The Nanostructure, Wear and Corrosion Performance of Arc Evaporated CrB_xN_y Nanocomposite Coatings

K. Polychronopoulou^{1,2,*}, M.A.Baker³, C. Rebholz², J. Neidhardt¹, M. O' Sullivan⁴,
A.E. Reiter⁵, K. Kanakis⁶, A. Leyland⁶, A. Matthews⁶, C. Mitterer¹

¹*Christian Doppler Laboratory for Advanced Hard Coatings at the Department of
Physical Metallurgy and Materials Testing, University of Leoben, Franz-Josef-
Strasse 18, A-8700 Leoben, Austria*

²*Department of Mechanical and Manufacturing Engineering, University of Cyprus,
1678, Nicosia, Cyprus*

³*The Surface Analysis Laboratory, Faculty of Engineering and Physical Sciences,
University of Surrey, Guildford, Surrey, GU2 7XH, United Kingdom*

⁴*PLANSEE Composite Materials GmbH, Siebenbürgerstraße 23, D-86983 Lechbruck,
Germany*

⁵*Oerlikon Balzers AG, Iramali 18, FL-9496 Balzers, Liechtenstein*

⁶*Department of Engineering Materials, University of Sheffield, Sheffield S1 3JD,
United Kingdom*

*Corresponding author: K. Polychronopoulou (kyriakip@ucy.ac.cy; Tel: +357 22
892772; Fax: +357 22 892254).

Abstract

The composition, nanostructure, tribological and corrosion behaviour of reactive arc evaporated CrB_xN_y coatings have been studied and compared to CrN. The CrB_xN_y coatings were deposited on a commercial Oerlikon Balzers RCS coating system employing 80:20 Cr:B targets. To vary the composition, the nitrogen fraction was adjusted ($N_2 \text{ fraction} = N_2 / (Ar + N_2)$) and a moderate bias voltage of -20 V was applied during coating growth. The coating composition and nanostructure was determined using time-of-flight elastic recoil detection analysis (TOF-ERDA), x-ray

diffraction (XRD) and x-ray photoelectron spectroscopy (XPS). Ball-on-disc dry sliding wear tests were conducted using an alumina ball counterface both at room temperature and at 500°C with the relative humidity controlled at 20 %. Potentiodynamic corrosion tests were undertaken in 3.5 % NaCl aqueous solution. The wear tracks were examined using optical profilometry and scanning electron microscopy (SEM); the surface composition inside and outside of the wear tracks were investigated using Raman spectroscopy and XPS. All coatings exhibit nanocomposite structures and phase compositions which are in fair agreement with those expected from the equilibrium phase diagram. The lowest wear rate at room temperature and 500°C was found for $\text{CrB}_{0.14}\text{N}_{1.14}$, which was shown to exhibit the highest hardness and possesses a nanocomposite nc-CrN/a-BN structure. $\text{CrB}_{0.12}\text{N}_{0.84}$ coatings showed the lowest passive current density in potentiodynamic corrosion tests.

Keywords: hard coatings, wear, corrosion, SEM, Raman, XPS.

1. Introduction

Nanocomposite coating materials have recently attracted increasing interest due to the possibility of synthesizing materials with technologically useful property combinations, e.g. hardness, low elastic modulus and low friction [1,2]. Much work has been undertaken on TiN-Si₃N₄ [3], Ti-B-N [4, 5], Cr-Cu-N [6-7] and MeC-DLC systems [8]. Such coatings are promising candidates for limiting or even replacing environmentally problematic lubricants when deposited onto tools or engineering components subjected to sliding contacts. Therefore, much effort is being put into the development of such coatings for industrial applications.

It is well known that CrN coatings have superior hot corrosion resistance properties and lower friction coefficients than TiN. CrN has a variety of applications such as on automotive components [9], machining tools [10], replacement for electroplated Cr [11] and molds for plastics processing [12]. On the other hand, chromium boride coatings are promising candidates for protective coatings such as tools, molds and dies due to their high hardness and good oxidation resistance [13-15]. Although ternary Cr-B-N films have been also studied by some researchers [16-18], the microstructures and mechanical properties obtained within this system have not been fully explored. With specific regard to the friction coefficient, Zhou et al.

[18] have reported that Cr-B-N films with low friction coefficients can be deposited, ascribing this to the presence of a h-BN phase in the coatings. However, it should be noted that previous research on Ti-B-N and Ti-Al-B-N coatings with similar BN phase regions to Cr-B-N in the equilibrium phase diagram have failed to show the presence of low friction coefficients and an amorphous BN phase rather than h-BN was observed [5,19,20].

Although most nitride, boride and carbide coatings deposited by physical vapour deposition (PVD) are chemically inert, one of the main obstacles for wider application in corrosive environments have been the sensitivity to crevice corrosion and higher costs (compared with electrochemically deposited coatings) [21,22]. On the other hand, in applications in which there is simultaneously a corrosive environment and abrasive loads, hard PVD coatings increase wear resistance and, in many cases, also improve corrosion resistance. It should be noted that the mechanical properties of the coatings (e.g. fracture strength, adherence) may be severely influenced by the corrosion processes. Therefore, it is important, from a technological and economical point of view, to improve both the wear and corrosion resistance of machine parts.

