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Abstract: This paper reports on the structure and mechanical properties of $\sim 2 \mu\text{m}$ thick nanocomposite (nc-) Ti(N,C)/ amorphous diamond like carbon (a-C:H) coatings deposited on 100Cr6 steel substrates, using low temperature ($\sim 200 \text{ oC}$) DC reactive magnetron sputtering. The carbon content was varied with acetylene partial pressure in order to obtain single layer coatings with different a-C:H carbon phase fractions. The nanocrystalline Ti(N,C) phase is approximately stoichiometric for all coatings and the a-C:H phase fraction increases from 31 - 47 at. % as the coatings stoichiometry changed from $\text{TiC}_{1.34}\text{N}_{0.51}$ to $\text{TiC}_{2.48}\text{N}_{0.48}$, respectively. $\text{TiC}_{1.34}\text{N}_{0.51}$ coatings showed the highest nano-indentation hardness (H) of $\sim 14 \text{ GPa}$ and a modulus (E_r) of $\sim 144 \text{ GPa}$; H reduced to $< 6 \text{ GPa}$ and E_r to $< 70 \text{ GPa}$ for $\text{TiC}_{2.48}\text{N}_{0.48}$ coatings. nc-Ti(N,C)/a-C:H coatings are promising candidates for applications where better matching of the modulus between relatively low modulus substrate, hard loading support layer and low modulus-high H/E ratio top layer is required.

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Dear Editor

Please find attached the revised Figure 3 as requested for the submitted manuscript titled "Structure and mechanical properties of low temperature magnetron sputtered nanocrystalline (nc-) Ti (N,C)/amorphous diamond like carbon (a-C:H) coatings", by C. Tsotsos, M. A. Baker, K. Polychronopoulou, P. N. Gibson, K. Giannakopoulos, A. Polycarpou, K. Böbel, C. Rebholz.

We increased the weight of lines and font size and improved the resolution of the graphs.

Thank you for considering our manuscript. We are looking forward to your response.

On the behalf of the authors.

Kind Regards

C. Tsotsos

Structure and mechanical properties of low temperature magnetron sputtered nanocrystalline (nc-)Ti(N,C)/amorphous diamond like carbon (a-C:H) coatings

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ABSTRACT

This paper reports on the structure and mechanical properties of $\sim 2 \mu\text{m}$ thick nanocomposite (nc-) Ti(N,C)/ amorphous diamond like carbon (a-C:H) coatings deposited on 100Cr6 steel substrates, using low temperature ($\sim 200^\circ\text{C}$) DC reactive magnetron sputtering. The carbon content was varied with acetylene partial pressure in order to obtain single layer coatings with different a-C:H carbon phase fractions. The nanocrystalline Ti(N,C) phase is approximately stoichiometric for all coatings and the a-C:H phase fraction increases from 31 – 47 at. % as the coatings stoichiometry changed from $\text{TiC}_{1.34}\text{N}_{0.51}$ to $\text{TiC}_{2.48}\text{N}_{0.48}$, respectively. $\text{TiC}_{1.34}\text{N}_{0.51}$ coatings showed the highest nano-indentation hardness (H) of $\sim 14 \text{ GPa}$ and a modulus (E_r) of $\sim 144 \text{ GPa}$; H reduced to $< 6 \text{ GPa}$ and E_r to $< 70 \text{ GPa}$ for $\text{TiC}_{2.48}\text{N}_{0.48}$ coatings. nc-Ti(N,C)/a-C:H coatings are promising candidates for applications where better matching of the modulus between relatively low modulus substrate, hard loading support layer and low modulus-high H/E ratio top layer is required.

Keywords: nanocomposite, a-C:H, Microstructure, Mechanical properties, Magnetron sputtering.

