Synthesis and characterization of Cr–B–N coatings deposited by reactive arc evaporation

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Nanocomposite Cr–B–N coatings were deposited from CrB_{0.2} compound targets by reactive arc evaporation using an Ar/N₂ discharge at 500 °C and –20 V substrate bias. Elastic recoil detection (ERDA), x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and selected-area electron diffraction (SAED) were used to study the effect of the N₂ partial pressure on composition and microstructure of the coatings. Cross-sectional scanning electron microscopy (SEM) showed that the coating morphology changes from a glassy to a columnar structure with increasing N₂ partial pressure, which coincides with the transition from an amorphous to a crystalline growth mode. The saturation of N content in the coating confirms the formation of a thermodynamically stable CrN–BN dual-phase structure at higher N₂ fractions, exhibiting a maximum in hardness of approximately 29 GPa.

I. INTRODUCTION

Transition metal nitride coatings, such as CrN and TiN, have been widely used as protective hard coatings

to increase the lifetime and performance of cutting and forming tools.¹ It is well known that CrN has superior hot corrosion resistance and lower friction coefficients compared to TiN.² Physical vapor deposition (PVD) CrN coatings have been investigated extensively and have attracted attention due to their excellent properties.³ In contrast to these binary coatings, only a few studies have been reported on coatings within the ternary Cr–B–N

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system.^{4–8} Additions of B have been reported to result in a substantial improvement of the mechanical properties and thermal stability of CrN coatings.^{5,8} For similar systems, such as Ti–B–N, B-enriched areas, covering TiN crystals and promoting the nucleation of TiB₂ (which itself has a low solubility for N) were reported.⁹ Similar segregation-driven processes occur for N in TiB₂. These processes periodically interrupt the epitaxial growth of individual crystallites and cause renucleation, leading to extremely small crystallite size of 2 to 3 nm for TiN–TiB₂ coatings. These effects have been attributed to the nucleation of boron as well as to boron diffusion and accumulation at grain boundaries.⁹ The addition of boron also promotes increased cohesion at the grain boundaries by affecting the local bonding at the interface (assuming that there is no oxygen, chlorine, or hydrogen uptake during deposition that would weaken the interfacial strength).^{10,11}

Although little is known about Cr–B–N thin films,^{4–8} bulk Cr–B–N is a multiphase material with a complex phase diagram,¹² consisting of CrN, Cr₂N, BN, and various Cr_xB_y phases (see Fig. 1), each of which exhibit different mechanical properties. The BN phase can crystallize in one of two forms, cubic (c-BN) or hexagonal (h-BN). These two polymorphic phases have different physical properties; c-BN is a very hard material with hardness approaching that of diamond, while h-BN is a soft material that generates a low friction coefficient in most dry sliding conditions due to its easily activated hexagonal shear systems with possible application temperatures up to 770 °C.¹³ However, in multiphase nanostructured coatings, BN is generally found to be present as an amorphous phase.^{7,13,14}

For other M–B–N (M stands for transition metal) ternary (or quaternary) systems, such as Ti–B–N,¹¹ Ti–Al–B–N,^{13,14} and Zr–B–N,^{15–19} it is generally agreed that improvement of the mechanical properties results from a

nanocomposite structure where virtually dislocation-free nanometer sized crystallites are separated by one to two monolayers of a strongly bonded amorphous phase at the grain boundaries. The crystallite size and the amorphous phase fraction can be finely adjusted by varying the target composition.²⁰ In the case of the Ti–B–N system, it has been reported that the formation of a nonequilibrium supersaturated solid solution of B in TiN might contribute to a further strengthening of the material, since the gliding of dislocations formed within the crystallites will be hindered by the additional B-induced strain fields.^{14,20} Due to the similarities in structure and properties between Ti–N and Cr–N phases, Cr–B–N coatings can be expected to exhibit properties similar to Ti–B–N.

The aim of the present study is the use of the higher energetic growth conditions provided by reactive arc evaporation for the synthesis of Cr–B–N coatings. The coatings microstructure and bonding structure is analyzed as a function of N₂ fraction and correlated to their respective hardness as determined by nanoindentation.

