Multifunctional Ti based carbonitride coatings for applications in severe environments

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Abstract:

In this work, the influence of NbZr and ZrSi addition to TiCN coatings are studied, aiming for their use as protective layers for parts subjected to severe corrosion and wear. The coatings with \( \text{C/N ratios ranging from 0.4 to 2.5} \) were deposited using the cathodic arc technique in a mixture of \( \text{N}_2 \) and \( \text{CH}_4 \) gases, on 316 stainless steel discs and Si (111) wafers. All the coatings exhibited residual compressive stresses, with values ranging from approximately -2.4 GPa to -3.5 GPa. The addition of Si led to an increase in hardness, regardless of the C/N ratio. All coatings with high C/N ratio (~2.5) presented slightly lower stress values and superior performance in 3.5\% NaCl corrosive solutions, the best performance being obtained for the TiSiZrCN coating, which exhibited the highest protective efficiency to corrosion (97.8 \%), due to its low corrosion current density (1.734 \( \mu \text{A/cm}^2 \)) and high polarization resistance (31.775 k\( \Omega \)). The tribological tests, performed at 23 °C and 250 °C, indicated that abrasion and oxidation were the predominant wear mechanism for all

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coatings. At 23°C, the friction coefficients of the coated specimens were significantly lower than those of the uncoated samples. When the collective performance across all of the experimental parameters was assessed, the coatings with C/N of about 2.5 proved to be the most suitable candidates to be used in severe service conditions.

**Keywords:** TiCN; hard coatings; corrosion and wear resistance; cathodic arc deposition.

1. Introduction

Materials used in severe environments should have the required properties for the specific application. For example, tribological materials used in marine applications, exposed to potentially high levels of corrosion, should have a high resistance to humidity and airborne chloride as well as a high resistance to wear. Material performance is crucial in safety-critical components, such as a ball valve used in nuclear power plant steam circuits. The ball and seal seat are commonly produced using 316L stainless steel (SS) and can fail prematurely as a result of the frequency of operation and the operating temperatures of the steam circuit. Malfunction and failure of these safety valves (predominantly via a galling mechanism) is completely unacceptable and could undermine the entire plant operation [1]. Various coating and surface engineering techniques can be used to reduce the potential limitations, and extend the operating envelope of these materials and components.

The coating of steel surfaces with non-oxide ceramic layers is widely used to improve component performance. Hocking et al. provided an extensive review of metallic and ceramic coatings offering an indication of the extensive research that has been conducted in this area [2].

Metal carbonitride coatings are the preferred choice for many marine applications or for those involving wear at moderate to high temperatures. They are durable and resistant to a broad range of severe conditions such as corrosive environments, high wear conditions, low or high
temperature, deep sea or space environments, or other extreme conditions. They can be easily deposited on metallic surfaces and generally provide strong adhesion, whilst being tolerant of imperfect surface preparation [3–6]. As a further iteration of the technology, transition metal carbonitride coatings poses further desirable characteristics such as chemical inertness, high hardness, and melting point, superior lubricating properties, high wear resistance, corrosion resistance in different environments, high thermal and electrical conductivity, and even glossy surfaces, and are used in a wide variety of applications [7,8].

The characteristics of the transition metal carbonitrides change with the C/N ratio, such as the specific properties of the surface can be tuned for a wide variety of industrial applications. Transition metal carbonitrides have good chemical stability in most alkaline solutions and dilute acids, with the exception of oxidizing and hydrofluoric acids [7]. One of the most common transition metal carbonitride coatings is TiCN, which combines the high hardness and the low frictional properties of TiC with the high toughness and bonding strength of TiN. The C/N ratio is critical for example, when optimising tribocorrosion resistance in saline solutions [9], or minimising tribological damage in unlubricated tests over a range of temperatures. This is in part due to the high sp² carbon content in TiCN coatings, which provides high hardness and wear resistance [9]. It has also been reported that the defect density in TiCN coatings increases with CH₄ fraction used for deposition, which determines its beneficial mechanical and tribological properties [10]. Various authors have attempted to enhance these characteristics by adding different elements to the TiCN structure. Nb is one of these elements which be partially substituted for Ti, forming TiNbCN coatings. Adding Nb leads to an increase in hardness and resistance to corrosion relative to TiCN [11,12]. A promising combination is TiHfCN, which again leads to improved hardness and the tribological properties, compared to TiCN coatings [13–16].
Vanadium carbonitrides coatings (VC\textsubscript{x}N\textsubscript{1−x}) have self-lubricating ability and high hardness (33 GPa) making them a good alternative coating cutting tools [17]. Bondarev et al. showed that the addition of Ag into VCN coatings increased wear resistance during sliding, scratching and impact loading [18]. TiAlCN is another potential alternative coating, which can form a mixture of hard nanocrystalline and amorphous compounds with a hardness of 41 GPa (with a C/N ratio of about 1.1) and good wear resistance [19–23]. Quaternary TiAlCN coatings formed by the simultaneous addition of Al and C into a TiN matrix system have high thermal stability [20] and at high levels of carbon content, leads to the presence of a free carbon phase leading to self-lubricating properties [25].

