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DOI: 10.1590/1516-1439.266514

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Effect of Low Temperature Nitriding of 100Cr6 Substrates on TiN Coatings Deposited by IBAD

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Received: January 24, 2014; Revised: December 10, 2014

In this paper we studied the influence of pre-treating the surface of 100Cr6 steel by ion beam nitriding at low temperature (380°C) on the surface topography and wear resistance of thin TiN coatings deposited by reactive ion beam assisted deposition. The specimens were characterized by grazing incidence X-ray diffraction, scanning electron microscopy and atomic force microscopy. The wear resistance of the TiN-coated specimens was evaluated by means of ball on disc tests. The results showed that application of a preliminary ion beam nitriding treatment slightly increased the surface roughness but improved the wear resistance of the 100Cr6 steel due to the formation of a diffusion zone containing the γ' -Fe₄N nitride combined with the TiN coating.

Keywords: *ion beam nitriding, TiN, IBAD, wear, steel*

1. Introduction

Nitriding processes comprise a series of thermo-chemical surface treatments which are largely applied in industry with the objective of improving performance of steel parts by diffusion of N into the steel surface. Surface hardness, corrosion resistance, fatigue resistance and wear resistance are properties which can be substantially improved by nitriding¹⁻⁴. The introduction of N into steel can be accomplished either by inserting the work piece into a high temperature N-rich environment (either gas or liquid) or by plasma assisted bombardment of N ions (ion beam nitriding). Among these, ion beam nitriding is of particular interest because it allows for excellent parameter control and higher efficiency at low temperatures (300-450 °C) resulting in a more chemically uniform surface layer⁵. The typical plasma nitrided steel surface consists of an outermost thin iron nitride layer (commonly referred to as “white layer”) followed by a relatively thicker N-rich diffusion zone close to the steel substrate⁶. The formation of the white layer can be suppressed in plasma nitriding by tuning process parameters⁷. Depending on its chemical affinity with elements present in the steel substrate and on the nitriding process parameters, N may remain in solution or give rise to a number of other nitride compounds. The main phases present in the nitrided zone on steel surfaces are ϵ -Fe_{2,3}N and γ' -Fe₄N nitrides, which exhibit very high

hardness (around 70HRC) and good corrosion resistance, thus improving the mechanical, chemical and tribology properties of the constructional parts⁸⁻¹⁰.

Physical Vapor Deposition (PVD) techniques are also commonly applied for enhancing surface properties of steels. PVD coatings include TiN, TiC, TiCN and TiAlN, which have a high hardness, low friction coefficient and high wear resistance. Since PVD coatings are very thin, any applied loads which cause the surface and sub-surface to deform must also be sustained by the steel base material: if the substrate undergoes extensive plastic deformation the coating might collapse and fail prematurely¹¹. Hence, duplex coatings have been developed whereby a preliminary nitriding treatment is applied followed by a hard coating deposition. By combining these two processes a composite layer is formed with the thin ceramic coating supported by the N-strengthened substrate, which leads to superior fatigue and wear resistance^{6,12}. The effectiveness of a duplex coating can be hampered by insufficient adhesion between the hard coating and the nitrided steel and by softening of the substrate due elevated temperatures during PVD. According to Kamminga^{7,13}, bad adhesion may be caused by porosity in the nitride layer or by its decomposition during application of high temperature PVD processes leaving a relatively softened α -Fe layer behind. The presence of an iron nitride layer may also impair adhesion of the PVD coating and improvements

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in performance have been observed by conducting the deposition process after removal of the nitrided white layer¹⁴.

