PVD coatings influence (TiCN, BCN, and CrAlN) on the fatigue life behavior of AISI 1045 steel for automotive applications

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Abstract
This work evaluated the influence of titanium carbide-nitride (TiCN), chromium aluminum nitride (CrAlN), and boron carbide-nitride (BCN) coatings deposited on AISI 1045 steel and their behavior in fatigue life. Suitable deposition parameters were established to obtain appropriate deposition times for polycrystalline growth and desired stoichiometry, as well as a stable layer thickness of ~ 3 μm. The physical and chemical properties of the obtained coatings were established by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and nanoindentation. Scanning electron microscopy (SEM) was used for analyzing the fracture surfaces of the samples subjected to fatigue. The analysis of the fatigue behavior of the uncoated and coated substrates was performed under rotary bending conditions applying maximum alternating stresses in the interval of 55 to 70% of the ultimate strength value, i.e., from 479 to 610 MPa, respectively. The test was conducted at room temperature. It was established that the fatigue resistance properties increased for the three types of coated samples, TiCN, BCN, and CrAlN, with values of 9.6%, 4.2%, and 3.9%, respectively, calculated for $1 \times 10^6$ cycles. The highest value in fatigue life improvement corresponded to the TiCN coating. This is associated with the increase in the mechanical properties of the coating, as well as the lower presence of tensile type stresses. The mechanical and fatigue results found in these ternary coatings deposited on AISI 1045 steel open up the possibility of future applications in mechanical devices, e.g., automotive applications with high fatigue demands in service conditions.

Keywords Physical vapor deposition PVD · Fatigue · AISI 1045 steel · Carbo-nitrides and nitrides transition metals · TiCN · CrAlN · BCN

1 Introduction
The physical vapor deposition (PVD) technique has been widely used in various industrial applications because coatings improve the morphological, mechanical, and tribological properties in various classes of substrates [1]. At present, there is limited information on the variable load properties of machine elements with PVD coatings. The technical literature review, including the works and developments carried out in the last years for obtaining and improving the physicochemical, mechanical, and tribological properties of PVD coatings, points out that the fatigue resistance of certain substrates will significantly increase with the addition of these coatings, due to an improvement in the fracture behavior for the material. This improvement in mechanical behavior is attributed to the added TiCN, TiN, and other layers, which prevents the propagation of cracks through the material [2–5]. An example of mechanical elements that must comply with solicitations to support variable loads and efforts are the components of an internal combustion engine, in particular the piston pin made of AISI 1045 steel, which is subjected to flexion fatigue, and the cubes (holes) in which it is lodged inside the engine must resist a surface pressure (pressure on the sliding surface) of 30 to 60 MN/m$^2$ [6]. Therefore, the new advanced-surface treatments are progressively spreading in the production of industrial elements, including those belonging to the automotive industry. The development of these new coatings simultaneously requires the study of other added properties, such as fatigue resistance, to extend their application in certain operating...
conditions for a mechanical element. The improvement in the morphological and mechanical properties of the material will serve as a basis for its use in the manufacture of coatings for steels used in elements and parts of the automotive industry. In light of the above, TiCN, CrAlN, and BCN coatings are expected to show better hardness, as well as other properties, relevant to applications of elements subjected to high stress and severe wear [5, 7]. Unfortunately, literature shows few research works focused on studying the fatigue resistance of TiCN, CrAlN, and BCN coatings deposited on AISI 1045 steel. Although some authors [2, 5], Puchi-Cabrera et al. [2], have studied the fatigue properties of steel substrates coated with TiCN layers, these studies do not address the TiCN, CrAlN, and BCN coatings’ performance in non-lubricated environments. Therefore, the aim of this work was to study the influence of carbo-nitride and transition metal nitride (TiCN, CrAlN, and BCN) coatings deposited on AISI 1045 steel under rotational fatigue behavior for protection synergies with potential applications for the metal-mechanic industry, which opens up the possibility of future applications in mechanical devices, e.g., automotive applications with high fatigue demands in service conditions.

