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Structural and mechanical properties study of CNx/MoS2 multilayer coatings obtained by sputtering

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Abstract

This work documents the study of samples of CNx/MoS2 multilayer coatings, deposited by magnetron sputtering technique, using 10% and 16% of N2 concentration in the Ar/N2 gas mixture to obtain two sample sets with different nitrogen concentrations in the CNx layers. The samples were grown on Si (100) and AISI 304 steel substrates to carry out different characterizations. The microstructure of the samples was investigated by scanning electron microscopy (SEM), atomic force microscopy (AFM) and x-ray diffraction (XRD). The chemical structure and vibrational modes present in the multilayer coatings were evaluated using x-ray photoelectron spectroscopy (XPS), and Raman spectroscopy, respectively. The analysis revealed that the CNx layers are amorphous, while the MoS2 layers show a polycrystalline structure with basal planes perpendicular to the substrate surface. Finally, the mechanical properties were evaluated by nanoindentation and pin on disk tests, respectively. The results revealed that the concentration of N in the CNx layer is fundamental in determining the mechanical properties. In the test carried out in a humid environment, the samples with the lowest concentration of N in the CNx layers present lower values in the coefficient of friction.

1. Introduction

Multilayer structure in coatings allows the combination of two or more materials to improve their individual properties. The selection of the materials and multilayer coating design (number of layers, thickness, deposition method, and interface thickness) are fundamental aspects that define their structural, mechanical, and tribological properties, as well as their applications [1–9]. Holmberg et al [3] recommend that with a suitable multilayer design it is possible to improve the load support and crack propagation resistance to achieve the required mechanical, and tribological properties. The combination of soft and hard materials as a bilayer is widely used in multilayer arrangement due to the soft layer acting as a buffer, which reduces the propagation of a subsurface fracture [4–9], while the hard layer provides support and hardness to the coating.

Currently, several studies have indicated that molybdenum disulfide (MoS2) is a solid lubricant due to its relevant tribological properties, such as low coefficient of friction (COF) and wear resistance; these coatings have also been used in vacuum and aerospace applications with excellent results [10–15]. The sputtered MoS2 films show a coefficient of friction between 0.1 and 0.3 in ambient conditions. [13, 15–17]

However, MoS2 is prone to rapid oxidation under humid or ambient conditions; this degradation due to oxidation results in poor tribological performance [10–19]. Researchers have developed a means to improve the mechanical and tribological properties of MoS2 films, looking for terrestrial applications in humid, corrosive environments and at high temperatures. For this purpose, different strategies have been followed, among which
is the doping of MoS₂ with metals (e.g., Au, Ti, Ni, Pb, or Cr), or composites with metallic and ceramic nanoparticles, seeking that these nanoparticles and metallic dopants provide protection against oxidation of MoS₂, and in turn increase its hardness and wear resistance, maintaining its lubricating properties [13, 18–21]. These investigations as well as studies of nanostructured coatings, bilayer or multilayer coatings of MoS₂ and metals or hard nitrides (TiN, CrN, etc) account for most of the recent major work [16–21]. Zhao et al [19] deposited DLC/MoS₂ multilayer by magnetron sputtering, and they reported better tribological properties of multilayer coatings due to the reduction of MoO₃ presence. Chhowalla and Amaratunga [15] report films made up of hollow MoS₂ fullerene-like nanoparticles synthesized by high local pressures of electric arc, in which the nanoparticles present curved planes of S-Mo-S, which prevent oxidation of MoS₂ and supply basal planes (0002) parallel to the surface, allowing low coefficients of friction in conditions with 45% of relative humidity [15].