1. Introduction

Tribological coatings for demanding wear resistant applications are required to combine a range of different functional properties such as high hardness, corrosion resistance, thermal stability and low friction coefficients [1]. For that reason physical vapour deposition (PVD) coatings based on the TiCN system have gained considerable attention, since they combine

properties of both TiN and TiC, and are known to offer enhanced wear resistance when deposited on tool steel and cermet substrates [2-4]. This combination of transition metal nitrides and carbides offered by the TiCN system has been investigated with particular attention for coatings containing up to 20 at. % C [5-6]. These studies show that coatings deposited in a reactive gas atmosphere using electron beam physical vapour deposition (EBPVD) processes at relatively low substrate bias (-70 V) and temperatures (~400 °C), exhibit a columnar structure [5]. The deposition of TiCN coatings using magnetron sputtering techniques at similar temperatures (~350 °C) and similar (relatively low) substrate biases (-60 V) resulted in much denser structures with a glassy like cross-sectional microstructure [5,7]. The sputter deposition of TiCN, in either combinatory reactive gas atmospheres or by composite target sputtering, results in an increase on the intrinsic stress at increasing C and N contents and increasing substrate bias. A correlation of early, cohesive, coating failure during wear testing and high intrinsic stress is noted for the above system [7]. Coatings containing up to 15 at. % C display a significant improvement in the wear resistance and a relatively good balance of hardness – in cases reported to be – in excess of 30 GPa and elastic modulus ~ 300 to 400 GPa, although on cermets substrates, elastic moduli as high as 500 to 600 GPa have been reported [7]. Previous work on the TiC_x system demonstrates that a desirable improvement in wear performance (sliding and abrasion) is provided for coatings containing 45 to 65 at. % C [8,9]. Stoichiometric TiC is also achieved at flow rates between 40 and 50 sccm acetylene. These coatings were deposited by reactive magnetron sputtering at temperatures ~ 200 °C without substrate bias; and exhibited dense glassy like microstructures. Although no evidence was presented regarding the intrinsic coating stresses, it is probable that the TiC coatings deposited

without substrate biasing offer an advantage over biased processes due to lower intrinsic stresses. Furthermore, coatings containing 40 to 60 at. % C content display a relatively high hardness (H)/ modulus (E) ratio ≥ 0.1 , expected to be beneficial for wear applications due to the increased coating toughness, resilience to permanent deformation and compatibility with the substrate elastic modulus [10,11].

In this study nc-Ti(N,C)/a-C:H coatings have been examined in order to further improve the friction coefficient and wear performance of coatings by incorporating N into the Ti-C based system. The resultant mechanical (and tribological) properties of the Ti-C-N coating system can be improved further through hybrid/duplex techniques e.g. pre-nitriding and/or multilayer TiN/TiCN coatings [13,14] with a beneficial load bearing support being offered by the hard TiN interfacial layer. The TiN layer can also beneficially act as a diffusion barrier between the TiCN layer and the substrate at elevated temperatures [12]. An approach to demonstrate the amount of energy dissipated under oscillating loaded sliding contact conditions using classical Wohler fatigue fretting curves showed that the amount of dissipated energy is significantly reduced after a large number of cycles for single layer TiN and TiCN coatings, due to cracking phenomena [15]. Therefore multilayer TiN/TiCN with additional top layers of TiC or a-C:H coatings can dissipate greater energy resulting in gradual debris formation and coating ejection at higher wear cycles thus prolonging coating durability [15]. It should be noted that the evaluation of the endurance of coatings through the classical Wohler-curves approach is a concept developed not as a function of maximum applied pressure but as a function of friction [14]. In practice, lower coating durability than that calculated has been observed due to coating decohesion. Coating durability and wear

resistance is affected by a series of mechanical factors and their interactions, including layer cohesion/adhesion, coating micro-strain and stress (inherent to the deposition process) and their effect on internal adhesion forces, stress distribution within the contact area, nominal thickness of coating layers, tribochemistry and thermal stability etc.

In this paper we deposit a set of Ti-C-N based coatings with varying amounts of C using low temperature DC magnetron sputtering. The process was selected specifically to be below 250 °C in order to avoid tempering of the heat treated 100Cr6 substrate. The aim of this work is to develop a multilayer coating consisting of a Ti/TiN support layer and a top Ti(N,C)+a-C:H layer with graded a-C:H content to form a a-C:H rich top-coat. Three coatings were deposited at constant nitrogen/acetylene ratios of 1:1. The flow rate was progressively increased for the each coating from 20 sccm to 30 sccm and 40 sccm to provide an increase in the carbon content. The chemical and phase composition, relative phase fraction, nanostructure and mechanical properties of these TiCN coatings are assessed in this paper.

