Influence of substrate pre-treatments by Xe\textsuperscript{+} ion bombardment and plasma nitriding on the behavior of TiN coatings deposited by plasma reactive sputtering on 100Cr\textit{f} steel

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\textbf{Highlights:}

- 100Cr\textit{f} steel substrates were Xe bombarded with 1.0 KeV
- The XRD patters confirms that the previous Xe ion bombardment increase nitrogen implantation in plasma nitriding process
• The AFM shows that the impact energy in combination with plasma nitriding cause a significantly increase roughness

Abstract

In this paper the influence of pre-treating a 100Cr6 steel surface by Xe$^+$ ion bombardment and plasma nitriding at low temperature (380°C) on the roughness, wear resistance and residual stresses of thin TiN coatings deposited by reactive IBAD was investigated. The Xe$^+$ ion bombardment was carried out using a 1.0 keV kinetic energy by a broad ion beam assistance deposition (IBAD, Kaufman cell). The results showed that in the studied experimental conditions the ion bombardment intensifies nitrogen diffusion by creating lattice imperfections, stress, and increasing roughness. In case of the combined pre-treatment with Xe$^+$ ion bombardment and subsequent plasma nitriding of samples with relatively high average roughness, the wear volume increases in comparison to the substrates exposed to only nitriding or ion bombardment.

**Keywords**: Ion implantation, nitrides, ion beam-assisted deposition, thin films, wear.

1. Introduction

The performance of cutting tools and dies can be largely improved by surface modification techniques, such as plasma nitriding and hard coating deposition, which are widely applied to steels leading to increase hardness, oxidation and corrosion resistance, wear resistance and overall superior tribological properties [1-5]. Plasma nitriding allows for excellent parameters control and high efficiency nitrogen diffusion at relatively low
temperatures (300-450°C), which results in a more chemically uniform compound layer (“white layer”) and maintaining the material original hardness in comparison to conventional gas nitriding processes [6].

Typically, plasma nitrided steel work-pieces have a compound layer (“white layer”) formed at the surface which is composed by nitrides. This layer can be formed by ε-Fe$_{2-3}$N and γ'-Fe$_{4}$N or only a monolayer with one type of nitrides. Bellow of the compound layer there are a diffusion zone, which is composed by the α-phase saturated of nitrogen and the fine precipitates nitrides [7]. The nitrides ε-Fe$_{2-3}$N and γ'-Fe$_{4}$N can exhibit very high hardness, lower friction coefficient and good corrosion resistance, thus improving mechanical, chemical and tribological properties [8-11].

Deposition of hard coatings such as TiN, TiC, TiCN and TiAlN, which exhibit very high hardness, good wear resistance and low friction coefficient is also commonly utilized for enhancing surface characteristics of steel parts. The hard ceramic coating can be applied both directly on the metallic substrate as well as on a previously nitrided material [12-14]. In the latter case a duplex scale is formed with superior fatigue and wear resistance due to increased compatibility between the hard external coating and the strengthened underlying substrate [15, 16], e.g. if the substrate is much softer than the hard coating, it might undergo plastic deformation in service causing the outer layer to collapse and fail prematurely [17]. Ion Beam Assisted Deposition (IBAD) is a Physical Vapor Deposition (PVD) process for hard coating deposition that may be combined with ion bombardment. The additional energy of the ion beam allows for coating deposition at lower temperatures, avoiding some of the difficulties associated with conventional PVD processes on nitried substrates, such as bad adhesion, creation of porosities or decomposition of the nitride layer leaving a relatively soft iron layer behind [18,
The IBAD technique also allows for better densification of the hard coating in comparison to PVD processes, as well as independent control of several parameters [20, 21].

