Behavior to wear and corrosion of steel with chromium silicon nitride coatings

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Abstract. Chromium silicon nitride coatings were deposited via physical vapor deposition using a reactive sputtering magnetron, on steel specimens, with a chromium silicate target, purity of 99.5% and argon/nitrogen gas ratio (%) of 80/20. The coating characterization was carried out by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy and nano hardness. The erosion-corrosion analysis was performed with a pin on disc tribometer, with a zircon pin, load of 1 N, applying three rotation speeds of the system (250 rpm, 400 rpm and 500 rpm) with an electrolyte composed of water, silica sand (0.05 mm, 0.1 mm and 0.15 mm) and 1% of sodium chloride. The electrochemical techniques used were resistance to polarization, electrochemical impedance spectroscopy and potentiodynamic polarization. The coating decreases the rate of substrate wear between 32% and 56%. The coefficient of friction decreases by almost 50% with the application of the film. Finally, the coating reduces by an order of magnitude the corrosion rate of steel in systems subject to wear and in 3 orders of magnitude in steel systems in static conditions, increasing the useful life of industrial facilities.

1. Introduction
At a global level, there are problems in the operation of industrial facilities. Predominantly due to faults in conduction pipes caused by wear and corrosion phenomena [1-4], which entails, the interruption in the service provided associated with possible human, environmental, economic and social losses for both the company and the community [5].

The coatings consist of one of the most efficient techniques for protecting substrates because they produce a barrier between the metal and its environment [6]. The application of these coatings via physical vapor deposition (PVD) have improved the operating conditions of a wide variety of substrates, due to the possibility of depositing a wide variety of materials and compounds, through the use of less polluting equipment and gases [7-16], particularly, chromium-based nitride (CrN) coatings, have been shown to have very high ductility and elevated fracture resistance, with low friction coefficient and good resistance to oxidation and corrosion [17], likewise, coatings in CrSiN have been the subject of studies and research projects, to look for the improvement of the characteristics of it when it is applied to different substrates submitted to different environments [18], finding an upgrade in the wear and corrosion resistance, in the properties of various substrates (steels, aluminum, silicon, alloys) which are exposed to distinct environments (dry and wet), when it is adding Si to CrN [18-22].
In order to reduce operational interruptions due to corrosion and erosion phenomena, avoiding the use of potentially very expensive materials, we propose a novel solution for this kind of industries, evaluating the behavior of CrSiN coatings deposited via PVD on API 5CT N80 steel substrates, material used in the manufacture of pipes used for water injection in hydrocarbon extraction facilities, subjected to the action of an aggressive fluid with different sizes of silica sand (SiO₂) and addition of NaCl. By using varied characterization techniques and equipment pin on disc equipped with device for erosion-corrosion tests, and connected to a Gamry potentiostat-galvanostat used for electrochemical measurements, to establish its properties to wear and corrosion.

2. Methodology
A PVD unit was employed for deposition process, using the balanced sputtering magnetron technique, with a chromium silicate target with a CrSi2 composition and purity of 99.5%. The deposit conditions were defined with a distance of 5 cm between the target and the substrate. The base pressure was always less than 4*10⁻⁶ mbar while the working pressure was 4*10⁻³ mbar. The coatings were deposited in N₂ (20%) and Ar (80%) atmosphere. Plasma generation was performed using a pulsed DC source with 120 mA of current, 60 W of power and 480 W during 30 min.

The erosion-corrosion analysis of the samples was carried out employing a Gamry potentiostat-galvanostat installed on a pin on disc microtest MT / 60 / NI Tribometer and was necessary to implement an attached cell in this one, to allow the electrolyte use and the different electrodes (work, reference and counter electrode) required to perform the test. The electrolyte is composed with water, silica sand of different sizes in a concentration of 20% and 1% NaCl. The test was worked with three electrode rotation speeds. The electrochemical techniques used to determine the parameters of corrosion of the specimens were the polarization resistance, electrochemical impedance spectroscopy and potentiodynamic polarization.