2. Experimental details

nc-Ti(N,C)/a-C:H coatings were deposited onto 100Cr6 steel substrates (app. 10 mm x 10 mm x 3 mm) by reactive pulsed DC magnetron sputtering. The substrates were heat treated, quenched and tempered to achieve ~ 9.3665 GPa micro-hardness and subsequently polished to a mirror finish prior to deposition. An industrial deposition chamber was used, which contains a single magnetron consisting of a segmented Ti target (5.7 W/cm²) of 1000 mm x 175 mm x 11 mm. Deposition occurred in argon/nitrogen/acetylene (Ar/N₂/C₂H₂) gas

mixtures, at a base pressure of 10^{-3} Pa and deposition pressure of 0.3 Pa to 0.33 Pa, this variation being dependant on the N_2/C_2H_2 flow rate ratio. To improve the coating to substrate adhesion, a ~ 0.1 μm Ti interlayer was initially deposited in Ar atmosphere and at a substrate bias of -50 V with target power and voltage of 10 kW and 430 V, followed by the deposition of a ~ 0.1 μm TiN load support layer at a substrate bias of -75 V with target power and voltage of 10 kW and 470 V to 520V. The N_2 flow rate was kept constant for both the TiN and the Ti(N,C) layer deposition i.e. 20, 30 and 40 sccm for coatings A, B and C respectively. The Ti target power was set at 10 kW for the duration of the deposition of the coating which was performed without a substrate bias and the target voltage was between 540 V to 610 V. The substrate temperature and target to substrate distance were kept constant at ~ 200 $^{\circ}C$ and 200 mm, respectively, and no substrate bias voltage was applied. Prior to deposition, the 100Cr6 steel substrates were ultrasonically cleaned in a 3 step sequence: a 5 min. rinse in acetone followed by isopropyl alcohol, then methanol and finally left to dry in warm air (~ 50 $^{\circ}C$). Each coating run consisted of a batch of 10 coated substrates (5 x 100Cr6 and 5 x Si wafers). The chemical composition of the coatings was determined by x-ray photoelectron spectroscopy (XPS), using a VG-Thermo Advantage Sigma Probe spectrometer employing a monochromatic $AlK\alpha$ source and a hemispherical analyser. Argon ion etching was performed at an incident energy of 3 kV and an etch current of ~ 0.75 μA over an area of approximately 18 mm². The coatings were etched until the O 1s peak intensity no longer decreased. The XPS high resolution spectra (N 1 s and C 1 s) were recorded at a 20 eV pass energy and step of 0.2 eV. Quantification was performed using instrument modified Wagner sensitivity factors after a Shirley background subtraction. The binding energies were referenced to sp^2 C at 284.5 eV as an internal

standard to take into account charging effects. Peak fitting was undertaken with the VG Thermo Advantage software employing a mixed Gauss/Lorentz function. Fracture cross-sections of coated samples were prepared for scanning electron microscopy (SEM) morphology and topography studies. Hardness (H) and reduced elastic modulus (E_r) values were determined using a Hysitron TriboScope, equipped with a Berkovich indenter. Loads were varied between 3 to 6 mN, with a sequence of 15 indentations taken at each load. H and E_r were measured using the procedure proposed by Oliver and Pharr [16]. The Berkovich indenter area functions used for calculation of H and E_r were derived by fitting nanoindentation data on a fused quartz sample to a standard equation [17]. X-ray diffraction analysis was performed using a dedicated glancing-angle x-ray diffractometer, employing monochromated Cu $K\alpha$ radiation at a tube voltage of 35 keV and current of 30 mA. Cross section transmission electron microscopy (TEM) analysis of films deposited onto Si wafer was performed using a Philips CM 20 operating at 200 kV equipped with an energy dispersive spectroscopy detector. 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 μm , followed by Ar ion etching (milling) down to electron transparency.

3. Results

3.1. Composition

Table 1 displays the elemental composition and stoichiometry for the three TiCN coatings as determined by XPS. These compositions have been entered on the Ti-C-N ternary plot in Figure 1.