In all of the examples presented above, the C or N contents within the coatings were tuned in order to get improved characteristics targeted at specific applications. Carbonitride coatings, MeCN, where Me can be either Ni, Cr, Fe, Al, Hf, Ti, Zr, Si, or a combination of these have been used for dies and cutting tools due to their good resistance to oxidation and to thermal cycling [7,19], wear resistant [25–28], microelectronics [29], responsive sensors [30], hot work tool steels [31], diffusion barrier coatings [25,26,32], coatings with high toughness [4], anticorrosive coatings [33–36]. Due to their high hardness and low friction coefficient, TiCN coatings deposited on a broad range of substrates are widely used in many industries, aiming for a variety of applications accepting low service temperatures (e.g. -10°C). CrCN coatings produced by PVD processes by the industry (e.g. Eifeler Plasma Beschichtungs GmbH) are used for protecting lathes, milling, cutting and drilling tools when machining non-ferrous metals – mainly Ti and Cu alloys. Also, PVD industrially produced (e.g. Voestalpine AG), ZrCN coating has excellent resistance against corrosion and abrasive wear, combined with high hardness and toughness, needed in applications where increased abrasion resistance is required, as for machining Si-containing Al alloys.
Further elements (i.e. Cr, Zr, Nb, Hf, Al, Y, Si, etc.) can be added to the base Ti-based carbonitrides coatings to further improve properties [7,24,37–42]. In this study, the addition of Si and Nb into TiZrCN coatings is assessed, with the aim of improving thermal stability, wear and oxidation resistance as well as increasing coating hardness, corrosion resistance, and tribological performance. TiNbZrCN and TiZrSiCN coatings have been prepared and characterised under conditions that are representative of the steam circuit within nuclear power plants.

2. Experimental details

The coatings were prepared simultaneously on both SS discs and Si wafer substrates, depending on the analysis that was carried out. The coatings were deposited in a mixture of CH₄ and N₂ reactive gases, using a cathodic arc system, equipped with two cathodes made of Zr (99.99% purity) and Ti85 at.%-Nb15 at.% or Ti88 at.%-Si12 at.%, respectively. Details of the deposition system may be found in [43]. The targets were supplied by Cathay Advanced Materials Limited, Guangdong, China. The SS samples were first polished to a surface roughness Rₐ in the range of 48 to 54 nm. Before deposition, all substrates were ultrasonically cleaned in isopropanol for 10 min, then rinsed with dry nitrogen, and finally positioned on a rotating holder in the deposition chamber, with the aim of improving the coating uniformity and the repeatability of the deposition process. The base pressure in the deposition chamber was of 6 × 10⁻⁴ Pa. Prior to coating, the samples biased at −1000 V were ion sputter-etched for 10 min in an Ar atmosphere at a pressure of 0.2 Pa. The deposition parameters were carefully chosen, by adjusting the arc currents on the cathodes, for obtaining coatings with 3–9 at. % concentration values for Zr, Nb and, Si. For each coating combination (TiNbZrCN and TiZrSiCN). Two types of sample were prepared, the first with a C/N ratio of ~ 0.4, a low ratio and from this point forward referred to as coating – 1. The second coating had a C/N
ratio of 2.5, a high ratio and is referred to as coating – 2. For coating – 1, the gas mass flow rates were maintained at 25 standard cubic centimetres per minute (sccm) for CH\(_4\) and at 65 sccm for N\(_2\), while for coating – 2, the CH\(_4\) flow rate was maintained at 65 sccm and for N\(_2\) the flow rate was decreased to 25 sccm. Preliminary tests on the deposition rates were performed for each type of coating and coatings with a thickness of ~4 µm were produced.

Table 1 presents the deposition conditions of the coatings. Each type of coating was deposited in the same run on a Si (111) wafer and ten SS discs (\(\phi = 20\) mm), in order to get the necessary number of replications for characterisation. To facilitate stress measurement, a thinner coating, controlled by the deposition time (5 minutes) was applied to (111) cut Si wafers.

