Surface properties of Mo-implanted PVD TiN coatings using MEVVA source

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\section*{Article Info}

\begin{tabular}{l}
\textbf{Article history:} \\
Received 25 January 2013 \\
Received in revised form 2 May 2013 \\
Accepted 3 May 2013 \\
Available online 13 May 2013
\end{tabular}

\section*{Abstract}

To further improve the tribological properties of TiN coatings used on mechanical parts, Mo ions were implanted into PVD TiN coatings with Metal Vapor Vacuum Arc (MEVVA) source at the implantation dose as high as \(1 \times 10^{18}\) ions/cm\(^2\). Surface morphology, microstructures, and nano-hardness of TiN coatings were investigated by optical profilometer, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Nano Indenter System. The tribological properties were investigated on a ball-on-disk friction and wear tester. The XRD results demonstrated that the diffraction peak of TiN appeared in the Mo-implanted TiN coatings. However, there was obvious decrease of nano-hardness due to the soft Molybdenum phase and its oxides. It was approved that Mo-implanted TiN coatings could greatly improve their tribological properties and that the implantation at dose of \(1 \times 10^{18}\) ions/cm\(^2\) could result in much lower friction coefficient. The existence of soft molybdenum, luscious molybdenum oxides and titanium oxides resulted in the remarkable reducing of the friction coefficient of TiN coatings with Mo-implantation.

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\section*{1. Introduction}

Titanium nitride (TiN) coatings have been used as wear resistant coatings for cutting tools and dies owing to their high hardness, good wear and corrosion resistance. In recent years, TiN coatings started to be used on machine parts like automobile parts and in some industries which required low friction [1–5]. As a result, low friction coefficient becomes essential to TiN coatings. Therefore, some studies have been carried out to investigate friction coefficients of TiN coatings. Azushima et al. [2,3] studied the influences of preferred grain orientations on friction coefficients of TiN coatings with different counter ball materials under dry condition. They revealed that a \(\{1 1 1\}\) preferred grain orientation could obtain a lower friction coefficient than a \(\{2 0 0\}\) preferred grain orientation for TiN coatings when the counter ball materials are SUJ2, SUS304, SUS440C and SWRM10. And they proposed that titanium oxide film on the contact surface of counter balls for TiN coatings with the \(\{1 1 1\}\) preferred grain orientations resulted in lower friction coefficients. On the other hand, lots of ions like C, N, Al, V and Zr [6–10] were implanted into TiN coatings and showed obvious effects on improving tribological performance of TiN coatings. As a result, ion implantation has been proved to be an effective way to improve the tribological properties of TiN coatings. However, there were few studies of Mo ion implantation on tribological properties of TiN coatings. Deng, et al. [11] investigated the effects of Mo and Mo+C ion implantations on PVD TiN coatings. They reported that nano fiber phase rich in Mo was found in TiN coatings after Mo implantations and that higher implantation dose could enhance the hardness, and decrease the wear rate and friction coefficient. Thus, it is possible to obtain much lower friction coefficient of TiN coatings by further increasing Mo ion implantation dose. This is because besides forming some special microstructure, higher implantation dose may provide more Mo element which may produce more molybdenum oxides with Magneli phase structure [12,13] as lubricant under dry friction. However, the dose of Mo ion implantation in the former study [11] was no more than \(4.5 \times 10^{17}\) ions/cm\(^2\). Moreover, there were lack of further studies on the surface morphology and worn surfaces, which were very critical for TiN coatings with Mo implantation applied on machine parts and in relevant industries.

In this paper, Mo ions with dose as high as \(1 \times 10^{18}\) ions/cm\(^2\) are implanted into PVD TiN coatings with MEVVA source. The microstructure, surface morphology and mechanical properties of TiN coatings are investigated. Ball-on-disk sliding friction and wear tests are carried out to investigate their tribological properties,
2. Experimental methods