2 Material and experimental detail

A multi-target sputtering magnetron was used for the deposition of the coatings, which facilitated the in situ deposition of both monolayers and multilayers. It has four magnetrons (Torus—4”, 10 cm Kurt J. Lesker) with diametric dimensions of 10 cm each; three radio frequency sources r. f. (13.56 MHz, RFX 600A); and three direct current (MDX 500, Advanced Energy). The design of the equipment establishes the location of the magnetrons facing and equidistant from the central point, where the samples to be coated are fixed. It has a system for measuring and controlling pressure (Baratron, MKS) and a flow meter or gas flow controller with four channels. The heating process is by temperature radiation with a maximum of 400 °C (Athena 500), and it includes a rotational sample holder system and another planetary system for coating coin-type and cylindrical-type specimens, respectively (see Fig. 1a–b). The target materials were 4 in. in diameter (~ 10 cm), 5 mm thick. 99.9% pure, silicon substrates with a crystallographic orientation (100) were used, and AISI 1045 steel substrates (coin-type, with 12.7-mm diameter and 5-mm thickness) were machined. All
the substrates were subjected to surface cleaning to remove organic contaminants, beginning by pickling in a solution of 50% hydrogen peroxide and 50% ammonia, for 40 min; then, drying at 100 °C for 15 min; finally, in an ultrasound system, the samples are cleaned in a sequence of alcohol and acetone for 15 min for each cycle. The crystallographic structure determination of the TiCN, BCN, and CrAlN coatings was analyzed by X-ray diffraction (PANalytical X’pert proTM), using a Cu-Kα radiation source with a wavelength of $\lambda = 1.5405$ Å. For X-ray photo-electron spectroscopy (XPS) studies, a SAGE HR100 (SPECSTM) equipment was used with a monochromatic source (Mg Kα 1253.6 eV), to determine the chemical composition of coatings; that is, in order to obtain the qualitative and quantitative character of the component elements in the thickness of the analyzed layer, it is fundamentally necessary to establish the relationship of areas enclosed under each peak for the different elements. Once the percentage of each one was established, the CasaXPS V2.3.15dev87™ software was used. Mechanical characterization for all coatings was carried out with nano-indentation test by using a Ubi1-HysitronTM device, with a Berkovich diamond tip at variable loads. From the nanoindentation test, the loads as function displacement curves were obtained for the three coatings. Taking into account these curves, the hardness and elastic modulus were determined with Oliver and Pharr’s method [8]. For the mechanical characterization of the AISI 1045 steel specimens, the ASTM 466–15 Standards were employed [9] for fatigue tests.

To perform the fatigue test in rotary bending on the AISI 1045 steel substrates with TiCN, BCN, CrAlN coatings and on the uncoated steel substrate, it was necessary to conduct tensile and hardness tests beforehand. The tension test in the AISI 1045 steel samples (Standard E8/E8M-13a) (see Fig. 2a) [10] was made to obtain properties, such as the elastic modulus ($E$), yield strength ($S_y$), ultimate strength ($S_u$) and breaking strength ($S_{br}$). Data corresponding to yield strength and ultimate strength were used to determine the load regimes in the fatigue tests. One hundred and forty samples were made for the rotary fatigue tests. Calibrated AISI 1045 steel bars of 5/8 inches in diameter and 6 m in length were used, which were later machined in a CNC lathe, according to the dimensions specified in Standards ASTM 466—15 and ASTM E606/E606M—12 (see Fig. 2b) [9, 11]. In the sanding process, sandpaper was used: 240, 280, 400, and 600; then, the samples were finally polished with diamond paste (2–4-μm range, mesh size #8000) to obtain the final finish. It was verified that the average roughness ($R_a = 0.044$ μm) was below 0.2 μm, in compliance with the specifications of the standard used. Once the samples were prepared, they were coated with the three materials (TiCN, BCN, and CrAlN). A calibration of the machine was

![Fig. 2](image_url)
made by comparing theoretical deformation values ($\varepsilon_t$) with test deformation ($\varepsilon_r$), with a maximum error of 5.6%, which is acceptable. In this sense, the AISI 1045 steel samples were made according to the dimensions specified in Standards ASTM 466—15 and ASTM E606/E606M–12 due to the fact that this geometrical form can simulate the steel pin, associated to the gudgeon pin. Therefore, Fig. 2c simulated a mechanical condition where there was an interaction of the assembly (metal-ceramic) associated with the coating and the metal surface of the hardened steel pin, as it would happen, for example, in the gudgeon pin assembly inside the internal combustion engine (automotive applications).

