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Investigating the wear characteristics of engineered surfaces: low-temperature plasma nitriding and TiN + MoS_x hard-solid lubricant coating

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Abstract Significant progress has been made in the past decade in plasma nitriding with a majority of the research work focusing on improving hardness and wear resistance of the nitrided surface through the reduction of nitriding temperature, pressure or time. Hard-solid lubricating coatings have also been extensively studied for lowering the wear rate and coefficient of friction of traditional hard coatings such as TiN by the combined effect of hardness and solid lubrication. In this study, the wear characteristics of low-temperature plasma-nitrided steel substrate performed using a Saddle-field fast atom beam source and TiN + MoS_x hard-solid lubricant coating deposited by a closed-field magnetron-sputtering technique have been investigated. The thin hard layer in plasma-nitrided substrates exhibited much higher hardness and lower wear compared to the untreated substrate in pin-on-disc wear testing. In addition, the study of the wear track morphology of the nitrided samples evidenced significant reduction of deeper ploughing and plastic deformation due to higher hardness and load supporting of the nitrided layer. On the other hand, due to the incorporation of MoS_2 in TiN coating, the wear resistance and coefficient of friction were greatly improved in TiN + MoS_x coating compared to pure TiN coating. In contrast to TiN coating, a relatively smoother wear track with less abrasive wear also supported the beneficial effects of adding MoS_2 in TiN coating.

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Introduction

Surface engineering either by modifying near-surface properties (e.g., nitriding) or by applying a layer of hard materials (e.g., coatings) has gained the attention of surface engineering researchers for controlling wear and friction at the contact surfaces and extending the service life. Thermochemical diffusion processes such as nitriding can improve the tribological and mechanical properties of steels by enriching the near-surface region with nitrogen. Plasma or glow discharge nitriding enjoys several advantages such as higher cleanliness, less distortion, higher hardness and wear resistance over the conventional nitriding processes. Recently, more attention has been paid to low-temperature (below 500 °C) plasma nitriding to acquire more enhanced surface properties (e.g., tribological and mechanical) without losing inherent corrosion resistance and to control the nitrided layer formation in a short processing time [1–6].

On the other hand, thin hard coatings (i.e., TiN, CrN, TiAlN, etc.) have been widely accepted particularly in the cutting and forming tool industries to enhance the tool life. However, many of these coatings have higher coefficient of friction, which does not protect the opposing surface and sometimes in a closed tribological system, the eroded hard coating particles act like grits, which propagate the failure of the coatings before the expected life [7]. Solid lubricants are often used in industrial applications to reduce friction between sliding surfaces in contact. However, solid lubricants usually have lower hardness and poor wear resistance and easily oxidise in humid air, which do not make them ideal for surface engineering applications. In recent years, hard-solid lubricating coating has been investigated to lower the wear rate and coefficient of friction by the combined effect of soft and hard phases [8–11].

In this paper, low-temperature plasma-nitrided steel substrates and hard-solid lubricant coating (TiN + MoS_x) have been investigated to exploit their wear characteristics in pin-on-disc wear tests.

Experimental procedure

Plasma nitriding

A low-temperature plasma nitriding of 316 stainless steel was conducted by a new process (Saddle-field neutral fast atom beam source) in an existing Plasma-Enhanced Chemical Vapour Deposition (PECVD) chamber (Fig. 1). The sample was etched with an overall pressure of 2×10^{-1} Pa for 15 min after achieving a base pressure of approximately 10^{-4} Pa. The sample was then heated to a required temperature level (420 °C) by an auxiliary heater, and a gas mixture of nitrogen (20%) and argon (80%) was introduced into the beam source to produce a neutral beam by the application of a high voltage (1,800–2,200 V) to the anodes of the source. A beam current of 0.4 A and a pressure of around 1×10^{-1} Pa were applied for 1, 3, 6 and 9 h during the nitriding process.

Coating deposition

The coatings were deposited on stainless steel substrates using a magnetron-sputtering technique where two facing magnetrons fitted with Ti and MoS_2 targets and other two facing magnetrons fitted with Ti targets were arranged in a closed-field arrangement (Fig. 2). The substrate was sputter cleaned in argon plasma with an overall pressure of 1 Pa for 15–20 min. After achieving a base pressure of 10^{-3} Pa, the deposition pressure was fixed at 3×10^{-1} Pa. First a very thin Ti interlayer (~0.15 μm) was deposited onto the substrate fixed to a rotatable substrate holder (at 3 rpm) approximately 80 mm away from the target. TiN + MoS_x coating was deposited for 60 min when the substrate passed in front of Ti and MoS_2 targets in the nitrogen gas environment. Two facing magnetrons with Ti target (current density, 15 mA/cm^2; and target voltage, 410 V) and MoS_2 target (current density, 0.9 mA/cm^2; and target voltage, 460 V) were activated during the coating deposition. The nitrogen flow rate was controlled by a Reactaflo reactive sputtering controller to form stoichiometric TiN. TiN and MoS_x coatings of same thickness were also deposited as references with the same parameters used during TiN + MoS_x coating deposition.