The ion bombardment of metallic surfaces produces a variety of microstructural changes, such as the creation of lattice defects, phase transformations, material removal (sputtering) and amorphization on the annealed 100Cr6 steel [22]. Recent studies have demonstrated that the atomic bombardment of steel substrates with Xe$^+$ ions improves the diffusion of nitrogen in the material by prompting stress, grain refinement, defects creation and diffusion channels in the 4140 (quenched and tempered) steel [23, 25-27]. This process can also be used to modify the substrate surface on the atomic level by increasing the surface roughness and thus improving the adherence of hard coatings to the treated areas [7, 28]. Thus, the development of processes which allow improving the performance of tools and dies can benefit from the understanding of pre-treating techniques for metallic substrates aiming at the subsequent deposition of ceramic coatings with enhanced hardness and thermal stability. In this work we report on individual and combined surface processing involving the bombardment with Xe$^+$ ions and plasma nitriding at low temperature, i.e. 380°C, of annealed 100Cr6 steel substrates, as pre-treatment alternatives for the deposition of TiN hard coatings.

2. Materials and Methods

2.1. Substrate material

The substrate material was an annealed 100Cr6 bearing steel. Its chemical composition is given Table 1. The steel specimens were employed in the annealed instead of quenched and tempered condition in order to avoid phase transformations during processing by ion plasma
nitriding. The samples used in all experiments were in the form of 20 mm diameter discs with 2 mm thickness. Prior to application of all surface modification techniques, the steel samples were ground with SiC grinding paper, polished in 6, 3 and 1 µm diamond paste and finally polished in a 0.25µm colloidal silica suspension.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition [wt.%]</td>
<td>1.00</td>
<td>0.25</td>
<td>0.35</td>
<td>1.5</td>
</tr>
</tbody>
</table>

2.2. Surface modification and TiN deposition

Samples from the 100Cr6 steel were submitted to preliminary Xe⁺ ion bombardment and plasma nitriding prior to TiN film deposition. The Xe⁺ ion bombardment/implantation and TiN deposition processes were performed using an ion beam assisted deposition (IBAD) system located at the Ionic Implantation and Surface Treatment Laboratory of the Campinas State University (Unicamp, Brazil). The system consists mainly of a deposition chamber equipped with two Kaufman ion sources of 3 cm diameter, a support for four targets and a temperature controlled (<1000 °C) sample holder. More details regarding this system can be found in the work of Hammer et al. [29].

For ion bombardment a xenon gas flux was introduced into the ~3 cm diameter ion beam Kaufman sources (9.9995%) and ions produced were accelerated to 1.0 keV. The samples were bombarded perpendicularly to the polished surface with a ~2.8 mA/cm² current density for 30min. During Xe⁺ bombardment, the substrate temperature was kept below 260 °C and the
work pressure in this case was 0.15 Pa. Plasma nitriding was performed using a 0.2 keV N\(^+\) beam with ~2.7 mA/cm\(^2\) current density focused on the 100Cr6 sample surface for 30min. The temperature of the process was set to 380 °C and the working pressure was 0.015 Pa for all nitrided samples. The deposition of TiN coatings was accomplished by sputtering a titanium target with an argon ion beam of 1.45 keV (80 mA) in a N\(_2\) atmosphere. The deposition N\(_2\) pressure was 0.055 Pa and the substrate temperature was set to 400 °C. The deposition time was 120 min for all the samples.

All those processes were carried out independently in the following manner: initial sputter cleaning of the substrates using a 600 eV Ar\(^+\) beam for 5 minutes, followed by Xe\(^+\) ion bombardment and/or nitrogen implantation when applicable, and finally, TiN coating deposition. Thus, a series of four samples was produced by combining the processes described above yielding the samples described in Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>Steel + TiN</td>
</tr>
<tr>
<td>SN</td>
<td>Steel + nitrided layer + TiN</td>
</tr>
<tr>
<td>S1000</td>
<td>Steel + Xe(^+) bombarded layer + TiN</td>
</tr>
<tr>
<td>S1000N</td>
<td>Steel + Xe(^+) bombarded and nitrided layer + TiN</td>
</tr>
</tbody>
</table>

2.3. Phase analyses and Microstructure
Angle-dispersive X-ray diffraction (XRD) using synchrotron radiation was carried out at the experimental station XPD of the Brazilian Synchrotron Radiation Laboratory (LNLS, Campinas) in order to assess the phase composition within the TiN coated samples subjected to the different surface pre-treatment procedures. The radiation energy was set to 10.5 keV (\(\lambda = 1.1823 \text{ Å}\)) and the beam was 4 mm wide and 1 mm high. Diffractograms were obtained both under a grazing incidence angle (\(\omega\)) of 1°, which corresponds to an average penetration depth \(\tau\) of 500 nm, and also using the symmetric \(\theta-2\theta\) mode.