Fatigue failure, from $N=1$ to $N=1000$ cycles, is considered to be low-cycle fatigue, while high-cycle fatigue corresponds to failure in stress cycles greater than $10^3$ cycles. In addition, it was determined that the S–N curve has ranges of finite and infinite life. In the transition range, which is the region between the finite and infinite life ranges, the fatigue resistance limit is determined, which is related to the number of technological cycles (Ng), located somewhere between $10^6$ and $10^7$ cycles in the case of steels. This study was carried out with high-cycle fatigue, and the value of Ng = $1 \times 10^6$ cycles was considered as the border between the finite and infinite life regions [5, 7, 9, 11–13]. For the construction of the S–N curves of each material (AISI 1045, TiCN, BCN, and CrAlN steel), five (5) samples were used for each level of stress; that is, approximately thirty (30) samples were tested for each type of curve obtained. For each level of stress, an error percentage was established that did not exceed 15%, using a 90% confidence level. The following Eq. (1) was used to determine the percent error [14, 15].

\[
\text{Percent error} = \pm \left\{ \frac{\sum_{i=1}^{n} (x_l - \bar{x}_l)^2}{n-1} \right\}^{1/2} \frac{t_{\alpha/2,v}}{\sqrt{n}}
\]

where $x_l = \text{sample life logarithm}$, $\bar{x}_l = \text{sample log average of life}$, $n = \text{sample size}$, $v = \text{degrees of freedom (n-1)}$, $t_{\alpha/2,v} = \text{value of t statistics}$, and $\alpha/2 = \text{degree of confidence}$.

For this study, the determination of the crystallographic structure of the TiCN, BCN, and CrAlN coatings was performed using an X-ray diffractometer (PANalytical X’pert pro™) with a Cu radiation source Kα and with a beam wavelength of $\lambda = 1.5405$ Å. The thickness of the coatings was verified using a KLA Tencor D-120 profilometer; the thickness of all the coatings was 3 μm. The conditions used to produce the coatings were based on earlier works, and certain parameters were also optimized for this research [1, 16, 17]. Two samples were used for thickness measurement at various sites of the formed step. Appropriate deposition time was determined to obtain equal thicknesses in the three coatings. Table 1 shows some values of the cross section thickness. The analysis of the fracture surfaces was conducted by scanning electron microscopy (SEM) with a JEOL Model JSM-6490LV™ (Phenom FEI) equipment. Fatigue

| Sample number | TiCN StpHt (μm) | BCN StpHt (μm) | CrAlN StpHt (μm) |
|---------------|----------------|----------------|------------------|
| 1             | 3.06           | 3.01           | 2.06             |
| 2             | 2.95           | 2.95           | 3.05             |
| 3             | 3.15           | 3.24           | 2.96             |
| 4             | 2.98           | 2.95           | 3.10             |
| Average       | 3.035          | 3.038          | 2.793            |
| Standard deviation | ±0.090 | ±0.138 | ±0.492 |

StpHt (μm) = coating thickness

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**Table 1** Cross-section thickness for coatings: TiCN, BCN, and CrAlN

**Fig. 3** Mechanism and main parts of the rotary fatigue testing equipment
tests were performed in a rotary bending machine HUNG TA Instrument Cia. Ltd., which is designed to apply totally inverted stresses with a ratio of efforts \( R_e = -1 \). The tests were carried out at 3600 rpm, with a frequency of 60 Hz. A diagram of the operating mechanism and main parts of the rotary bending equipment can be seen in Fig. 3.

3 Results and discussion

3.1 X-Ray diffraction analysis

Figure 4a–c show the diffraction patterns obtained for the TiCN, BCN, and CrAlN coatings, which are the product of the analysis on the silicon substrates (100). The diffraction lines in the patterns show an order along the \( 2\theta \) axis, corresponding to a face-centered cubic structure (FCC), NaCl type, and space group Fm3m [18]. The substitution mechanism predominated in the formation of the three coatings, both for TiCN [19] and BCN; the carbon atoms (C) substituted the nitrogen atoms (N), which created a Ti-ordered, B-ordered, and C-N disordered system. For the CrAlN coating, the aluminum atoms (Al) were replaced by chromium atoms (Cr), creating an ordered Cr-Al system, while the nitrogen atoms (N) were located in interstitial positions. In all three coatings, the crystallization process formed a NaCl type FCC structure, the Ti, B, Cr, and Al atoms were arranged in the Wyckoff 4a site, while the C and N atoms were arranged randomly in the Wyckoff 4b site. The international indexing records JCPDF 00–042-1488 and JCPDF 00–035-1293 for titanium and boron carbide nitride were taken as reference, while two indexings