X-ray photoelectron spectroscopy (XPS) was used to determine the elemental compositions and chemical bonds in the coatings. XPS spectra were taken with a VG ESCA 3MKII spectrometer, using AlK\(_\alpha\) radiation. The system was equipped with an electron energy analyser (Phoibos 150) and operated in the analysis described with fixed analyser transmission mode. All the measurements were performed in UHV conditions (~ 10\(^{-7}\) Pa). A 4 keV Ar\(^+\) ion beam was used for sputter etching of the specimens (10 min). The sample preparation and the spectral processing were similar to those described in [44]. Casa XPS spectra software (Kratos Analytical UK), version 2.3.15 was used to analyse the obtained spectra [45].

X-ray diffraction (XRD) was used to determine the crystalline structure, phase composition, texture, and grain size of the coatings using a Rigaku MiniFlex II diffractometer, with Cu K\(_\alpha\) radiation (1.5405 nm) set-up in 20/0 geometry. The crystallite size was calculated using the Scherrer formula [46].

Nanoindentation was used for measurement of hardness (H\(_I\)) and reduced Young’s modulus (E\(_r\)), using a nanoindenter (TI Premier Hysitron) equipped with a Berkovich–type diamond
tip with a tip radius of 150 nm. Ten indents on the surface of each specimen, at least 5 µm apart, were made using a 5 mN load. The penetration depth was lower than 10% of coating thickness. Both hardness and elastic modulus were calculated using the Oliver and Pharr method [47].

The residual stress was evaluated by the Stoney model [48], by measuring the radii of curvature of Si (111) wafer substrates before and after coating, using a surface profilometer (Dektak 150).

The adhesion of the coatings to the SS substrates was determined according to ISO EN 1071-3:2005, by scratch testing. The tests were carried out by applying a uniformly rising load upon the indenter moving horizontally across the coated surface, until visual failure, signalled by the coating flaking from the substrate. The scratch tracks were analysed using an optical microscope, and the critical load value, \( L_c \), was determined.

The corrosion behaviour was examined in 3.5% NaCl solution (pH=8), at room temperature (RT, 22 ± 1 °C), using a VersaSTAT 3 Potentiostat/ Galvanostat. Tests were conducted using a typical three-electrode cell, with a Pt and saturated Ag/AgCl (0.197 V vs. NHE) counter and reference electrodes. The open-circuit potential (\( E_{OC} \)) in the corrosive solution was continuously monitored for 1h. Then, potentiodynamic curves from -1 V to +1 V were recorded. The working electrode was placed in a Teflon sample holder with an exposure area of 1 cm². The electrochemical measurements were performed with a scanning rate of 0.167 mV/s (as given in ASTM G 59–97). Tests were repeated at least two times for each sample.

The corrosion potential (\( E_{i=0} \)), corrosion current density (\( i_{corr} \)), anodic slope (\( b_a \)) and cathodic slope (\( b_c \)) were determined by graphical extrapolation of the two branches of the polarization curves in the range of ±50 mV, as per the method detailed in [49]. Versa Studio software (Princeton Applied Research) was used for calculating the electrochemical parameters. The polarization resistance (\( R_p \)) was calculated using the Stern-Geary equation [50]:

\[
R_p = \frac{\sigma}{2\pi b} \ln \left( \frac{d}{r} \right)
\]
More details about this procedure can be found in [50, 51].

The tribological performance of the coatings was assessed using a TE77 high-frequency reciprocating test rig (Phoenix Tribology, Berkshire, UK). Tests were performed using a 6 mm AISI 316 pin and a coated plate. A 5 N normal load was applied at a reciprocating frequency of 2 Hz, with a stroke of 12.4 mm, in the air with ambient humidity (c.50%) at 23°C and at 250°C. All the results were compared with those obtained on Ti carbonitride coatings without alloying elements published in [52]. The wear rate (K) was calculated by normalizing the worn volume (V) over the normal load (F) and the sliding distance (d):

\[
K = \frac{V}{Fd}
\]

(2)

An Alicona Infinite Focus G5 was used to assess surfaces topography using optical profiles of surface roughness contours. The worn volume was determined by measuring the cross-sectional areas of the wear scar at 3 points on each track.

The XPS, stress measurements and nanoindentation tests were carried out on coated Si (111) substrates. The coated SS discs were used for the XRD measurements, as well as for the corrosion and tribological tests.