The microstructure of the 100Cr6 steel substrate and the TiN coatings was investigated by scanning electron microscopy (SEM) using a Philips XL-30 FEG microscope. The sample cross-sections were etched to reveal the material microstructure with 3% Nital solution. Transmission Electron Microscopy (TEM) of sample cross-sections was used to characterize the size and distribution of the iron nitrides formed during plasma nitriding and to visualize the impact of atomic peening on the microstructure of the steel surface by using a JEOL 2100 microscope. Suitable thin samples were prepared applying a wedge shaped thin slice, i.e., polishing by gentle abrasive rubbing of a specimen with a slight tilt (0.3-0.7°) to obtain an electron transparent wedge with smooth and highly polished surfaces (20 µm). Finally, electron transparent areas were then obtained by low energy ion polishing.

2.4. Topography, wear and coating adhesion

The influence of each pre-treatment procedure on the surface topography of the coated samples was evaluated by atomic force microscopy (AFM) using the tapping mode in a FlexAFM 3 – Nanosurf equipment. To evaluate the adhesion of the coatings, an Anton Paar Nanoscratch-Tester (NST) was employed using a linear increase of the applied normal force up
to 500 mN. The wear resistance of the TiN coatings deposited on the different substrate surfaces was evaluated by means of ball on disc tests. A ball of cemented carbide (WC-Co) with 3.0 mm radius and 5 N normal load were applied to the tests. The total sliding distance was set to 1000 m.

2.5. Residual Stress Analysis

The effect of Xe bombardment and plasma nitriding on the average residual stresses of the TiN films was determined by applying the $\sin^2\psi$ method at a fixed penetration depth of 500 nm using a four-circle diffractometer located at the experimental station XPD of the Synchrotron facilities (LNLS, Campinas, Brazil) [30, 31]. The radiation energy was 10.5 keV ($\lambda = 1.1823$ Å) and beam dimensions were 1 x 1 mm. A fixed penetration depth was chosen in order to suppress the influence of stress gradients, which typically occur in thin surface films, on the stress evaluation procedure. Owing to the weak macroscopic texture of the IBAD deposited TiN films, unrestricted lattice spacing measurements could be performed for all sample directions defined by the inclination angle $\psi$ and the azimuth $\phi$.

The penetration depth $\tau$ of the synchrotron X-rays depends on the incident ($\alpha$) and exit ($\beta$) angles of the incoming and diffracted X-rays, respectively. This can be also expressed as a function of the diffractometer angles according to Eq.(1):

$$\tau = \frac{\sin\alpha \cdot \sin\beta}{\mu[\sin\alpha + \sin\beta]} = \frac{\sin\omega \cdot \sin(2\theta - \omega) \cdot \cos\chi}{\mu[\sin\omega + \sin(2\theta - \omega)]}$$

(1)

where $\mu$ is the linear absorption coefficient of TiN and $\omega$, $2\theta$ and $\chi$ represent the instrumental angles of a four-circle diffractometer. The azimuthal $\phi$ and the inclination $\psi$
angles, which define the sampled specimen directions, can be also expressed in terms of the
diffractometer angles according to Eq. (2) and (3):

\[ \psi = \arccos \left[ \cos \chi \cdot \cos(\omega - \theta) \right] \]  
(2)

\[ \phi = \varphi + \arctan \left[ \frac{-\sin \chi}{\tan(\omega - \theta)} \right] \]  
(3)

Considering Eq. (1) to (3), a \( \sin^2 \psi \)-based stress analysis can be carried out at a constant
penetration depth by applying the following procedure:

(I) the penetration depth \( \tau \) of interest is chosen taking into account e.g. the film
thickness;

(II) a diffraction line (hkl) of the material under consideration is chosen, thus fixing the
diffraction angle \( 2\theta = 2\theta_{hkl} \);

(III) a list of the azimuths \( \varphi \) and the inclination \( \psi \)-angles has to be defined, taking
into account the symmetry of the stress state, the crystallographic texture of the material and
the required measurement accuracy;

(IV) a list of diffractometer settings (\( \omega, \chi, \phi \)) has to be determined for each specimen
direction (\( \varphi, \psi \)) using Eq. (1) to (3).