Carbon nitride (CNₓ) coatings deposited by sputtering demonstrate a relatively high hardness and wear resistance; however, a high N concentration in CNₓ films causes a decrease in these properties [22–25]. The concentration and bonding state of nitrogen in amorphous CNₓ films determine their chemical and physical properties, including tribological performance. Amorphous CNₓ films with low N concentration are used in industrial applications, but the most common function of amorphous CNₓ films is as a protective coating. Several studies are focused on improving the wear rate and friction coefficient of CNₓ films. The coefficient of friction of CNₓ is in the range from 0.07 to 0.45 in ambient air conditions. [22–26] Moreover, CNₓ, a-CNₓ, and fullerene-like CNₓ are chemically inert, and this could decrease the oxidation of MoS₂ under environmental conditions [27, 28].

After a large number of publications on solid lubricant coatings, there is still no solid lubricant that provides excellent wear resistance and low friction coefficients, especially when exposed to room temperature and high temperatures. Therefore, the combined amorphous phases produced in CNₓ coatings with the crystallized phases in MoS₂ coatings, forming a multilayer coating of modulated composition, could significantly improve hardness, fracture toughness, friction coefficient, and adhesion, and therefore improve their resistance to wear.

In this work, we studied two sets of CNₓ/MoS₂ multilayer coatings with different percentages of nitrogen in the CNₓ layer. The effect of N% on the multilayer coating properties has been evaluated and compared among them. The microstructure, chemical composition, and mechanical properties of CNₓ/MoS₂ multilayer systems were analyzed.

Studying the effective mechanical properties of the combination of CNₓ and MoS₂ properties in multilayer systems, looking for an adequate number of periods that improve their mechanical properties.
2. Methods

Initially, MoS$_2$ and CN$_x$ single layers were grown on Si wafers to characterize the microstructure and determine their growth rate deposition. The MoS$_2$ rate deposition was $\sim 195$ nm min$^{-1}$, while CN$_x$ rate deposition was $\sim 15$ nm min$^{-1}$ over Si wafer under the deposition conditions given in table 1. Next, the MoS$_2$ and CN$_x$ layers were deposited alternately as a multilayer coating. Two sets of multilayer coatings were deposited on Si (100) wafers and polished AISI 304 steel substrates by magnetron sputtering using two targets as cathodes with a diameter of 2 inches and a target-to-substrate distance of 5 cm; the first one was graphite and the other molybdenum disulfide. The deposition chamber was pumped down to around $4.0 \times 10^{-5}$ mbar; the multilayers were then obtained as the design of the schematic representation of figure 1 shows. The CN$_x$ layer was deposited by DC sputtering from the graphite target under a reactive N$_2$/Ar atmosphere (10/90 and 16/84%). Thereafter, the substrate was rotated to the second target position (commercial target of MoS$_2$, obtained from substrata materials, with a purity of 99.9%) to deposit the MoS$_2$ layer in an Ar atmosphere by DC pulsed at 20 kHz with a pulse length of 48 $\mu$s. The main deposition parameters of each set of samples are shown in table 1.

The reasons for selecting this range of N$_2$ concentrations in the N$_2$/Ar gas mixture are the following: (i) For a higher concentration of N$_2$, the growth rate of the coating is very low and (ii) according to previous reports, a higher concentration of N$_2$ in the gas mixture causes saturation in the CN$_x$ coating, and it ceases to be incorporated [28]. In this study, two sets of coatings with N$_2$ concentrations of 10% and 16% were deposited in the N$_2$/Ar gas mixture; the films were designated as samples A and B, respectively. The CN$_x$/MoS$_2$ bilayer, which is called the period, is repeated up to five times (figure 1). The sample label is indicated with the period number followed by the letter A or B, depending on the sample set to which it belongs.

The properties of the multilayer coatings were analyzed by several characterization techniques. The morphology and microstructure were carried out with a Field Emission Scanning Electron Microscope (Jeol 7610 F) using SEI and GB-High detectors with 1–2 kV. The multilayer coatings on Si wafers were observed in a cross-sectional manner to analyze the morphology, homogeneity, and final thickness of the multilayer arrangement. The thickness of each layer and the total thickness of the multilayer arrangement were measured in a cross-section image using PC_SEM software by Joel.

The topography images of the coatings were measured using a Park XE7 atomic force microscope (AFM); the AFM equipment was operated in tapping mode with a scanning rate of 0.2 Hz in 256 $\times$ 256 pixel images.