The samples characterization was carried out by using different techniques. Initially X-ray diffraction (XRD) was carried out to establish the crystallinity of the coating, after using a Carl ZEIZZ EVO MA10 equipment, the thickness of the coating was defined by utilizing the scanning electron microscopy (SEM); as well as its chemical composition by energy dispersive X-ray spectroscopy (EDS), finally, a Hysitron TI 750 UBI nano hardness tester with Berkovich diamond tip was used to determinate the presence and hardness of the coating. Analyzes on the generated tracks in the test pieces were carried out at the end of the wear test, both to establish the volume of material loss (LEICA DVM2500 high resolution optical microscope) and for the morphological and chemical analysis (ESM and DSE respectively).

3. Results and discussion
In this section, the coating characterization will be presented, to afterwards present and analyze the results obtained.

3.1. Coating characterization
By SEM images taken on the cross section of N80 steel specimens coated with a CrSiN film with an increase level of 1 K, it was determined that the coating reached an average thickness of 3 μm. Figure 1 shows correspondence between the theoretical and experimental XRD patterns of the CrSiN, the obtained coatings exhibited a face center cubic (f c c) CrN-type structure (Cr,N) with diffraction peaks of (1 1 1), (0 0 2) and (0 2 2), likewise, between 30° to 60° angles there is a bulge in the analyzed coating pattern, which is characteristic of amorphous materials, a characteristic attributed to silicon nitride Si₃N₄ corresponding to a compound present in the coating in an amorphous way [22-24].

The EDS technique allowed establishing the percentage composition of the coating characterized by weight like this: N (73.77%), Si (22.49%) and Cr (3.74%). The hardness of the coating is 6.52 GPa, value that improves the results of the substrate, however, this values not reached as high as the maximums reported by other investigations with different combinations of the components of the coating [19-21], this may be because for this investigation, the content of Si present in the film exceeds
the critical value cited, where the value of this property decreases with the increase of Si [19,20,25]. The decrease in hardness it is attributed to the increase in the volume of the amorphous fraction present in the coating [19].

![XRD patterns](image)

**Figure 1** XRD patterns.

### 3.2. Wear rate

Defined from the classical wear equation [18,26,27], presented in Equation (1).

\[
W = V(S \ast L)^{-1}
\]  

higher in the CrSiN coating as the sliding velocity increases, which may be due to the increase in the number of fractures of the coating surface [28] and from the periodic removal of the coating film by abrasion, this same behavior was found in other materials [29,30]. Likewise, it is evidenced that the rate of wear from CrSiN coating is lower than for the base material analyzed (Steel N80), achieving a decrease in the rate between 32% and 56% which depends on the size of the particles and the system rotation speed as it is seen in Figure 2. It is also shown in Figure 3 the relation between the rate of material loss and the size increase of particles, where the larger the size of the particles there is an increase in the rate of wear of the material, which may be due to the abrasive wear caused for largest particles added to electrolyte that can act as hard protuberances increasing the wear rate [30].

![Wear rate with constant particle size](image)  
**Figure 2.** Wear rate with constant particle size. 

![Wear rate with constant rotation speed](image)  
**Figure 3.** Wear rate with constant rotation speed.
3.3. Friction coefficient
Figure 4 shows the friction coefficient behavior for N80 steel and CrSiN specimens depending on the sliding distance, rotating against a Zirconium pin with a constant load of 1 N. N80 steel specimens presents a mean value of 0.57, while decreases until values between 0.3 and 0.4 (depending on the rotation speed) for coating film in CrSiN, demonstrating an excellent lubricating behavior of the coating, and thus improving the conditions of the substrate, this decrease may be due to the lubrication of oxides \((\text{Si(OH)})_4\) formed on the sliding surface by the tribochemical reactions \(\text{Si}_3\text{N}_4\) with \(\text{H}_2\text{O}\), this effect is more evident in coatings with high Si content [31] or by the presence of the amorphous phase \(\text{Si}_3\text{N}_4\) in the coating [22],[31].

Besides, the friction coefficient presents a slight decrease in its value as the sliding velocity increases, this is consistent with the behavior of other materials in this same speed range [32], which may be due to the variation presented in the tangential velocity of the system. The curves of the friction coefficient initially have presented high values which can be attributed to solid–solid contact between tribo-pairs, this contact can be easily formed if the sliding interface is unsmooth, then, at 115 m, achieve a lower value in state of equilibrium, which may be due to the polishing of the roughness and cleaning of the surfaces [10] and for the rapid wear of coating, which causes the interface between tribo-pairs to become smoother and reduce the solid–solid contact region [18], likewise, the little difference of the values of the coefficient found in the equilibrium state may be due to the fact that the wear of the coating was produced by the same mechanism [10].