The Ti/N ratio was similar for all three coatings ranging from 1.86 to 2.02. The N_2/C_2H_2 flow rate ratio was kept constant for all film depositions however an increase in the C_2H_2 relative flow rate results in a reduction of the Ti sputter yield as a thin layer of graphite forms on the surface of the Ti target [18], thus the coatings deposited at 30 sccm and 40 sccm C_2H_2 are more similar in composition than the coating deposited at 20 sccm C_2H_2 . SEM cross section analysis (Figure 2) indicates that the coating total thickness progressively reduces from 2.7 μm to 2.5 μm and 2.2 μm for coatings A ($TiC_{1.34}N_{0.51}$), B ($TiC_{2.04}N_{0.54}$) and C ($TiC_{2.48}N_{0.48}$), respectively.

The resultant cross-sectional microstructure of the films is also affected by the C_2H_2 flow rate. As the a-C:H phase fraction in the film increased, the coatings exhibited a more dense structure. Coating A showed a fine columnar structure, coating B, a semi-columnar structure and coating C, a dense glassy-like structure.

3.1.1. Chemical bonding environment (XPS)

The XPS data for the coatings is presented in Figure 3. For all samples there was a small charge shift to higher binding energies. The main C 1s component clearly corresponds to a-C:H - sp^2 C and this is known to have a binding energy of 284.5 eV [19]. Consequently, all of the XPS data was charge shifted such that the a-C:H - sp^2 C component was located at binding energy of 284.5 eV.

In Figure 3 (a), the C 1s peaks for coatings A ($TiC_{1.34}N_{0.51}$), B ($TiC_{2.04}N_{0.54}$) and C

($\text{TiC}_{2.48}\text{N}_{0.48}$) are presented in Figure 3 (b) the C 1s and N1s peaks for coating A have been peak fitted, and in Figure 3 (c) the Ti 2p peak for coatings A is presented. The Ti $2p_{3/2}$ peak occurs at 455.2 eV and the N 1s peak at 397.1 eV. These peak positions are consistent with those for TiN [20].

The GAXRD scans presented in Figure 5 (and described in detail later) show that the only Ti-containing phase in these TiCN coatings is a cubic nanocrystalline TiN (NaCl-type) phase. With this information, the C 1s peak fit for coatings A ($\text{TiC}_{1.34}\text{N}_{0.51}$, Figure 3 (b)) can now be considered in detail. The lowest energy C 1s component (component A) at 282.2 eV corresponds to Ti-C bonding [9]. Hence the nanocrystalline phase being formed in these coatings is actually Ti(N,C). The small carbon component is approximately 1 eV higher than the Ti-C peak (component B) and corresponds to carbon atoms located at the edge of the Ti(N,C) crystallites [9,21]. At 282.2 eV, the Ti-C binding energy is higher than that for pure TiC/a-C:H coatings [9,20] since this corresponds to carbon incorporated into TiN, to form Ti(N,C), and the presence of the more electronegative nitrogen in the local environment causes the binding energy of the carbon to increase slightly. As the C/Ti ratio increases, the intensity of this Ti-C component apparently decreases (Figure 3), but the carbon concentration in the coatings is actually rising and analysis of the peak fits shows that in fact the total amount of C bonded to Ti (component A + component B) remains at between 14 and 16 at. % for all three coatings. The binding energy of the Ti-C component for the three coatings progressively increases from 282.2 – 282.7 eV as the Ti concentration increases. This is due to the carbon atoms in the Ti(N,C) phase existing in an increasingly more electropositive environment.

Components C (284.5 eV) and D (285.2 eV) in the C 1s peak fit correspond to a-C:H sp^2 C and sp^3 C respectively [20]. The higher binding energy components (E and F) are associated with C-O bonding.

The N 1s peak shape shown in Figure 3 (b) is typical of that for TiN [22], the tail to higher binding energies corresponding to the presence of some N-O bonding. There is no strong evidence of C-N bonding in the C 1s or N 1s peak fits in any of the TiCN coatings contrary to what is reported for Ti(N,C) coatings deposited by co-reactive sputtering of Ti and graphite targets for similar compositions [23]. The Ti 2p peak has not been fitted due to the complex nature of the fit required for TiN [24] and the limited extra information such a peak fit would provide.