Characterisation techniques

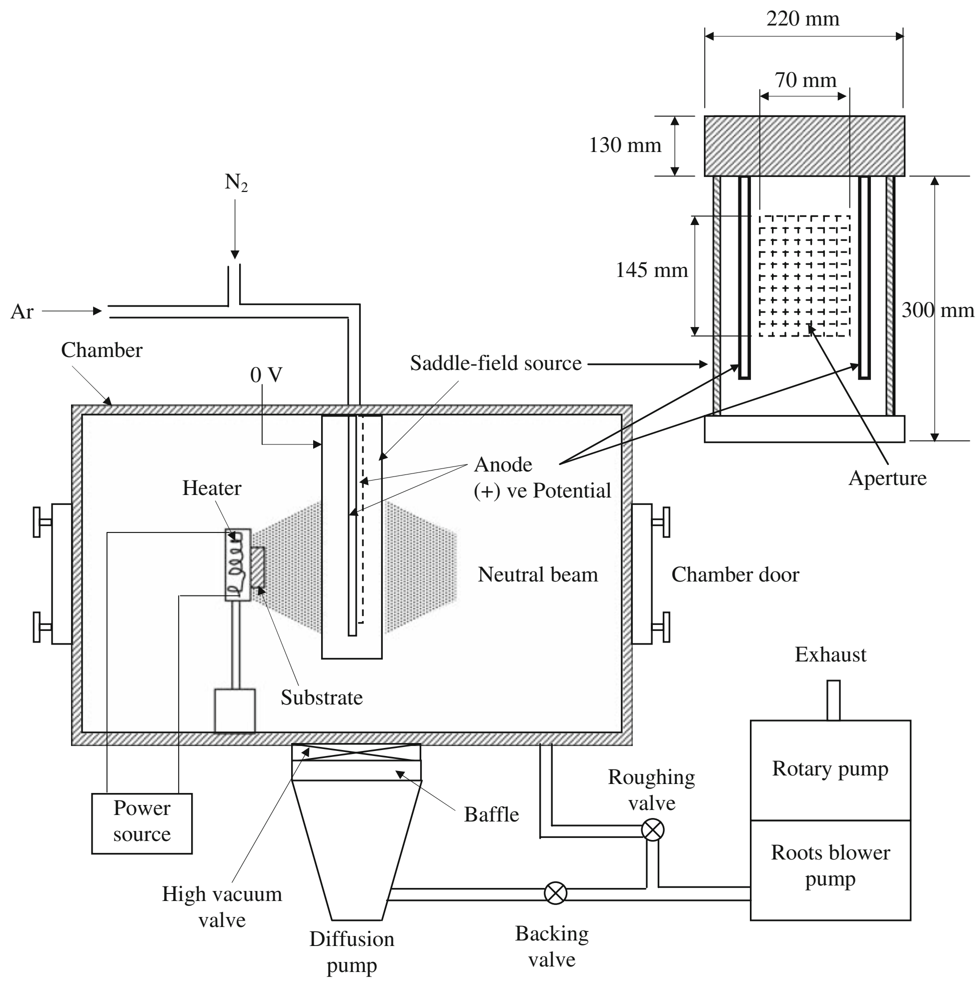
Glancing-Angle X-ray Diffraction (GAXRD) was performed by a Bruker D8 diffractometer with CuK_α radiation at an incident angle of 3°. A Princeton Gamma-tech Energy Dispersive X-Ray (EDX) spectroscope was employed to obtain the chemical composition of nitrided surface and coating. Vicker micro-hardness measurements were carried out using a Leitz MiniLoad micro-hardness tester with a maximum load of 15 g for coated samples and 25 g for nitrided samples. Coating thickness was measured by a Teer BC-2 ball-cratering device. Ball-cratering device grinds a small crater (diameter ~1 mm) through the coating with a steel ball of known diameter to provide a tapered cross-section of the coating when viewed under an optical microscope. Geometrical measurement of the resultant crater allows the calculation of the coating thickness using a simple equation (Fig. 3). The pin-on-disc wear tests were carried out using an Implant Sciences ISC-200PC tribometer. Each sample was tested to 9,000 revolutions, at a speed of 60 rpm and a cylindrical track diameter of 9 mm in laboratory air (40–50% RH). A normal load of 2 N on a 3-mm diameter tungsten carbide ball (pin) was also used for each sample. The computer controlled pin-on-disc tester automatically calculated the coefficient of friction (ratio of frictional force measured by a load cell and applied normal force) using a specialised software. The depth and width of the wear tracks were measured using a WYKO NT1100 Optical profilometer. A Reichert "MeFe2" Universal Camera Optical Microscope and the optical profilometer were employed to investigate the wear tracks.