The XRD patterns were obtained in coatings deposited on AISI 304 steel substrates using a Rigaku Dmax2100 diffractometer with Cu K$_\alpha$ radiation using 30 kV, 20 mA in the range $2\theta$ of 20°–55° with step 0.2°. Raman spectra were measured on a HORIBA LabRam HR Evolution Raman Spectrometer in the range of 10 to 2000 cm$^{-1}$; the excitation source was He–Ne laser at 632.8 nm line with 20 mW of power.

![Figure 2. (a) SEM and (b) AFM images of the CNx surface of sample A. (c) SEM and (d) AFM images of CNx surface of sample B. (e) SEM and (f) AFM micrographs of the MoS2 surface.](image-url)
X-ray photoelectron spectroscopy (XPS) was carried out using a spectrometer Alpha 110 Thermo-Fisher Scientific with a monochromatic source of Al Kα (hv = 1486.6 eV) as an x-ray source. The high-resolution spectra (C1s, N1s, Mo3d, and S2p) were analyzed by carrying out the fitting of each spectrum with Avantage® software applications, such as peaks with a mix of Gaussian-Lorentzian form (30% Lorentzian form) and Smart background. The percent atomic was determined by calculating the normalized areas of peaks, taking into account the sensitivity, equipment operating, and energy compensation factors, then the normalized areas were divided by the sum of normalized areas of all peaks of the spectrum.

The mechanical properties measurements were carried out in coatings deposited on AISI 304 steel substrates. The friction coefficient was evaluated by a CMS Pin-on-disk tribometer against a steel ball in ambient conditions, and with relative humidity around 45%. The test parameters were: 1 N for a normal load for 5500 laps of sliding with a linear speed of 5 cm s⁻¹. The hardness and reduced elasticity modulus were carried out with an IBIS nanoindentation system using a Berkovich indenter, and the indentation load was from 30 to 12 mN. Both mechanical properties were calculated from load-unload displacement curves by IBIS nanoindentation software using the Oliver & Parr model [29].

3. Results

3.1. Morphological characterization

The morphology of CNₓ and MoS₂ single layers were analyzed using SEM and AFM. In figures 2(a) and (c), SEM images present a granular surface on CNₓ films. However, sample A shows a dense morphology of hemispherical agglomerates with a grain size around 30 nm, made up in turn of smaller spherical particles of around 5 nm, while the surface of sample B exhibits small cracks indicating a certain degree of porosity and the hemispherical agglomerates are smaller than those of sample A. Furthermore, the lamellae of MoS₂ tend to grow perpendicular to the substrate surface over the CNₓ layer, with random orientation; this causes a ‘worm-like’ morphology [10, 11] whose microstructure is observed in figure 2(e), where the average width of worms is 9 nm and the length of the structures up to 400 nm. The inset of figure 2(e) shows the cross-section of the MoS₂ film with the columnar growth and the lamellar structure perpendicular to the substrate surface [13]. The AFM results in figures 2(b), (d), and (f) show similar morphology to the SEM images [figures 2(a), (c), and (e)], where the average area roughness of MoS₂ layer is 7.5 nm and CNₓ layers are around 10 nm.

3.2. SEM Characterization

The cross-sectional SEM images of sets A and B multilayer coatings deposited on silicon are shown in figure 3. All multilayer coatings display a columnar structure that is characteristic of coatings grown by the sputtering
technique. SEM images also show a well-defined alternate multilayer arrangement, where the MoS$_2$ layer has a higher average atomic number than CN$_x$. This results in the bright layers corresponding to MoS$_2$ and dark layers to CN$_x$.

The thickness of the MoS$_2$ layer is lower when grown directly on Si than when it is grown on the CN$_x$ coating under the same conditions. The total thickness of the coatings of both sets was between 1.6 and 3.2 micrometers. The thickness ratio of CN$_x$ to MoS$_2$ layers varied from 1:4 to 1:1, and the thickness ratio of 4 A and 4B samples was 1:4 and 1:2, respectively.