![Diffraction patterns](image-url)
were made, taking the structure of chromium nitride (CrN) JCPDF 00–031-157 and aluminum nitride (AlN) JCPDF 00–025-1495 for the coating of chromium aluminum nitride [19]. It is evident in Fig. 4c that the ternary material, CrAlN, was the result of the combination of CrN and AlN, which have the same NaCl type FCC crystalline structure and the space group 225- Fm3m. On one hand, from the diffraction patterns of the TiCN and BCN coatings, high-intensity peaks were obtained with an orientation (111) corresponding to the angles $2\theta = 36.34^\circ$ and $43.22^\circ$. On the other hand, a high-intensity peak was obtained for CrAlN with an orientation (200) corresponding to the angle $2\theta = 41.64^\circ$. Jointly, small displacements were present in the peaks (111) and (200) towards smaller angles. The results obtained for the lattice parameters ($a_0$) in the TiCN, BCN, and CrAlN coatings were 4.278 Å, 3.622 Å, and 4.334 Å, respectively. We can establish from the analyzed results that the diffraction angles and lattice parameters were affected by the type of coating material.

### 3.2 Chemical composition of coatings by using XPS analysis

Table 2 shows the XPS results for all coatings. Since the elemental signals spectra were obtained for the TiCN, BCN, and CrAlN coatings, the signals for the coatings allow locating and defining the respective binding energies, which facilitate the determination of the chemical composition and stoichiometry of the ternary layers. For TiCN: Ti (2p3) = 458.4, N (1 s) = 396.80, C (1 s) = 284.8, and Si (2p) = 61.6; for BCN: N (1 s) = 400, C (1 s) = 285.6, and B (1 s) = 192.8; and for CrAlN: Cr (2p) = 475.99, N (1 s) = 396.97, Al (2 s) = 119, and Al (2p) = 74. Therefore, the binding energy values of the coatings and XRD results (Fig. 4) confirm the formation of CrAlN ternary compound [20, 21]. Finally, the stoichiometry was established for the three coatings (Ti32.45-C35.83-N31.72, B48.63-C31.22-N20.15, and Cr40.27-Al38.01-N21.72) [18].

### 3.3 Mechanical properties of coatings by using nanoindentation test

Table 3 shows the mechanical properties for all coatings from nanoindentation results. Here, the coatings’ influence in the hardness and elastic modulus can be appreciated. It is also shown that the material with the lowest values for mechanical properties was TiCN ($H = 28$ GPa, $E = 224$ GPa), followed by CrAlN ($H = 30$ GPa, $E = 335$ GPa), and then BCN ($H = 33$ GPa, $E = 251$ GPa). Taking into account the last results, the elastic modulus ($E$) is related to the type of material, but not to the material microstructure; in this sense, the $E$ depends on crystal structure and lattice parameter [18]. Also, the hardness difference of the three coatings is due to the different crystallographic directions analyzed from XRD results in Fig. 4. It was possible to determine that the TiCN, BCN, and CrAlN coatings showed a preferential orientation in the (111), (111), and (200) planes, respectively. It is necessary to emphasize that the hardness of the interstitial nitrides in transition metals depends on the crystalline orientation, and, in general, the orientation (111) and (200) showed the highest hardness; therefore, the BCN coatings show the highest hardness in relation to the TiCN and CrAlN coatings.

### 3.4 Tension and hardness tests

The material used as a substrate was AISI 1045 steel, and the chemical composition in the state of supply is shown in Table 4. It was necessary to carry out the tensile test in advance to determine certain mechanical properties of the substrate, as this was fundamental for the planning of the test and the verification of the state of supply of the material. All tests were carried out at room temperature. Table 5 shows the results obtained in the tensile and Rockwell C (HRC and Vickers (HV)) hardness tests. Three samples were used, and they were made of calibrated AISI 1045 steel (in supply state), obtaining a yield strength of $S_y = 787.783$ MPa and an ultimate strength of $S_u = 871.624$ MPa. The $S_y/S_u = 0.904$ ratio of the material helped establish the stress relations applied in the

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**Table 2**  Atomic percent of the chemical composition and stoichiometric relation for all TiCN, BCN, and CrAlN coatings from XPS results

| Coatings | Chemical elements | N/(Ti + C) | N/(B + C) | N/(Al + Cr) |
|----------|-------------------|------------|-----------|-------------|
| TiCN     | 35.83 31.72 32.45 | –  –  –    | 0.46      | –  –  –     |
| BCN      | 31.22 20.15 –     | 48.63      | –  –  –    | 0.25  –     |
| CrAlN    | –  21.72 –        | 40.27 38.01| –  –  –    | 0.27  –     |

**Table 3**  Mechanical properties for all TiCN, BCN, and CrAlN coatings from nanoindentation results

| Coatings | Mechanical properties | Elastic modulus (GPa) |
|----------|-----------------------|-----------------------|
|          | Hardness (GPa)        |                       |
| BCN      | 33                    | 251                   |
| CrAlN    | 30                    | 335                   |
| TiCN     | 28                    | 224                   |
fatigue test, which had to be less or equal to the established ratio. This ensured that the behavior of the material remained within the linear-elastic range while being subjected to the load levels used in fatigue.