Results and discussions

Characteristics and wear behaviour of plasma-nitrided samples

The plasma-nitrided samples exhibited distinct microstructures under optical microscope with *grain boundaries* and *twins* as shown in Fig. 4, possibly due to formation of the nitrided layer [1, 12]. The twins were more visible when nitriding time was increased from 3 to 9 h. This surface irregularity was also reflected in the linear increase of surface roughness with the increase of nitriding time

Fig. 1 Schematic diagram of plasma-nitriding experimental set-up



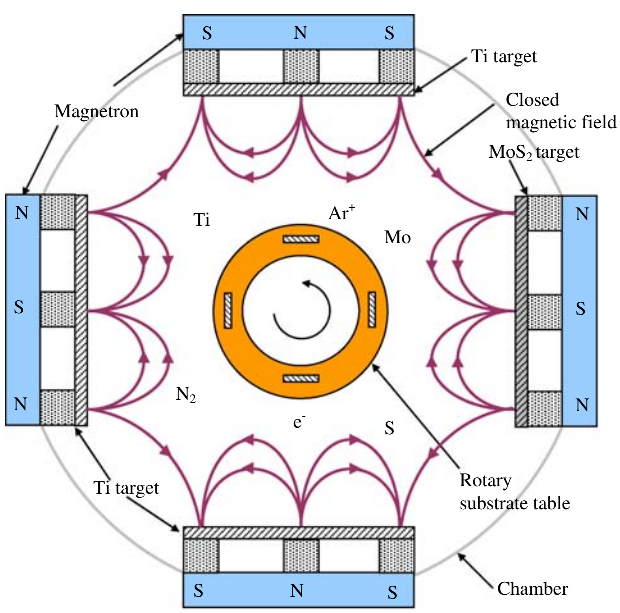


Fig. 2 Cross-section of the closed-field magnetron sputtering chamber

(30 nm for the untreated sample to a value of approximately 170 nm after 12 h). A thin nitrided layer (3–4 μm) was observed in case of the sample nitrided for 1 h. However, the nitrided layer thickness was measured to be as high as 25 μm in this study when the sample was nitrided for 8 h. The formation of a comparatively thicker nitrided layer at low temperature and within a short processing time, possibly due to the energetic atom beam, showed the potential of this new nitriding process. The formation of a relatively thick nitriding layer increased the composite hardness (1200 $HV_{0.025}$) of the samples, which was up to four times higher than the untreated sample. X-ray diffraction patterns of the nitrided sample reported in the author's previous publication [6] confirmed the formation of a metastable phase called "expanded austenite" or "S phase" [13]. EDX analysis of the nitrided samples also confirmed the presence of nitrogen in the nitrided layer having increasing intensity of nitrogen peak with the nitriding time [6].

For better understanding of the tribological properties of nitrided surfaces, pin-on-disc wear tests were carried

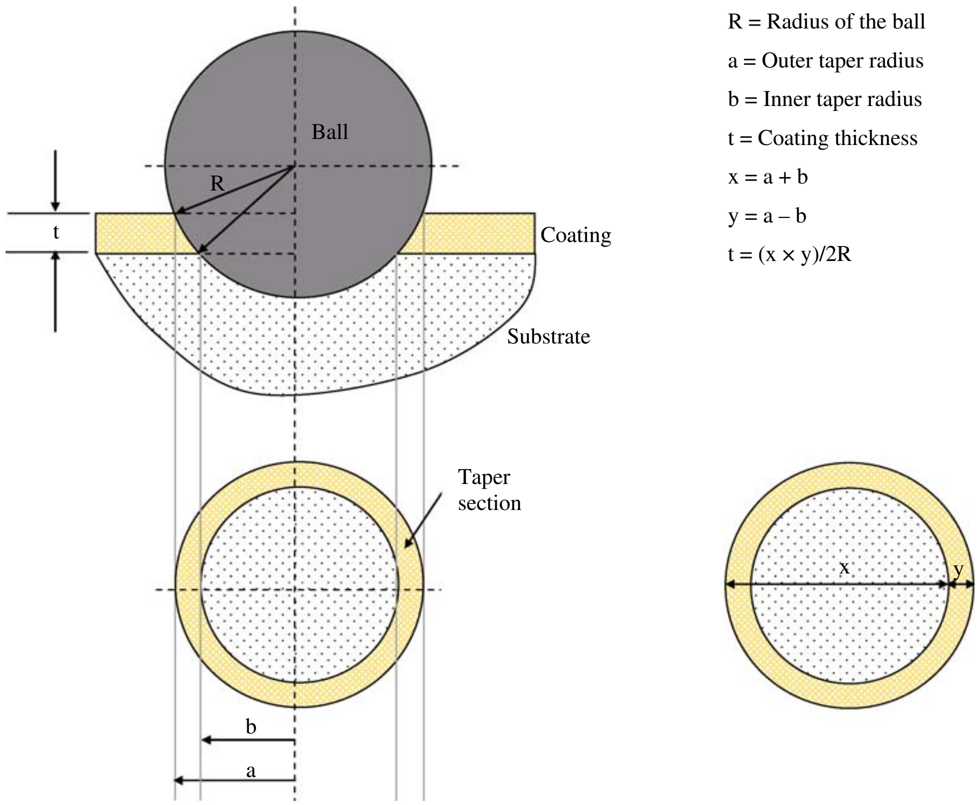


Fig. 3 A schematic diagram of the crater formed through the coating by ball-cratering equipment and the geometry used to determine the coating thickness