Table 2 summarizes the bilayer thickness and CN$_x$ to MoS$_2$ thickness ratio of all obtained samples. The layer thickness of MoS$_2$ is several times greater than that of the CN$_x$ layers. Meanwhile, the sputtered rate of CN$_x$ layers was the same in both sets regardless of N$_2$% but not the granular size.

The bilayer thickness decreases when the period’s number is increased, from 2.8 to 0.4 μm for the A set and from 2 to 0.5 μm for the B set, but not proportionally. Apparently, the same occurs for the thickness of the interfaces. The thickness and roughness of coatings are factors that contribute to the mechanical behavior[3, 4]. Figure 4 shows the average roughness values for the two sets of samples, the outer layer of which is MoS$_2$ in both sets; with the number of periods, the thickness of this outer layer decreases from 2.29 μm for sample 1A to 0.3 microns for sample 5A, and the roughness is in the range of 8 to 20 nm. The sample with the lowest average roughness was 4A (8 nm).

The deposition time in both sets was the same, and it was determined considering the growth rates of materials (MoS$_2$ is 195 nm min$^{-1}$, and CN$_x$ is 15 nm min$^{-1}$) on Si wafer and the number of periods in each sample. The thickness ratio expected was (1:1) for all samples; however, table 2 shows different values, indicating that the sequence of film growth (substrate/CN$_x$/MoS$_2$) modified the growth rate for both materials. Furthermore, the morphology of the CN$_x$ layers also contributed to the alteration in the deposition rate.

The surface morphology of the CN$_x$ growing on Si and MoS$_2$ are very similar; however, the growth rate on MoS$_2$ was higher than that on Si. In the case of MoS$_2$, the surface morphology is very similar when it is growing on Si and CN$_x$.10. Whereas in the case of MoS$_2$ grown on CN$_x$16, the dimensions of the worm structure decreased by approximately half.

The dependence of the growth rate of MoS$_2$ on the CN$_x$ layers can be inferred from the evolution of the thickness ratio of the CN$_x$/MoS$_2$ bilayer with the increase in numbers of bilayers. For series A, the thickness ratio ranges from 1:5 for sample 1A to 1:2 for sample 5A, which shows that initially MoS$_2$ increases its growth ratio over CN$_x$, up to 5 times compared to its growth ratio on Si, by increasing the number of bilayers. The influence of CN$_x$ growth over the MoS$_2$ layer is observed; its growth ratio also increases in such a way that the thickness ratio of the bilayer is now between 1:3 and 1:2.

![Figure 4. Average roughness of the outer layer of both sets of samples, over Si substrate.](image-url)
The increase in the growth ratio of MoS$_2$ is lower in series B, as shown by the evolution of the ratio of bilayer thicknesses, which goes from 1.2 for sample 1B to 1:3 for sample 5B.

### 3.3. XPS analysis

The high-resolution XPS spectra of Mo3d and S2p is shown in Figure 5. Figure 5a shows the two deconvoluted doublets revealed from the Mo 3d XPS spectrum; the first doublet at 229.4 and 232.4 eV belongs to Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$, respectively; it has 3.1 eV of spin–orbit splitting and both peaks are typical for Mo bonded to S with Mo$^{4+}$ chemical state. The second doublet located at 232.6 eV (Mo3d$_{5/2}$) and 235.6 eV (Mo3d$_{3/2}$) has 3 eV of spin–orbit splitting, and it is distinctive of Mo bonded to O with Mo$^{6+}$ chemical state; its chemical state may be caused by Mo–O bonds. The formation of MoO$_3$ is due to the degradation of MoS$_2$ under environmental conditions. Additionally, a peak at 226.7 eV corresponding to S2s presented. As figure 5b shows, the S2p spectrum is fitted by four peaks. The first two peaks located at 161.8 eV and 162.9 eV belong to S2p$_{3/2}$ and S2p$_{1/2}$, respectively; these peaks have 1.1 eV of spin–orbit splitting, which is characteristic for S bonded to Mo with S$^{2–}$ chemical state. The last two peaks are located at 163.3 eV(S2p$_{3/2}$) and 164.5 eV(S2p$_{1/2}$); these peaks have 1.2 eV of spin–orbit splitting, and are distinctive of S$_{2}^{2–}$ chemical state. The doublets indicate the existence of S$^{2–}$ and S$_{2}^{2–}$ ligands. The presence of S$^{2–}$ ligands can suggest that MoS$_2$ is partially amorphous. The atomic
percentage of MoS₂ calculated from XPS was 15.7 at.% Mo, 29.22 at.% S and 55.11 at.% O. Since the depth of analysis of the XPS technique is very small, on the order of nm, we can say that the surface of MoS₂ is partially oxidized\cite{30–32}.