The application of PVD at low temperatures is difficult because of reduced ad-atom mobility, which decreases coating density leading to inferior mechanical performance¹⁵. In the Ion Beam Assisted Deposition (IBAD) process, PVD is combined with ion bombardment. The additional energy of the ion bombardment allows deposition of ceramic coatings at lower temperatures, thus avoiding some of the difficulties involved in the application of high temperature PVD on nitrided substrates¹⁶⁻¹⁸. Indeed, by comparing the IBAD and PVD processes applied to previously quenched and tempered steel substrates, Škorić and co-workers showed that IBAD led to improved properties due to densification of the hard coating¹⁹. The IBAD process can thus be used to produce dense and hard coatings with strong adhesion and also allows for the independent control of several parameters e.g. ion bombardment energy, ion to atom arrival ratio, ion current density and ion angle of incidence, which influence the properties of the growing films¹⁸.

In the present article, the influence of applying ion beam nitriding to a 100Cr6 bearing steel prior to the deposition of TiN films by IBAD was investigated. Wear resistance, microstructure and phase composition were investigated for IBAD TiN coatings applied both on previously nitrided surfaces and also on untreated surfaces.

2. Material and Methods

2.1. Substrate material

The substrate material prior to surface treatment was an annealed 100Cr6 bearing steel. Its nominal chemical composition is given Table 1. The steel specimens were used in the annealed state instead of the quenched and tempered condition, which is common for bearing steels. The reason for this was to avoid phase transformations during the nitriding treatment (carried out at 380°C), which could influence N diffusion throughout the process.

The specimens used for plasma nitriding and PVD coating were in the form of 20mm diameter discs with 2mm thickness which were all cut from the same rod. Prior to surface treatment, all samples were prepared by conventional grinding from 220 to 4000 SiC grid size, followed by polishing using 6.0, 3.0, 1.0 µm diamond paste and 0.25 µm colloidal silica suspension.

2.2. Ion beam nitriding and TiN deposition

TiN coatings were deposited on substrates with and without previous nitriding treatments. Both processes (ion beam nitriding and film deposition) were performed using an IBAD system, located at the Photovoltaic Conversion

Laboratory of the Physics Institute of the Campinas State University (Brazil). This system consists mainly of a deposition chamber with two Kaufman ion sources with 3 cm diameter, a support for four targets and a temperature controlled (<1000 °C) sample holder. For more details regarding this system the reader is referred to Hammer et al.²⁰. The base pressure of the chamber was less than 10⁻⁴ Pa. Both processes, ion beam nitriding and TiN deposition, were carried out independently following a sequence which began with sputter cleaning using a 600 eV Ar⁺ beam for 5 minutes, followed by nitriding (when applicable) and posterior TiN coating deposition. Identification of the samples used in the present work is presented in Table 2.

Nitriding of the substrate was performed using a N⁺ beam of 0.2 keV and 19 mA that was directed to the substrate during 30 min. The temperature of the process was set to 380 °C and the working pressure was 1.5×10⁻² Pa for all nitrided samples. Following the nitriding process, TiN films were deposited by IBAD by sputtering a Ti target with a 1.45 keV (80 mA) Ar ion beam in a N₂ atmosphere. The N₂ pressure was 5.5×10⁻² Pa and the substrate temperature was set to 400 °C. The deposition time was 120 min for all samples. The hardness of the TiN coatings on both S and SN samples was measured with a CSEM Nanohardness tester using a diamond indenter and a load of 5N.

2.3. Microstructure and phase analyses

The microstructure of the 100Cr6 steel substrate and the TiN coatings was investigated after etching the samples with Nital 3% using by scanning electron microscopy (SEM) using a Philips XL-30 FEG microscope. In order to assess the phase constitution within the TiN coated samples, angle-dispersive X-ray Diffraction (XRD) experiments were carried out. The measurements were performed at the experimental station XPD of the Brazilian Synchrotron Radiation Laboratory (LNLS) at Campinas (Brazil). The radiation energy was set to 10.5 keV ($\lambda = 1.1823 \text{ \AA}$). The beam size was 4 mm × 1 mm. Diffractograms were obtained under a grazing incidence angle (ω) of 1°, which corresponds to an average penetration depth τ of 500 nm.