3. Results

3.1. Elemental and phase compositions

The chemical binding state and elemental compositions of the coatings were investigated by XPS. The coating’s composition was determined from Ti2p, Nb3d, Cr2p, Zr3d, Si2p, N1s, C1s and, O1s peaks. Fig.1 shows, as an example, the metal peaks of the TiNbZrCN – 1 coating, taken after 5 min of sputtering (approximately 0.5 nm in depth) [53–55]. The obtained results are in good agreement with existing data [56–62], including the Ti2p3/2 peaks at 455.6 eV, 457.1 eV and, 458.7 eV were associated with TiCN, TiOx and TiO2.
compounds, respectively; the Nb3d$_{5/2}$ peaks at 204.1 eV and 206.0 eV to NbCN and NbO$_2$, respectively; the Zr3d$_{5/2}$ peaks at 180.1 eV and 182.0 eV to ZrCN and ZrO$_2$, respectively. The XPS results indicated the formation of an oxide rich region at the topmost layer of the coating, as a result of surface oxidation in an open atmosphere. This effect is typical for transition metals carbonitrides, due to the metals high reactivity to oxygen (e.g. [56,63]). The increase of the sputter duration to 60 min led to a marked decrease in the amount of oxygen found. The atomic concentrations of the elements determined under these conditions were considered to represent the compositions in the bulk coating, and are summarized in Table 2. It should be noted that the Zr contents in the coating composition were in the range of 7.9 – 8.8 at.%. It can also be seen that, as intended, the (C+N)/(metal+Si) ratio was in the range 0.96 – 1.10, while C/N ratios were of 0.41 – 0.42 and 2.47 – 2.49 for coating – 1 and – 2, respectively.

All coating exhibited pure fcc solid solutions, with (111) preferred orientation (Fig.2). The (111) texture, specific to a coating deposited by the cathodic arc method [34,64], could be explained by the intense ion bombardment of the growing coating, resulting in a high amount of residual stress. Ion impacts generated growth defects (vacancies, grain boundary voids, stacking faults, and twins), compositional gradients, non-equilibrium structures, grain packing, mutual impingements of grains and porosity, all these contributing to the intrinsic stress increase. If the “lowest overall energy conditions” dictates the coating texture [34,64,65], the observed (111) preferred orientation suggests that strain energy was dominant, compared to surface energy, since the lowest strain energy plane is (111).

It should also be noted that there was a decrease of the coating crystallinity with increasing C/N ratio. The grain size values were derived from the (111) peak using the Scherrer formula. This tendency was also reported for other carbonitride coatings [7,9–12,14–16,19–21,23,34,66]. The grain size of TiNbZrCN was 9.1 nm for coating – 1 and 7.0 nm for coating
2. The reduction in the grain size for the TiNbZrCN – 2 coatings is to be expected due to the increase of the carbon content, which amorphized the coatings [56]. The TiSiZrCN –1 coating exhibited a polycrystalline structure with a grain size value of 7.7 nm, while the grain size of TiSiZrCN – 2 coatings could not be calculated due to coating amorphization and furthermore the addition of Si also affected the amorphization of the coating. This behaviour was expected when the constituent elements present large atomic radii differences (Ti=1.54 nm; Zr=1.33 nm; Nb=1.60 nm; Si=1.90 nm), which favours amorphization, as evidenced by XRD diffraction patterns. This has been previously reported for different coatings [67–69].

3.2. Mechanical properties

Fig. 3 presents the measured values of the hardness (H), reduced elastic modulus (E_r), intrinsic stress (σ) and the surface roughness (R_a) of the coatings. The coating – 2 series was harder in comparison with those of coating – 1, a result of the decrease in the grain size and amorphization, revealed by XRD. The increase of the hardness in rich carbon coatings was also reported in [20–22,26,31, 33, 56,59,60]. The highest hardness value was measured for the TiSiZrCN-2 coating, with an amorphous structure, as revealed by the XRD analysis (Fig.2). The increase of the hardness concomitantly with the grains size reduction may be ascribed to the formation of strong interfaces, without grain boundary sliding, and this is an effect which is more pronounced with the addition of Si.

The reduced elastic modulus values (E_r) presented the same trend as the hardness values, with the highest values obtained for coatings – 2. The E_r value depends on the composition of the coating [72], as well as on the specific deposition conditions, such as ion bombardment of the growing coating in terms of energy and density, deposition rate and temperature [73]. Si-containing coatings presented higher modulus values compared to the TiZrNbCN coatings.
The residual stress ($\sigma$) measurements revealed that all of the coatings exhibited compressive stress, with values ranging from about -2.4 GPa to -3.5 GPa, values specific for the coatings deposited by the cathodic arc method. Higher values were measured for the coatings containing Si, the same was also observed for TiSiCN coating, compared to the TiZrCN and TiNbCN coatings [33]. This increase may be ascribed to the lattice distortion as a result of adding Si into the coating matrix. Si has an atomic radius that is much larger than the neighbouring atoms within the coating. For the coating – 2 series, lower stress values were measured due to the increase of the amorphous carbon phase [56]. The surface roughness ($R_a$) values for the all of the coatings were significantly reduced as both C/N ratio and Si increased, the lowest roughness being obtained in the amorphous TiSiZrCN-2 coating.