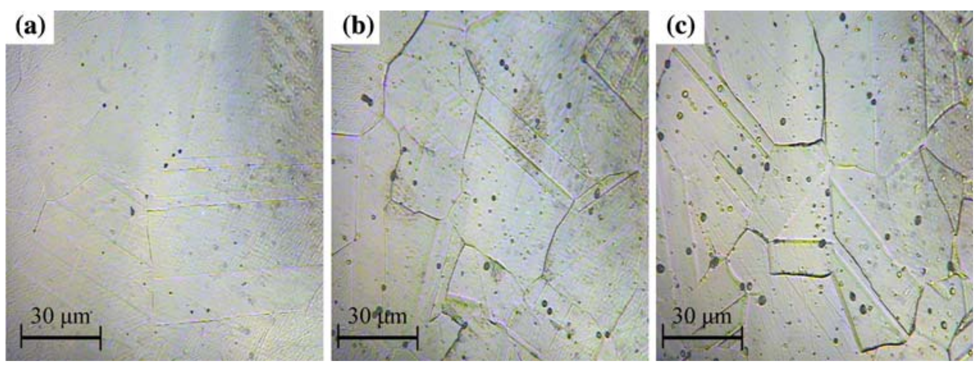


Fig. 4 Surface morphology of the nitrided surfaces (without chemical etching) treated at 420 °C for (**a**) 3 h, (**b**) 6 h and (**c**) 9 h

out on both as-nitrided and polished nitrided samples. The untreated and polished nitrided (9 h) samples showed steady-state friction values of approximately 0.76 and 0.55, respectively. However, the steady-state friction coefficient value for as-nitrided sample (9 h) was approximately 0.64 possibly due to slightly rougher surface. The plasma-nitrided samples showed a lower, more stable and smoother coefficient of friction compared to the untreated sample due to the hard nitrided surface leading to lower contact area and the prevention of asperity welding. Figure 5 shows the wear depth values of both treated and untreated samples in pin-on-disc wear test under the same operating condition. It was found that low-temperature plasma nitriding significantly improved the wear resistance of 316 stainless steel. The wear depth value of the 1-h nitrided sample (polished) was recorded to be as low as 0.5 µm, which was approximately 13 times lower than the untreated sample. This was due to hard nitrided surface leading to a decreased contact area with the counter-part surface at the time of wear test. It was interesting to note that the wear depth value increased as the nitriding time increased. This fact could be attributed to the build up of higher residual stress in the topmost layer of the nitrided sample with increased nitriding time as observed in XRD analysis [6]. The formation of relatively harder and larger abrasive wear particles in the samples with longer nitriding period could also be responsible for higher wear. The wear depths of all the nitrided samples were significantly lower than that of the untreated sample. However, the polished nitrided samples showed slightly lower wear depth

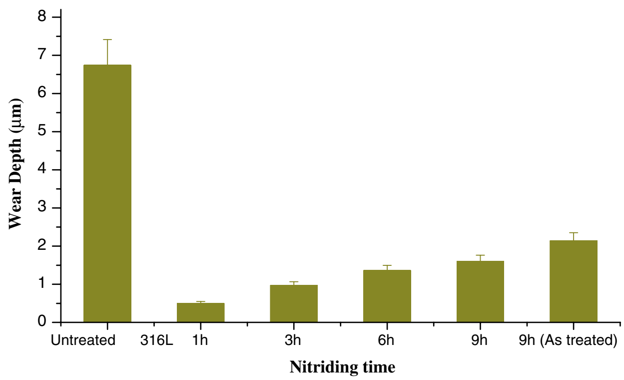


Fig. 5 Wear depth of the untreated and treated samples with different treatment times

compared to the as-treated ones, possibly due to the influence of lower surface roughness.

A very wide, rougher and deeper wear track was clearly observed for the untreated sample in the pin-on-disc wear test (Fig. 6a). The wear track of the untreated sample showed large plastic deformation and deeper ploughing line and severe material pile up at the edge of the wear track. A large amount of wear debris was distinctly found on the wear track of the untreated sample, and this wear debris produced a parallel deep ploughing line along the wear track. Therefore, the wear mechanism in the untreated sample could be characterised by a severe abrasive and deformation type wear. On the other hand, different wear behaviour was characterised for the nitrided sample compared to the untreated sample. From Fig. 6b, a narrow, relatively less rough and shallow wear track was observed in the nitrided samples. The wear track width of the nitrided sample treated for 1 h (240 μm) was almost half of the untreated sample (503 μm). Nitrided samples showed a modest polished type micro-abrasive wear, no severe plastic deformation or no material pile up at the edge of the wear track due to a very hard and higher load-supporting layer of nitride.