Figures 6(a)–(d) displays the C 1 s and N 1 s XPS spectra of CNₓ single layer with different N₂ (10\% and 16\%) concentrations in the N₂/Ar gas mixture, corresponding to samples A and B, respectively. The high-resolution XPS spectra were deconvoluted into three peaks using the Voight function to fit. Figure 6(a) and (c) shows C 1 s spectra fitted by three peaks located at 284.9, 286.2, 287.9 eV, which correspond to C sp²–C (C=C), C sp²–N (C=N), and C sp³–N (C–N), respectively. Peaks labeled as C=C and C=N bonds decrease their intensities, whereas the intensity of the C–N peak increases in sample B concerning sample A. These suggest greater incorporation of N atoms in sample B\cite{33}. The N incorporation may be the outcome of the C atoms being mainly bonded to N with sp² hybridization.

The N 1 s spectra (figures 6(c)–(d)) split into three peaks; the first peak is at 397.4 eV and is attributed to sp³ N–C bonds, the second peak is located at 401.5 eV and corresponds to sp³ N–C bonds, and the third peak at 404.5 eV is typical for N–O bonds due to the oxygen absorbed at the surface. It is evident that peak sp³ C–N bonds incrementally increase in intensity, whereas sp³ C–N and N–O bonds decrease their intensity peak. The C 1 s and N 1 s spectra fitted suggest that atoms of N are incorporated into the CNₓ layer as sp³ C–N bonds, which is the outcome of increment of N₂ concentration on deposition environment. The atomic percentage of sample A calculated from XPS was 42.52 at.% C, 38.98 at.% N, and 18.49 at.% O, while that of sample B was 44.05 at.% C, 40.72 at.% N and 15.24 at.% O\cite{33, 34}.

Figure 7. XRD pattern of 4 A and 4B multilayer coatings deposited on 304 steel substrates.

Figure 8. Raman spectra of multilayer coatings samples. (a) set A and (b) set B.
3.4. Structural characterization

Figure 7 displays the XRD pattern of 4 A and 4B coatings. The peak located at \(2\theta = 34^\circ\) corresponds to (100) plane of MoS\(_2\) in its hexagonal phase (card No. 87-2416). Both samples showed the same peak and only differed by the intensity; this is due to the bilayer thickness, which suggests a lower period thickness in 4 A than in 4B [17]. Moreover, the CN\(_x\) peaks were not detectable and this indicated that the layer of CN\(_x\) was amorphous.

Additionally, two peaks at 44° and 51° angles correspond to AISI 304 stainless steel substrate (card No. 33-0397). According to the XRD patterns reinforced with SEM images, it is observed that the growth of MoS\(_2\) on the CN\(_x\) coating is in a polycrystalline form with the basal planes oriented perpendicular to the surface of the substrate with a small crystallite size on the order of 4 nm estimated by Debye–Scherrer’s formula [35].

