

## Structure characterization and tribological study of magnetron sputtered nanocomposite nc-TiAlV(N,C)/a-C coatings

Quanshun Luo,<sup>\*a</sup> Shun Cai Wang,<sup>b</sup> Zhaoxia Zhou<sup>c</sup> and Linghao Chen<sup>a</sup>

Received 16th February 2011, Accepted 20th April 2011

DOI: 10.1039/c1jm10707k

Grown by reactive unbalanced magnetron sputtering in a mixed N<sub>2</sub> and CH<sub>4</sub> gaseous medium, heterogeneous nanocomposite coatings in the Ti–Al–V–N–C system show extraordinarily excellent tribological performance of coated machining tools. Using analytical high-resolution TEM, EELS, FEG-SEM, XRD, and Raman spectroscopy, this paper reports detailed structural and chemical characterization of the coatings grown at various CH<sub>4</sub> : N<sub>2</sub> ratios. Meanwhile, the mechanical and tribological properties were also measured, including hardness, Young's modulus, residual stress and the dry-sliding friction and wear at varying environmental humidity. When CH<sub>4</sub> gas was introduced in the deposition, the structure of the coatings has been found to experience a change from nano-scale TiAlN/VN multilayer architecture to a complex mixture of columnar grains of nc-TiAlV(N,C)/a-C nanocomposites and inter-column network of sp<sup>2</sup>-type amorphous carbon. Carbon incorporation and segregation also shows remarkable influence on the columnar growth model by leading to finer grain size. As compared to the carbon-free nitride coating, the nanocomposite coatings showed substantially reduced residual stress owing to the free-carbon precipitation, whereas the coatings maintained comparable hardness to the carbon-free TiAlN/VN. Their tribological properties were found to be strongly dependent on the environment. In humid air at RH > 30%, the coatings showed low friction coefficient less than 0.4 and extremely low wear rate at a scale of ~10<sup>-17</sup> m<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>.

### Introduction

Hard coatings of transition metal nitrides (TMN) grown by magnetron sputter deposition are important wear resistant materials. In recent years, several technological advances have been made in the synthesis of multi-functional coatings, such as multicomponent alloying, nano-multilayer designing, and self assembly of nanocomposite structures. In the first process, alloying the binary nitride TiN with aluminium and chromium can significantly enhance its oxidation resistance, such as in the development of magnetron sputtered metastable Ti<sub>0.5</sub>Al<sub>0.5</sub>N coating.<sup>1,2</sup> In the ternary Ti–Al–N system, further increase of the Al content leads not only to increased oxidation resistance, but also to spinodal precipitation of hexagonal AlN nano-phase in the cubic crystalline matrix to form a nanocomposite structure.<sup>3</sup> Secondly, nano-multilayer TiN/VN coatings having the TiN and VN bi-layer thickness within a few nanometres were reported to have superhardness over 50 GPa, a value double the hardness of the binary nitride components.<sup>4</sup> The

concept of lamellate structure with super hardness and strength was first introduced by Koehler.<sup>5</sup> Up to now, polycrystalline multilayer nitride coatings have been successfully developed to show excellent mechanical properties, wear resistance and good performance in various industrial applications.<sup>6–8</sup> Another model of superhard structure, comprising TMN nano-crystallites and a grain boundary phase of resin-like SiN<sub>x</sub>, was first proposed by Veprek and co-workers in the Ti–Si–N system<sup>9,10</sup> and then extended to other systems, such as CrSiN<sup>11</sup> and TiBN.<sup>12</sup> Subsequently comprehensive studies have been carried out on the nanocomposite structure, interface and the hardening mechanisms *e.g.* in refs. 11–16. Despite the superhardness and/or excellent oxidation resistance, however, most TMN coatings exhibit high friction.<sup>17</sup>

Incorporation of carbon during the sputtering growth of TMN coatings can bring about dramatic changes in the structure and properties. Carbon is known to have multiple sp, sp<sup>2</sup> and sp<sup>3</sup> binding characteristics, and thereafter may have a series of different condensed structures having diverse physical and mechanical properties. Considering the fact that carbon coatings, mostly diamond like carbon (DLC), have environment-dependent low friction coefficient, more recently the research interests have been focused in the growth of carbon-containing TMN coatings, such as Ti–N–C,<sup>18–21</sup> Ti–Al–N–C,<sup>22–24</sup> Zr–N–C<sup>25</sup> and Ti–Si–C–N,<sup>26,27</sup> which show both high hardness and environment-dependent low friction. It has been found that

