Comparison of the structural and tribological properties of nitride-based coatings on industrial steels

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Abstract. This paper presents an analysis and comparison of the tribological performance of titanium carbonitride, chromium aluminum nitride and aluminum titanium nitride coatings, deposited by Magnetron Sputtering on S600 steel punches. The films were studied structurally and morphologically, carrying out tests by means of X-ray diffraction, atomic force microscopy and scanning electron microscopy. The correlation between the wear behavior in rolling contact and the mechanical properties of ternary coatings is reported using the Pin-on-disk technique. The wear marks are studied to observe the deformation behavior produced by the tests carried out. The influences of the structure and composition of the coatings on the mechanical and tribological behavior during the rolling wear tests are discussed. Chromium aluminum nitride was the material that presented the lowest wear rate, due to its hardness, elastic modulus, and critical load (resistance to scratching). These physical characteristics are also present in the titanium carbonitride and aluminum titanium nitride coatings which provide conditions that benefit wear resistance, expecting an improvement in performance in industrial steel.

1. Introduction
The processes of cutting and punching by means of dies are widely used in the metalworking industry, mostly by companies that are dedicated to the transformation of raw materials, for the manufacture of products such as metal sheets or plates. These processes are usually easy, fast, and inexpensive to obtain the desired shapes, sizes and finishes when compared to casting, forging, and machining [1]. However, dimensional, position, shape and surface errors in the pieces are generated by errors in punching [2] and directly affect the quality of the pieces, since the punch’s wear induces different defects during cutting [3,4]. Common errors include edge stretch, crack penetration depth, and burr height [5]. To improve the quality of sheet products, it is proposed to apply physical vapor deposition (PVD) coatings with tribological properties that help to increase the useful life of punching and cutting tools in die cutting processes.

In previous studies such as those carried out by Högman [6], the punchability in ultra-high-strength steels, tool wear, and wear reduction due to the addition of PVD films to the punches were observed. Klocke, et al. [7] studied PVD coated tools and found that the highest mechanical stresses appear on the cutting edge and surface of the coating, where the tribological conditions of the process lead to temperatures of approximately 400 °C and contact pressures of more than 3000 MPa. Çöl, et al. [8] studied the performance and wear of punches coated; trough field tests they were able to observe how the useful life of the tools increased when these coatings were applied. Podgornik, et al. [9] evaluated the coatings in terms of the adhesion of the coating to the substrate, the load capacity, resistance to wear.
under dry and lubricated sliding, performance of the coating on the punch, and the evolution and magnitude of the punching force.

In the embossing process, the material is pushed down and towards the walls of the female die, generating a pressure on the surface of the punch. This pressure causes the material to adhere to the punch, generating understandable efforts now of exit which produces wear on the surface of the punch in different ways. At first an adhesive wear and at another time an abrasive wear, which are types of wear caused on the punch material by the compound punching process. This research seeks to analyze and compare the structural and tribological behavior of the titanium carbonitride (TiCN), chromium aluminum nitride (CrAlN) and aluminum titanium nitride (TiAlN) coatings deposited on industrial steels.

2. Methodology
The coatings’ deposition process was carried out in a magnetron sputtering system-Intercovamex-V4. Silicon substrates with crystallographic orientation (100) and S600 steel substrates were used, which were washed with water in abundance and subsequently subjected to a coating in an ultrasonic tank with acetone for 30 minutes. For the TiCN, TiAlN and CrAlN coatings, titanium carbide (TiC), titanium-aluminium (Ti-Al), and chrome and aluminium (Cr-Al) targets were used, respectively; with an approximate purity of 99.99%. Silicon substrates with crystallographic orientation (100) and S600 steel substrates were used. A surface cleaning of the substrate was carried out in an ultrasound system. Prior to the start of the depositions, a vacuum pressure of 1.4 x 10^-4 mbar was generated.