2.4. Topography and wear

The influence of the nitriding pre-treatment on surface topography of the coated samples was evaluated by Atomic Force Microscopy (AFM) in contact mode. The analyses were conducted in a CSM instruments Nano-Scratch Tester (NST). The wear resistance of each sample was studied by applying ball on disc tests. For these experiments, a 3.0 mm radius cemented carbide (WC-Co) sphere was used with a 5 N load over a total distance of 1000 m.

Table 1. Nominal chemical composition of the 100Cr6 steel used in the present investigation.

Element	C	Si	Mn	Cr	Fe
Composition (wt.%)	1.0	0.25	0.35	1.5	Balance

Table 2. Sample series and respective sample structures.

Sample	Sample structure
S(TiN)	Steel + TiN
SN(TiN)	Steel + Nitrided Zone + TiN

3. Results and Discussion

3.1. Microstructure and phase analyses

The surface hardness of the as-received and nitrided 100Cr6 substrates were, respectively, 2.6 ± 0.2 GPa and 3.5 ± 0.2 GPa. After TiN deposition, the surface hardness increased and the values obtained for both S and SN samples were between 22 and 26 GPa. Determination of the hardness values for the TiN coatings was difficult because of their reduced thickness, which required the use of a small applied test load (5 N). Because of this, the measurements were very sensitive to variations in surface roughness, hence the large variance in experimental values (22 to 26 GPa).

A cross-section SEM micrograph of the SN(TiN) sample is presented in Figure 1. The microstructure of the annealed hypereutectoid steel consists of a ferritic matrix with dispersed spheroidized cementite particles. It can also be observed that the average thickness of the TiN coatings deposited by IBAD amounts to about 400 nm, and the coatings present a columnar grain structure. The TiN coating of the S(TiN) sample also exhibited a thickness of approximately 400 nm (not shown). From the micrograph presented in Figure 1, it is not possible to state whether the ion beam nitriding process conducted at

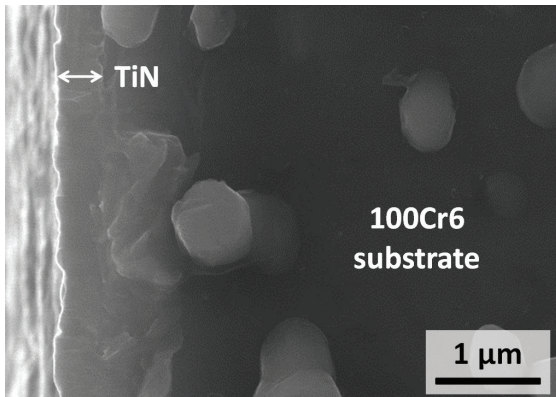


Figure 1. Cross section micrograph of the SN(TiN) nitrided sample (20,000X).