<sup>a</sup>Materials and Engineering Research Institute, Sheffield Hallam University, Sheffield, UK S1 1WB. E-mail: q.luo@shu.ac.uk; Fax: +0044 114 2253501; Tel: +0044 114 2253649

<sup>b</sup>School of Engineering Sciences, University of Southampton, Southampton, UK SO17 1BJ

<sup>c</sup>Department of Engineering Materials, University of Sheffield, Sheffield, UK S1 3JD

a transition from columnar nitride crystallites to a dual-phase structure occurs as a result of the precipitation of free carbon in the coating structure. It is known that many nitride coatings grown by vapour deposition show columnar structure, where the relationship between the deposition conditions and the coating morphology has been established in several models.<sup>28</sup> When carbon is incorporated, it may partially dissolve in the nitride lattice depending on its solubility, whereas the remaining carbon precipitates as a secondary free-carbon phase to form the nanocomposite structure.<sup>18–27</sup> Therefore, the coating growth involves redistribution or segregation of the impinging atoms/ions on the growth front. For a dynamically rough growing surface which often happens in magnetron sputtering deposition, the energy distribution of impinging species depends strongly on the local roughness. In particular, the cone-like column tops receive more incident atoms/ions than the column boundary regions because of the shadowing effect of the latter. Such inhomogeneous energy distribution would influence the structural and chemical characteristics of the carbon phase, such as its crystalline structure, chemical bonding, size and shape, and segregation. Unfortunately, these growth-dependent structural characteristics are less mentioned in previous publications. Up to date, there is still lack of knowledge about evolution of the heterogeneous structure in the sputtering growth of carbon containing TMN coatings.

This paper reports experimental findings of the structural characterisation of magnetron sputtered multicomponent TiAlVCN coatings along with mechanical and tribological tests. The coatings were grown by co-sputtering of TiAl and vanadium targets in a mixed gaseous medium of N<sub>2</sub> and CH<sub>4</sub>. Previously TiAlN/VN multilayers have been developed as candidate coatings for wear protection of machining tools. The TiAlN/VN was found to have high hardness and toughness, lower dry-sliding friction coefficient than other nitride coatings, and extremely low wear rate.<sup>7,8,29</sup> By incorporating carbon in the TiAlN/VN, the deposited coating was found to show substantially extended tool lifetime in dry machining a wrought aluminium alloy.<sup>30</sup> Preliminary research indicated that the outstanding performance should be attributed to the carbon-modified structure of the TiAlVCN coatings although detailed understanding was not available.<sup>31</sup> This paper reports comprehensive structural characterisation of the carbon-incorporated TiAlVCN coatings by using analytical and high-resolution transmission electron microscopy (TEM) with electron energy loss spectroscopy (EELS), field emission gun scanning electron microscopy (FEG-SEM) energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and Raman spectroscopy. The experimental findings reported in this paper are expected to improve the understanding of carbon–TMN nanocomposite coatings regarding the chemical states of carbon and the related phase segregation, which therefore contributes to a better control of the mechanical and tribological properties.

## Experimental

### Coating deposition

Multicomponent TiAlVCN coatings were grown on hardened and polished high speed steel coupons (M2, nominal chemical

compositions in wt%: C 0.8, Si 0.3, Mn 0.3, Cr 4.0, Mo 6.0 and V 2.0; hardness HV 7.9 GPa) by unbalanced magnetron (UBM) sputtering using an industrial scale PVD unit, the Hauzer HTC-1000-4 system. Two pairs of face-to-face pure vanadium targets and Ti<sub>0.5</sub>Al<sub>0.5</sub> targets were employed in the sputtering deposition. After pre-heating to 450 °C in the vacuum chamber, the samples were etched by mixed vanadium and argon ions when one of the two vanadium targets was operated at cathodic glow discharge mode at –1200 V. Then the system was operated under UBM sputtering mode at a substrate bias voltage of –75 V, to grow a VN base layer, 0.4 μm thick, and then the TiAlVCN coating. During the TiAlVCN deposition, carbon was incorporated by introducing a mixed N<sub>2</sub> + CH<sub>4</sub> + Ar atmosphere with separately controlled N<sub>2</sub> and CH<sub>4</sub> fluxes. By adjusting the inletting gas fluxes to make the N<sub>2</sub> to CH<sub>4</sub> ratios to be 3 : 1, 2 : 1 and 1 : 1 in a rank of increasing CH<sub>4</sub> incorporation, three versions of TiAlVCN coatings were grown, namely TiAlVCN-1, TiAlVCN-2 and TiAlVCN-3 as shown in Table 1. The total coating thickness was 3.0–3.2 μm as determined using the calotest method.