3.5 Fatigue tests

For the fatigue test, the stress-life method is used. This model is called the S–N curve or Wöhler diagrams [2, 22, 23]. The fatigue tests were performed on a HUNG TA model rotary bending machine, which applies loads that produce fully inverted sinusoidal stresses with a stress ratio of Re = −1. An equivalent load analysis was done for the fatigue machine and this, along with the applied stress levels, was necessary to define the loads that were used. Equation 2 comes from the equation of normal bending stress, and it was also considered that the moment of inertia of the critical cross-section was circular with a diameter ds = 6.35 × 10⁻³ m. This, along with the selected stress levels, was used to determine the weights applied in the test. The following relationships were chosen to determine the applied stress levels: 70%, 65%, 60%, and 55% of the ultimate strength value [2, 5, 7, 12, 13, 23].

\[ S = \frac{(M)(c)}{I} \rightarrow S = \left( \frac{Wa}{I} \right) \left( \frac{ds}{7} \right) \rightarrow S = \frac{16(Wa)}{\pi(ds)^3} \rightarrow W = \frac{\pi(S)(ds)^3}{16a} \]  

(2)

where \( S = \) normal bending stress (N/m²), \( M = \) maximum bending moment (Nm), \( c = \) distance of the element furthest from the neutral axis (m), \( I = \) moment of inertia of the area with respect to the reference axis (m⁴), \( W = \) applied weight (N), \( a = \) fixed distance (0.2 m), and \( ds = \) diameter of the cross Sect. (6.35 × 10⁻³ m).

Standards were established to carry out the fatigue test as follows: the tests were considered complete when the number of technological cycles \( 1 \times 10^6 \) (for infinite life) was exceeded or when the failure of the material occurred before reaching that cycle number, \( Ng \) (for finite life). In addition, as a test validity criterion, it was determined that those in which the failure took place in the critical section of the sample would be accepted; otherwise, they would be discarded. ASTM 468–11 and ASTM 739–10 standards were used for the representation of the results [14, 15]. The points on the graphs represent the data obtained experimentally, and the continuous lines represent the trend adjustment lines; additionally, 95% confidence bands are attached. Figure 5 shows the S–N curve of the uncoated material. With respect to the levels tested on the AISI 1045 steel for the transition range, the samples exceeded \( 1 \times 10^6 \) cycles for stress levels of 50% and 45% of the ultimate strength value, which correspond to stresses of 435.81 MPa and 392.23 MPa, respectively. These values obtained in the fatigue tests of the uncoated steel, as well as previous studies of substrates with coatings similar to the ones in this study, served as a reference for the determination of the stress levels applied in the transition range of the studied materials [5, 24].

Figure 6 shows the S–N curve for TiCN-coated steel. An increase in fatigue resistance is observed when the graph is placed over the curve of the uncoated steel, which is consistent with previous studies conducted on metallic substrates with titanium carbo-nitride (TiCN) and titanium nitride (TiN) coatings [2, 5, 7, 23]. For the TiCN-coated steel, the increase in the \( 1 \times 10^6 \) cycles was 9.625%. The transition range was located for stress levels of 47.5% and 45% of the ultimate strength value, corresponding to stresses of 414.02 MPa and 392.23 MPa, respectively.

The behavior of the BCN-coated steel is shown in Fig. 7. Similar to the previous case, the graph is on top of the base curve (uncoated steel). Previous studies on various metallic substrates coated with tungsten nitride titanium (WTiN), tungsten titanium (WTi), tungsten nitride (WN), and zirconium nitride (ZrN) have shown an improvement in the fatigue behavior [4, 13]. There was an increase in the \( 1 \times 10^6 \) cycles of 4.215%. The transition was established for stress levels of 45% and 40% of the ultimate strength value, corresponding to stresses of 392.23 MPa and 348.65 MPa, respectively.