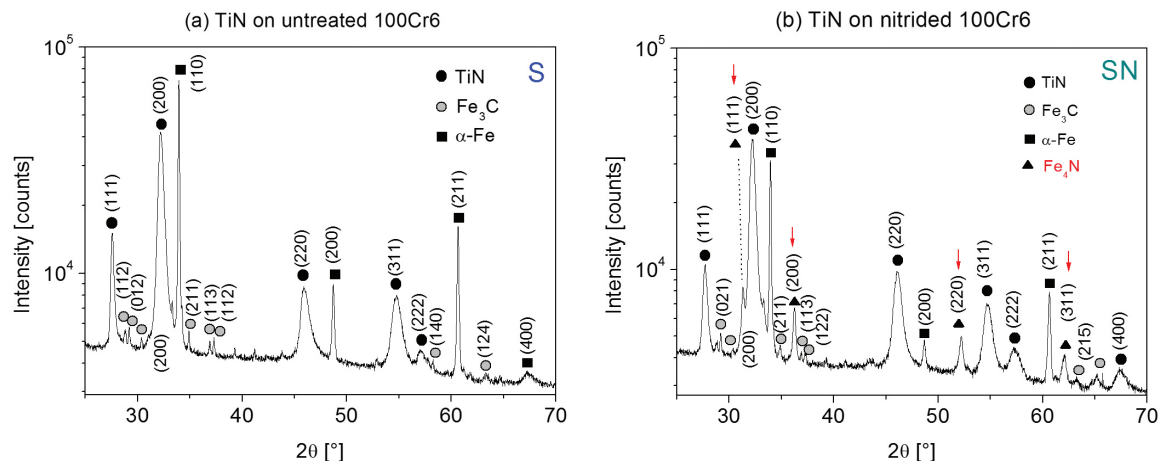


Figure 2. Grazing incidence X-ray diffraction patterns obtained for (a) untreated S(TiN) and (b) nitrided SN(TiN) samples.

380 °C led to the formation of a white compound layer, but no indication on the formation of such layer was found (adhesion of the TiN coating, wear performance). The application of higher resolution microscopy techniques would be necessary to clarify the issue.

The results from phase analysis conducted by XRD on the S(TiN) and SN(TiN) samples are presented in Figures 2a and 2b, respectively. The differences with respect to the phase composition in both samples become clear by analyzing the XRD patterns. For the S(TiN) sample, phase analysis reveals the presence of ferrite and Fe_3C that stem from the 100Cr6 substrate and TiN from the coating. In the SN(TiN) sample, which was nitrided prior to TiN deposition, it was possible to identify the presence of iron-rich γ' - Fe_4N by the reflections of the (111), (200), (220) and (311) planes, as indicated in Figure 2b. In both Figures 2a and 2b, the TiN reflections are well defined but exhibit broadening (e.g. in comparison to the Fe reflections from the substrate), indicating small crystallite size and possibly a nanostructured layer. In addition, it is possible to notice that for both S(TiN) and SN(TiN) samples, the stronger reflections correspond to the (200) planes. The relative intensity of the diffraction lines may indicate the presence of preferential orientations in the coating. The results presented in Figures 2a and 2b indicate, therefore, that the preliminary nitriding treatment did not influence texture of the TiN coatings deposited by IBAD.

The development of preferential orientations in TiN coatings depends on a number of factors, such as ad-atom mobility, stoichiometry and surface energy, which are in turn influenced by deposition process parameters such as temperature, ion energy, ion current density and angle of ion incidence²¹. Owing to its NaCl type crystal structure, the crystallographic planes with highest atomic density in TiN belong to the {001} family²². In the present case, since the (200) planes exhibit the strongest diffraction peaks, texture in the TiN films appears to be controlled by the lower surface energy of the dense {001} type planes. These results are in agreement with previous investigations of TiN coatings produced by IBAD^{19,23}. A more detailed explanation on texture development in TiN coatings is provided by Gall et al.²⁴.

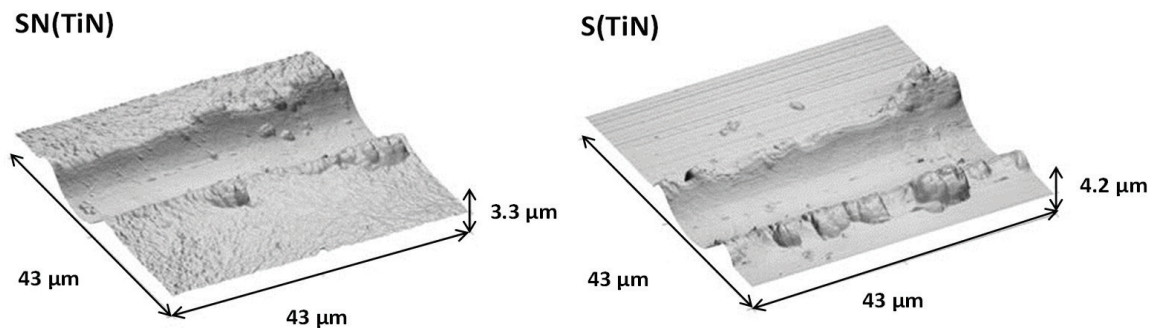


Figure 3. Profiles of surface sample topography by atomic force microscopy.