In a previous study, the correlation between the microstructure and mechanical properties of arc-evaporated CrB_xN_y coatings with varying N contents were studied [23]. In this paper, in addition, the tribological performance at elevated temperatures and corrosion behaviour have been investigated. After dry sliding wear tests were undertaken, optical profilometry, scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and Raman spectroscopy were used to elucidate the wear mechanism. Initial data on the corrosion behaviour was recorded through potentiodynamic scans of the coated samples exposed in 3.5 mol. % NaCl solution.

2. Experimental Details

2.1. Coating Deposition

CrB_xN_y coatings, 3.9-5.4 μm thick, were deposited in a commercial Oerlikon Balzers RCS coating system with a chamber volume of 1000 liters, and a base pressure in the range of 10^{-6} mbar (10^{-4} Pa). Coupons of high speed steel (HSS DIN 1.3343), polished to a 1 μm finish, and cemented carbide cutting inserts were used as substrates. Prior to

coating deposition, the substrates were heated to 500°C and Ar ion etched for approximately 20 min using a secondary gas discharge. In particular, the substrates were mounted on a carousel in the plane of the upper sources and two-fold rotated during the process. The substrate holder was situated at a distance of 22 cm in front of the targets. Prior to deposition they were rapidly heated by extended electron bombardment from a secondary gas discharge from an additional ionization chamber. For the subsequent Ar etching process the polarity of the sample holder was switched in order to attract the gas ions from the same source. Radiation heaters were kept at 500°C at the chamber walls under etching and deposition conditions applied. The preheating at 500°C was used for cleaning the substrate surfaces prior to any deposition.

Four arc sources were equipped with Cr/B (80/20 at.%) targets (PLANSEE Composite Materials GmbH, Germany) and controlled at a constant arc current of 150 A during deposition. The N₂ fraction ($N_2 \text{ fraction} = N_2 / (Ar + N_2)$) was set to 0, 0.10, 0.15, 0.20, 0.25, 0.5 and 1, respectively, and back-filled with Ar to a constant total pressure of 2 Pa, regulated by a capacitive gauge. A moderate bias voltage of –20 V was applied during deposition to assist growth, without triggering detrimental high levels of intrinsic stress. In addition, a CrN reference coating was deposited using pure Cr instead of the Cr/B targets, keeping the rest of the parameters exactly the same.

2.2. Coating Analysis

The elemental composition of the coatings was determined by time-of-flight elastic recoil detection analysis (TOF-ERDA) using a primary beam of 350 MeV Au ions [23]. A detection system with a solid angle of 0.4 msr (milli-steradians) and a large detection angle of 60° which enables simultaneous detection of all elements (including H) was employed [24,25]. The coating thickness was measured on HSS and cemented carbide cutting inserts by ball cratering and verified by cross-sectional SEM analysis (Zeiss Evo 50). XRD was undertaken using a Siemens D 500 x-ray diffractometer employing Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). XPS was used to investigate the presence of amorphous phases and provide general information on chemical bonding. XPS was undertaken on a Thermo VG Scientific Sigma Probe spectrometer using monochromatic Al K α radiation (1486.6 eV). Elemental peak scans were recorded at

a pass energy of 20 eV, giving an energy resolution of <0.5 eV. To remove the surface contamination, the sample surface was sputter cleaned using a 3 keV rastered argon ion beam with a current of 0.3 mA for some minutes. However, some oxide still remained at the surface for the coatings after this cleaning process. The binding energies (BE) were referenced to the C 1s peak (285.0 eV), corresponding to hydrocarbon contamination [26].

The wear scars and the volume of the worn-off counterpart ball were examined by optical microscopy. The coating wear volumes were in turn evaluated by white light optical profilometry (Veeco NT1100) to calculate the wear rate, which is defined as the worn-off volume divided by the applied normal force and total running distance [27].

Raman spectroscopy was employed to identify oxide phases inside and outside the wear tracks. This was undertaken using a JOBIN-IVON LabRam HR800 instrument at a laser-wavelength of 633 nm (He-Ne laser). SEM images recorded on a TESCAN VEGA instrument were used to investigate the wear tracks on the coatings and to examine the oxides on the surface after tribological testing at elevated temperature. The indentation response of the films was analyzed using a UMIS microindentation system. The shape of the Berkovich three-sided pyramidal diamond tip was calibrated using the Oliver and Pharr method with fused silica as the reference material [28]. To determine mechanical properties, the coatings were indented with a constant maximum load of 20 mN. The indentation hardness and reduced modulus were then calculated using the Oliver and Pharr method in accordance with the European standard [29] from at least 20 indents. The stresses were evaluated by measuring the deflection of two parallel laser beams reflected from the sample surface and applying the Stoney formula [30]. The coated Si(100) samples were heated in vacuum to measure the temperature dependence of stress (Biaxial Stress Temperature Measurements, BSTM). The substrate used for BSTM stress measurements was Si.