The data obtained in the fatigue tests for CrAIN-coated steel is detailed and represented in Fig. 8. Similar to the previous cases, the graph is located on top of the curve of the uncoated substrate; however, it showed the lowest improvement compared to the other two coatings (TiCN and BCN). The increase in fatigue resistance is lower to that obtained by BCN, as for the \( 1 \times 10^6 \) cycles, an improvement of 3.95% was obtained. The transition range was established at stress levels of 45% and 40% of the ultimate strength value, which corresponds to stresses of 392.23 MPa and 348.65 MPa, respectively.

### Table 4 Chemical composition for calibrated AISI 1045 steel

| Standard | %C  | %Mn | %Si  | %P   | %S  |
|----------|-----|-----|------|------|-----|
| SAE 1045 | 0.43–0.50 | 0.60–0.90 | 0.15–0.25* | 0.030 | 0.050 max |

*SAE 1045 standard bars contain silicon as of 1 1/8"

### Table 5 Tensile and hardness test results for calibrated AISI 1045 steel

| Samples   | E (GPa) | \( S_y \) (MPa) | \( S_{ut} \) (MPa) | \( S_{rot} \) (MPa) | Hardness HRC | Hardness HV |
|-----------|---------|-----------------|-------------------|-------------------|--------------|------------|
| AISI 1045 | 204.563 | 787.783         | 871.624           | 717.045           | 21.913       | 403.375    |
| Standard deviation | ± 29.662 | ± 13.625 | ± 22.600 | ± 10.691 | ± 3.517 | ± 21.725 |
Finally, all the curves for the uncoated steel and with the three coatings (TiCN, BCN, and CrAlN) are shown in Fig. 9. For the three cases of the coated samples, an increase in fatigue resistance was found; this improvement in descending order corresponds to TiCN, BCN, and CrAlN materials with 9.6%, 4.2%, and 3.9%, respectively. The highest gain in fatigue life corresponds to TiCN coating, followed by BCN. This can be explained by the presence of titanium in the material coating, where titanium carbide (TiC) and nitrogen (N) in the buffer layer, very important for the compatibility of the whole, were used, as well as in the final single layer of TiCN, which provides good adhesion in the coatings and the improvement in fatigue resistance. In this sense, it is possible to establish that the biaxial deformation in the planes was affected by the type of coating material. The values obtained determine the presence of tensile-type stresses, being the lowest of them for the TiCN coating [18]. In the XRD analysis (Fig. 4), it was determined that these materials formed a NaCl-type FCC structure; therefore, the Ti and B atoms were located in the Wyckoff 4a site, while the C and N atoms were randomly located in the Wyckoff 4b site. The presence of titanium with a high atomic radius (ra = 2 Å) and boron with an intermediate atomic radius (ra = 1.17 Å) in both structures influenced the mechanical properties (hardness and elastic modulus) (Table 2) that affect the improvement of fatigue resistance. The increase of these mechanical properties, together with the excellent adhesion of such coatings to the substrate, indirectly causes a delay in the nucleation process of fatigue cracks [4, 18, 25]. The above can be applied to the CrAlN coating, in which titanium is not present and has intermediate mechanical properties, compared to the other coatings, which links to its low fatigue resistance.
To estimate the alternating stress for each one of the materials, with a number of technological cycles \(1 \times 10^6\) (for infinite life), the equations are used as follows: TiCN: 
\[907.353(\pm 25.403)(N)^{-0.043(\pm 0.002)}\], BCN: 
\[976.774(\pm 24.869)(N)^{-0.052(\pm 0.002)}\], CrAlN: 
\[987.883(\pm 24.869)(N)^{-0.053(\pm 0.002)}\], steel: 
\[990.526(\pm 24.336)(N)^{-0.056(\pm 0.002)}\].

Figure 10a establishes the maximum alternating stress for the steels coated with TiCN, BCN, CrAlN, and the uncoated steel, with values of 500.93 MPa, 476.21 MPa, 475.01 MPa, and 456.91 MPa, respectively. Figure 10b shows the reported percentages of improvement in fatigue resistance for the three materials TiCN, BCN, and CrAlN in comparison with the uncoated steel.

### 3.6 Fractographic analysis of fracture surfaces

Selected fracture surfaces of the TiCN-, BCN-, and CrAlN-coated and uncoated AISI 1045 steel, which were subjected to fatigue, were analyzed by scanning electron microscopy (SEM). The fractographic analysis of the sample surfaces only included higher maximum alternating stresses; that is, it was done at a stress level of 70% of the ultimate strength value. The purpose of the study of these fracture surfaces was to allow the identification of crack nucleation sites [25] and of the appearance of coating delamination, to explain the fracture process of the substrate-coating systems, and, particularly, to identify the way in which fatigue cracks propagate after nucleation.