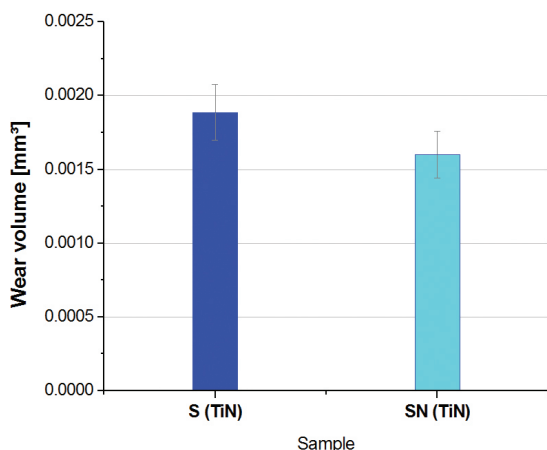


Figure 4. Average volume loss of TiN after ball on disc tests for the S(TiN) and SN(TiN).

3.2. Topography and wear

Figure 3 displays the surface topography of the samples investigated obtained by AFM in the vicinity of the wear tracks after the ball on disc tests. The average surface roughness (R_a) of the samples were determined and the values obtained were $0.077 \pm 0.008 \mu\text{m}$ and $0.083 \pm 0.008 \mu\text{m}$ for the S(TiN) and SN(TiN) samples, respectively.

The S(TiN) sample exhibits the lowest level of surface roughness, compatible with the surface finishing of metallographic polishing to which the substrates were initially subjected. Ion beam nitriding leads to an increase in surface roughness, which can be explained by a number of different mechanisms which involve: 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^{25,26}. 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.

The average volume losses of each sample after the wear tests are compared in Figure 4. The SN(TiN) duplex layered sample exhibited superior wear resistance in comparison to the S(TiN) sample, as can also be noticed by the larger amount of detached material shown in Figure 3. It is likely that this is due to hardening of the substrate with formation of γ' -Fe₄N caused by the ion beam nitriding process, since in both materials the TiN coatings exhibited similar hardness (22-26GPa, Table 2) and also because the thin TiN coatings were completely removed during the wear tests. Thus, on the S(TiN) specimen removal of the hard outer layer exposed a soft annealed substrate leading to higher wear rates compared to the SN(TiN) sample.

4. Conclusions

In the present work, TiN deposition was performed by IBAD on annealed and ion beam nitrided substrates of 100Cr6 steel. In both cases, the TiN films were approximately 400 nm thick. The application of the preliminary nitriding treatment was found to increase surface roughness slightly in comparison to TiN films deposited on non-nitrided 100Cr6 samples, and also led to the formation of γ' -Fe₄N. It was possible to show that the duplex coating formed by nitriding and TiN deposition of 100Cr6 steel has superior wear resistance properties in comparison to plain TiN coatings deposited on non-treated substrates.

Acknowledgements

This work was supported by the NanoCom Network Project, 7th Framework Program – IRSES – Project Nr. 247524. SSV, FA and HP are CNPq fellows.