3.1.2. Phase Composition and Relative Phase Fractions

From the peak fits, it is possible to determine the phase composition and relative phase fractions. Due to the absence of a CN_x phase and considering the GAXRD results (see section 3.2), show only the formation of a cubic nanocrystalline Ti(N,C) phase together with the results of the C 1s peak fits, it can be stated that these Ti-C-N based coatings have a two phase nanocomposite nc-Ti(N,C)/a-C:H structure.

The relative phase fractions can be determined on the basis that: (a) the XPS peak intensities for the Ti 2p and N 1s peaks correspond solely to the Ti(N,C) phase; (b) the carbon components A and B correspond to the Ti(N,C) phase; (c) the carbon components C

and D correspond to the a-C:H phase; (d) the carbon components E and F are associated with the Ti(N,C) and a-C:H phases (and the amount of C-O bonding in each phase is assumed to be in proportion to the relative fractions of carbon bonded in the two phases). The resulting phase fractions and Ti(N,C) stoichiometries are given in Table 2.

It can be seen from Table 2 that the Ti(N,C) nanocrystalline phase is approximately stoichiometric, but the carbon fraction in this phase increases as the total carbon concentration in the coating increases, as might be expected.

3.2 Structure (TEM and XRD)

TEM analysis performed on coatings A ($\text{TiC}_{1.34}\text{N}_{0.51}$) indicates that the coating thickness for low reactive gas flow rates (i.e. 20 sccm for N_2 and C_2H_2) is $\sim 2.7 \mu\text{m}$, which is similar to that measured by SEM. Over the whole coating thickness, four layered regions can be resolved. The change in structure between the two outermost layers can be seen in the higher magnification TEM dark field image and selected area diffraction patterns (SAED) in Figure 4 (b). The layer at the surface has a very fine featureless structure, whereas the inner layer exhibits a columnar structure. Energy dispersive x-ray analysis showed that there is a higher carbon concentration in the $\sim 450 \text{ nm}$ thick outermost surface region compared to the underlying columnar layer. The average grain size for the Ti(N,C) nanocrystalites in this $\sim 450 \text{ nm}$ thick surface for coatings A ($\text{TiC}_{1.34}\text{N}_{0.51}$) was found to be approximately 3 to 4 nm. The outermost layer corresponds to the nc-Ti(N,C)/a-C:H region, with a relative phase fraction of 31 at. % a-C:H and 69 mol. % Ti(N,C). The layer beneath this surface region also corresponds to nc-Ti(N,C)/a-C:H, but with a lower a-C:H phase

fraction with larger grain sizes of 7 to 9 nm. The reason for this increased carbon content in the outermost layer is target poisoning by C_2H_2 in the later stages of the deposition. The two layers close to the coating/substrate interface are the Ti interlayer and the TiN support layer.

GAXRD data for the TiCN coatings are presented in Figure 5. All coatings contain a nanocrystalline phase similar to the f.c.c. TiN structure with a (111) preferential orientation. Nanocrystalline phases not containing Ti will not be detected in the GAXRD scans unless they make up the majority of the coating structure. Comparison of the peak widths and heights between θ -2 θ scans (not shown here) and the GAXRD scans suggests a columnar structure, though interference with substrate and interlayer peaks in the θ -2 θ scans makes definite conclusions somewhat difficult in this respect. As stated previously in conjunction with the XPS analysis, the coating nanocrystalline phase can be characterised as a cubic Ti(N,C) (NaCl-type) phase. Coatings B ($TiC_{2.04}N_{0.54}$) exhibit the ‘poorest’ crystallinity in the group while GAXRD scans obtained for coatings C ($TiC_{2.48}N_{0.48}$) are indicative of a larger crystalline size. The GAXRD scans for coatings C can be misleading; from the XPS and TEM results, this coating contains an a-C:H phase fraction of more than 45 at. %. As the crystallinity deteriorates with increasing a-C:H content (see Table 2) coatings C ($TiC_{2.48}N_{0.48}$) probably become x-ray amorphous i.e. the material may still be crystalline but have a crystallite size which is too small to result in x-ray diffraction. This happens with nanocrystallites having a grain size of approximately < 1.5 nm. In this case, the grains are so small that the order within the crystal has become distorted and the nanocrystalline structure is thus not resolvable by XRD. Therefore the film can be described as a more