The mechanical behaviour of the coatings was characterized by the ratios $H/E_r$ and $H/E_r^2$ and the elastic recovery ER (%) [19]. The $H/E_r$ ratio indicates the amount of strain a coating can stand before a permanent deformation happens, so a higher $H/E_r$ ratio indicates a better wear resistance [74–78]. A coating characterized by a relatively low elastic modulus and consequently, a high $H/E_r$ value is supposed to make possible the redistribution of the applied load over a larger area, hindering the failure of the coating/substrate system as a result of high interfacial stresses [79]. Coatings with an augmented resistance to plastic deformation and overload possess $H/E_r$ ratios greater than 0.1. This limitation has been confirmed by a variety of coatings, from nitrides and carbides to oxides [80–85]. The $H/E_r$ ratio calculated for the deposited coating is presented in Fig.4a. The $H/E_r$ ratio increase with the amount of Si and this again has been reported in a comparison of TiN, TiAlN and TiSiN coatings [86]. Also, the coating – 2 series, with increased carbon content, had a higher $H/E_r$ ratio than coating – 1 series.

The $H/E_r^2$ ratio can also be correlated with resistance to abrasive and erosive wear [87].

Based on the measured data, Fig.4b presents comparatively the results obtained for the tested
coatings. It can be seen that the coating – 1 series present lower \( H/E_r^2 \) ratio values, indicating that the coating – 2 series have the highest resistance to plastic deformation. In each series, the coatings with added Si had a higher \( H/E_r^2 \) ratio than the corresponding all-metal carbonitrides, indicating that when Si was added to the coatings hardness increased.

The measured adhesion of the coatings to the substrate, quantified as the critical force \( L_c \), is presented in Fig. 4c. The measured \( L_c \) values confirmed that the coatings with higher \( H/E_r \) and \( H/E_r^2 \) values were highly elastic (ER > 60%) [88] and present a superior resistance to crack initiation and propagation. Based on the load-displacement curve, the calculated ER (%) values are presented in Fig. 4d. It shows that both a higher C/N value and added Si increased ER values. As the intrinsic stress in the coatings is also an important factor influencing adhesion, high adhesion is usually related to reduced stress. All the investigated coatings exhibited a good adhesion (\( L_c \geq 34N \)), the obtained values correlating well with the trends described from the \( H/E_r \), \( H/E_r^2 \), ER and stress values.

3.3. Corrosion resistance

The variation of the open circuit potential (\( E_{oc} \)) during 1 h of immersion is shown in Fig. 5. The most significant result is that all of the coatings demonstrated more electropositive E_{oc} values than that of the uncoated substrate, signifying that the coatings improved the corrosion resistance of the uncoated steel. Based on the results presented in Fig. 5, for the TiNbZrCN coatings, the increase of C/N ratio leads to an increase of \( E_{oc} \), while for the TiSiZrCN there was a slight decrease (from -93 mV to -130 mV). TiNbZrCN-2 coatings have a more electropositive \( E_{oc} \). A constant evolution of the open circuit potential was recorded during the tests for all of the investigated surfaces, indicating the formation of stable protective layers.
The potentiodynamic polarization curves of the investigated surfaces are presented in Fig.6. For TiSiZrCN-1, a breakdown potential is seen around 168 mV, while for TiNbZrCN-2 around 283 mV. For the other two coatings and substrate, no breakdown potential was observed. By comparing all of the investigated samples, passivation plateau ranging from 0.5 to 1 V was noted for TiSiZrCN-2 coating.

Based on the potentiodynamic curves, the main electrochemical parameters (Fig.7) were determined as follows:

- the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) by graphical extrapolation of the anodic and cathodic branches of curves from +25 mV to −25 mV, method detailed in Ref.[49,89];
- the polarization resistance (R_p) by Stern–Geary equation [50];
- the porosity (P) using Elsener’s equation [90];
- the protective efficiency (P_e) by equation proposed by Nozawa and Aramaki [91].

The corrosion resistance was estimated according to a set of four criteria.