References

- Menthe E, Rie KT, Schultze JW and Simson S. Structure and properties of plasma nitrided stainless steel. *Surface and Coatings Technology*. 1995; 74-75:412-416. [http://dx.doi.org/10.1016/0257-8972\(95\)08246-8](http://dx.doi.org/10.1016/0257-8972(95)08246-8).
- Lei MK and Zhang ZL. Microstructure and corrosion resistance of plasma source ion nitrided austenitic stainless steel. *Journal of Vacuum Science & Technology A*. 1997; 15(2):421-427. <http://dx.doi.org/10.1116/1.580501>.
- Renevier N, Collignon P, Michel H and Czerwec T. Low temperature nitriding of AISI 316L stainless steel and

- titanium in a low pressure arc discharge. *Surface and Coatings Technology*. 1999; 111(2-3):128-133. [http://dx.doi.org/10.1016/S0257-8972\(98\)00722-1](http://dx.doi.org/10.1016/S0257-8972(98)00722-1).
4. Leite MV, Figueroa CA, Corujeira Gallo S, Rovani AC, Basso RLO, Mei PR, et al. Wear mechanisms and microstructure of pulsed plasma nitrided AISI H13 tool steel. *Wear*. 2010; 269(5-6):466-472. <http://dx.doi.org/10.1016/j.wear.2010.04.037>.
 5. Zagonel LF, Bettini J, Basso RLO, Paredez P, Pinto H, Lepienski CM, et al. Nanosized precipitates in H13 tool steel low temperature plasma nitriding. *Surface and Coatings Technology*. 2012; 207:72-78. <http://dx.doi.org/10.1016/j.surfcoat.2012.05.081>.
 6. Sun Y and Bell T. Plasma surface engineering of low alloy steel. *Materials Science and Engineering A*. 1991; 140(7):419-434. [http://dx.doi.org/10.1016/0921-5093\(91\)90458-Y](http://dx.doi.org/10.1016/0921-5093(91)90458-Y).
 7. Kamminga JD, Hoy H, Janssen GCAM, Lugscheider E and Maes M. First results on duplex coatings without intermediate mechanical treatment. *Surface and Coatings Technology*. 2003; 174-175:671-676. [http://dx.doi.org/10.1016/S0257-8972\(03\)00578-4](http://dx.doi.org/10.1016/S0257-8972(03)00578-4).
 8. Ochoa EA, Figueroa CA and Alvarez F. Nitriding of AISI 4140 steel by a low energy broad ion source. *Journal of Vacuum Science & Technology A*. 2006; 24(6):2113-2116. <http://dx.doi.org/10.1116/1.2356480>.
 9. Walkowicz J, Smolik J and Miernik K. Research on physico-chemical bases of the ion nitriding process control with the use plasma spectroscopic diagnostics. *Vacuum*. 2000; 56(1):63-69. [http://dx.doi.org/10.1016/S0042-207X\(99\)00167-0](http://dx.doi.org/10.1016/S0042-207X(99)00167-0).
 10. Tillman W, Vogli E and Momeni S. Mechanical and tribological properties of Ti/TiAlN duplex coatings on high and low alloy tool steels. *Vacuum*. 2010; 8(3):387-392.
 11. Dong H, Sun Y and Bell T. Enhanced corrosion resistance of duplex coatings. *Surface and Coatings Technology*. 1997; 90(1-2):91-101. [http://dx.doi.org/10.1016/S0257-8972\(96\)03099-X](http://dx.doi.org/10.1016/S0257-8972(96)03099-X).
 12. Garcia J and Pitonak R. The role of cemented carbide functionally graded outer-layers on the wear performance of coated cutting tools. *International Journal of Refractory Metals & Hard Materials*. 2013; 36:52-59. <http://dx.doi.org/10.1016/j.ijrmhm.2011.12.007>.
 13. Kamminga JD, Doerwald D, Schreurs M and Janssen GCAM. Industrial feasibility of the nitrocoat process. *Surface and Coatings Technology*. 2005; 200(5-6):1837-1841. <http://dx.doi.org/10.1016/j.surfcoat.2005.08.008>.