2.3 Wear and Corrosion Tests

Ball-on-disc dry sliding tests were conducted on the CrB_xN_y coated HSS substrates at room temperature (RT) and 500°C under ambient conditions with a controlled relative humidity of 20 %, using a CSM Tribometer at a constant velocity of 10 cm/s and track radius of 10 mm. Alumina balls (purity of 99.8% and Ø 6 mm) were employed as counterparts under a load of 5 N. The corrosion behavior was

studied using potentiodynamic corrosion tests in 3.5% (0.57 M) NaCl aqueous solution. A three-electrode cell employing a saturated calomel reference electrode and platinum counter electrode was connected to a Solatron 1286 ECI potentiostat. Prior to corrosion testing, the samples were immersed in the electrolyte at the open-circuit potential for one hour to achieve equilibrium. The potentiodynamic polarization curves were recorded at a sweep rate of 1.66 mV/s.

3. Results and Discussion

3.1. Coating Elemental and Phase Composition

The elemental composition of the coatings as a function of N₂ flow was determined by TOF-ERDA and is given in Table 1. For the coatings investigated, the Cr/B ratio was found to be relatively constant (varying between 7.3 and 8.3) and the Cr/N ratio decreases from 3.0 to 0.9 as the N₂ fraction increased from 0.10 to 0.5. A lower concentration of B in the coatings compared to the Cr/B target is a common occurrence for metal boride coatings grown at high pressures and is caused by preferential scattering of the light B atoms during transfer through the process gas from target to substrate [31]. The coating compositions have been superimposed on the equilibrium CrB_xN_y phase diagram in Figure 1 [32].

The crystalline nature of the coatings was investigated by XRD and the spectra recorded for all of the coatings are presented in Figure 2. The standard line positions for face-centered cubic (fcc) CrN (JCPDS No. 76-2494), hexagonal Cr₂N (JCPDS No. 79-2159), and metallic Cr (JCPDS No. 06-0694) are included in this figure. For the coatings synthesized in pure Ar only peaks attributable to Cr are observed. Since these coatings contain 10.7 at.% B, any Cr₂B phase present must be amorphous. With increasing N content (0.1 and 0.15 N₂ fractions, giving rise to N contents of 23 and 29 at.%, respectively), there is a single reflection at approximately 44.8° with a broad tail to higher angles. It is difficult to give an unambiguous interpretation, but it seems most likely that there are two nanocrystalline phases present, Cr(N) and either Cr₂N or CrN. It has previously been shown by Rebholz et al. [33] that up to 16 at.% N can be interstitially incorporated into a pure Cr coating for reactively sputtered Cr–N coatings. Considering the positions of these coatings in the

phase diagram, the Cr_2N phase may be expected to form. As the nitrogen fraction is increased (≥ 0.2), the single feature at approximately 44° narrows and shifts toward lower angles, suggesting the formation of CrN with an approximately stoichiometric composition (in accordance with its position in the phase diagram). Furthermore, additional reflections emerge, confirming the formation of CrN. A slight peak shift to lower angles together with a progressive change from a (200) to a (111) texture is noticeable for coatings deposited at higher N_2 fractions. For coatings deposited at N_2 fractions of 0.25, 0.5, and 1, the crystallite size of CrN, estimated using the Scherrer equation [34] was found to be 5.9, 6.7, and 10.4 nm, respectively. On the other hand, the coatings deposited at low N_2 fraction probably show smaller grain sizes (but peak overlap makes a clear determination of grain size untenable).

XPS B 1s and N 1s core-level spectra of the coatings are presented in Figure 3. Despite the sputter cleaning prior to analysis, many spectra still exhibited residual oxygen related bonding, e.g. B–O bonds at 191.5 eV. For the B1s peak, two components are observable, the peaks at approximately 187 eV and 190 eV corresponding to Cr–B and B–N bonding respectively [35]. The results indicate that a Cr_2B phase is being formed in the coatings with N contents up to 42 at.%. Considering the absence of any Cr_2B peaks in the XRD spectra, it has to be assumed that this phase is amorphous. With increasing N concentration, the Cr_2B phase is progressively replaced by an amorphous BN phase. With regard to the N 1s spectra, Cr_2N and CrN are reported to occur at binding energies of 396.4 and 397.4 eV, respectively [36,37], and BN at 190.4 eV [35]. It has already been established from the B 1s spectra that BN is present in the coatings at higher N concentrations. It is also clear from the low total B content in these coatings (and their position in the phase diagram) that in all coatings, BN represents a small amount of the total phase fraction. This is reflected in the low intensity of the BN component in the N 1s region. Considering the N peak maximum, at a N_2 fraction of 0.1, the peak maximum occurs at 397.5 eV. As the N_2 fraction increases the peak moves to progressively lower binding energies, being 396.0 eV for N_2 fractions of 0.5 and 1.0. This would suggest that for N_2 fractions of 0.1 and 0.15 (corresponding to N contents of 23 and 29 at.%, respectively), the chromium nitride phase present in the coatings is Cr_2N and for N_2 fractions of ≥ 0.2 , CrN is the predominant phase.