The first criterion stated that the corrosion resistance of a surface increased by increasing corrosion potential (E_{corr}) to more electropositive value. All the coatings exhibited a more electropositive E_{corr} as compared to the uncoated substrate. TiNbZrCN-2 had the most positive E_{corr}, followed by TiSiZrCN-1, TiNbZrCN-1 and, TiSiZrCN-2 coatings. The observed differences were due to the different composition of the coatings, where the presence of Si did not promote the formation of a passive layer on the surfaces of the coatings. As reported previously, the passive coatings formed on the metallic glasses are likely to be amorphous in nature and due to the absence of grain boundaries, diffusion of ions along the passive coating would be restricted, thereby increasing the corrosion resistance. The corrosion resistance was predominantly determined by the formation of a strong passive protective coating. The protective ability of the passive coating depended on the supply of
corrosion resistant ions to the passive coating. For instance, it has been reported for metal-
metalloid amorphous alloys, that the corrosion resistance increased with an increase in Nb concentration [92].
The second criterion states that a surface has high corrosion resistance when it has a low
value of $i_{\text{corr}}$ and high value of $R_p$. All the coatings showed lower $i_{\text{corr}}$ and higher $R_p$ than that
of uncoated substrate, indicating that the coatings enhanced the corrosion performance of the
stainless steel. The coatings – 2 showed lower $i_{\text{corr}}$ and higher $R_p$ values compared with
coatings – 1, meaning that the increase in the C/N ratio led to an increase in corrosion
resistance.
The third criterion relates to porosity. Important porosity differences were found for the
investigated coatings. In the case of the TiNbZrCN coating, the porosity decreased with
increasing C/N ratio, while for TiSiZrCN it increased with C/N ratio.
Regarding the corrosion protection ($P_e$), for both types of coatings, the $P_e$ value increased
with the C/N ratio, the highest value recorded for the TiNbZrCN-2 coatings. However, all
coatings had a $P_e$ value greater than 93%, showing high protective efficiency to NaCl
corrosive attack.
Considering all the results of the electrochemical tests, TiSiZrCN-2 can be considered as the
coating with the best corrosion resistance due to its high protective efficiency ($P_e=97.8\%$),
acceptable porosity ($0.425x10^{-3}$), low corrosion current density ($1.734\ \mu A/cm^2$) and high
polarization resistance ($31.775\ \text{k}\Omega$), then the TiNbZrCN-2 coating.

3.4. Tribological performance
All of the tribological experiments were carried out in comparison with carbo-nitride coatings
without alloying elements, taken as reference coatings. The data represents the average of at
least three tests for each temperature. Friction performance of the results of the tribological
tests was expressed in terms of the change in the coefficient of friction versus time, and the wear rate (K). Figs. 8a and 8b show the evolution of the coefficients of friction as a function of time at 23 °C, and 250 °C, respectively. It can be observed that the values are quite constant during the test.

Fig. 9 shows the average coefficients of friction recorded at 23 °C and 250 °C, calculated after a ‘running-in period’ of 1000 s to remove initial contact instabilities, including the oxide layer formed due to ambient exposure. At 23 °C the friction coefficients for the coatings were more than 3 times lower than those of uncoated samples, with the lowest friction coefficient measured in the TiNbZrCN-1 coating; all other coatings presented similar values for the friction coefficients. At 250 °C, the average friction coefficients of the coatings were higher than those measured at 23 °C, while for the bare substrate a lower value was measured, probably due to the oxide layer formed at high temperature, which promotes friction reduction. Again, all coatings presented quite similar values of the average friction coefficients, except for the TiSiZrCN-2 coating which presented a lower value. The obtained results are consistent with previously reported data on friction performance of carbide or carbonitride coatings [93–95].

Fig. 10 shows the wear rate K, calculated post-testing. Lower wear rates were measured for the coated specimens compared with the uncoated specimens. For the coatings, the wear rates at 250 °C were higher than those measured at 23 °C, likely because of a more intense oxidation process of the carbonitrides, with damaging effects.

The optical micrographs and surface profiles of the wear tracks at the end of the sliding tests are shown in Figs. 11 and 12 and provide a map of the dominant wear mechanisms. The presence of grooves parallel to the sliding direction is indicative of the abrasive nature of the wear. The deepest wear tracks were found in the TiSiZrCN-2 and TiNbZrCN-2 coatings subjected to high temperatures, while the largest width occurred on the TiNbZrCN-2 surface.
also under the high temperature. Deeper wear scars and larger tracks correlated with an increase in the friction coefficients, as confirmed by the results given in Figs. 10 and 11, which also show increased friction coefficients for the coatings tested at 250 °C.

The uncoated 316L steel specimens showed the formation of micro/macro pitting and galling, as well as debris and a fractured surface, showing severe wear damage and low wear resistance. In contrast, the coated samples were much less affected by wear. For these, besides some minor abrasive wear, a mild polishing can be seen.