Figure 11a–c show the fracture surfaces for the TiCN-coated substrate tested at high stress. Figure 11a shows the fracture surface of a coated sample subjected to a maximum alternating stress of 610.137 MPa and which failed at 45,422 cycles. It can be stated that the failure of the specimen was the product of the simultaneous propagation of a series of cracks. Nucleation sites were located at the periphery of the surface, which led to the location of the fracture zone.
in the center of the fault surface. The presence of several fracture traces was examined, and it indicated the appearance of several nuclei at different sites along the contour of the sample. The results are consistent with information and studies reported in reference to similar deposition processes and types of coatings [2, 5, 7, 12, 13, 23]. Figure 11b shows detail in square (A), where the starting site of one of the fatigue cracks is present. The direction of crack propagation is suggested by the white arrows on the fracture surface, and the direction of the arrows determines the subsequent expansion of the cracks. In this case, it can be observed that the core that originates the fatigue crack appeared at the periphery of the sample and not in the substrate, at the interface between coating and substrate. The detailed view of the area represented in square (B) is seen in Fig. 11c, which reveals the fracture of the sample at this crack initiation site.

Figure 12a–c show the fracture surfaces for the BCN-coated steel tested at high stress. Figure 12a defines the failure surface of a sample tested at 610.137 MPa and which failed at 28,428 cycles. Image analysis indicates that the sample failure was established by a crack protruding from the surface contour. The fracture occurred as a result of the propagation of the A-nucleated crack, and this led to the fracture zone being located at the opposite end of the sample. Other adjacent cracks are observed on the fracture surface. Similar failure processes as described above with different coatings are consistent with other results obtained [4, 13, 26]. The magnified view of the area identified in square (A) is shown in Fig. 12b; here, the direction of the propagation of the cracks can be clearly established. An additional magnified view of the crack initiation site is shown in Fig. 12c, which also illustrates the partial delamination of the coating at the site where the crack was probably nucleated in square (B).

The fracture surfaces for the last highly stressed CrAlN coating substrate are shown in Fig. 13a–c. Figure 13a determines the fracture surface of a coated specimen tested with a maximum alternating stress of 610.137 MPa and which failed at 10,482 cycles. Image analysis corroborates that the sample fracture was the result of multiple propagations of a series of cracks, which nucleated at the sample contour and guided the fracture zone to the center of the surface. The presence of several traces of cracks indicates that they nucleated at different sites on the periphery of the fault.
surface. These surface results are consistent with similar coating studies \[13, 26\]. The area in detail in square (A) determines one of the probable starting points of one of the cracks, shown in Fig. 13b. The white arrows in the section of the fracture suggest the direction of expansion, and the direction of the arrows establish the growth of the crack. It can also be stated that the crack nucleated at the edge of the section and not in the substrate, near the substrate-coating interface. Figure 13c is an enlargement of the area represented in square (B), and it shows the final fracture of the specimen at the starting site of the analyzed crack.

Finally, for comparison purposes, Fig. 14a–c show the fracture surfaces of uncoated AISI 1045 steel, tested at high stress. Figure 14a shows the surface of an uncoated specimen tested at 610.137 MPa and which failed at 11,312 cycles. It was determined that the sample fracture is the result of the propagation of a single crack, instead of multiple cracks, initiated at the periphery. The surface did not have a flat appearance typical in fatigue, showing irregularity in the entire analyzed section. The fracture zone was located at the opposite end from the beginning of crack formation at A. Figure 14b shows an enlargement of the A area, where the direction of crack propagation is defined by the white arrows. An enlargement of the crack nucleation start site is shown in Fig. 14c, where the final fracture of the substrate was verified.

The results obtained on the fracture surfaces are consistent with the established theory that fractures have their beginning in material discontinuities where the cyclic stress is maximum. The fracture surfaces are flat and perpendicular to the stress axis, and they follow the determined theoretical sequence: stage I is the beginning of one or more microcracks; in stage II, the microcracks form parallel surfaces in
the shape of plateaus, known as beach marks; and stage III consists of sudden and fast fractures. Fatigue studies using surface treatment, such as plasma nitriding, establish the same sequence for the fracture; however, they have higher increases in fatigue strength limit (23.76%) [25]. It is worth mentioning that processes of thermal spray coating HP/HVOF of tungsten carbide and hard chrome plating have adverse effects on the fatigue resistance of steels [27].