The XRD and XPS results can now be combined to yield the phase composition of the CrB_xN_y coatings as a function of N_2 fraction. The coating deposited in pure Ar has a nanocomposite nc-Cr/a- Cr_2B structure. For N_2 fractions of 0.1 and 0.15, an unambiguous assignment is difficult, but it would appear that a three-phase structure of nc-Cr(N)/nc- Cr_2N /a- Cr_2B is formed. At a 0.2 N_2 fraction, a three-phase nc-CrN/a-BN/a- Cr_2B or four phase nc-CrN/nc- Cr_2N /a-BN/a- Cr_2B coating is deposited. At a N_2 fraction of 0.25, again the actual phase composition is not clear, but probably this coating has a three phase nc-CrN/nc- Cr_2N /a-BN structure. At a 0.5 N_2 fraction a two-phase nanocomposite nc-CrN/a-BN structure is formed. These phase compositions are in fair agreement with the positions of the coatings in the equilibrium phase diagram. However, CrN appears to form at lower N contents than expected (at the expense of Cr_2N).

3.2. Mechanical Properties

The indentation hardness and the reduced elastic modulus as well as the biaxial macroscopic stress values of the tribologically tested coatings (see next section) are presented in Figure 4. It can be seen that the hardness H for the nanocomposite coatings with N_2 fractions of 0.1 to 0.25 show little variation ($H = 23$ - 24 GPa), but the elastic modulus E progressively drops to the lowest value of 315 GPa for the coating deposited at 0.25 N_2 fraction. E then rises slightly for N_2 fractions of 0.5 and 1.0. This drop in E is most probably associated with the presence of the a-BN phase (at similar phase fractions) in these coatings. The hardness can be seen to increase to 29 GPa for the 0.5 N_2 fraction coating. The XRD and XPS data indicate this coating to have a nc-CrN/a-BN structure. The XPS data shows that all of the B is bonded as BN, so based upon the elemental composition given in Table 1 and the reasonable assumption that the two phases are approximately stoichiometric, the phase fractions for this $\text{CrB}_{0.14}\text{N}_{1.14}$ coating can be simply calculated to be 88 mol.% nc-CrN and 12 mol.% a-BN. The grain size for $\text{CrB}_{0.14}\text{N}_{1.14}$ was determined to be 6.7 nm. Using the expressions given by Baker [38], it can be calculated that approximately 13 mol.% of a-BN is required to achieve a-BN monolayer coverage of 6.7 nm nc-CrN grains. For similar nanocomposite systems, Veprek et al. [3] have shown that monolayer coverage of the grains leads to the highest hardness. Consequently, it is this nc-CrN/a-BN structure with monolayer coverage of the nc-CrN grains which is most probably leading to the high hardness (29 GPa) observed

for this coating. All CrB_xN_y coatings (and the CrN reference) show only small compressive stresses (Figure 4).

3.3. Tribological Properties

Three of the CrB_xN_y coatings, $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2), $\text{CrB}_{0.12}\text{N}_{0.84}$ (0.25 N_2) and $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2), were selected for tribological testing at room temperature (RT) and at 500°C. A CrN standard coating deposited using a pure Cr (instead of the Cr/B) target) was also studied as a reference.

3.3.1. Tribological Tests at Room Temperature

Figure 5 shows the friction coefficient as a function of sliding distance for $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2), $\text{CrB}_{0.12}\text{N}_{0.84}$ (0.25 N_2) and $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2), respectively, sliding against alumina ball at RT. The friction coefficient of CrN coatings deposited using a pure Cr (instead of Cr/B) target is also presented for comparison purposes (sliding distance 500 m). For the $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2) coatings, the test ran for 750 m to avoid wearing through the whole coating. The friction curve for the $\text{CrB}_{0.12}\text{N}_{0.84}$ (0.25 N_2) coatings starts with a long running-in period with a friction coefficient of approximately 0.7. After this running-in period, the friction coefficient drops sharply to a value of approximately 0.45, where it remains constant during the whole test period of 4000 m. $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2) coatings show a high initial friction coefficient of 0.7 for the first 2000 m sliding distance, after which the friction coefficient decreases to a steady state value of 0.55. For the $\text{CrB}_{0.12}\text{N}_{0.84}$ (0.25 N_2) coatings, the high friction values during the first 500 m sliding distance are associated with high adhesive and/or abrasive (ploughing) forces acting at the sliding interface. However, with increasing sliding distance the friction coefficient is reduced, possibly due to the adhered material becoming detached, resulting in a smooth contact spot [39]. Interestingly, $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2) has a much longer run-in period than $\text{CrB}_{0.12}\text{N}_{0.84}$ (0.25 N_2). This may simply be due to the higher hardness of $\text{CrB}_{0.14}\text{N}_{1.14}$ (the ball needs to slide against this hard material for a longer time before a lower friction tribofilm is formed), but could also be associated with the different phase compositions and nanostructures of these two coatings.