### Mechanical and tribological tests

A Mitutoyo MVK-H2 Knoop hardness tester was used for coating hardness measurements. The applied indenting load was 25 g, making the indenting depth less than 10% of the coating thickness. A Fischerscope H100 depth-sensitive indentation tester was used to measure the Young's modulus at an indentation load of 50 mN. The *E* values were calculated by following the Oliver–Pharr model.<sup>32</sup>

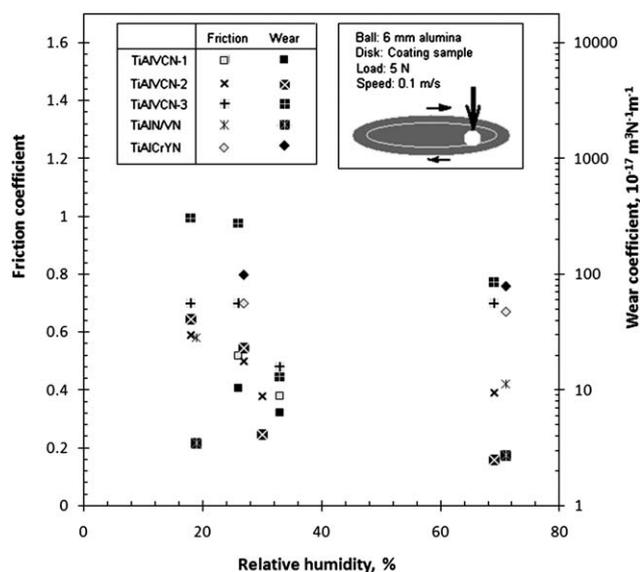
A room-temperature ball-on-disk tribometer was employed to investigate the friction and wear properties at ambient conditions. A schematic sketch is inserted in Fig. 1 to show the ball-on-disk configuration. The applied tribo-test conditions were: applied normal load of 5 N, linear sliding speed of 0.1 ms<sup>–1</sup>, a 6 mm diameter alumina ball as the sliding counterface, and a range of atmospheric relative humidity between 18 and 72%. Prior to each test, both the disc and ball samples were cleaned with acetone and dried in air. During each tribo-test, the coefficient of friction was continuously acquired to the computer at a preset frequency of 1 Hz to obtain the friction curve and to calculate the steady friction coefficient. After each test, the obtained wear track was scanned using a laser profilometer to measure the wear track cross-section and thereafter to calculate the wear coefficient.

### Characterizations

A FEG-SEM, FEI Nova-200, was employed to observe the coating surfaces. Chemical compositions of the deposited coatings were determined using the attached ultra-thin windowed EDX system. Since SEM-EDX is known for its limited precision in analysing light elements other complementary analyses were applied to determine the carbon and nitrogen. Raman microspectroscopy was conducted by employing a Renishaw-2000 Raman System to characterize the substructures of nitride and free carbon in the deposited coatings. The instrument utilizes a He–Ne laser with an excitation wavelength of 632.8 nm, allowing a lower spectral limit of 150 cm<sup>–1</sup> and upper limit of