3.5. Raman analysis

The normalized Raman spectra of A and B are shown in figure 8. The spectra were obtained using the 632.8 nm He-Ne laser line. All samples display the E\(_{2g}\) and A\(_{1g}\) modes corresponding to MoS\(_2\) bonds, located at 383 and 407 cm\(^{-1}\), respectively. The peaks at 180, 454 and 634 cm\(^{-1}\) also correspond to MoS\(_2\) [36, 37]. The period thickness in the multilayer coatings modifies the Raman intensity. This fact is observed in two peaks, which are located at 1580 and 1350 cm\(^{-1}\) corresponding to D and G Raman bands related to amorphous CN\(_x\) [38–40]. The D and G peaks were observed from samples with three and five periods, since the bilayer thickness is minor and this allowed the laser beam to penetrate and excite the CN\(_x\) layer.

In addition, Raman spectra display a peak between 200 and 300 cm\(^{-1}\), which indicates the characteristic MoO\(_2\) formation; the peak located at 997 cm\(^{-1}\) is also associated with MoO\(_3\). The presence of these oxides confirms that MoS\(_2\) is prone to oxidize under environmental conditions. [37].

Ferrari et al.[39] proposed that there are four basic types of carbon nitride films: (1) a-C: N, (2) ta-C:N, (3) a-C:H:N and (4) ta-C:H:N. The main difference between them is the fraction of sp\(^2\) and sp\(^3\) bonded atoms. The
Table 3. G peak position and the intensity $I(D)/I(G)$ ratio of D and G peaks.

| Coating | G peak position (cm$^{-1}$) | $I(D)/I(G)$ |
|---------|-----------------------------|-------------|
| 3 A     | 1557.6                      | 1.1         |
| 3B      | 1531.4                      | 1.1         |
| 4 A     | 1568.2                      | 1.4         |
| 4B      | 1564.4                      | 1.3         |
| 5 A     | 1565.2                      | 1.1         |
| 5B      | 1567.6                      | 1.4         |

Figure 11. Friction coefficient of both sets measured under ambient conditions.
CNx layer grew in both sets A (10%N2) and B (16% N2) and could be classified as type 1 (a-C: N) amorphous carbon films with a high fraction of sp² due to the deposition technique used. Apart from a high-intensity ratio, I(D)/I(G), is also attributed to a higher sp² cluster content. This fact is due to D and G peaks corresponding only to sp² sites [38–40]. To obtain the I(D)/I(G) intensities, the D and G peaks were fitted with two Gaussians with Fityk software (free version) and the area ratio was used (figure 9).

Zhou et al [41] have reported that the sp³ fraction increases when the thickness of G peak decreases. As shown in table 3, the G peak position in sample set A is located at a higher wavenumber than in set B. This indicates that the sp³ fraction is higher in set B than set A. However, the I(D)/I(G) intensity ratio (1.1–1.4) of samples indicate a greater fraction of sp³ bonds between C, and N atoms in both sets, which is corroborated by XPS analysis (figure 3) [39–41].

3.6. Mechanical characterization

The hardness and elastic modulus of set A and B as a function of the number of periods in multilayer coatings are shown in figure 10. The indentation load was from 30 to 12 mN, with the maximum indentation depth around 1 μm in all the samples with thicknesses between 1.6 and 3.2 micrometers, which indicates that the hardness and elastic modulus are effective values of the multilayer system. It was expected that the mechanical properties increase with the number of periods; however, the interface and the thickness are parameters to be considered. [42–46]. Set B presents this trend, but the improvement of hardness and elasticity modulus is slight. Instead, set A has similar values of these mechanical properties (H and E) in all the coatings. In our case, the hardness is very low (between 0.2 and 0.6 GPa), because as we can see from XPS analysis, the N concentration in the films reaches high values (close to 40% for both A and B samples). It is well known that similar behavior has been reported in the literature by other authors [26, 47]. These results agree well with Raman’s analysis, because as the N content increases a more graphitic material is obtained, which is associated with low hardness values as shown in table 3. On the other hand, according to Leyland and Matthews [44], the H/E ratio is an indicator of the material plasticity, which is related to wear resistance. The maximum values of H/E ratio display the samples with two periods in both sets because they showed a drop in the hardness and elasticity modulus. In addition, figure 1(c) shows that by increasing the number of periods the H/E ratio decreases, which suggests that the multilayer coatings have more plasticity if the number of periods is increased.