From the 2D profilometric images presented in Figure 5, the maximum wear depth after testing for $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2), $\text{CrB}_{0.12}\text{N}_{0.84}$ (0.25 N_2) and $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2) is 4.2, 1.2 and 0.04 μm , respectively. No measurable wear was observed for

CrN coatings after testing for 500 m. The profilometry results suggest that a different wear mechanism is occurring for the different CrB_xN_y coatings. At RT, the wear track for $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2) coatings is deep with a high roughness, indicative of severe abrasive wear, whereas there is a significant amount of material build-up at the edge of the wear track for $\text{CrB}_{0.12}\text{N}_{0.84}$ (0.25 N_2) coatings, suggesting an adhesive wear mechanism. In the case of high N containing coatings, $\text{CrB}_{0.14}\text{N}_{1.14}$ (deposited at 0.5 N_2 fraction), the wear track is very shallow, but the profilometry results would suggest the occurrence of both abrasive and adhesive wear.

The wear rate varies significantly between the coatings, with values ranging from $4.5 \times 10^{-6} \text{ mm}^3/\text{Nm}$ for $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2) to $1.9 \times 10^{-8} \text{ mm}^3/\text{Nm}$ for $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2) coatings. The significantly lower wear rate for $\text{CrB}_{0.14}\text{N}_{1.14}$ is clearly associated with its highest hardness due to the large CrN phase fraction, whereas the phase composition of $\text{CrB}_{0.12}\text{N}_{0.45}$ includes a softer metallic Cr phase and a lower hardness value.

3.3.2. Tribological Tests at 500°C

Figure 6 presents the friction coefficient curves for the CrN and CrB_xN_y coatings recorded during ball-on-disk experiments against alumina balls at 500°C for a sliding distance of 300 m. For the $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2) coatings, the first 50 m sliding distance present a high initial friction coefficient of 0.7, whereas for the remaining of the test, the friction coefficient decreases to a value of 0.5. This drop can possibly be explained by loosely adhered material detaching from the ball. For the $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2) coatings, a different friction profile was obtained where there is a change between regimes of lower and higher friction coefficient. From the 2D profilometric images, it can be seen that $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2) coatings exhibits a ploughed groove more than 10 μm deep and 350 μm wide after testing at this temperature evidencing complete failure. For the $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2) coatings, the wear track is 1.8 μm deep and 200 μm wide. For the pure CrN coatings, the friction coefficient profile is rather stable at 500°C and the wear depth is higher than in the case of CrB_xN_y , even exceeding coating thickness. The wear rates are found to be 1.1×10^{-5} , 2.1×10^{-6} and $1.9 \times 10^{-8} \text{ mm}^3/\text{Nm}$ for $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2), $\text{CrB}_{0.12}\text{N}_{0.84}$ (0.25 N_2) and $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2) coatings, respectively. However, it should be noted that for coatings $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2) and $\text{CrB}_{0.12}\text{N}_{0.84}$ (0.25 N_2) the wear depth measured through 2D profilometry is much deeper than the coating thickness. The wear depths

for all coatings are substantially higher when tested at 500°C. For example, the wear depth for CrB_{0.12}N_{0.45} (0.15 N₂) increased from 4.2 µm at RT to 10.6 µm at 500°C, whereas the wear rate for CrB_{0.14}N_{1.14} (0.5 N₂) increased from 1.9 x 10⁻⁸ mm³/Nm to 4.1 x 10⁻⁸ mm³/Nm. At 500 °C, the CrN reference coatings showed inferior wear behavior (wear depth of 12.4 µm) than all of the CrB_xN_y coatings, whereas at room temperature it reached the best wear behaviour (for 500 m sliding distance).

With regard to the wear mechanism, at the higher temperature of 500°C, profilometry for CrB_{0.12}N_{0.45} (0.15 N₂) and CrN shows a profile corresponding to a depth of 10.6 and 12.4 µm, i.e. far beyond the thickness of these two coatings, making it impossible to draw any firm conclusions on the wear mechanism since the alumina balls were sliding against the steel substrates for a prolonged period of time. However, it is probable that abrasive wear has led to the severe wear scars observed for these two coatings. The 2D optical profilometry image for CrB_{0.14}N_{1.14} (0.5 N₂) indicates that adhesive wear is occurring for this coating.

The alumina ball counterpart wear rate was found to be in the 1.3 to 48x10⁻¹⁷ m³/Nm range. The minimum wear rate was found in the case of coatings deposited at higher N₂ fractions. This seems to be surprising, but could be attributed to the softer and less abrasive amorphous BN phase found in these coatings (XPS studies).