x-ray transparent i.e. the penetration of x-rays through the x-ray amorphous. Thus narrower peaks obtained for coatings C ($\text{TiC}_{2.48}\text{N}_{0.48}$) arise mainly from the Ti-rich sublayer and/or from the TiN interlayer where the crystallinity is expected to be more pronounced. In fact, narrower XRD peaks are already visible in the XRD data for coatings B, from the more crystalline (low a-C:H content nc-Ti(N,C)/a-C:H) sublayer. It should be noted that coatings C ($\text{TiC}_{2.48}\text{N}_{0.48}$) have the lowest thickness out of the three coatings with an average thickness of 2.2 μm , so that the XRD signal from the sublayers will be further enhanced. Full width half maximum (FWHM) of the x-ray peaks were determined using the Scherrer equation [25]

$$\text{grain size} = 0.9\lambda/\cos\theta \text{ FWHM}$$

where λ is the wavelength of the incident radiation and θ the Bragg angle. On the assumption that peak broadening is due to grain size variation only, the FWHM analysis indicated that the Ti(N,C) crystallite size for coatings A ($\text{TiC}_{1.34}\text{N}_{0.51}$), B ($\text{TiC}_{2.04}\text{N}_{0.54}$) and C ($\text{TiC}_{2.48}\text{N}_{0.48}$) are 4 nm, 2 nm and 7 nm respectively. This is in good agreement with TEM where the nanocrystalline size measured for coatings A is between 3 to 4 nm. It is possible that the crystallite size of the intermediate nc-Ti(N,C)/a-C:H layer with a low a-C:H content remains constant for all three coatings at approximately 7 to 9 nm as indicated by TEM for coatings A and GAXRD data for coatings C.

3.3. Nanohardness and modulus

H and E_r data for coatings A ($\text{TiC}_{1.34}\text{N}_{0.51}$), B ($\text{TiC}_{2.04}\text{N}_{0.54}$) and C ($\text{TiC}_{2.48}\text{N}_{0.48}$) are

summarised in Figure 6. The penetration depth for all coatings was approximately 15 % of the Ti(N,C)+a-C:H layer total thickness where the obtained hardness measurements were similarly constant. A decline in H and E_r is noted with increased a-C:H content. Coatings A ($\text{TiC}_{1.34}\text{N}_{0.51}$) are the hardest of the group with a hardness of $\sim 13.8 \pm 0.1$ GPa and $E_r \sim 144$ GPa. Coatings B and C with > 40 at. % a-C:H demonstrate the lowest hardness and elastic moduli. $H = 4.8 \pm 0.2$ GPa to 9.2 ± 0.1 GPa and $E_r = 59$ GPa to 94 GPa for coatings C ($\text{TiC}_{2.48}\text{N}_{0.48}$) and B ($\text{TiC}_{2.04}\text{N}_{0.54}$) respectively. The H/E ratio for coatings A, B and C is found to be 0.096, 0.097 and 0.081, respectively. It is noted that up to ~ 31 at. % a-C:H the coatings indicate a higher resistance to plastic deformation, whereas a further increase of a-C:H phase fraction to more than 40 at. % increases the plasticity of the coatings. According to Tsui et al [26] in a rigid-ball on elastic/plastic plate contact the H/E is proportional to the yield pressure (i.e. resistance to plastic deformation) P_y . This is given by the equation (1)

$$P_y = 0.78 r^2 (H^3/E^2) \dots (1)$$

In (1) r is the contacting sphere radius.

This suggests that H^3/E^2 can be used to indicate the coating's resistance to plastic deformation in these types of loaded contact. It should be taken in account that in this paper the nanoindenter is not spherical however based on Tsui et al [26] it could be assumed with caution that lower H/E values could indicate lower resistance to plastic deformation of the films.