All substrate samples were made from 316L stainless steel with dimensions of 70 mm × 30 mm × 1 mm with Ra of 4.13 nm and the hardness of 150 HV0.2. After ultrasonically cleaned for 15 min with acetone and alcohol, respectively, about 1.6 μm thick PVD TiN coatings were deposited on the surface of substrate samples by an MIP-10-800 Multi Arc Ion Plating. The parameters of TiN deposition included a nitrogen pressure of 0.6 Pa, an arc current of 60 A, a duty cycle of 30%, a temperature of 200 °C, a substrate bias of 200 V, and TiN deposition for 90 min after Ti deposition for 5 min. Before Mo ion implantation, the TiN coating samples were again ultrasonically cleaned for 15 min with acetone and alcohol, respectively. Then a MEVVA II A-H source, made by Beijing Normal University, China, was utilized to implant Mo ions into the TiN coatings. The parameters of Mo-implantation included a vacuum of 2 × 10⁻⁴ Pa, an average ion energy of 80 keV, a current density of 24 μA/cm², and an accelerating voltage of 26 kV. The implantation temperature was room temperature at the beginning and without heating in the whole process. To further control the surface temperature lower than 100 °C during the whole implantation, the sample surfaces of TiN coatings were kept out of implantations for 10 min by a sample shutter every 20 min. And the two doses of Mo ion implantation were 3 × 10¹⁷ ions/cm² and 1 × 10¹⁸ ions/cm² (corresponding to the 3E17 and 1E18 in the following part of the paper, respectively).

NanoMap-D optical profilometer was used to measure surface morphology of TiN coatings and their roughness. PHI-710 scanning Auger microprobe (SAM) was adopted to detect the Mo element profile on the TiN coating surface and it was found that the implantation depth was about 200 nm. ESCALAB 250 X-ray photoelectron spectroscope (XPS) was employed to analyze the chemical states of the elements of the coating surfaces after sputter for 10 nm by Ar ions. D/max-2500 X-ray diffraction (XRD) with 2° incidence angle of fixed omega was utilized to characterize the phases of the surface coatings. Nano-hardness and elastic modulus of the samples were surveyed by MTS XP Nano Indenter System with a Berkovich indenter tip in the Continuous Stiffness Mode (CSM).

Friction and wear tests were conducted on an MS-T 3000 ball-on-disk friction and wear tester with a 4 mm diameter Si₃N₄ ball sliding on the TiN samples under an applied load of 1.96 N. The ball was static while TiN coating disk was rotating during the dry friction driven by a motor. The tests were carried out at a sliding velocity of 0.126 m/s with the wear track radius of 3 mm for 60 min under dry friction in air. The room temperature was 20 ± 3 °C and the relative humidity was 45 ± 5%. The volumes of wear tracks were measured by the NanoMap-D optical profilometer and the Scanning Probe Image Processor (SPIP) software, and calculated by the following formula:

\[ V = \frac{V_I}{1 - \tan \alpha} \times \pi \times d \]

where \( V \) is the total wear volume of the wear tracks (μm³); \( L_1 \) is the arc length of a part of the wear tracks (μm); \( V_I \) is the wear volume of the part of wear track with the arc length of \( L_1 \) (μm³); and \( d \) is the wear track diameter (μm).

Then the wear volumes were calculated into wear rates. JEOL JSM-7001F scanning electron microscope (SEM) and Energy-Dispersive X-ray Spectrometer (EDS) were used to analyze the morphologies and element distribution of the worn surfaces of samples.

Mo implantations can obviously change the surface color of TiN coatings from golden yellow to silvery white with a little light yellow for TiN coatings with Mo dose of 3E17 and to bright silvery white for TiN coatings with Mo dose of 1E18, by naked-eye observation. Fig. 1 shows the three-dimension morphology of the TiN coating surfaces with different Mo implantation doses. It can be seen that there are several droplets and pits on all TiN coatings. However, droplets are a little smaller after Mo implantation due to the sputter effect on PVD TiN surfaces during the implantation process. Furthermore, their roughness with a measuring area of 0.5 mm × 0.5 mm is listed in Table 1. The results show that Mo implantations do not cause increase of surface roughness of TiN coatings. And from the results of morphology and roughness, it can be seen that Mo implantation may not result in higher friction coefficients and is beneficial to TiN coatings used in machine parts.