3.3.3. Wear track characterization

Raman spectroscopy was employed to examine the phases present inside and outside the wear track after the 500°C tests for the CrN reference and CrB_xN_y coatings. The results are shown in Figure 7. Spectrum I was taken from outside the wear track and spectra II, III and IV from different points inside the wear track. In the case of the CrB_{0.12}N_{0.45} (0.15 N₂) coatings (Figure. 7a), inside the wear track, Raman peaks were observed at 225, 290, 411, 554, 609 and 656 cm⁻¹, corresponding to iron oxides Fe₂O₃ and Fe₃O₄ [40, 41] originating from the substrate. For CrB_{0.14}N_{1.14} (0.5 N₂) coatings (Figure 7b), Raman peaks were found at 305, 355, 557 and 613 cm⁻¹, corresponding to Cr₂O₃ [40, 41] formed by oxidation during the ball-on-disk test inside the wear track. For the CrN reference coatings (Figure 7c), peaks from both iron and chromium oxides were identified inside the wear track. Outside the wear track, the Raman spectrum for CrB_{0.12}N_{0.45} (0.15 N₂) (Figure 7a) shows a strong Cr₂O₃ peak, whereas for the CrB_{0.14}N_{1.14} (0.5 N₂) and CrN reference coatings, smaller Cr₂O₃

peaks are observed. It should be also mentioned that Raman (and Energy Dispersive X-ray Analysis, EDX) studies were performed after 500°C tribological testing in order to study the material transfer from ball to coating and vice versa. For all the coatings examined, no peaks from the alumina balls were identified. On the contrary, examination of the alumina balls after sliding against coatings $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2) and $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2) revealed the presence of Fe_2O_3 and Cr_2O_3 .

The f.c.c. crystal structure of bulk CrN gives rise to high symmetry and would not allow any first order Raman scattering [42]. However, PVD deposited coatings, due to the rapid quenching times, usually exhibit a somewhat disordered and defective structure; allowing first order bands to be observed [43]. Typically such spectra are composed of optic and acoustic bands. For the coatings investigated here, it is expected that the total density of peaks in the area between the optic and acoustic bands increases as a more complex multiphase CrB_xN_y coating is grown, compared to the more ordered, single phase CrN reference sample.

Different points, inside the wear tracks were randomly selected for investigation. The presence of Fe_2O_3 and Cr_2O_3 inside the wear tracks and only Cr_2O_3 in the case of 0.15 N_2 and 0.5 N_2 coatings, is in good agreement with a lower wear depth and a friction coefficient reduction for the 0.5 N_2 coatings. Compared to the sample surface outside the wear track it is clear that more pronounced oxidation takes place inside the wear track. Based on the spectra recorded, the coatings which show the least evidence of wear debris are the 0.5 N_2 coatings.

It was also noticed that the intensity of some of the oxide Raman peaks change depending on the area being investigated. This can be mostly attributed to a varying degree of crystallinity of oxide debris in different areas of the wear track (resulting from differing temperatures and tribo-chemical conditions experienced in the contact zone) and a variation of the incident beam angle with the crystalline oxide particles [44]. It is also worthwhile mentioning that Raman bands are employed as stress indicator for thin films. Therefore, different degrees of stress in the oxide layers and particles can also give rise to peak intensity variations.

XPS Cr 2p and O 1s core level spectra were also taken from inside and outside the wear track after tribological tests at 500°C for the $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2) and $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2) coatings are shown in Figure 8. For both coatings (inside and outside the wear track), the Cr 2p_{3/2} peak position is 576.8 ± 0.1 eV and the O 1s position is 530.5 ± 0.2 eV. Both these peak positions are in agreement with the

presence of Cr_2O_3 at the surface [45]. The shoulder at higher binding energies on the O 1s peak corresponds to the presence of some chromium hydroxide (and also possibly adsorbed water) at the surface, resulting from exposure of the sample to atmosphere.

Figure 9 shows SEM micrographs, secondary electron (SE) (Figure 9 a & c) and backscatter electron (BSE) modes (Figure 9 b & d), of the wear track after testing at 500°C for the $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2) and $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2) coatings. The base of the wear track for $\text{CrB}_{0.12}\text{N}_{0.45}$ is rough due to ploughing and the edge of the wear track appears smooth, with no evidence of adhesive material. The SE and BSE images show clear evidence of wear debris, corresponding to the iron and chromium oxides identified by Raman spectroscopy. On the contrary, the $\text{CrB}_{0.14}\text{N}_{1.14}$ coatings exhibit a topography which is significantly different to that observed for the $\text{CrB}_{0.12}\text{N}_{0.45}$ coatings. The wear track base is smooth and a rougher surface is observed at the wear track edge. The wear debris in this case is much finer. This would suggest that the larger particulates observed for $\text{CrB}_{0.12}\text{N}_{0.45}$ are iron oxide and the chromium oxide wear debris are smaller. The SEM results are in good agreement with the 2D profilometry results.