Thus, in order to maintain a constant penetration depth during a \( \sin^2 \psi \)-based stress
analysis, the traditional \( \chi \) or \( \omega \) tilting, which are used individually at a certain \( \varphi \)-azimuth, has
to be replaced by a coordinated movement of the diffractometer angles \( \omega, \chi \) and \( \phi \). As a
consequence of the controlled penetration depth, only a limited region within the \( \sin^2 \psi \)-plot is
accessible for a certain hkl reflection. For further details regarding this technique, the reader is
referred to [30].

The lattice strains were measured for the \{220\} diffraction line of TiN. This reflection
was chosen based on a compromise between the ease for separating this line from neighbouring
ones, its intensity and the highest possible 2θ-angle. The Diffraction Elastic Constants (DEC) were calculated based on the Eshelby-Kröner model using the single crystal elastic constants for TiN [31].

3. Results and Discussion

3.1. Microstructure

The microstructure of the 100Cr6 steel subjected to Xe\(^+\) bombardment followed by plasma nitriding and TiN deposition (sample S1000N) is presented in Figure 1. The SEM image initially reveals that the annealed hypereutectoid steel substrate consists of a ferritic matrix with embedded spheroidized cementite particles. It can also be observed that the average thickness of the TiN coatings deposited by IBAD amounts to about 400 nm. Plasma nitriding conducted at 380 °C did not lead to the formation of a white compound layer but only to a restricted diffusion zone, which cannot be visualized using SEM analyses.
Figure 1: Cross section micrograph of the S1000N sample showing the TiN coating (20,000X).

The results of the phase analyses conducted by XRD on the S, SN, S1000 and S1000N specimens are presented in Figure 2. The XRD patterns of non-nitrided samples (S and S1000) contain reflections that correspond to ferrite and Fe₃C from the substrate, as well as TiN from the deposited hard coating. For the SN sample, which was not subjected to Xe⁺ bombardment, the diffractograms reveal additionally the presence of the iron-rich γ’-Fe₄N nitride. With regards to the S1000N sample, which was in turn bombarded with Xe⁺ prior to nitriding, both ε-Fe₂₋₃N and γ’-Fe₄N iron nitrides could be detected. The formation of ε-Fe₂₋₃N nitride confirms that the previous ion bombardment was responsible for increasing nitrogen retention [26, 27] on the steel surface during the plasma nitriding process. In addition, it is worth noticing that the volume fraction of γ’-Fe₄N appears to be larger in the S1000N specimen than in the SN sample, as indicated by the difference in the relative intensity of the respective diffraction lines. This probably happens because bombardment with Xe⁺ ions texturized the treated surface, causing the generation of lattice defects and stress which accelerate the nitrogen diffusion into the first atomic surface layers [26, 27]. Overall, the TiN reflections exhibit line broadening (e.g. in comparison with the reflections which stem from metallic iron in the steel substrate), an indication of small crystallite size and possibly nanostructured layer (i.e., disorder). In addition, there appears to be no strong preferential orientation in the TiN coatings deposited on the different substrates since in all cases several TiN reflections could be detected with no marked difference in their relative intensities, in agreement with a recent investigation [33].

The microstructure of the S1000N specimen was further investigated by TEM (Figures 3 and 4). Observation of Figure 3 indicates elevated dislocation density in the sub-surface region of the steel substrate (approximately 0.5μm thickness), likely caused by plastic strain.
associated with the $\text{Xe}^+$ ion bombardment. Possible sources of deformation caused by ion bombardment include: formation of gas bubbles from within the substrate lattice, phase transformations and the peening effect itself caused by ion collision [21, 24].
The presence of lattice defects accounts for the higher diffusivity necessary for the formation of the nitrogen-rich $\varepsilon$-Fe$_{2.3}$N nitride layer detected by XRD (Figure 2). Figure 4 displays a TEM image of the coating/substrate interface in S1000N sample. The interface between the steel substrate and TiN coating exhibit fringes due to very fine nitride formation (red arrows). Analyses of the electron diffraction data from the coating-steel interface indicate two distinct superposing patterns, corresponding to the $\varepsilon$-Fe$_{2.3}$N and $\gamma'$-Fe$_4$N nitrides, as indicated in the inset of Figure 4, thus corroborating the results of the XRD analysis presented in Figure 2.
Figure 4: TEM image and electron diffraction pattern from the sample S1000N showing the presence of $\text{Fe}_2\text{N}$ and $\gamma'$-$\text{Fe}_4\text{N}$ nitrides.