II. EXPERIMENTAL DETAILS

A. Synthesis

Cr–B–N coatings were deposited using a commercial Oerlikon Balzers RCS coating system with a chamber volume of 1000 l and a base pressure in the range of 10^{−6} mbar (0.1 Pa). Si (100), high speed steel (HSS DIN 1.3343), cemented carbide (grade 10) cutting inserts, and Fe foil substrates were used as substrates. The substrates were heated to 500 °C and Ar ion etched for approximately 20 min using a secondary gas discharge. Four sources were equipped with sintered Cr/B (80/20 at.%) cathodes and fixed at a constant arc current of 150 A during deposition. The N₂ fraction (N₂/Ar + N₂) was set to 0, 0.1, 0.15, 0.2, 0.25, 0.5, and 1, respectively, and backfilled with Ar to a constant total pressure of 2 Pa as 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. A Cr–N coating was deposited for comparison purposes using metallic Cr targets (instead of Cr/B compound targets) and the same parameters.

B. Analysis

Coating thickness was measured on high-speed steel and cemented carbide cutting inserts by ball cratering and verified by scanning electron microscopy (SEM) cross-sectional analysis (Zeiss Evo 50, Oberkochen, Germany) on fractured Si (100) samples. The compositional depth profiles of the coatings were determined by time-of-flight (TOF) elastic recoil detection analysis (ERDA) using a primary beam of 350 MeV Au ions.²¹ The forward-scattered coating atoms were analyzed using a

FIG. 1. Composition of the coatings as determined by ERDA in respect to the simplified ternary Cr–B–N phase diagram.

detection system with a solid angle of 0.4 msr (milli-radians) and a large detection angle of 60° ,²² which enables simultaneous detection of all elements (including H). The crystal structure of the coatings was examined using a Siemens D 500 x-ray diffractometer (XRD; Cu $K\alpha = 1.5418 \text{ \AA}$; Bruker, Karlsruhe, Germany). As XRD only provides information about crystalline phases, x-ray photoelectron spectroscopy (XPS) was used to investigate amorphous phases and provide general information on chemical bonding. XPS was undertaken on a Thermo VG Scientific Sigma Probe spectrometer (Sussex, UK) using monochromatic Al $K\alpha$ radiation (1486.6 eV). For individual elemental peak scans, a pass energy of 20 eV was used, giving an energy resolution of $<0.5 \text{ eV}$. To remove the surface contamination, the sample surface was sputter cleaned by a 3 keV rastered argon ion beam with a current of $0.3 \mu\text{A}$ for some minutes. However, some oxide still remained at the surface for the coating with no N and those with low N contents after this cleaning process. The binding energies (BE) were referenced to the C 1s peak (285.0 eV), corresponding to hydrocarbon contamination. In addition, high-resolution transmission electron microscopy (HRTEM) was used to further investigate the coating nanostructure. Coatings deposited onto Si substrates were prepared for cross-sectional and plane view imaging by cleaving and mechanical polishing (thinning) of the samples up to a thickness of about $10 \mu\text{m}$, followed by Ar ion etching (milling) down to electron transparency.²¹ The samples were analyzed firstly in a Philips CM20 TEM (Eindhoven, The Netherlands) and then a JEOL 2010F field emission gun (FEG) TEM, both operated at 200 keV.

The indentation response of the films was analyzed using a UMIS nanoindenter. The shape of the three-sided pyramidal diamond tip (radius of approximately 100 nm) of Berkovich geometry was calibrated using the method suggested by Oliver and Pharr with fused silica as reference material.^{23,24} After polishing to a $1 \mu\text{m}$ finish (to a surface roughness value of $R_a = 0.05 \mu\text{m}$), the coatings deposited to a thickness larger than $3 \mu\text{m}$ on high-speed steel were indented with a constant maximum load of 20 mN. The indentation hardness H and reduced modulus E were then calculated using the Oliver and Pharr

method²⁴ (in accordance with the European standard²⁵) from at least 20 indents. The temperature-dependent stress state was evaluated by curvature measurements of coated Si(100) substrates ($7 \times 20 \times 0.3 \text{ mm}^3$), measured by laser deflection following Stoney's equation under vacuum for temperatures up to 700°C .²⁶

III. RESULTS

After removal from the deposition chamber, the 3.5 to $4.6 \mu\text{m}$ thick coatings (Table I) exhibited a silver gray coloration independent of the N_2 fraction. At the same time, the deposition rate was found to increase from 35 nm/min at low N_2 fractions to 50 nm/min in a pure N_2 discharge. The deposition rate was calculated using the coating thickness (obtained from SEM cross-sectional studies) and the coating deposition time.