![Fig. 1. Morphology of the TiN coating surfaces with different Mo implantation doses](image-url)
Phase structures of TiN films with Mo implantation are analyzed by XRD (Fig. 2). It can be seen that there is only TiN phase on the TiN coating samples, while the TiN coatings after Mo-implantation at dose of both 3E17 and 1E18 ions/cm² show similar structures of Ti₂N (2 0 0) besides TiN [14,15]. It suggests that Mo-implantation may generate high energy and activate elements in TiN coatings to cause new Ti₂N structures. To further investigate the influence of Mo ion implantation on microstructures of TiN coatings, the XPS studies of TiN coatings and Mo-implanted TiN coatings at 1E18 dose were carried out after surface etching for 10 nm. The results are shown in Fig. 3 and Table 2. It reveals that Mo implantation does not cause any change of the chemical states of Ti element of TiN coatings, and that Ti element on the surfaces of TiN coatings both un-implanted and implanted is composed of Ti₂N, TiN, Ti₂O₃, and TiO₂. However, the chemical state of Ti₂N should exist only at a very superficial layer for the un-implanted TiN coating according to the sole TiN phase of its XRD result. Moreover, after Mo-implantation, TiN coating surfaces display the existence of Mo and MoO₂, which is helpful to decrease the friction coefficients of TiN coatings.

Fig. 4 displays the nano-hardness and elastic modulus of the un-implanted and Mo-implanted TiN surfaces at 1E18 dose. It can be seen that Mo ion implantations could obviously lower mechanical properties of TiN coatings. Taking 50 nm to 150 nm displacement into surface as the steady part of the curves, the average values of TiN, TiN-Mo-3E17 and TiN-Mo-1E18 are shown in Table 3. It verifies that Mo implantation could decrease the nano-hardness and elastic modulus of TiN coatings, while higher Mo implantation doses can obtain much lower average nano-hardness and elastic modulus, with dropping range of 21.17% and 15.2% respectively for TiN coatings after Mo implantation at 1E18 dose. Also, it proves that the existence of soft Mo and its oxides lead to the distinct hardness decrease although there is hard Ti₂N phase in the TiN coatings.

### 3.2. Friction and wear performance

Fig. 5 demonstrates the wear rates and friction coefficients of the un-implanted and Mo-implanted TiN surfaces along with time. As shown in Fig. 5a, the average wear rates of TiN, TiN-Mo-3E17 and TiN-Mo-1E18 coatings are 20.120 × 10⁻⁶, 13.807 × 10⁻⁶ and 12.982 × 10⁻⁶ mm³/Nm, respectively. The Mo-implanted TiN coatings can obviously decrease wear rates of TiN coatings by 31.38% for TiN-Mo-3E17 and by 35.48% for TiN-Mo-1E18. And higher dose of Mo implantation does not further display remarkable reducing of wear rates comparing with the lower dose. In Fig. 5b, it can be seen that the friction coefficient curve of TiN samples

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**Table 1**

<table>
<thead>
<tr>
<th>Roughness (nm)</th>
<th>TiN</th>
<th>TiN-Mo-3E17</th>
<th>TiN-Mo-1E18</th>
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<tr>
<td>Ra</td>
<td>9.95</td>
<td>9.58</td>
<td>8.00</td>
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<td>Rq</td>
<td>62.67</td>
<td>58.60</td>
<td>47.86</td>
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**Table 2**

<table>
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<tr>
<th>Samples</th>
<th>Binding energy (eV)</th>
<th>Chemical state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti 2p₃/₂</td>
<td>Mo 3d₅/₂</td>
</tr>
<tr>
<td>TiN</td>
<td>454.63, 455.8, 457.2, 458.45</td>
<td>TiN, Ti₂O₃, TiO₂</td>
</tr>
<tr>
<td>TiN-Mo-1E18</td>
<td>454.21, 455.95, 457.6, 458.6</td>
<td>227.5, 228.6 TiN, Ti₂O₃, TiO₂, Mo, MoO₂</td>
</tr>
</tbody>
</table>

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**Table 3**

<table>
<thead>
<tr>
<th>Mechanical properties (GPa)</th>
<th>TiN</th>
<th>TiN-Mo-3E17</th>
<th>TiN-Mo-1E18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average nano-hardness</td>
<td>35.53</td>
<td>33.04</td>
<td>28.01</td>
</tr>
<tr>
<td>Average modulus</td>
<td>491.38</td>
<td>463</td>
<td>416.69</td>
</tr>
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</table>
profiles 3.3. Fig. each} 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Mechanical properties of the TiN surfaces of un-implanted and Mo-implanted at 1E18 dose (a) nano-hardness; and (b) elastic modulus.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{Wear rates and friction coefficients of the TiN coating surfaces with Mo implantation at different doses (a) wear rates; and (b) friction coefficients.}
\end{figure}