The coatings’ deposition was carried out and in that sense; for the TiCN coating a working pressure of 5.7 x 10^-2 mbar was used in a mixture of 50 sccm of argon (Ar) and 16 sccm of nitrogen (N_2) at 250 °C, and power target of 400 W was applied on the TiC target. For the TiAl coating, a pressure of 5.6 x 10^-2 mbar was used in a mixture of 50 sccm (Ar) and 5.5 sccm (N_2) at 250 °C, and power target applied to the Ti target and Al target was 400 W and 300 W, respectively. For CrAlN coating a pressure of 5.7 x 10^-2 mbar was used in a mixture of 50 sccm (Ar) and 3.7 sccm (N_2) at 250 °C, power target applied to the Cr target was 350 W and Al target was 200 W.

The structural characterization was carried out in a Panalytical X’Pert PRO X-ray diffractometer (XRD), with Cu-Kα radiation source (λ = 1.5406 Å) in Bragg-Brentano configuration(θ / 2θ). Roughness and grain size were measured by atomic force microscopy (AFM) - Asylum Research MFP-3D®- in non-contact mode in a surface area of 10x10 µm, 20x20 µm and 14x14 µm. They were studied in the software -Scanning Probe Image Processor (SPIP®). The mechanical properties were obtained in a Nanovea nanoindenter with a Berkovich type tip and a compliance of 0.00035 µm/mN, the results were analyzed based on the Oliver and Pharr method. The tribological study was carried out following the ASTM G99-17 standard [10] on a Microtest MT 4001-98 tribometer, with a tungsten carbide (WC) counterpart, the parameters used for the test were a speed of 10 m/s, normal load of 10 N and a total distance of 400 m.

3. Results and discussion
This section presents the analysis of the structural, morphological, mechanical and tribological properties of TiAlN, TiCN and CrAlN coatings by the magnetron sputtering technique.

The X-ray diffraction patterns for the TiAlN, TiCN, and CrAlN coatings are shown in Figure 1. These coatings were deposited on silicon substrates (100). The Figure 1 show a sequence of 20 diffraction lines for a face-centered cubic structure (FCC), NaCl type with an fm-3m space group [11].

The TiAlN, Figure 1(a), ternary system presented a NaCl-type FCC structure with space group fm-3m and a preferential orientation in the (200) plane. TiCN, Figure 1(b), is related to a substitution mechanism, in which carbon (C) atoms replace nitrogen (N) atoms, resulting in C-N system ordered by titanio (Ti), and not ordered for the TiCN coating. The CrAlN material, Figure 1(c), is the result of the coupling of two FCC phases of aluminum nitride (AlN) and the chromium nitride (CrN), which generate a conjugated complex where the aluminum (Al) and chromium (Cr) atoms are located in the reticular
positions and the aluminum atoms (Al) are replaced by the atoms (Cr) while nitrogen is located in interstitial positions of the CrAlN crystal.

The TiAlN, TiCN and CrAlN coatings crystallized forming a NaCl-type FCC structure, in which the Ti, Cr and Al atoms would be in the Wyckoff 4a site, while the C and N atoms randomly occupied the Wyckoff 4b site [12,13]. Furthermore, it is observed in Figure 1(c) that the CrAlN material is formed from CrN and AlN, sharing the same NaCl-type FCC crystal structure and the same 225-Fm3m space group.

![Figure 1. XRD patterns. (a) TiAlN; (b) TiCN; (c) CrAlN.](image)

The morphological characterization was carried out by AFM, it was used for the quantitative analysis of the surface morphology of the TiAlN, TiCN and CrAlN coatings, the coatings were deposited on silicon (100) substrate, in order to obtain values surface roughness (Ra) and grain size (D). AFM images for all coatings are shown in Figure 2(a), Figure 2(b), and Figure 2(c). The morphological images show the textures generated on the surface of the layers after deposition. Morphologically the surface of the samples varies in uniformity according to the films deposited on S600 steel.

![Figure 2. Topographic images. (a) TiAlN; (b) TiCN; (c) CrAlN.](image)

In Figure 3(a) and Figure 3(b), it is evidenced that CrAlN has a susceptibility to grow with low roughness compared to other materials, thus demonstrating a decrease in grain size and consequently greater compaction. The film with the highest value in these parameters is TiAlN. TiCN shows a decrease of 23.53% and 11.98% in roughness and grain size values respectively, compared to TiAlN. Regarding CrAlN, a decrease of 42.23% and 17.57% is observed for roughness and grain size respectively, compared to TiCN.