4. Discussion

4.1. Coating nanostructure

With regard to understanding the phase composition of these PVD TiCN coatings, although it is clear that PVD deposited coatings are growing under non-equilibrium conditions and kinetics as well as thermodynamics influence the nanostructure which develops, it is useful to consider the free energy of formation, $^f\Delta G_{298}^0$ for the various phases which may form when Ti, N and C atoms arrive at the coating surface. The free energy of formation at 298K ($^f\Delta G_{298}^0$) for TiN and TiC has been reported to be -309.6 kJ/mol and -180.7 kJ/mol, respectively, whereas for a-C:H phase formation this value depends on structure adopted; 0 for graphite and 2.9 kJ/mol for diamond [27]. $^f\Delta G_{298}^0$ for CN_x will be dependant on the compound stoichiometry and structural phase. Most PVD CN_x coatings have low N content (< 30 at. %) [19] and considering that no a-C:H-like CN_x phases exist naturally, it is to be expected that $^f\Delta G_{298}^0$ for such materials will have a value close to 0 kJ/mol.

Consequently, it can be seen that the largest thermodynamic driving force is for the formation of TiN. The results in this paper indicate that the addition of C initially results in the formation of Ti(N,C). Hence, the thermodynamic driving forces and kinetics of PVD thin film growth have resulted in the formation of Ti(N,C) rather than TiN + TiC. Only when the C content is in excess of that required to form approximately stoichiometric Ti(N,C) does a-C:H start to form as a separate phase. CN_x never forms as a separate phase, as the Ti/N ratio is always > 1 (hence the entire N immediately bonds with Ti to form the TiN based phase, due to the high $^f\Delta G_{298}^0$ for TiN) and there is little (if any) thermodynamic

driving force for the formation of a CN_x phase.

4.2. Mechanical properties

From XPS data and using the method described in previous work [28] it can be approximated that for coatings A ($TiC_{1.34}N_{0.51}$) and B ($TiC_{2.04}N_{0.54}$) the amount of a-C:H present which is ~ 31 at. % and ~ 43 at. %, respectively is sufficient for ~ 1.5 to 2 monolayer coverage (estimates made using 4 nm Ti(N,C) nanocrystallites for coating A and 2 nm for coating B). A reduction of the nanocrystallite size below 2 nm and a concomitant increase in the a-C:H content may compromise the fracture toughness of the coatings due to a reduction in the nanocrystalline phase fraction. According to Veprek et al [29] when considering the design of a nanocomposite structure consisting of a crystalline phase surrounded by an amorphous (metallic, ceramic or carbon) phase dislocation action is prohibited because the grains are smaller than the critical dimension D for Frank-Read sources and the separation of the grains by the by the matrix is also small. Thus the probability of dislocations forming in nanocrystals is little since the stress required to form dislocations (e.g. from Frank-Read sources of dislocation multiplication) and move such dislocations from grain to grain (through grain boundary pile up), is a lot higher at smaller grain sizes and for smaller separation of the grains by an amorphous matrix. In the case of the nc-Ti(N,C)/a-C:H coatings when the separation of the nanocrystallites by the a-C:H matrix becomes greater than a critical size the ability of the coating to reduce cracking during large elastic deformations is compromised [29]. Although coatings A ($TiC_{1.34}N_{0.51}$) and B ($TiC_{2.04}N_{0.54}$) possess very similar H/E ratios the nanostructure of coatings A

(TiC_{1.34}N_{0.51}) should be more effective in limiting initial crack size and hindering crack propagation [29,30] since coating B possess a smaller crystalline size and higher volume of the a-C:H phase. The optimum hardness previously reported in literature for hydrogen terminated a-C:H matrices is up to 20 GPa [18]. As the amorphous phase coverage for coatings A (TiC_{1.34}N_{0.51}) is greater than 1 monolayer, grain boundary sliding can occur at lower shear stresses due to low interfacial bond strength of the hydrogen terminated amorphous sp² rich a-C:H phase. Coatings A (TiC_{1.34}N_{0.51}) have an average grain size of approximately 4 nm. The reduction in H and E_r observed for coatings B (TiC_{2.04}N_{0.54}) may well be attributed to lattice incoherence strains and a high volume of grain boundaries at low grain sizes. Below approximately 3 nm, the geometry of the Ti(N,C) nanocrystallites becomes more rounded and less angular [18, 30, 31] with a potential increase in grain boundary defects. Even though the H values obtained for coatings B (TiC_{2.04}N_{0.54}) and C (TiC_{2.48}N_{0.48}) are relatively low, the increased plasticity of the a-C:H-rich Ti(N,C)+a-C:H top layer (~400 to 450 nm) forming near the surface is expected to contribute significantly to these measured values. The aim of this layer is to act as a ‘bedding’ layer in wear applications operating in a critical manner either by sacrificially offering a friction reducing transfer layer to the counterpart, controlling the wear rate [32-34] or by both increasing energy dissipation and reducing friction under contact to potentially increase the fretting resistance of the coatings [14]. In a separate study by the authors [35] coatings A (TiC_{1.34}N_{0.51}) and B (TiC_{2.04}N_{0.54}) display good tribological properties when subjected in high contact pressure tribological testing.