A. Composition

The composition of the samples as determined by ERDA is displayed in Table I. It is noteworthy that despite the moderate base pressure ($\sim 10^{-6} \text{ mbar}$, 0.1 Pa), the level of impurities in the Cr–B–N coatings such as O, H, and C does not exceed a total of $0.5 \text{ at.}\%$. With respect to the main constituents, the coatings can be divided into three groups. The first is the coating synthesized in pure Ar, which in the ideal case should mirror the Cr/B target composition of (4/1). However, the Cr/B ratio for all the coatings was found to be approximately two times higher than the target ratio (Table I). This result indicates that a synthesis-related consistent boron loss was observed for all N_2 partial pressures, which moderates slightly for the coating synthesized at higher N_2 fraction (≥ 0.5), suggesting that the B loss might be gas scattering related. The second group, synthesized at lower N_2 fractions (0.1 and 0.15), represents in terms of nitrogen a transition, where approximately 23 to 29 at.% N is incorporated. This results in a Cr/(B + N) ratio of approximately 2 (Table I). The respective positions of these coatings within the ternary phase diagram (shown in Fig. 1) suggest that the chromium-rich films might contain a large fraction of Cr_2N . Increasing the N_2 fraction further to 0.20 gives a Cr/(B + N) stoichiometry of approximately 1. Thus, there could be a metastable solid solution of B

TABLE I. Composition of the Cr–B–N coatings deposited at the stated N_2 fractions, as determined by ERDA, along with the respective ratios and coating thickness values.

N_2 fraction	Composition (at.%)						Ratios			Thickness (μm)
	Cr	B	N	O	H	C	Cr/B	(Cr + B)/N	Cr/(B + N)	
0	88.8	10.7	...	0.1	0.1	0.2	8.3	...	8.3	3.5
0.1	68.8	7.9	22.9	0.1	0.1	0.2	8.7	3.3	2.2	3.9
0.15	63.3	7.6	28.7	0.1	0.1	0.1	8.3	2.5	1.7	3.8
0.2	56.2	6.6	36.5	0.2	0.2	0.2	8.5	1.7	1.3	3.9
0.25	50.5	6.2	42.6	0.3	0.2	0.2	8.1	1.3	1.0	4.6
0.5	43.7	6.0	49.7	0.2	0.2	0.1	7.3	1.0	0.8	3.9

in CrN. The N concentration saturates at N_2 fractions exceeding 0.5, corresponding to a (Cr + B)/N stoichiometry of 1 (Table I). This suggests a dual-phase structure along the quasi-binary tie line between CrN and BN (Fig. 1).

B. Coating structure

1. XRD

The crystal structure of the coatings was investigated by XRD and the corresponding patterns are given in Fig. 2. The standard 2θ positions for face-centered cubic (fcc) CrN (JCPDS No. 76-2494), hexagonal Cr_2N (JCPDS No. 79-2159), and metallic Cr (JCPDS No. 06-0694) are included in the figure. For the coating synthesized in pure Ar only peaks attributable to Cr are observed. Since this coating contains 10.7 at.% B, any eventually formed chromium boride phase present must be amorphous. This XRD pattern suggests strongly textured film growth, since no other peaks are observed. With increasing N content (0.1 and 0.15 N_2 fractions, giving rise to N contents of 23 and 29 at.%, respectively), there is a single reflection at $\sim 44.8^\circ$ 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 Cr_2N or CrN. It has previously been shown by Rebholz et al.²⁷ that up to 16 at.% N can be interstitially incorporated in α -Cr for reactively sputtered Cr–N coatings. A shift of the Cr_2N or CrN peak to higher angles would be consistent with the

presence of a substoichiometric CrN or Cr_2N phase. Considering the positions of these coatings in the phase diagram, the formation of Cr_2N may be expected. As the nitrogen fraction is increased (≥ 0.2), the single feature at $\sim 44^\circ$ 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,²⁸ 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).

2. TEM

TEM images of the 0 N_2 coating (deposited in Ar using the 80/20 Cr/B target) are shown in Fig. 3. This coating shows the presence of columnar growth, with the column diameters ranging between 50 and 400 nm. Figure 3(b) is a dark-field image of one of the columns at higher magnification, and a multilayer structure with a period of 24 nm can be observed. This multilayer effect has previously been reported for Ti–B–N coatings deposited using the same equipment (employing similar mixed Ti/B targets to those used in this work).^{29,30} The origin of this multilayer structure is the different annular Cr and B emission from the target. Thus, the multilayer effect is caused by a small periodic change in the Cr/B ratio.³⁰ For the coating deposited at 0.1 N_2 fraction the dark field images [Figs. 3(c) and 3(d)] show a uniform grain size.