There is always a compromise to be made between hardness, residual stress, and adhesion when optimising a coating for a given application. In this respect, as can be seen in Figs. 3, 4, 9 and 10, the coating – 2 series would be a suitable solution for ball valves exposed to steam generated in a nuclear power plant circuit, due to the combined mechanical and tribological performance.

4. Discussion

A wide variety of binary hard carbides or nitrides have been successfully used in many applications. From this platform, the carbonitride class of coating has been developed, which combines the properties of nitrides and carbides. These properties can be tailored by changing the C/N ratio [7,21,96]. The addition of NbZr or ZrSi into TiCN coatings targets the fabrication of protective layers for parts subjected to severe corrosion and wear. It was found that the C/N ratio led to an increase of the resistance to plastic deformation of coatings, more evident for in the coatings – 2 tests. Moreover, by adding Si, a further increase of resistance to plastic deformation was found. This result can be related to the amorphized structure and small grain size values determined for these coatings.

In the literature, tensile stress promotes crack propagation, leading to a reduction in hardness. Thus, this stress should be minimised and is generally undesirable in industrial protective
coatings. Compressive stresses are far more desirable for these applications, especially if the value is around 1 GPa. Higher values are associated with low adhesion between coatings and the substrate. It can be seen that all of the investigated coatings compressive stress, with the lowest value (-2.4 GPa) being recorded for the TiNbZrCN-2 coatings. Comparing the results, the TiNbZrCN-2 showed low stress, high adhesion to the metallic substrate \( (L_c=38 \text{ N}) \) and high hardness (34.2 GPa). Moreover, this coating presented the lowest wear rate in the tribological tests performed at 23 °C and high protective efficiency (97.8 %) in the saline corrosive solution.

For the coating – 2 series, the intrinsic stress values were lower than the one for coating – 1 series, probably due to the amorphization of the structure as a result of the increase of C and with the added Si (i.e. TiZrSiCN-2 coatings). Stress relaxation determined how well the coating adhered to the substrate, and its corrosion resistance and tribological performance. The coating – 2 series, with C/N ratio of 2.5, presented the best corrosion performance in the 3.5% NaCl solution, this was due to the good coating adhesion to the substrate and also to the amorphous structure and small grain size \( (\approx 7 \text{ nm}) \). Comparing the two coatings of series-2, the TiZrSiCN-2 coating showed the best corrosion resistance, ascribed to the small electronegativity difference \( [97,98] (\Delta \chi=0.637) \), compared to the \( \Delta \chi=0.664 \) value of the TiNbZrCN-2.

Regarding the tribological tests performed at 23 °C, the TiNbZrCN-2 coatings exhibited the lowest friction coefficients and wear rates. This can be related to low residual stresses and high adhesion. In the case of TiZrSiCN-2 tested at 250 °C, the lowest measured wear rate could also be attributed to the superior adhesion, but also to the higher hardness, low roughness and, good elastic recovery. Moreover, the TiZrSiCN-2 coatings showed the highest resistance to plastic deformation, and this is a further reason for the wear resistance at high
temperatures. This result can be related to the increase of carbon content, leading to the formation of a finer surface with smaller grain sizes.

The results presented in the current work showed that both TiNbZrCN and TiZrSiCN coatings with a C/N ratio of 2.5 are promising candidate coatings for components exposed to severe corrosive conditions. Furthermore, TiNbZrCN coatings with the same C/N ratio also work equally well under non-corrosive conditions at 23°C. The same can be said for the TiZrSiCN coatings at 250°C. As a possible application, these coatings can be used for the ball valves, such as it will be worth to investigate them further for the novel generation of nuclear power plant components. Besides, cryogenic ball valves can be another potential field of application to be explored.

5. Conclusions

In this work, two series of TiNbZrCN and TiZrSiCN coatings were deposited by the cathodic arc technique. It was found that the structure, mechanical, anticorrosive and tribological properties of both types of coatings had a strong dependence on the C and N content. The coating with low C/N ratio proved to have reduced friction coefficients at 23°C and 250°C, while the coatings with a high C/N ratio exhibited lower wear, higher hardness and good corrosion resistance in 3.5% NaCl, whatever the coatings composition. Considering the coatings with high C/N ratio, the TiSiZrCN coating exhibited the highest hardness (35.4 GPa), while TiNbZrCN the lowest intrinsic stress (-2.4GPa). The results presented in the current work showed that both TiNbZrCN and TiZrSiCN coatings with a C/N ratio of 2.5 are promising candidate coatings for components exposed to severe corrosive conditions. Furthermore, TiNbZrCN coatings with the same C/N ratio also work equally well under non-corrosive conditions at 23°C. The same can be said for the TiZrSiCN coatings at 250°C.
Acknowledgements