3.3.4. Consideration of the Tribological Behaviour at RT and 500 °C

At RT, the friction coefficient of the CrB_xN_y coatings (and CrN reference) does not vary significantly with coating composition and after the running-in period it is in the range of 0.4 – 0.6. These results are in agreement with other work in which it has been observed that for TiB_xN_y and CrB_xN_y coatings with varying a-BN contents, the friction coefficient remains in the range 0.4 – 0.6 [46-48]. The friction coefficient for the coatings at 500°C is similar to that obtained at RT, suggesting that oxidation does not have a strong effect on the friction coefficient.

According to the crystal chemical approach suggested by Erdemir [49,50], oxides with higher ionic potentials are more likely to provide low friction when present at a sliding interface. Conversely, oxides with lower ionic potentials will lead to high friction and hence high third-body wear. Indeed, Cr_2O_3 is an oxide well known for its abrasive character and has a low ionic potential of 4. Raman and XPS confirmed that Cr_2O_3 is formed at the surface for all coatings at 500°C. The increased growth of Cr_2O_3 at 500°C leads to a higher degree of abrasive three body wear causing an overall increase in the wear coefficient for the CrN and CrB_xN_y coatings.

The highest relative increase in wear at elevated temperatures was obtained for CrN, followed by CrB_{0.14}N_{1.14} (0.5 N₂) and CrB_{0.12}N_{0.45} (0.15 N₂). These results indicate that the single phase CrN coating has a lower resistance against abrasive wear than the nanocomposite CrB_xN_y coatings. As stated in section 3.2, nanocomposite coatings are known to offer increased hardness compared to single phase nitride coatings, but – possibly even more important for wear resistance the nanocomposite structure also leads to higher H/E ratios and fracture toughness [6,20,35]. Furthermore, the oxidation resistance for TiN and CrN based nanocomposite coatings has also been found to increase compared to single phase nitrides due to the strong bonding between the nanocrystallites and amorphous grain boundary phase, hindering cation and anion diffusion and resulting in lower oxidation rates at the surface [3,51]. Consequently, the substantial improvement in wear resistance for the nanocomposite CrB_xN_y coatings (in particular CrB_{0.14}N_{1.14} – comprised of 89 mol.% nc-CrN + 11 mol.% a-BN) compared to single phase CrN at elevated temperatures is associated with their nanocomposite structure offering a higher resistance to abrasive wear and oxidation.

3.4. Corrosion Studies

Initial corrosion measurements have been undertaken on the CrB_xN_y coatings. Potentiodynamic polarization curves for all CrB_xN_y coatings in 3.5% NaCl solution are presented in Figure 10, together with reference data from the uncoated HSS substrate and CrN for comparison. Compared to the substrate, the corrosion potential, E_{corr} , for the CrB_xN_y and CrN coatings is shifted to more noble values, indicative of better corrosion resistance. The steel substrate shows no passive region, but the CrB_xN_y and CrN coatings exhibit passivity over a region ranging approximately from –200 to +700 mV. CrB_{0.12}N_{0.84} (0.25 N₂) coatings give rise to the lowest passive current density ($7 \times 10^{-6} \text{ Acm}^{-2}$) and CrB_{0.14}N_{1.14} (0.5 N₂) coatings show the highest passive current density ($2 \times 10^{-3} \text{ Acm}^{-2}$). CrN exhibits an intermediate passive current density of approximately $8 \times 10^{-5} \text{ Acm}^{-2}$.

The four coatings deposited with a N₂ fractions of 0.1 to 0.25 show a trend of decreasing passive current density with increasing N₂ fraction. However, the coatings with a N₂ fraction of 0.5 exhibit the highest passive current density. There is no obvious explanation for the dramatic change in the current density from the lowest value for the coatings deposited at 0.25 N₂ fraction (CrB_{0.12}N_{0.84}) to the highest value at 0.5 N₂ fraction (CrB_{0.14}N_{1.14}). The chemical composition, phase composition and

grain size for these two coatings are relatively similar. $\text{CrB}_{0.12}\text{N}_{0.84}$ and $\text{CrB}_{0.14}\text{N}_{1.14}$ coatings show respectively (200) and (111) CrN preferential orientations. Lee has reported that CrN coatings preferentially oriented in the (200) direction possess improved corrosion resistance properties compared to those exhibiting a (111) preferential orientation [52]. However, it seems unlikely that this difference in preferential orientation would lead to the dramatic change in the passive current density observed. Hence these initial corrosion results are somewhat inconclusive. However, it is clear that nanocomposite CrB_xN_y coatings can exhibit similar and even better corrosion resistance than CrN coatings, but further work is required to fully understand the factors which influence these corrosion properties and how to maximize the corrosion resistance.