5. Conclusions

nc-Ti(N,C)/a-C:H coatings were deposited onto 100Cr6 polished coupons and Si wafers using DC magnetron sputtering at ~200 °C. Progressively increasing the C₂H₂/N₂ flow rate ratio resulted in both an increase in the carbon content in the films and in the a-C:H phase fraction. The resultant a-C:H phase fractions were ~31 at. %, ~43 at. % and ~47 at. % for coatings A (TiC_{1.34}N_{0.51}), B (TiC_{2.04}N_{0.54}) and C (TiC_{2.48}N_{0.48}), respectively. XPS and XRD results indicated that a two phase nanocomposite structure of cubic Ti(N,C) nanocrystallites surrounded by an amorphous a-C:H phase was formed. When the C content is in excess of that required to form approximately stoichiometric Ti(N,C), a-C:H starts to form as a separate phase. No formation of CN_x is noted since the Ti/N ratio is always > 0.9, thus (due to the high $^f\Delta G_{298}^0$ for TiN) there is little thermodynamic driving force for the formation of a separate CN_x phase. TEM indicates that a a-C:H rich Ti(N,C)+a-C:H layer of approximately 450 nm in thickness is formed at the surface, where an increase in C occurs due to progressive Ti target poisoning and a reduction of the average crystalline size is noted. For greater a-C:H volume fractions (> 40 at. %) a reduction in hardness and modulus is observed declining sharply from 13.8 GPa (~ 31 at. % a-C:H) to between ~5 and ~9 GPa (~ 43 to 47 at. % a-C:H), respectively. A similar decline in modulus is exhibited with increasing a-C:H content ranging from 144 GPa to less than 70 GPa from ~31 at. % to ~47 at. % a-C:H. The optimum composition in terms of mechanical properties and H/E ratios (> 0.09) are obtained for coatings A (TiC_{1.34}N_{0.51}) and B (TiC_{2.04}N_{0.54}). These films can be promising candidates for graded multilayer coatings where an enhanced lubricity, whilst still maintaining a relatively high H/E ratio, is required.

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Table 2. Relative phase fractions and Ti(N,C) stoichiometries for the TiCN Coatings.

Table 1.

Coatings No.	Stoichiometry	Ti (at.%)	C (at. %)	N (at. %)	Ti/N
A	TiC _{1.34} N _{0.51}	35	47	18	1.94
B	TiC _{2.04} N _{0.54}	28	57	15	1.86
C	TiC _{2.48} N _{0.48}	25	62	12	2.02

Table 2.

Coatings No.	Stoichiometry	Ti(N,C) (mol.%)	a-C:H (at.%)	Ti(N,C) _x phase stoichiometry	Ti(N,C) phase stoichiometry
A	TiC _{1.34} N _{0.51}	68.9	31.1	Ti(N,C) _{0.97}	Ti(N _{0.51} C _{0.45})
B	TiC _{2.04} N _{0.54}	57.4	42.6	Ti (N,C) _{1.05}	Ti(N _{0.54} C _{0.51})
C	TiC _{2.48} N _{0.48}	52.7	47.3	Ti(N,C) _{1.07}	Ti(N _{0.48} C _{0.59})

Figure 1 (Ternary)
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Figure 2 (SEM cross section)
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Figure 3 (XPS)

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Figure 4 (TEM)

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Figure 5 (XRD)
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Figure 6 (Mechanical Properties)
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