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Table 1. Deposition conditions for the coatings

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Total (CH₄+N₂) mass flow rate</td>
<td>90 sccm</td>
</tr>
<tr>
<td>CH₄ mass flow rate</td>
<td>25/65 sccm</td>
</tr>
<tr>
<td>N₂ mass flow rate</td>
<td>65/25 sccm</td>
</tr>
<tr>
<td>Arc current</td>
<td>90 A for Zr, 110 A for TiNb and TiSi</td>
</tr>
<tr>
<td>Substrate bias voltage</td>
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</tr>
<tr>
<td>Deposition temperature</td>
<td>320 °C</td>
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<tr>
<td>Deposition duration</td>
<td>40–50 min</td>
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Table 2. Elemental composition (XPS method)

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<thead>
<tr>
<th>Coating</th>
<th>Ti</th>
<th>Zr</th>
<th>Nb</th>
<th>Si</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>(C+N)/(metal+Si)</th>
<th>(C+N+Si)/(metal)</th>
<th>C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiNbZrCN-1</td>
<td>34.4</td>
<td>8.8</td>
<td>5.6</td>
<td>-</td>
<td>14.2</td>
<td>34.9</td>
<td>2.1</td>
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<td>1.01</td>
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<tr>
<td>TiNbZrCN-2</td>
<td>34.9</td>
<td>7.9</td>
<td>4.9</td>
<td>-</td>
<td>35.9</td>
<td>14.4</td>
<td>2.0</td>
<td>1.05</td>
<td>1.05</td>
<td>2.5</td>
</tr>
<tr>
<td>TiSiZrCN-1</td>
<td>38.8</td>
<td>8.8</td>
<td>-</td>
<td>3.9</td>
<td>13.6</td>
<td>32.1</td>
<td>2.8</td>
<td>0.96</td>
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</tr>
<tr>
<td>TiSiZrCN-2</td>
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<td>2.1</td>
<td>1.10</td>
<td>1.09</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Figures caption

Fig.1. XPS Ti2p, Nb3d and Zr3d spectra of TiNbZrCN-1 coating taken after 5 min of sputtering (approximately 0.5 nm in depth)

Fig.2. XRD patterns of the investigated coatings

Fig. 3. Mechanical properties of the investigated coatings: (a) hardness \( H \); (b) reduced elastic modulus \( E_r \); (c) residual stress \( \sigma \); (d) surface roughness \( R_a \)

Fig. 4. Mechanical properties of the investigated coatings: (a) \( H/E_r \); (b) \( 10^4H/E_r^2 \); (c) critical force for adhesion \( L_c \); (d) elastic recovery \( E_R \)

Fig. 5. The open circuit potential evolution during the 1h of immersion for the coated and bare substrates

Fig. 6. Potentiodynamic polarization curves of the uncoated and coated substrates

Fig. 7. The main electrochemical parameters (\( E_{i=0} \) – corrosion potential; \( i_{corr} \) – corrosion current density; \( R_p \) – polarization resistance; \( P_e \) – protective efficiency; \( P \) – porosity) of the investigated samples

Fig. 8. Evolution of the friction coefficients for coated samples vs. time at 23 °C (a) and 250 °C (b) of the coated and bare substrates

Fig. 9. The average friction coefficients of the coatings at 23 °C and 250 °C of the coated and uncoated substrates

Fig. 10. Wear rate (K) of the coated and uncoated samples calculated after the tribological tests

Fig. 11. Optical images and cross-sectional wear profiles of the wear tracks for the coatings tested at 23 °C: TiNbZrCN-1 (a and b), TiNbZrCN-2 (c and d), TiSiZrCN-1 (e and f), TiSiZrCN-2 (g and h) and uncoated sample (i and j).
Fig. 12. Optical images and cross-sectional wear profiles of the wear tracks for the coatings tested at 250 °C: TiNbZrCN-1 (a and b), TiNbZrCN-2 (c and d), TiSiZrCN-1 (e and f), TiSiZrCN-2 (g and h) and uncoated sample (i and j)
Fig. 1.

- Ti 2p:
  - A, D: TiCN
  - B, E: TiO_x
  - C, F: TiO_2

- Zr 3d:
  - A, C: ZrCN
  - B, D: ZrO_2

- Nb 3d:
  - A, C: NbCN
  - B, D: NbO_2

Binding energy (eV) vs. Intensity (arb. units)
Fig. 2.
Fig. 3.
Fig. 4
Fig. 5.
Fig. 6.
Fig. 7.
Fig. 8.

23 °C

250 °C
Fig. 9.
Fig. 10.
Fig. 11.
Fig. 12.
Figure 4