![Friction Coefficient Behavior](image)

**Figure 4.** Friction coefficient behavior.

3.4. Corrosion rate
As seen for some alloys where the corrosion current during wear increases with the increasing speed of the pin [29], Figure 5 shows the increase of corrosion rate of the samples for higher sliding velocity, which is due to the increase in the wear rate [29] that degrades the coating leaving the bare steel in contact with the electrolyte and the increase in speed does not allow corrosion products to adhere as corrosion barriers leaving the active material, followed by metal oxidation.

The results indicate that the coating decreases in an order of magnitude the corrosion rate of N 80 steel in specimens subject to wear processes, demonstrating that the coating in CrSiN significantly improves corrosion resistance, in addition, improves in 3 orders of magnitude the corrosion rate of N80 steel specimens under static conditions, verifying that the increase in the wear of the coating produces an increase in the corrosion rate of the samples, this behavior was presented for systems with the three particle sizes used.
3.5. Open circuit potential

Figure 6 shows the behavior of the open circuit potential for both N80 steel and CrSiN specimens before, during and after the wear test. Before and after the performance of the wear test, the coated specimens have better resistance to the corrosion phenomenon than the N80 steel specimens, which is reflected in the low values of potential of the latter in comparison with the obtained values for the specimens with CrSiN film, in which a decrease in charge transfer between the substrate and the electrolyte is generated.

During the wear test, initially the value of the open circuit potential decreases until the moment in which the pin begins to eliminate part of the coating forming chromium oxides Cr$_2$O$_3$ [31,33], protecting the system from corrosion, represented in the increase in the value of the potential (registered phenomenon for a time of 1300 s) until a relatively stable value is obtained, when comparing the
potential values for static conditions (initial and final) it can be seen that the final potential is a little lower, which indicates a degradation of the covering.

Initially in the test, for the N80 steel samples, it is shown an increase in the potential value, caused possibly by the formation of iron oxides Fe₂O₃ [34]. When these are eliminated by the system's rotation processes produce a decrease in the value of the potential, as well as the corrosion resistance of the steel samples, whose final values are below those obtained for the specimens with CrSiN coating both for movement and static conditions. This indicates that although the degradation is present in the coating, there is no total wear of it.

3.6. Scanning electron microscopy image analysis materials

The Figure 7 shows, that there isn’t any adhesion between the pin material and the substrate, indicating that the system exhibits cohesive wear, also, the presence of small abrasive wear is evident in some sectors due to the presence of particulate material, likewise, the base of the traces do not present undulations, presenting a uniform wear, which may be due to the nature of the material. Figure 8 shows the ductile behavior of the substrate, which can be concluded by the dragging of material presented in some of the tracks analyzed.

![Figure 7. Wear type.](image1)

![Figure 8. Drag material.](image2)

For tests with silica particle size of 0.15 mm, there are marks outside normal stringency to the normal roughness generated by the pin, which can be produced by the silica particles present in the electrolyte and defined as oxides of silicon or iron [34], the above, taking into account that in the analysis of energy dispersive X-ray spectroscopy taken on these marks, the presence of elements such iron, silicon and oxygen can be seen, but not others such nitrogen and chromium.

4. Conclusion

Employing the described technique and the established parameters, a CrSiN coating with an average thickness of 3 μm was obtained, characterized by two compounds, Cr₄N₄ with diffraction peaks of (1 1 1), (0 0 2) and (0 2 2) and Si₃N₄ present in the coating amorphously.

The application of the coating of CrSiN on N80 steel samples improves the wear response, achieving a decrease of up to 56%. In addition to this, is achieved decrease one order of magnitude the corrosion rate for systems subject to wear and three (3) orders of magnitude for systems in static condition. There is no kind of adhesion of material between the pin and the substrate, so it can be said that the type of wear presented is mainly cohesive with the presence of abrasive wear. At the end of the wear test, it occurred the degradation of the coating, although not the total destruction of it.
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