For the Cr–B–N coatings, TEM shows a pronounced suppression of columnar growth with increasing N_2 fraction. At 0.5 N_2 fraction, the columnar structure seems to be weak and the featherlike structure is indicative of continual renucleation [Figs. 3(e) and 3(f)]. This is in agreement with the SAED pattern for this coating [Fig. 3(f)], which shows little evidence of texture [the (200) preferential orientation seen for the coatings deposited at lower N_2 fractions now being suppressed]. The SAED is in agreement with CrN with space group $Fm\bar{3}m$ and a unit-cell dimension $a = 4.148 \text{ \AA}$.

3. XPS

Figure 4 shows the Cr 2p, B, and N 1s core-level spectra of the coatings. Despite the sputter cleaning prior to analysis, many spectra still exhibited residual oxygen-related bonding, e.g., B–O bonds at 191.5 eV.³¹

The Cr 2p spectra exhibit two broad features characteristic for the Cr 2p $1/2$ and 2p $3/2$ orbitals. For the coating deposited in pure Ar, a shoulder at lower binding

FIG. 2. XRD patterns of the coatings deposited at various N_2 fractions.

FIG. 3. Cross-sectional TEM micrographs of the coatings deposited with (a) 0 N_2 fraction (bright-field), (b) 0 N_2 fraction (dark-field), (c) 0.10 N_2 fraction (dark-field) + SAED pattern, (d) 0.10 N_2 fraction, higher magnification (dark-field), (e) 0.50 N_2 fraction (bright-field), and (f) 0.50 N_2 fraction (dark-field) + SAED pattern.

FIG. 4. XPS spectra of the Cr 2p, B 1s and N 1s core level spectra for the coatings deposited at the stated N_2 fractions.

energies (E_B) is detected that is associated with metallic Cr-Cr bonds. The contribution at higher E_B could be assigned to Cr-B bonds,³² while the contamination-related contributions of Cr-N and Cr-O might also be present. This is in accordance with the expected mixture

of metallic Cr with CrB_x . As soon as N_2 is introduced to the discharge, the metallic Cr-Cr contribution vanishes and the spectra narrows at an E_B characteristic for Cr-N bonds indicating the CrN-dominated environment at higher N_2 fractions.^{33,34}

The B 1s peak indicates 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 driven mainly by thermodynamics.

The N 1s spectra are more difficult to interpret. In the literature, Cr_2N and CrN are reported to occur at binding energies of 396.7 and 397.4 eV, respectively, and BN is found at 398.1 eV.^{31–35} It has already been established from the B 1s spectra that BN is present in the coatings with 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 N 1s peak at the BN peak position. Considering the N peak maximum, it can be seen that with increasing N content the peak maximum shifts from higher to lower binding energies. 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 , but CrN is formed at higher N contents.

C. Mechanical properties

The indentation hardness (H_{IT}) and reduced elastic modulus (E_r) for the coatings deposited at different N_2 partial pressures are presented in Fig. 5. The maximum hardness of $\sim 29.5 \pm 0.9$ GPa (corresponding modulus value of $\sim 322 \pm 7$ GPa) is observed for coatings deposited at higher N_2 fractions ≥ 0.5 . For lower N_2 fractions, lower—but still acceptable—hardness values (23–24 GPa) were observed. Within the same region the modulus is increasing from 324 to 362 GPa, with a maximum for the N-free coating. The modulus of 342 ± 11 GPa of the CrN reference sample deposited under similar

FIG. 5. Indentation hardness and reduced elastic modulus values for Cr–B–N coatings, including a CrN reference deposited under similar conditions.

conditions is comparable. However, the hardness of 18.5 ± 0.6 GPa is inferior to the B-containing coatings.

IV. DISCUSSION

A. Influence of N_2 fraction on structure evolution

The N_2 partial pressure has a significant effect on the bonding and microstructure of the arc-evaporated Cr–B–N coatings. Combining the ERDA, XRD, and XPS results, the coating deposited in pure Ar consists of metallic nanocrystalline (nc-) Cr and amorphous (a-) Cr_2B . As N_2 is introduced in the discharge (0.1 and 0.15 N_2 fraction), an unambiguous assignment is difficult, but it would appear that a three-phase structure of nc-Cr(N), a- Cr_2B and substoichiometric nc- Cr_2N (or less likely nc-CrN) phase is formed. At a 0.2 N_2 fraction, a three-phase nc-CrN, a-BN, and a- Cr_2B coating is deposited. Then for higher N_2 fractions, a dual-phase nc-CrN and a-BN structure is formed.