5. Conclusions

The nanostructure, tribological and corrosion properties of CrB_xN_y arc-evaporated coatings deposited at different nitrogen fractions have been investigated. The tribological testing was undertaken at room temperature (RT) and 500°C using an alumina ball as a counterface and corrosion properties were studied in a 3.5% NaCl aqueous solution. The following conclusions can be drawn:

- (1) The CrB_xN_y coatings all exhibit nanocomposite structures with phase compositions which are in fair agreement with the Cr-B-N equilibrium phase diagram.
- (2) After a running-in period, the friction coefficient for the CrB_xN_y and CrN coatings at RT and 500°C was found to be in the range of 0.4 – 0.6.
- (3) Of the CrB_xN_y coatings deposited, the $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2) coatings with a nanocomposite structure of nc-CrN/a-BN exhibited the highest hardness (29 GPa) and best tribological properties at both RT and 500°C. At RT compared to the CrN reference coatings, the $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2) coatings had a similar performance and the other CrB_xN_y coatings exhibiting a worse tribological performance. However, at 500°C, all CrB_xN_y coatings exhibit a better performance than CrN and $\text{CrB}_{0.14}\text{N}_{1.14}$ coatings showed a wear coefficient of $4.05 \times 10^{-8} \text{ mm}^3/\text{Nm}$ compared to $8.2 \times 10^{-5} \text{ mm}^3/\text{Nm}$ for CrN.

(4) For all coatings, at RT and 500°C, oxidation leads to the formation of Cr₂O₃ at the surface. Exposure to higher temperatures increases the oxidation rate and fracture of the thicker Cr₂O₃ layer leads to the formation of hard Cr₂O₃ debris and enhanced three body abrasion. The improved wear behavior of the CrB_xN_y coatings at 500°C is attributed to increased hardness and excellent resistance of the nanocomposite structure to oxidation and abrasive wear.

(5) The corrosion resistance of CrB_xN_y and CrN coatings is good, with passive behavior being exhibited over a large voltage range (-200 to +700 mV). CrB_{0.12}N_{0.84} coatings show the lowest passive current density of $7 \times 10^{-6} \text{ Acm}^{-2}$ compared to $8 \times 10^{-5} \text{ Acm}^{-2}$ for CrN. Further work is required to understand how to maximize the corrosion resistance of these CrB_xN_y coatings.

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Table 1: Composition and stoichiometry of the CrB_xN_y coatings (as determined by TOF-ERDA)

N_2 fraction	Composition (at.%) ± 0.5						Ratios		Stoichiometry
	Cr	B	N	O	H	C	Cr/B	Cr/N	
0	88.8	10.7	-	0.1	0.1	0.2	8.3	-	$\text{CrB}_{0.12}$
0.1	68.8	7.9	22.9	0.1	0.1	0.2	8.7	3.0	$\text{CrB}_{0.11}\text{N}_{0.33}$
0.15	63.3	7.6	28.7	0.1	0.1	0.1	8.3	2.2	$\text{CrB}_{0.12}\text{N}_{0.45}$
0.2	56.2	6.6	36.5	0.2	0.2	0.2	8.5	1.5	$\text{CrB}_{0.12}\text{N}_{0.65}$
0.25	50.5	6.2	42.6	0.3	0.2	0.2	8.1	1.2	$\text{CrB}_{0.12}\text{N}_{0.84}$
0.5	43.7	6.0	49.7	0.2	0.2	0.1	7.3	0.9	$\text{CrB}_{0.14}\text{N}_{1.14}$

List of Figure Captions:

Figure 1: The composition of the coatings (determined by TOF-ERDA) superimposed onto the ternary CrB_xN_y phase diagram for the temperature of 1000°C [32].

Figure 2: XRD patterns of the CrN reference and CrB_xN_y coatings [21]. JCPDS line positions for Cr, Cr_2N and CrN have been superimposed onto the XRD data.

Figure 3: XPS B 1s and N 1s spectra for the CrB_xN_y coatings.

Figure 4: Indentation hardness, reduced elastic modulus and biaxial stresses for the CrN reference and CrB_xN_y coatings.

Figure 5: In situ friction coefficient measurements and 2D profilometric studies of the wear tracks produced after tribological testing at room temperature for the CrN reference and CrB_xN_y coatings.

Figure 6: In situ friction coefficient measurements and 2D profilometric studies of the wear tracks produced after tribological testing at 500°C for the CrN reference and CrB_xN_y coatings.

Figure 7: Raman spectra of the CrN reference, $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2 fraction) and $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2 fraction) coatings after tribological testing at 500°C . Spectrum I has been taken outside the wear track and spectra II, III and IV taken from different points inside the wear track.

Figure 8: XPS spectra of the Cr 2p, and O 1s core level spectra for the $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2) and $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2) coatings inside and outside of the wear track after tribological testing at 500°C.

Figure 9: SE-SEM (a and b) and BSE-SEM (c and d) micrographs of the wear tracks produced on the $\text{CrB}_{0.12}\text{N}_{0.45}$ (0.15 N_2) and $\text{CrB}_{0.14}\text{N}_{1.14}$ (0.5 N_2) coatings after tribological testing at 500°C against alumina balls.

Figure 10: Potentiodynamic curves for CrB_xN_y coatings as well as the CrN and HSS substrate references measured in 3.5% NaCl aqueous solution.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10