3.2. Topography, wear and coating adhesion

The surface topography of the samples investigated by AFM is displayed in Figure 5. It is possible to verify that the different types of pre-treatment lead to marked differences in the surface roughness of the TiN films. The sample S exhibits the lowest levels of roughness, compatible with the surface finishing of the metallographic preparation to which the substrates were initially subjected. Thus, the non-treated sample represents the reference state for the purpose of comparison. Plasma nitriding of the substrate (sample SN) leads to a small increase in roughness, which can be explained by different mechanisms such as: volumetric expansion of the substrate lattice due to incorporation of N in solid solution and formation of nitrides, sputtering of the surface due to the impact of N ions during deposition, as well as redeposition of the sputtered material [34, 35].
The bombardment with Xe$^+$ ions at 1.0 keV kinetic energy produces a more significant increase of roughness in the sample S1000 than the nitriding process. This occurs due to a more intense atomic attrition prompted by the heavy Xe$^+$ ions. As previously shown reduction the Xe$^+$ bombardment kinetic energy diminishes surface roughness [22, 26]. Finally, the exposure of the 100Cr6 steel surface to prolonged atomic attrition caused by the combination of ion bombardment and plasma nitriding leads to the roughest surface profile in the sample S1000N. The evolution of the average surface roughness of the TiN coatings as a function of the pretreatment technique applied to the 100Cr6 substrates is presented in Figure 6.

The average worn volumes obtained after ball on disc tests are presented in Figure 7. The lowest wear rates were observed for the samples subjected to individual treatments of nitriding (SN) or ion bombardment (S1000) instead of a combination of both plasma nitriding and Xe$^+$ ion bombardment (S1000N).
Figure 6: Evolution of average roughness $R_a$ as a function of surface pre-treatment in TiN coating.

This indicates that the bombardment with Xe$^+$ ions causes strain hardening of the steel surface that is comparable with the hardness increase promoted by nitride formation, or possibly a combination of surface hardening with slightly increased roughness that contributes to enhance the coating adhesion to the substrate. Both effects, i.e. increased substrate hardness and coating adhesion, ought to be considered here because in all cases the thin TiN coatings (~400 nm, Figure 1) from all samples appear to have been completely removed during the wear tests. The wear behavior of the S1000N specimen was found to be comparable to the untreated sample S. In this case, excessive surface roughness causes insufficient TiN adhesion on the substrate. As the tribological system investigated (cemented carbide against TiN) involves materials of elevated hardness, the main wear mechanism appears to be abrasive, thus leading to appreciable breakup of the sharper coating asperities.
Figure 8 exhibits the scratch scars and the critical loads for coating delamination obtained during the nano-scratch tests. It is possible to observe chevron cracking, indicating cohesive failure; the dashed rectangles highlight the start of chipping failure (adhesive failure).

These values indicate a transition point in the wear behavior, which can occur due to plastic deformation, increase in temperature [36] or initial failure of the coating (microcracking, surface flaking, loss of cohesion) [37]. In the present case, the critical load is an indicative of adhesion of the TiN coating to the substrate material. The highest critical load was observed on the SN sample, consistent with the minimum wear volume observed in Figure 7. The same trend is observed for the remaining samples, within the error margins of the experiment.

Figure 7: Average wear volume of the different samples after ball-on-disc tests.
Figure 8: a) Image of the scratch scars and b) critical load for TiN coatings deposited onto the different substrates.
3.3. Residual stress analyses

Residual stress in thin coatings produced by deposition can usually be ascribed to two sources. On one hand, the energetic ions cause atoms from the substrate to be shifted from their original lattice positions producing residual interstitials. This leads to an outwards expansion of the thin film from the substrate. In the plane of the coating, however, expansion is restricted and the entrapped atoms cause elevated compressive stress [38]. In addition to these intrinsic stresses, additional residual stresses arise during cooling from the deposition temperature due to incompatibility of thermal expansion between substrate and coating [39, 40]. These cooling stresses are therefore influenced by the surface pre-treatments which can alter the phase composition and the average thermal expansion coefficient near the interface with the hard metal coating.

