Evaluation of corrosive behavior of chromium silicon nitride under hydrodynamic conditions in aggressive environments

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Abstract. In order to analyze corrosion resistance and wear behavior, steel cylinders were coated with chromium silicon nitride via physical vapor deposition, using a reactive sputtering magnetron, with base and working pressures of $4 \times 10^{-6}$ mbar and $8 \times 10^{-3}$ mbar respectively. The diffraction patterns correspond to chromium nitride and the amorphous phase of silicon nitride, hardness of 6.52 GPa, thickness of 3 μm and chemical composition characterized by nitrogen, silicon and chromium. The corrosion behavior was determined with a rotating cylinder electrode, rotating at different speeds and connected to a Gamry potentiostat galvanostat, using the techniques of polarization resistance, electrochemical impedance spectroscopy and dynamic potentiation polarization. The tests were carried out in solutions composed of water, 1% of sodium chloride and silica sand, with temperatures of 25 °C and 45 °C. Limiting current density behavior was evidenced. The coating corrosion rate was reduced by up to two orders of magnitude compared to that found for steel samples and was affected by the system rotation speed, particle size and electrolyte temperature.

1. Introduction

Extreme operating conditions to improve production technologies can result in increases in temperature and flow velocity in pipes and other components of industrial processes [1,2]. The above, added to the presence of corrosive fluids, can favour the occurrence of wear and corrosion in pipes, which are responsible for much of the operating problems of industrial facilities worldwide [3-6].

To improve the materials used in these facilities, coating films have been used that create a barrier between the metal and the environment [7]. Among these, the transition metal nitrides deposited by physical vapor deposition (PVD) have been the subject of numerous investigations due to their excellent mechanical properties [8-[12]. Among these, the coatings of chromium nitride (CrN) have shown to have a high hardness, low friction coefficient and good wear resistance to corrosion [18][22].

In last years, efforts have been made to improve the properties of CrN coatings, introducing a third element within the coating and obtaining CrXN [18] films, which reported considerable improvements in the tribological and mechanical characteristics of CrN with the addition of Si [19-[23].

With the purpose of improving hydrocarbon production processes by increasing the useful life of water extraction and injection pipes, this work seeks to evaluate the behavior of CrSiN coatings, due to their resistance to wear and corrosion when applied to other types of substrates, deposited via PVD on API 5CT N80 steel substrates, materials used in the manufacture of tubes used in production wells for water injection and extraction with high content of particulate material and aggressive flows, in order to establish their response to corrosion and wear.
2. Methodology

The coating process was carried out using a reactive sputtering magnetron by means of PVD, with a chromium silicate target with a CrSi2 composition with 99.5% purity. As a consequence of the samples’ geometry, it was necessary to implement horizontal rotary axis in order to guarantee the uniformity of the film. The coatings were deposited in an N2 (20%) and Ar (80%) atmosphere, the distance between target and substrate was 5 centimeters, the plasma generation was performed using a pulsed DC source, with 120 mA, 480 V over 30 minutes.

The preparation of the substrates was carried out using a horizontal rotary axis for polishing the specimens with abrasive paper and cloth. Then, they were degreased with isopropyl alcohol and ultrasound for 20 seconds and, finally, manual cleaning and drying was carried out for 5 minutes.

The corrosive behavior determined using a rotating cylinder electrode (RCE) with three rotation speeds (250 rpm, 1250 rpm and 2000 rpm), connected to a Gamry potentiostat galvanostat. The electrolyte was composed of water, silica sand of different sizes (0.05 mm, 0.1 mm and 0.15 mm) at 20% and 1% NaCl, and at temperatures of 25 °C and 45 °C. The electrochemical techniques used were polarization resistance, electrochemical impedance spectroscopy and dynamic potent polarization.

X-ray diffraction (XRD) was used to establish the crystallinity of the coating. Its thickness was defined by means of scanning electron microscopy (SEM) while its chemical composition was determined by using energy dispersive X-ray spectroscopy (EDS). Its hardness was defined by using a Hysitron nanoindenter. Finally, visual analysis was carried out using a scanning electron microscope in order to qualitatively analyze the degree of wear on the coating.

3. Results and analysis

3.1. Coating characterization

The diffraction patterns were obtained using the thin film configuration, finding chromium nitride Cr4N4 with face-centered cubic (FCC), CrN-type structure and diffraction peak with preferred orientation of (1 1 1), peaks corresponding to the CrN (0 0 2) and CrN (0 2 2) were also observed. Between the angles 30° and 60° there was a bulge in the pattern of the coating proper to amorphous materials. This characteristic is attributed to silicon nitride Si3N4 and corresponds to a compound present in the amorphous coating [14,21,22]. Figure 1 shows the diffraction peaks as well as the correspondence between the theoretical and the obtained spectrum for the CRSiN coating.

![Figure 1. DRX patterns.](image)

The average thickness of the layer was 3 μm, with a percentage composition by weight of N (73.77%), Si (22.49%) and Cr (3.74%). The average hardness was 6.52 GPa which improved the substrate by 270%. However, it was lower than that found in different investigations. This may be due to the high percentage of Si present in the coating [18,19,24]. It is valid to highlight that hardness value ensures the presence of the protective film and improves wear resistance.
3.2. Limiting current density

Figure 2 shows that increasing the rotation speed of the system produced a displacement of the Tafel curves to the right, indicating an increase in the corrosion current and the corrosion rate of the system. It can be seen that the average corrosion current (defined by the vertical line on the current axis) for specimens with CrSiN coating was below the average found for N80 steel at around 1.7 orders of magnitude, which demonstrates the level of protection achieved with the use of the coating. Limiting current density ($i_L$) was obtained by the graphic method from the cathodic region of the Tafel curves, for the three sizes of particles used in the present investigation, $i_L$ increased as a function of the specimen rotation speed, which may be due to the wear process of the coating that facilitates the ion exchange, increasing the current density, as well as the corrosion rate of the system [1]. This behavior is characteristic of processes controlled by mass transfer [1,26], a control mechanism that can be verified by the verticality of the cathodic slopes of the Tafel curves [27].