The low H/E ratio values can be attributed to several factors: (i) the CNx layer does not contain an adequate percentage of N to be a hard coating, (ii) is required a major control of the thickness of periods to obtain abrupt interfaces, (iii) the thickness of the amorphous CNx layer is higher than the optimum required and (iv) the CNx layer has an amorphous structure, and MoS2 presented a polycrystalline structure as shown in figure 7, which causes lattice mismatch between two materials and favors the formation and propagation of cracks. [45]

The pin-on-disk test was performed under ambient conditions to determine the friction coefficient (COF) of the two sets. It is well known that in a humid environment the friction coefficient of MoS2) tends to increase rapidly due to the oxidation of MoS2. Figure 11 shows curves COF versus time where we compare coatings from set A and B with the same number of periods. The graph of COF versus time is divided into two zones for analysis: the first from 0 to 750 s, the second zone from 750 to 1500 s. Both sets of multilayer coatings in the first zone display low COF values, probably induced by the outer layer of MoS2, then in zone 2, most samples show fluctuations in the tribological test and the COF values increase gradually.

Samples of set A show average coefficient of friction values close to COF of MoS2 (0.1 to 0.3) reported in the literature when the test is performed in a humid environment [15]. Sample 1 A shows a stable behaviour of the friction coefficient with an average value of 0.24. Moreover, sample 4 A, in the first zone, exhibits the lowest coefficient of friction of 0.07, although in the second zone, the COF increases slightly until an average COF value of 0.09 with a stable behaviour is attained.

Sample 5 A displays a stable behaviour and a low COF of 0.1 in the first zone, but the fluctuations in the test occur as a consequence of the fall of the outer layer and the accumulation of material that corresponds with the adhesive wear, resulting in an increase of the coefficient of friction of 0.47 in the second zone.

However, all samples of set B in the first zone of the test show COF values close to 0.2, and in the second zone the COF values increase to around 0.4. These measurements show that the N concentration in the CNx layers has an important role in the microstructure of the MoS2 layer and therefore, on the coefficient of friction of the multilayer system, showing lower values for set A, which has a lower N concentration in the CNx layer.

The results of the coefficient of friction obtained revealed that the COF values are also influenced by the thickness ratio of the bilayer and the roughness. Sample 4 A, as shown in figure 11, displays the lowest friction coefficient value (0.09); that is related to the highest I(D)/I(G) intensity ratio (1.4) attributed to a higher sp² cluster content with a thickness ratio of the bilayer (1:4) and the lowest Ra value (8 nm) [16–21].
4. Discussion

The set of results of the multilayer systems CNx-MoS2 A and B obtained with different concentrations of N2 in the N2/Ar atmosphere shows important differences in their physicochemical properties. The XPS and Raman results indicate that the CNx layers contain a majority concentration of sp3 bonds rather than sp2. The morphology observed by SEM indicates smaller clusters of cauliflower-like particles in the case of samples B in addition to the presence of small fractures, whereas samples A present a uniform structure without fractures in both cases the XRD results show that the films are amorphous. The behavior of the ratio I_D/G > 1.1 indicates that the CNx films are graphite-type samples, which explains the low hardness values obtained [26, 47]. The MoS2 films grow with the basal planes perpendicular to the surface of the substrate, in a polycrystalline manner, with a crystallite size of around 4 nm, giving rise to the worm-like structure seen in SEM micrographs, and XRD data indicate growth in direction (100). The morphological characteristics of MoS2 films are prone to oxidize in ambient or humid conditions; it is well known that their mechanical properties can easily degrade [10–19]. It is important to mention that the growth ratio of MoS2 increased significantly when growing on CNx films relative to its growth on silicon, with a greater effect observed in samples A, resulting in a thickness relationship between CNx films and MoS2 between 1: 5 and 1: 2. In both multilayer systems, the external film exposed to the environment is MoS2, for which the XPS results show that it is partially oxidized. The modulus of elasticity and hardness in both sets of samples shows a slight increase with the number of periods of the CNx-MoS2 bilayer; however, both values are low: the hardness is at values lower than 1 GPa, and the values of modulus of elasticity less than 70 GPa. The H/E ratio presents a maximum for the case of two periods in both systems, and subsequently a decreasing tendency, which implies a more plastic behavior of the system as the number of periods increases.