The friction coefficients for the S600 steel systems, TiAlN, TiCN and CrAlN coatings, and tungsten carbide (WC) counterpart are presented in Figure 4. The coefficient of friction in the materials TiAlN, TiCN and CrAlN, is taken from the settlement distance. Therefore, the value of the friction coefficient will depend on the predominant effect related to the adhesive and interference mechanisms.
Figure 3. (a) Roughness vs. coating materials; (b) grain size vs. coatings materials.

Figure 4. Coefficient of friction for all surfaces depending on tracks.

Figure 5 shows the friction coefficients for steel, TiAlN, TiCN and CrAlN. The friction coefficient for steel is 0.48359±0.10546, for TiAlN it is 0.47222±0.1075, for TiCN it is 0.09257±0.0034 and for CrAlN it is 0.05823±0.0032. It is observed that the material with the best performance for the exposed application is CrAlN, with a decrease of 87.96%, compared to S600 steel. Considering the Archard model [14], when a material has a low roughness and a high hardness, the friction coefficient tends to decrease, therefore, it can be determined that the CrAlN coating has the lowest friction coefficient given its low roughness and high hardness with respect to the other deposited (TiCN and TiAlN) coatings.

The wear rate (K) generated by tribological tests is calculated using the Equation (1), Equation (2), and Equation (3) [15].

\[
K = \frac{V}{(F \times S)}, \quad (1)
\]

\[
V = 2 \times \pi \times r \times A, \quad (2)
\]

\[
S = 2 \times \pi \times R \times n, \quad (3)
\]

where K is the wear rate, V is the worn volume, r is the radius of the wear track, A the area of the track that relates the height and depth of the wear track, F is the force applied to the pin, S is the slip distance, and n is the number of turns during the tribological test.

In Figure 5 the images corresponding to the tribological tests are presented, where the width, depth and wear rate were studied. In Figure 5(a) the wear corresponding to the TiAlN coating is observed, where we can identify a track with a width of 0.5536±0.02768 and a depth of 3.443±0.2443, lower than those of the standard sample, but a considerable wear rate is still evident. Figure 5(b) and Figure 5(c) show the wear generated for the TiCN and CrAlN samples, where there is a considerable reduction in the width of 0.0748±0.03974 and 0.0484±0.03042, depth 1.054±0.2054 and 0.667±0.2667 of the tracks respectively; with respect to the standard sample, it refers to a lower wear rate.
Thus, the wear rate is directly related to the material resistance to be worn, then the CrAlN coating has the highest wear resistance and the TiAlN has the lowest resistance. The low wear rate for CrAlN coating depend on the mechanical and tribological properties of the material, which has superior properties such as hardness and elastic modulus, accompanied by a friction coefficient reduction, as previously demonstrated. These physical characteristics provide conditions that benefit wear resistance in the coatings analyzed. Exhibiting the lowest wear rate for the CrAlN coating. In Figure 6 the width and depth values of the four materials are compared. It is observed that the CrAlN coatings present a low rate of wear which correlates the data obtained in the XRD and AFM analyzes.

![Figure 5. 2D profiles of the wear tracks. (a) steel; (b) TiAlN; (c) TiCN; (d) CrAlN.](image)

![Figure 6. (a) width of wear tracks generated by the tribological test; (b) depth of wear tracks generated by the tribological test.](image)
4. Conclusions
Chromium aluminum nitride coatings have better structural, morphological, tribological and mechanical properties compared to aluminum titanium nitride, titanium carbonitride coatings due to the coexistence of the aluminum nitride and chromium nitride phases. The chromium aluminum nitride and titanium carbonitride coatings have fewer surface defects, due to the low values in the grain size, therefore, there is a decrease in the contact between asperities in the tribological pair, presenting a low COF, reducing the wear particles, and increasing the lifetime of the protective layer as observed in the Pin-on-Disk tests where a lower wear rate was obtained, contributing to better efficiency in industrial applications.

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