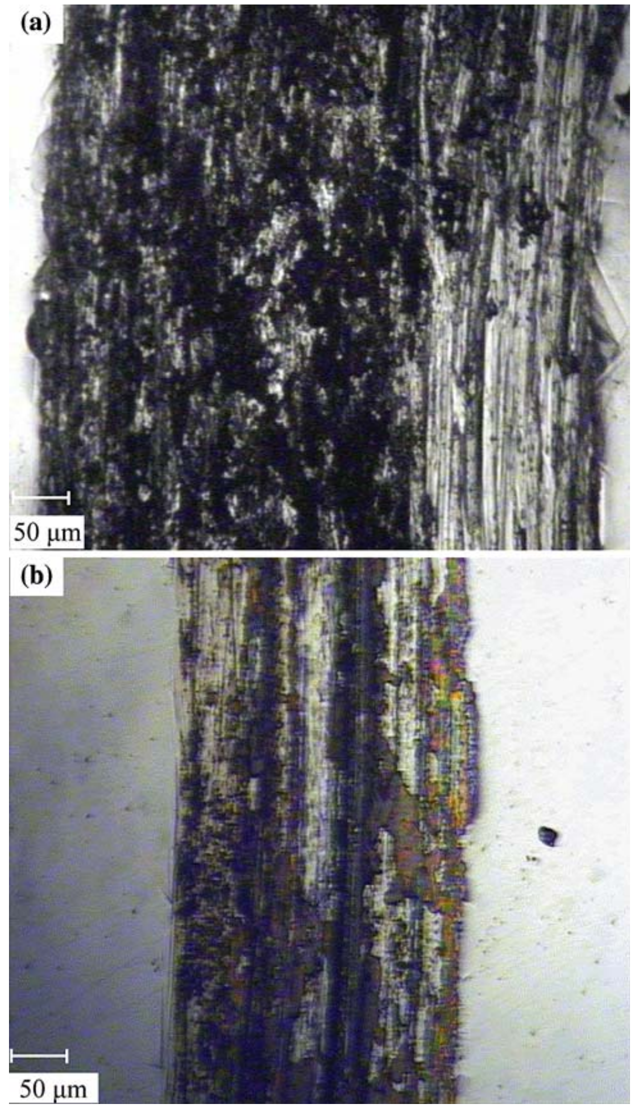


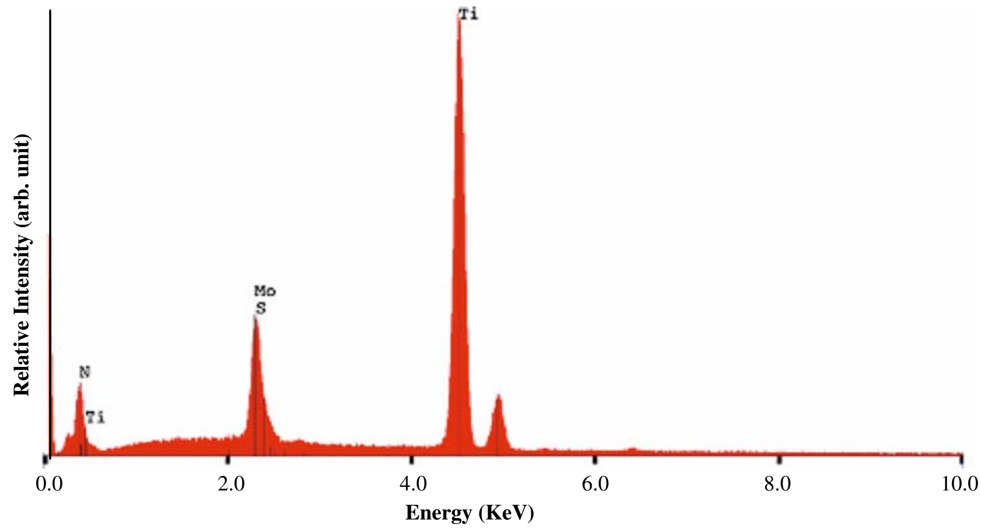
Fig. 6 Optical wear track morphology of (**a**) untreated and (**b**) treated samples (1 h)

Characteristics and wear behaviour of coated samples

TiN + MoS_x coating thickness was measured to be approximately 2 μm by the ball-cratering device, and the surface of the coating (R_a: 15–20 nm) was quite smooth compared to TiN coating and steel substrate. EDX analysis measured approximately 7 wt.% Mo + S in the TiN + MoS_x coating. A typical spectrum of EDX analysis on the TiN + MoS_x coating is shown in Fig. 7. XRD study revealed shifted TiN peak and no MoS_x phase in the coating suggesting that Mo and S atoms were possibly incorporated into the cubic TiN lattice or segregated at the grain boundaries (Fig. 8) [8]. TiN + MoS_x coating showed lower friction coefficient ($\sim$0.4) than pure TiN ($\sim$0.6), but higher than MoS_x coating (0.2). This fact can be explained by the formation of MoS_x from Mo and S atoms in the wear track during the run-in period as explained by Goller et al. [8].