B. Effect of microstructure on mechanical properties of the coatings

Figure 5 exhibits hardness and reduced elastic modulus of Cr–B–N coatings as a function of the N_2 fraction. The most significant findings can be summarized as follows: (i) The reference Cr–N coating exhibits a hardness value of 18.5 GPa. This hardness is in agreement with reported values for CrN.³⁶ (ii) The coating deposited in pure Ar (0% N_2) exhibits a hardness value of 25 GPa. This hardness is relatively high for a mainly metallic, Cr-base coating. However, the hardening effects of the Cr_2B phase, grain-size reduction associated with a dual-phase plasma-deposited microstructure and compressive stress might explain this high hardness.³⁷ For the coating deposited at 0% N_2 , the stress was found to be -1.5 GPa. All the arc-evaporated B-containing coatings deposited (with and without N) exhibit high hardness (22–29 GPa). This behavior could be attributed to boron segregation to the grain boundaries,⁹ which causes hindering of dislocation movement and the formation of amorphous Cr_2B and BN phases. These two mechanisms of hardness improvement are both valid for the coatings deposited at low and high N_2 fractions, respectively. (iii) For coatings deposited at N_2 fractions up to 0.25, the hardness remains constant and then increases for a N_2 fraction of 0.5. Consequently, the formation of a nanocomposite structure of nc-CrN and a-BN gives rise to the highest hardness. According to the phase diagram, this corresponds to a structure comprising approximately 89 mol% nc-CrN + 11 mol% a-BN. For a nc-CrN with an average grain size of approximately 5 nm, to give monolayer coverage an amorphous layer content of approximately 10 mol% is required.¹⁶ Hence, the highest hardness is obtained for a nc-CrN/a-BN coating with monolayer a-BN coverage of the CrN nanocrystallites.

Also, from Fig. 5 it is clear that increasing the N_2 fraction (from 0 to 0.25) causes a rather significant decrease in the elastic modulus values for the coatings deposited at low N_2 fractions (from 359 ± 6 to 312 ± 14 GPa). This would appear to correlate with a gradual decrease in the a-Cr₂B content. The coatings deposited at higher N_2 fractions have a dual-phase nc-CrN/a-BN structure, and this gives rise to the highest hardness combined with the lowest elastic modulus, yielding a H/E value of 0.09. This is in good agreement with previous work on nc-(Ti,Al)N/a-BN coatings, where a dual-phase structure comprised of 90 mol% (Ti,Al)N and 10 mol% a-BN gave rise to the highest H/E ratio.¹⁵

Biaxial stress measurements showed minimum intrinsic compressive stresses (-1.3 GPa and -0.8 GPa for 0.1 and 0.2 N_2 fraction, respectively) at the deposition temperature ($T_{\text{dep}} = 500$ °C) for coatings deposited at low N_2 partial pressure, whereas the opposite was found for coatings deposited at N_2 fraction >0.25 (-2 GPa for coating deposited at 0.5 N_2 fraction). The stress is dependent on many factors including ion bombardment, phase composition, and the thermal expansion coefficients of each phase present. This increased stress for higher N fractions is possibly the result of a two-phase (purely ceramic) nc-CrN/a-BN coating being deposited compared with the three-phase coatings with larger amorphous fractions and lower thermal expansion coefficients formed at lower N fractions.

V. CONCLUSIONS

In the present study it was demonstrated that nanocomposite coatings within the ternary Cr–B–N system can be deposited by high-rate reactive arc evaporation. The microstructure, chemical bonding environment, and mechanical properties of the coatings can be controlled (and designed) by adjusting the nitrogen fraction. By increasing the N_2 content, the columnar structure is suppressed by renucleation processes, and for coatings deposited at N_2 fractions ≥ 0.5 a dense growth mode was observed. Coatings deposited at low N_2 fractions consist mainly of metallic Cr, Cr₂B, and substoichiometric Cr₂N phases. Increasing the N_2 content leads to the formation of a two-phase stoichiometric nc-CrN and a-BN structure. The coating deposited at 0.5 N_2 had a nc-CrN/a-BN structure comprising approximately 90 mol% nc-CrN and 10 mol% a-BN and an average grain size of approximately 6.7 nm, corresponding to monolayer coverage of the nanocrystalline CrN grains. This nanocomposite coating had the highest hardness of 29 GPa and highest H/E value of 0.09.

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