![Figure 2. Tafel curves.](image)

The influence of temperature on the $i_L$ is observed in Figure 3, where it can be seen that for the same rotation velocity its increase produces an increase in the value of $i_L$, whose effect is intensified at higher system rotation speeds, mainly due to the increase of the kinetics of the reactions present in the system generated by the increase in temperature [25].

![Figure 3. Temperature influence on $i(L)$.](image)

3.3. Corrosion rate

As can be seen in Figure 4, there was a very significant decrease of up to two orders of magnitude between the values of the corrosion rate found for the coating of CrSiN with respect to the values found for the substrate (steel N80), indicating that the coating has a high resistance to corrosion in aggressive environments with the presence of chlorides, because Cr has a good resistance to corrosion due to its
self-passive mechanisms and Si generates a hard barrier. These characteristics are reflected in this study in a decrease of the degradation of the material.

3.3.1. Effect of flow velocity. Figure 4 shows that an increase in the speed of rotation, produced a rise in the corrosion rate. This behavior may be due to the wear of the coating due to the shear stresses produced by the fluid as well as the impact of the silica particles, presenting scratching and abrasion or dragging of the coating, producing areas of substrate without cover (API N80), generating direct steel-electrolyte contact and therefore an ion exchange between unprotected areas with the absence of the coating.

The products generated in the process (oxides) adhered to the surface of the metal generating a protective film, which diminishes the contact area and consequently the corrosion rates, however, as the increase in the speed of the flow produces an increment in the cutting speed, detaching the corrosion products from the specimens, the above added to the wear of the CrSiN film, facilitating mass transport, increasing the density and corrosion rate [25].

![Figure 4. Corrosion rate as a function of flow velocity.](image1.png)

3.3.2. Particle size effect. For electrolytes with small particles (0.05 mm and 0.1 mm) the increase in the particles’ diameter produces an increment in the corrosion rate, while with particles of considerable size (0.15 mm) this relationship disappears. Figure 5 shows that the lower corrosion rate occurs at a speed of 250 rpm and a particle size of 0.15 mm, while in systems with higher rotation the lowest corrosion velocity is presented for particles of 0.05 mm, indicating that in these systems a greater drag of particles towards the coating produces greater wear and, thus, increases the corrosion rate, generating erosion-corrosion mechanisms.

![Figure 5. Corrosion rate as a function of particle size.](image2.png)
The relationship between particle size and corrosion rate for particles less than or equal to 0.1 mm may be due to the increase in the kinetic energy of the particles that impact the surface of the coating produced by the increase in size [28]. The disappearance of this relationship for larger particles can be explained by the change in the morphology of the larger particles in which a decrease in points and edges is evidenced, to the decrease in impact energy due to the fragmentation of the bits [], or the impossibility that certain flow velocities can have of dragging particles of greater weight, with them remaining deposited at the base of the container, as happens in the pipes [].

3.3.3. System temperature effect. For the same rotation velocity, the increase in temperature produces an increment in the corrosion rate, due to the acceleration in the kinetics of the oxide - reduction reactions caused by the increase in the thermodynamics of the system. Figure 6 shows the typical behavior of this parameter, which is more evident at higher rotation speeds.

![Figure 6. Corrosion rate as temperature function.](image)

The above effect may be due to the fact that when raising the temperature, oxide - reduction reactions are generated with greater kinetics, allowing these reactions to occur with a higher frequency, causing a charge transfer in shorter periods of time, accelerating the process of deterioration of the material, or because the rise in temperature produces an increase in diffusivity and a decrease in viscosity increasing the speed of corrosion [27][30].

The CrSiN coating has a high efficiency against the phenomenon of corrosion, which is mainly influenced by the temperature and the speed of rotation of the system, the increase of which produces a tendency towards higher values of the limiting current density, causing an increase in the loss of mass of the substrate, which is due to the erosion-corrosion mechanisms generated by the presence of aggressive flows with contents of chlorides and particulate material, whose size influences the processes of wear and corrosion but depend on the speed of the rotation of the system.

3.4. Scanning electron microscopy images

Figure 7 shows the micrograph taken of the coating at the end of the tests, presenting the damage effected on the CrSiN. There are marks of drag and scratches, produced by the impacts of particulate material, damage which increased when the rotation velocity was higher. The samples subjected to a temperature of 45 °C presented greater degradation of the coating, where there were more marks of impacts and scratches, as well as material removal with oxidation processes that can be characterized by iron oxides (Fe₃O₄) [1] due to the wear of the coating by the particulate material. These zones with their respective chemical compositions can be observed in the micrograph presented in Figure 8.
4. Conclusions
The coating has two compounds silicon nitride Si$_3$N$_4$ present as an amorphous phase, and a face-centered cubic (f c c) CrN-type with diffractions peaks of (1 1 1), (0 0 2) and (0 2 2) corresponding to the Cr$_4$N$_4$ compound.

CrSiN films decrease the corrosion rate by up to two orders of magnitude. This behavior is mainly affected by the speed and temperature of the fluid and to a lesser extent by the size of the particulate material present, since in many cases the fluid velocity does not have the ability to transport larger particles.

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