Without implantation is entirely above that of the TiN samples with Mo-implantation. Taking the parts after the sharp increasing at the beginning of the friction coefficients curves as the steady stages, the average friction coefficients of TiN, TiN-Mo-3E17 and TiN-Mo-1E18 at the steady stages are 1.05, 0.63 and 0.43, respectively. It can be seen that the friction coefficients of TiN coatings decreased by 40% for TiN-Mo-3E17 and by 59.05% for TiN-Mo-1E18. In addition, the friction coefficient curve for TiN coating fluctuates more widely and begins to rise after wear for 50 min compared with the previous steady stage. However, the friction coefficient curves for Mo-implanted TiN coatings are stable without obvious increase. Moreover, the TiN-Mo-1E18 samples notably reduce the time of the sharp increasing of friction coefficients at the beginning of the wear. It suggests that Mo-implanted TiN coatings can reduce friction effectively and higher dose is greatly beneficial to the decrease of its friction coefficient. It is supposed that hard Ti₂N phase and soft phase Mo and lubricious phase MoO₂ play important roles in anti-wear and reducing friction during the dry friction process.

3.3. Worn surfaces analysis

The morphology of wear tracks and their typical cross-section profiles are displayed in Fig. 6. To examine the details of the wear tracks, two typical parts of flat area (red curves in Fig. 6d–f) and pit area (green curves in Fig. 6d–f) are analyzed respectively. It is found that all wear tracks have pits and furrows. The pits are similar to each other and all extend to the 316L steel substrates, while the furrows on the wear tracks show distinct differences. As seen in Fig. 6a, there are obvious furrows along the friction direction on the wear track for TiN coating with the width of 0.7 mm and the depth of near 2.0 μm (Fig. 6d). Some furrows and the bottom of the flat area of TiN coatings reach the 316L substrate which result in the wide fluctuation and rising of friction coefficient after wear for 50 min. After Mo-implantation at dose of 3E17, the wear track becomes narrower and shallower with the width of 0.6 mm and the depth of 1.0 μm (Fig. 6b and e). However, there are still lots of furrows on the wear tracks of the Mo-implanted TiN coatings at 3E17 dose. Furthermore, on the wear track of the Mo-implanted TiN coatings at 1E18 dose, the furrows are very few and much shallower (Fig. 6c and f), and the width sharply decreases to 0.4 mm with the depth of about 1.0 μm (Fig. 6f). It reveals that Mo implantation can greatly decrease severe degree of the friction and abrasive wear during dry friction.

SEM images of wear tracks in Fig. 7 display the similar results as Fig. 6. After Mo-implantation at dose of 1E18, the wear track becomes much narrower and shallower with fewer furrows and smaller pits (Fig. 7a and b) which are further proved by their relevant EDS results of element distribution of Ti and Fe on the wear tracks. Three points marked as 1, 2 and 3 (Fig. 7c and d) represent the areas of substrate, flat area and pit area of the wear tracks, respectively. It can be seen that the morphology of the substrates of both TiN and TiN-Mo-1E18 coatings is similar, while the wear tracks are quite different. First, there are much deeper furrows on the wear tracks of TiN coatings while there are no obvious furrows after Mo implantation, which reveals that severe abrasive wear is remarkably reduced by Mo implantation. Second, there are much bigger dark oxides pieces above the pits area of TiN coatings with many cracking on the oxides surfaces, while the smaller dark oxides pieces mainly disperse on the edge of pits and above flat area after
Mo implantation, which reveals that Mo implantation could also remarkably reduce the severe adhesive wear.