The \( \sin^2\psi \) versus lattice spacing plots are presented in Figure 9. As can be observed for all samples, residual stresses are compressive and the \{200\} lattice spacing varies linearly with \( \sin^2\psi \), in agreement with previous investigations [41, 42]. It is also important to observe that XRD measurements for residual stress analysis on all materials could be performed over a large range of sample tilt positions, indicating that no strong preferential orientation is present in TiN coatings, as expected from the results presented in Figure 2.
The residual stress values obtained for each coating procedure are presented in Figure 10. In all cases, stress values are highly compressive: (-6.25±0.2), (-4.55±0.05), (-6.77±0.12) and (-5.95±0.1) GPa for the S, SN, S1000 and S1000N specimens, respectively. By comparing the results obtained for samples S and S1000, it is possible to observe that Xe⁺ bombardment alone does not have a significant effect on the residual stress state on the deposited TiN coating.

However, plasma nitriding caused a significant reduction in the residual stresses. In duplex coatings, where a hard ceramic layer is deposited onto a nitrided substrate, a transition zone appears between substrate and coating [37, 43]. This happens because of the high ion energy during IBAD that promotes the transference of chemical elements across the substrate/coating interface, leading to the formation of a Ti-rich interlayer [33]. In the nitrided sample, this would lead to the reaction with nitrogen and an increase in adhesion and chemical compatibility between the TiN coating and substrate. This also contributes to reduce the residual
stresses in the TiN coating. For similar reasons, the SN sample exhibited superior wear characteristics (Figures 7 and 8) in comparison to the other tested materials.

![Figure 10: Average residual stress values in the TiN as a function of surface pre-treatment.](image)

The application of Xe⁺ bombardment prior to plasma nitriding causes an increase in the residual stresses of the TiN film to values similar to those of the untreated substrate in the S sample. This is because of the occurrence of ε-Fe₂₃N that has a Thermal Expansion Coefficient (TEC) greater than γ’-Fe₄N: TEC(γ’-Fe₄N) < TEC(ε-Fe₂₃N) < TEC(Fe).

4. Conclusions

The impact of individual and combined pre-treatments based on the bombardment with 1.0 keV Xe⁺ ions and plasma nitriding at 380°C on the adhesion and wear of TiN coatings deposited by IBAD onto spheroidized 100Cr6 steel was investigated. The results showed that the bombardment with Xe⁺ ions causes grain refinement, texturization, and increases the density.
of lattice imperfections at the treated surface, thus enhancing nitrogen diffusion at 380°C and probably causing strain-hardening as well.

The combined pre-treatment led therefore to a diffusion zone containing both ε-Fe₂₃N and γ′-Fe₄N nitrides, whereas simple plasma nitriding promoted the formation of only γ′-Fe₄N. The presence of ε-Fe₂₃N confirms an enhanced nitrogen retention in the diffusion zone and the formation of a more expressive nitride fraction. This corroborates the positive influence of Xe⁺ ion bombardment on the nitrogen retention during nitriding treatments.

Superior wear behavior was however verified for the application of individual plasma nitriding. Xe⁺ ion bombardment with 1.0 keV impact energy in combination with plasma nitriding caused sputtering of substrate and significantly increased surface roughness of the TiN film. In such condition, the wear rate of the TiN became similar to that observed in the substrate without pre-treatment. Reduction of the Xe⁺ ion energy shall lead to less sputtering and surface roughness. This might enhance the wear performance in the case of a combined pre-treatment due to a more pronounced nitrogen retention.

All TiN coatings evolved compressive residual stresses, ranging from -4.55 and -6.77 GPa. The lowest residual stress values were observed for the sample subjected to individual plasma nitriding due to the formation of only γ′-Fe₄N with reduced TEC and the increased chemical compatibility by a Ti-rich interlayer between substrate and coating during IBAD.

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