 14. Panjan P, Čekada M, Kirn R and Soković M. Improvement of die-casting tools with duplex treatment. *Surface and Coatings Technology*. 2004; 180-181:561-565. <http://dx.doi.org/10.1016/j.surfcoat.2003.10.119>.
 15. Patsalas P, Charitidis C and Logothetidis S. The effect of substrate temperature and biasing on the mechanical properties and structure of sputtered titanium nitride thin films. *Surface and Coatings Technology*. 2000; 125(1-3):335-340. [http://dx.doi.org/10.1016/S0257-8972\(99\)00606-4](http://dx.doi.org/10.1016/S0257-8972(99)00606-4).
 16. Škorić B and Kakaš D. Tribological Behavior of TiN and TiAlN Deposited on Substrates Plasma Nitrided at Low Pressure. *Materials and Manufacturing Processes*. 1995; 10(2):321-326. <http://dx.doi.org/10.1080/10426919508935025>.
 17. Škorić B, Kakaš D and Gredić T. Influence of plasma nitriding on mechanical and tribological properties of steel with subsequent PVD surface treatments. *Thin Solid Films*. 1998; 317(1-2):486-489. [http://dx.doi.org/10.1016/S0040-6090\(97\)00565-8](http://dx.doi.org/10.1016/S0040-6090(97)00565-8).
 18. Kakas D, Terek P, Kovacevic L, Miletic A and Skoric B. Influence of interfacial layer thickness and substrate roughness on adhesion of TiN coatings deposited at low temperatures by IBAD. *Surface Review and Letters*. 2011; 18(03n04):83-90. <http://dx.doi.org/10.1142/S0218625X11014497>.
 19. Škorić B, Kakaš D, Rakita M, Bibić N and Peruškob D. Structure, hardness and adhesion of thin coatings deposited by PVD, IBAD on nitrided steels. *Vacuum*. 2004; 76(2-3):169-172. <http://dx.doi.org/10.1016/j.vacuum.2004.07.005>.
 20. Hammer P, Victoria NM and Alvarez F. Electronic structure of hydrogenated carbon nitride films. *Journal of Vacuum Science & Technology A*. 1998; 16(5):2941-2949. <http://dx.doi.org/10.1116/1.581443>.
 21. Ma C-H, Huang J-H and Chen H. Texture evolution of transition-metal nitride thin films by ion beam assisted deposition. *Thin Solid Films*. 2004; 446(2):184-193. <http://dx.doi.org/10.1016/j.tsf.2003.09.063>.
 22. Combadiere L and Machet J. Reactive magnetron sputtering deposition of TiN films. I. Influence of substrate temperature on structure, composition and morphology of the films. *Surface and Coatings Technology*. 1997; 88(1-3):17-27. [http://dx.doi.org/10.1016/S0257-8972\(96\)02870-8](http://dx.doi.org/10.1016/S0257-8972(96)02870-8).
 23. Škorić B, Kakaš D, Rakita M, Bibic N and Rakita M. Microstructural studies of TiN coatings prepared by PVD and IBAD. *Surface Science*. 2004; 566-568:40-44. <http://dx.doi.org/10.1016/j.susc.2004.06.060>.
 24. Gall D, Kodambaka S, Wall MA, Petrov I and Greene JE. Pathways of atomistic processes on TiN(001) and (111) surfaces during film growth: an ab initio study. *Journal of Applied Physics*. 2003; 93(11):9086-9094. <http://dx.doi.org/10.1063/1.1567797>.
 25. Mahboubi F and Abdolvahabi K. The effect of temperature on plasma nitriding behaviour of DIN 1.6959 low alloy steel. *Vacuum*. 2006; 81(3):239-243. <http://dx.doi.org/10.1016/j.vacuum.2006.03.010>.
 26. Akbari A, Mohammadzadeh R, Templier C and Riviere JP. Effect of the initial microstructure on the plasma nitriding behavior of AISI M2 high speed steel. *Surface and Coatings Technology*. 2010; 204(24):4114-4120. <http://dx.doi.org/10.1016/j.surfcoat.2010.05.042>.