Figure 9 shows the comparison of the specific wear rate of TiN + MoS_x coating with pure TiN and MoS_x coatings. TiN + MoS_x coating showed the least wear among the different coatings under the same operating conditions, although the coating possessed a lower hardness value than TiN coating and a higher hardness value than MoS_x coating. It has been well established that the low coefficient of friction could be one of the reasons for lower wear rate in thin film coating [14]. Since there was no clear correlation between the hardness of the coatings and their tribological

Fig. 7 A representative EDX spectrum of TiN + MoS_x coating



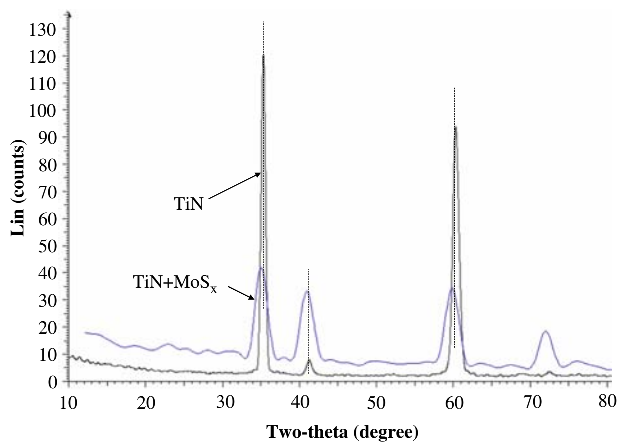


Fig. 8 XRD spectra of pure TiN and TiN + MoS_x coatings

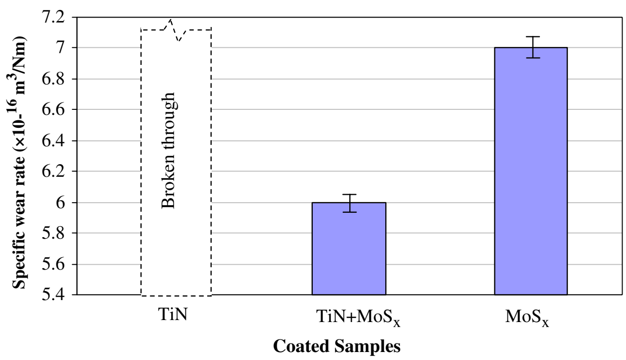


Fig. 9 Specific wear rates of TiN, TiN + MoS_x and MoS_x coatings in a pin-on-disc wear test

performance, it was inferred that the lubricity from MoS_x in the TiN + MoS_x coatings might be playing a role in lowering the wear rate in the TiN + MoS_x coating. The low wear in the TiN + MoS_x coating could be related to the fact that a low friction layer produced on the opposing surface (pin) in the pin-on-disc wear test. TiN showed the highest wear rate, as it was completely broken before reaching the same sliding distance for other coatings. This indicated that even if the wear depth in TiN coating was taken as equal to the coating thickness, the wear rate of TiN coating would be approximately *one order of magnitude* higher than that of TiN + MoS_x coating. The low wear in MoS_x coating compared to TiN coating could be attributed to easy sliding of the pin over the coating and possibly due to formation of a transfer layer on the pin making the contact only between the low friction layers. Although much lower friction was observed in MoS_x coating, the comparatively higher wear rate than TiN + MoS_x could be related to the lower hardness of MoS_x coating.

In general, the tribological behaviour of a thin coating is dominated by four main parameters: the ratio of coating to substrate hardness, the coating thickness, the surface roughness and the wear debris in the contact [15]. During the pin-on-disc testing, the transferred materials were compacted and mechanically mixed with coating materials, forming the surface layer usually referred to as wear debris, which plays an important role in controlling the wear and friction behaviour [14]. The good lubrication property of MoS_2 is generally ascribed to the ease of sliding of the basal planes of its hexagonal structure, which are held together by weak van der Waals bonding. It should be noted that although XRD study revealed no evidence of MoS_2 hexagonal phase in either MoS_x or TiN + MoS_x, a structural reorientation of Mo and S atoms in the coatings during sliding could be expected. This phenomenon was not in contradiction with the literature where it was reported that poorly crystalline or amorphous phase of MoS_2 transforms into well-developed hexagonal phase in sliding operation [16–18].

