pin. The particles with low fracture resistance will determine a viscous flowing. Figure 12 shows the wear scar on the spherical pin after the dry sliding test.
incorporation in the TiN structure. The hardness of N2 was incorporated with Ti in the film at ratios determined by the scratch test was found 4N and 16N for the TiN and TiN/MoS2 films, respectively. Coefficient of friction of the TiN/MoS2 film was lowered by factors of 2.5 and 5.25 compared to the coefficient of friction of the TiN films in dry conditions using testing loads of 1N and 5N.

The microhardness of the TiN films prepared by PVD was of about 22 GPa measured using 0.245 N load and 15 s indentation time. The deposition rate was higher than that of the TiN or TiN/MoS2 films prepared by ECR sputtering. Also the critical load was higher (55N compared to 4N or 16N, respectively). The coefficient of friction of the TiN films was lower also in the PVD case.

For the thin films based on Ti, supplementary addition of Al or Zr has a stabilizing effect at high temperatures, as for example cutting tools working at high speeds. The tools coated with thin films of (TiAl)N or (TiZr)N exhibit an excellent behavior for machining of steel. This effect is attributed to the low coefficient of friction at high temperatures due to the formation of a protecting oxide, with an inhibiting role of the diffusion on the tool surface. This phenomenon was observed when the coatings were tested in air, molecular oxygen, argon, or vacuum. The surface morphology of the worn surfaces was different after testing in different conditions. After the test in dry air the sliding surface was smooth, on the contrary after the test in vacuum, the surface was rough. For the TiN coatings, the low coefficients of friction in oxygen and water vapors can be explained by formation of tribo-chemical formation of Ti oxides. The Ti oxides act as lubricants in conditions of sliding contacts. In this way can be explained the decrease of the coefficients of frictions at temperatures that are over 400°C. Even if these films can be removed by mechanical action of the sliding counterpart, the formation speed of the oxides is so high to offer the needed tribological properties.

4. CONCLUSIONS

TiN and TiN/MoS2 films were prepared by a hybrid ECR-DC reactive sputtering deposition. The N2 was incorporated with Ti in the film at ratios determined by the partial flow ratios between Ar and N2 gases. The DC sputtering voltage applied to the target controlled the feeding with excited Ti atoms. The special arrangement of the sputtering target as a stack of Ti and MoS2 rings permitted MoS2 incorporation in the TiN structure. The hardness of the films was found to be in the range of 35 ± 5GPa for the TiN films and 52 ± 0.5GPa for the TiN/MoS2 films. Critical load (Lc), determined by the scratch test was found 4N and 16N for the TiN and TiN/MoS2 films, respectively. Coefficient of friction of the TiN/MoS2 film was lowered by factors of 2.5 and 5.25 compared to the coefficient of friction of the TiN films in dry conditions using testing loads of 1N and 5N.

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REFERENCES