The results of the coefficient of friction in tests carried out with a relative humidity content of 45% show important differences between the systems. Sample 1 A, in which the MoS2 layer is five times thicker than the CNx film, presents a COF value close to 0.25; this value is around that reported for pure MoS2 in similar humid conditions [15]. However, when increasing the number of periods, two differentiable regions of the COF are observed: the first stage covers up to the first 800 s, in which the friction coefficient is less than 0.1; for longer times the COF increases to values greater than 0.4, except for sample 4 A, which presents a low COF value, close to 0.05, in the first stage and later reaches a value close to 0.1, with a stable behavior. This sample presents the lowest COF values, with a thickness relationship of 1:4, and a low roughness of 8 nm. On the other hand, in the multilayer system B, the average COF values in the first stage are greater than 0.25 and subsequently increase to values greater than 0.4. This behavior in COF shows an important difference in the samples obtained from CNx with different concentrations of N2 in the plasma N2/Ar mixture. The best values of COF were obtained for the samples prepared with a lower concentration of N2 (samples A), in which a smaller and more compact granular structure is observed, free of cracks, on which the growth rate of MoS2 is higher.

5. Conclusions

Two sets (A and B) of CNx-MoS2 multilayer coatings were deposited by magnetron sputtering, where the difference between them consists of two different concentrations of N2 in the N2/Ar plasma mixture. The structural characterization showed a polycrystalline structure in the MoS2 layer, while the CNx layers were amorphous with a homogeneous distribution of cumulus with cauliflower shape.

Additionally, the C and N atoms are bonded with sp2 and sp3 hybridization as indicated in XPS analysis. However, a higher fraction of N atoms bind to C atoms with sp3 hybridization (CN), and high nitrogen incorporation values close to 40% were determined for both sets of samples A and B. Raman studies corroborate this result since the intensity ratio of the I_D/I_G (1,1–1,4) peaks of the samples indicates a higher fraction of sp2 bonds between the C and N atoms in both sets of samples. The mechanical behaviour of the two assemblies has been investigated and compared. In our case, the hardness is in the low range (between 0.2 and 0.6 GPa), because as can be seen in the XPS analysis, the concentration of N in the films reaches high values. These results agree well with the Raman analysis, since when the N content increases, a more graphitic material is obtained, which is associated with low hardness values.

The set B (higher concentration of N) exhibited a slight improvement in mechanical properties as the number of periods increased. Instead, set A (lower concentration of N) presented better COF values, and sample 4 A displays the best performance and the lowest value of the coefficient of friction. This is related to the highest I_D/I_G, intensity ratio (1.4) attributed to a higher sp2 cluster content with a thickness ratio of the bilayer (1:4) and the lowest Ra value (8 nm) (μ = 0.09). Summarized, the N concentration in the CNx layer is an important parameter to determine the mechanical properties of both sets of CNx-MoS2 multilayer coatings.
For this reason, the authors recommend that future work related to CN$_x$-MoS$_2$ multilayer coatings deposited by sputtering use small concentrations of N (<10%) in the Ar/N$_2$ mixture to reduce the amount of nitrogen that is incorporated into the CN$_x$ films, thus improving its mechanical properties. It would also be interesting to explore the effect on these properties of the design change of the bilayers from substrate/CN$_x$/MoS$_2$ to substrate/MoS$_2$/CN$_x$. Taking into consideration that CN$_x$ grows amorphously, MoS$_2$ has a crystalline structure, and the sequence of film growth modifies the growth rate for both materials. So too does the morphology, which in turn affects the mechanical properties strongly associated with the top layer.

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