The investigation of wear track with optical microscope or optical profilometer serves as a good tool to analyse wear behaviour of thin film coatings [19]. Optical micrographs revealed noticeable differences in the surface wear characteristics among TiN, TiN + MoS_x and MoS_x coatings. Figure 10 shows a typical wear track morphology created after the pin-on-disc test in TiN coating. The maximum depth (2.43 μm) in the three-dimensional wear track of TiN coating, higher than the coating thickness (~2 μm), confirmed the complete delamination. The exposure of the substrate was also apparent in the wear morphology under optical microscope. Wear grooves with features of cutting and ploughing, typical for a severe abrasive wear mechanism, were observed in the TiN coating. The generation of hard and abrasive coating particles due to the progressive removal of the TiN coating contributed to a pronounced abrasion mechanism, and hence a local removal of the TiN coating in the form of flakes exposing the substrate. The detachment of TiN coating could also be attributed to the loss of adhesion and the presence of debris originating from the steel substrate. Due to the higher hardness of TiN coating, it showed lower wear up to a certain sliding distance and the abrasive particle formed in the wear track that played the role of a third body in the tribological system and propagated the failure of the coating very rapidly [10].

In contrary to TiN coating, severe abrasive wear and brittle flaking of the coating were diminished in the TiN + MoS_x coating due to the solid lubricant effect coming from the solid lubricant part of the coating. A comparatively smooth surface in the wear track and less wear debris at the periphery of the wear track than TiN coating were observed as shown in Fig. 11. The optical

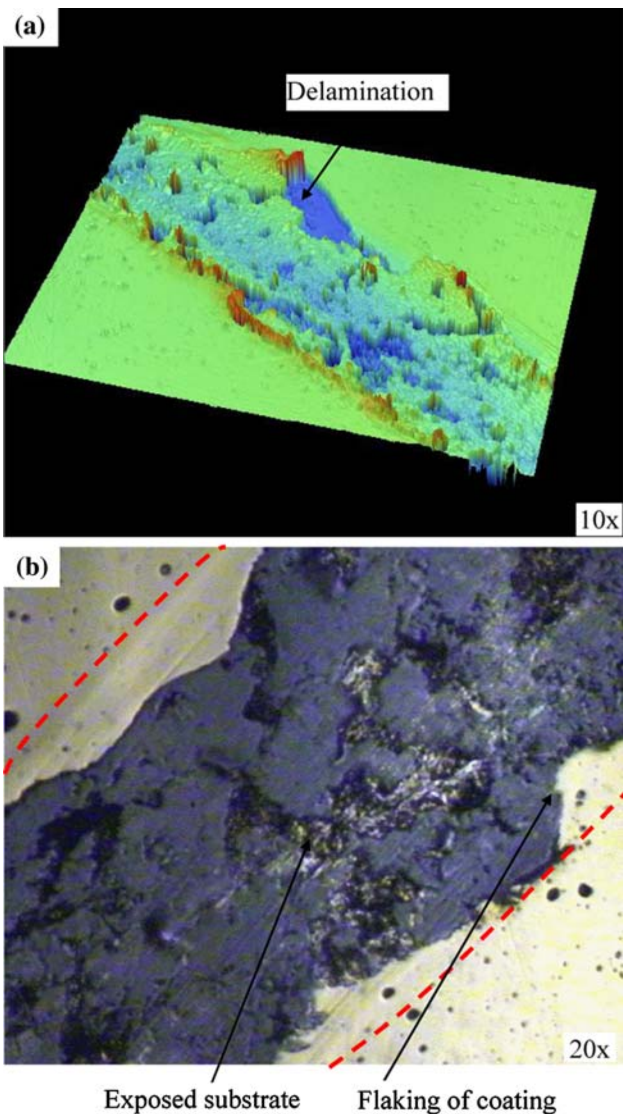


Fig. 10 Wear track morphology of TiN coating under (**a**) optical profilometer and (**b**) optical microscope