3.4. Discussion

Lubricious tribofilms like titanium oxides and molybdenum oxides could be formed and used as good lubricants during dry friction condition. They have the Magneli-phase structures with low shearing strength and could isolate friction surfaces effectively to reduce the wear and friction of surfaces [12,13,16]. However, the titanium oxide film begins to deteriorate over about 400 °C and increase its friction coefficient. As seen in Fig. 5b, the friction coefficient of TiN coatings shows a longer increase period at the beginning of the wear, which may be due to the deterioration of Ti oxides. On the contrary, Mo implantation could decrease the friction coefficients of TiN coatings and keep it much more stable. After Mo implantation, soft phase Mo of TiN coatings could be easily cut and adhere to worn surfaces during the wear process, which may effectively decrease the friction coefficient. Also Mo element may diffuse into deeper place of the worn surface of TiN coating under the high temperature during wear process. At the same time, a part of molybdenum can be gradually transformed to molybdenum oxides under high temperature of friction process. Besides the original MoO₂ on the surfaces, there could continuously produce lubricious molybdenum oxides on the worn surfaces of TiN coatings with Mo implantation during the dry friction process. Therefore, besides titanium oxides, there are Mo and molybdenum oxides as good lubricants which are beneficial to get smoother worn surfaces and maintain lower friction coefficients. Also, the existence of Mo and its oxides could be able to delay the temperature rising of the friction surfaces and prolong the valid lubrication time of the titanium oxides. In addition, TiN coatings with Mo implantation could remarkably improve their anti-wear properties. Firstly, the hard substrate phases of TiN can provide good load supports for the lubricious phases of titanium oxides, Mo and molybdenum oxides, which can greatly reduce their abrasive wear and adhesive wear for much longer time. Secondly, hard phases of Ti₂N may disperse on the friction surfaces and further enhance its wear resistance after Mo implantation.

Owing to its higher dose of Mo implantation, TiN coating with Mo-implantation at dose of 1E18 could get much more molybdenum on its surface than that at dose of 3E17. Also, it can provide

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**Fig. 6.** Morphology of wear tracks of the TiN coatings with and without Mo implantation (a) TiN; (b) 3E17 ions/cm²; and (c) 1E18 ions/cm² and its typical cross-section profile (d) TiN; (e) 3E17 ions/cm²; and (f) 1E18 ions/cm². (For interpretation of the references to color in text, the reader is referred to the web version of this article.)
much more molybdenum oxides produced during the wear process, along with the titanium oxides, to get much better lubrication effect for a much longer time. As a result, TiN coatings with Mo implantation at 1E18 dose can obtain the lowest friction coefficient, and remarkably improve the surface morphology of wear tracks. However, the wear resistance of TiN coatings with Mo implantation at 1E18 dose could not be further distinctly improved comparing to the 3E17 dose due to the obvious decreasing of surface hardness.

4. Conclusions

Mo ions were implanted into PVD TiN coatings at doses of $3 \times 10^{17}$ ions/cm² and $1 \times 10^{18}$ ions/cm² by MEVVA source at room temperature. From the XRD results, it was found that Mo implantations could produce the diffraction peak of hard phase Ti$_2$N at the two doses. And soft phases of Mo and MoO$_3$ were also detected by XPS which obviously reduced the nano-hardness and elastic modulus of TiN coatings after Mo implantation. The tribological properties of Mo-implanted TiN coatings, against Si$_3$N$_4$ ball were remarkably improved. The wear rates and friction coefficients decreased by 31.38% and 40% respectively for Mo-implanted TiN coatings at dose of 3E17, while that of the Mo-implanted TiN coatings at dose of 1E18 decreased by 35.48% and 59.05% respectively. The wear mechanism of TiN coatings un-implanted and implanted was both abrasive wear and adhesive wear. However, Mo implantation could remarkably reduce the abrasive wear and adhesive wear of TiN coatings resulting from its lubricious oxides and hard phases of Ti$_2$N and TiN. Furthermore, the TiN coating with Mo-implantation at 1E18 dose could obtain the lowest friction coefficient and the narrowest wear tracks, due to more soft molybdenum and molybdenum oxides as good lubricant and longer lubrication time of titanium oxides during wear process.

Acknowledgments

The authors would like to thank the Beijing Natural Science Foundation (3132023), the National Natural Science Foundation of China (51275494, 51005218), the Fundamental Research Funds for the Central Universities, the Program for Key International Science and Technology Cooperation Project of China (2010DFR50070) and the Tribology Science Fund of State Key Laboratory of Tribology (SKLTF11004) for their financial supports.

References