**Fig. 12** (a) Fracture surface of a BCN-coated sample tested at 610.137 MPa (70% $S_u$) and which failed at 28,428 cycles, (b) magnified view of the area identified in square (A), where the direction of crack propagation is clearly visible, and (c) partial delamination of the coating is shown, where the crack possibly nucleated from the square (B).

**Fig. 13** (a) Fracture surface of a CrAIN-coated sample tested at 610.137 MPa (70% $S_u$) and which failed at 10,482 cycles: some secondary cracks can be observed on the fracture surface; (b) enlarged view of the area identified in square (A): the direction of crack propagation is indicated by the arrows; and (c) detailed view of the area identified in square (B): crack initiation site.
3.7 Correlation between mechanical and fatigue properties

Figure 15a shows the relationship between coating nature, hardness, and fatigue resistance for all coatings deposited on the industrial steel substrates. It is clearly shown that the improvement in hardness ($H$) and elastic modulus ($E$) (Table 2), the increase of the maximum alternating tension ($S_a$) as a function of cycle number (Fig. 10a), and the increase of fatigue resistance (Fig. 10b) have incidence when the coating nature (type of material) was changed. From this correlation, it is possible to determine that one merit index

![Image](https://example.com/image1.png)

![Image](https://example.com/image2.png)

![Image](https://example.com/image3.png)

Fig. 14 (a) Fracture surface of an uncoated AISI 1045 steel sample tested at 610.137 MPa (70% $S_u$) and which failed at 11,312 cycles; (b) enlarged view of the area identified as (A), the direction of crack propagation is indicated by the arrows; and (c) detailed view of the area identified in square (B), possible crack nucleation site.

Fig. 15 (a) Correlation between mechanical and fatigue properties for the TiCN, BCN, and CrAlN coatings deposited as a function of the coating nature; (b) biaxial deformation as a function of the coating material.
[28] associates with the increment coatings hardness and the increase of fatigue resistance (%) at the same coating type. Therefore, the TiCN coating offers the best synergy for mechanical and fatigue properties with good hardness and a high maximum alternating tension (Sa), which is very important for mechanical applications in the devices, e.g., automotive applications with high fatigue demands in service conditions. We can establish from the Fig. 15b results that the biaxial deformation in the plane is affected by the coating material type, and the obtained values determine the presence of tensile-type stresses in the following order: \( \varepsilon = -3.1794 \times 10^{-3} \) for TiCN, \( \varepsilon = -0.0110 \) for BCN, and \( \varepsilon = -0.0447 \) for CrAlN. The TiCN coating has the lowest tensile stress value.

4 Conclusions

The TiCN, BCN, and CrAlN coatings were satisfactorily deposited on AISI 1045 steel substrates. So, from the diffraction analysis (XRD), chemical results (XPS), and nanindentation test, it was possible to establish that crystalline structure and stoichiometric relation are related to the improvement in the mechanical properties (hardness and elastic modulus), as well as to the adhesion of the coatings. In this sense, the increase in mechanical properties, together with the excellent adhesion of the coatings (TiCN, BCN, and CrAlN) to the substrate, indirectly causes a delay in the nucleation process of fatigue cracks, thus improving fatigue resistance.

The fatigue resistance property increased for tests with coated samples, and the material with the greatest improvement was TiCN with 9.63%, followed by BCN with 4.22%, and finally CrAlN with 3.95%, calculated for \( N = 1 \times 10^6 \) cycles. The highest values of fatigue life corresponded to TiCN material. This could be justified by the presence of titanium in the crystal structure where titanium carbide (TiC) and nitrogen (N) were used, providing the best mechanical properties and a good adhesion in the coatings, as well as by the lower presence of tensile type stresses for the TiCN coating.

The study of the fracture surfaces carried out on the tested steels (both coated and uncoated) clearly establishes that the nucleation sites were on the periphery of the surface. These originated the growth of the crack and led to the location of the fracture zone at the opposite end to the formation of the nucleus.

Finally, the study of mechanical properties and fatigue resistance in the TiCN, BCN, and CrAlN coatings simultaneously evidenced that the improvement of mechanical properties and maximum alternating tension (Sa) enables their application in high dynamic loads on the substrates that are used in the mechanical elements and parts of the automotive industry.
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