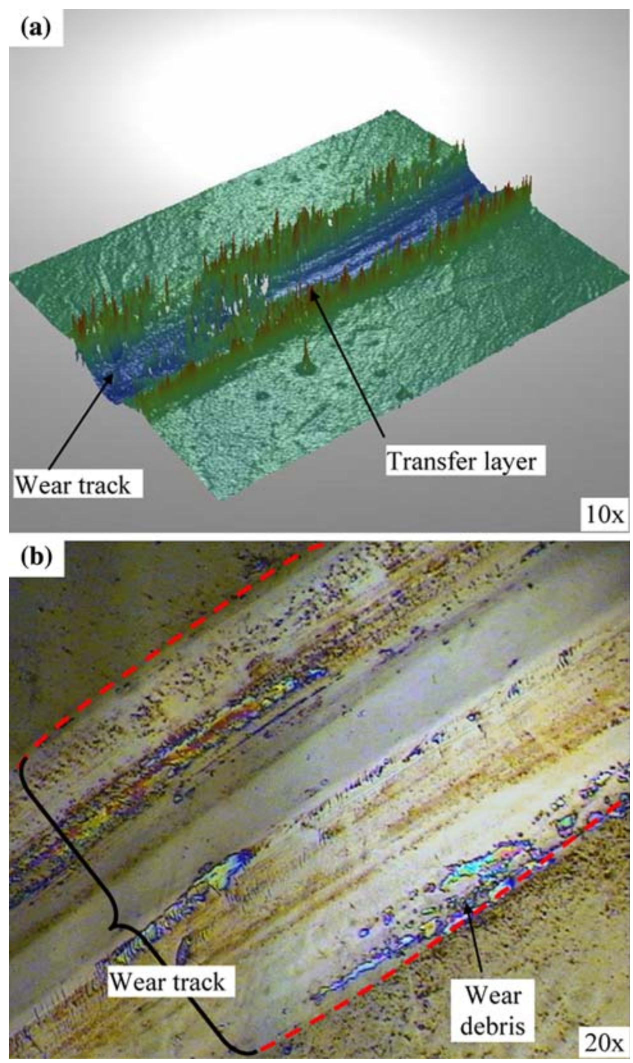


Fig. 11 Wear track morphology of TiN + MoS_x coating under (**a**) optical profilometer and (**b**) optical microscope

micrographs did not show any sign of delamination of the coating, as the wear depth (0.28 μm) in the TiN + MoS_x coating was much lower than the coating thickness. Although the middle of the wear track in the TiN + MoS_x coating was smooth, there were few places on the side of the track with deeper grooves. This could be reasoned by the non-uniform material transfer from the TiN + MoS_x coating or spalling of relatively bigger debris where there was a lack of lubrication.

Very smooth wear track with very little wear debris appeared for the MoS_x coating as shown in Fig. 12. The wear track was barely visible in optical microscope as if no wear track was formed. However, the wear track with deep groove was clearly visible in the three-dimensional optical profilometer. The smooth wear track formed due to the low friction properties of the MoS_x coating and the transfer layer formed on the opposing surface. The deeper groove formed due to the lower hardness of the coating compared to TiN and TiN + MoS_x coatings.

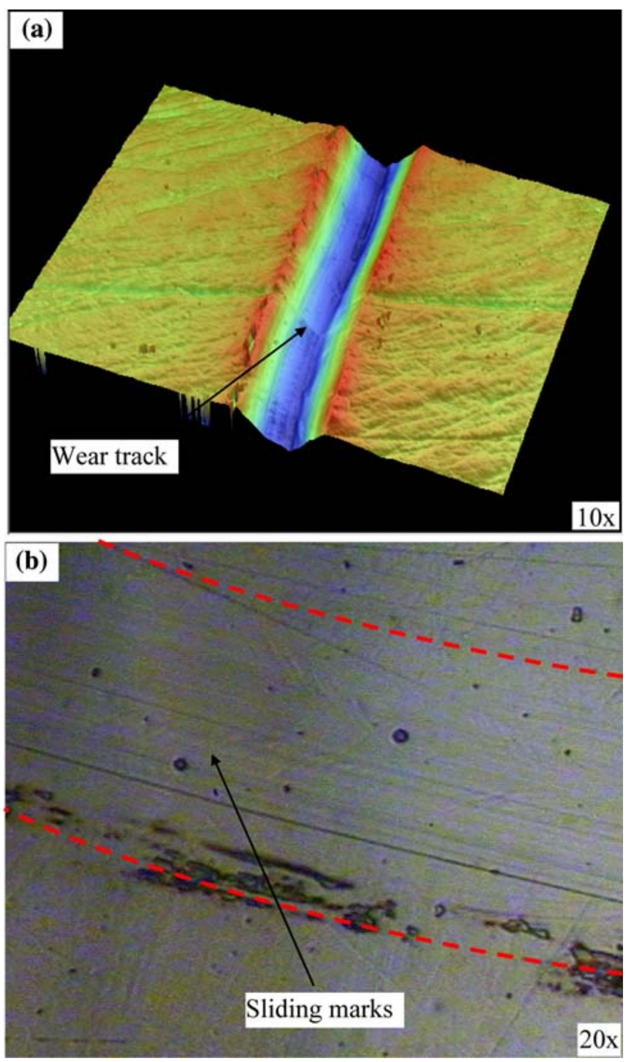


Fig. 12 Wear track morphology of MoS_x coating under (**a**) optical profilometer and (**b**) optical microscope

Conclusions

The low-temperature plasma nitriding on steel substrate by a Saddle-field fast atom beam source produced a thin hard nitrided layer having a surface characteristic of 'grain boundaries' with 'twins' within a short treatment period. Plasma-nitrided surface showed higher hardness (up to 4 times), higher wear resistance (4–13 times) and lower coefficient of friction compared to the untreated sample. The lowest wear rate was obtained in the sample with the shortest nitriding time (1 h). The pin-on-disc test revealed a relatively narrow track width and micro-abrasive wear mechanism in the wear track of the nitrided sample. The TiN + MoS_x hard-solid lubricant coating deposited by closed-field magnetron sputtering exhibited remarkable decrease of wear rate and coefficient of friction compared to the pure TiN coating in the pin-on-disc test possibly due to the combined hard and solid lubrication effects. Severe abrasive wear mechanism, revealed in TiN coating, was suppressed in the TiN + MoS_x coating and a comparatively smooth wear track with irregular patches of slightly deep grooves was characterised.

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