**Table 1** Chemical composition, Young's modulus and hardness of the investigated materials

	Composition (at%)					<i>E</i> /GPa	HK <sub>0.025</sub> /GPa
	C	N	Al	Ti	V		
TiAlVCN-1	2.95 ± 2.38	39.71 ± 6.02	13.02 ± 1.67	15.21 ± 1.71	28.94 ± 4.17	335.3 ± 27.0	29.3 ± 0.7
TiAlVCN-2	5.72 ± 0.47	36.83 ± 2.90	11.67 ± 0.41	15.38 ± 1.50	30.09 ± 1.54	296.9 ± 32.6	28.1 ± 1.4
TiAlVCN-3	6.48 ± 1.17	39.88 ± 4.44	12.14 ± 0.76	13.93 ± 1.23	27.20 ± 1.89	181.2 ± 14.1	9.9 ± 1.1
TiAlN/VN	—	38.63	14.36	17.08	29.94	417.0 ± 13.7	37.2 ± 2.6
C/Cr	C: 31.49		Cr: 68.51			212.3 ± 1.6	11.9 ± 1.6



**Fig. 1** Steady-state friction coefficient and wear coefficient of TiAlVCN, TiAlN/VN and TiAlCrYN coatings measured in various environment relative humidity in ball-on-disk sliding tests against an alumina ball counterface.

2000  $\text{cm}^{-1}$ . Spectra were acquired at frequency range of 200–1800  $\text{cm}^{-1}$  covering the acoustic and optical vibration bands of transition metal nitrides and the disordered and graphite bands of carbon. The crystallography and residual stress were analysed using a Philips X-Pert X-ray diffractometer operating with a Cu-K $\alpha$  radiation source (40 kV and 40 mA, wavelength  $\lambda = 0.154056$  nm). Residual stress measurements were undertaken using the XRD- $\sin^2\psi$  technique optimised in our recent research.<sup>33</sup> The {220} plane of the nitride phase was selected to collect the diffraction peaks at a series of fixed incident angles.

Extensive structure characterizations were carried out using analytical and high-resolution TEM, including Philips CM20 (200 kV, LaB<sub>6</sub>), JEOL 3010 (300 kV, LaB<sub>6</sub>), and JEOL 2010F (200 kV, field emission gun) equipped with EELS capability. For the EELS analysis, core loss spectra were acquired to show the C-K, N-K, Ti-L<sub>2,3</sub> and V-L<sub>2,3</sub> edges at a routine energy resolution of 1.2 eV. To ensure acquisition from sample areas thin enough to avoid the need for correction of the spectrum for plural scattering, it was verified that the plasmon intensity was less than one tenth of the zero-loss peak intensity. Cross-sectional TEM samples were prepared by using a Gatan-691 precision ion polishing system operating at 3.0–5.0 kV and low sputtering angles of 5°–8°.

## Results

### Chemical composition, mechanical and tribological properties

Table 1 lists the chemical compositions, hardness and elastic modulus of the TiAlVCN coatings. The properties of the carbon-free TiAlN/VN coating and a carbon-based C/Cr coating<sup>34</sup> are also listed for reference. The TiAlVCN coatings show similar chemical compositions to the TiAlN/VN except for their carbon contents. In the former, carbon incorporation has been detected. However, the EDX determined carbon contents are very low, which might be caused by high mass absorption of low energy X-rays, a well known limitation for SEM-EDX to measure light elements. More characterizations of carbon were carried out using both Raman spectroscopy and TEM-EELS, to be shown later.

Carbon shows remarkable influence on both the hardness and elastic property. The coatings TiAlVCN-1 and TiAlVCN-2, being deposited at CH<sub>4</sub> : N<sub>2</sub> ratios of 1 : 3 and 1 : 2 respectively, exhibit hardness and Young's modulus values only slightly lower than the TiAlN/VN. TiAlVCN-3, grown at a CH<sub>4</sub>:N<sub>2</sub> ratio of 1 : 1, is much softer and with lower elastic modulus, similar to the properties of the C/Cr coating.

Fig. 1 shows the steady state friction coefficient and wear coefficient of the TiAlVCN coatings measured in a range of relative humidity, RH = 18–70%. The experiment results of two carbon-free coatings, the TiAlN/VN multilayer and the TiAlN-based TiAlCrYN, are also included for comparison. All the coatings show environment dependent friction and wear coefficients, having lower friction and lower wear at higher humidity. The TiAlVCN coatings show pronounced dependence of both friction and wear on the environment humidity. The friction coefficients of the TiAlVCN-1 and TiAlVCN-2 coatings are higher than 0.5 and the wear coefficients in the range of 10<sup>-16</sup> m<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup> when the relative humidity is below 30%. A prompt decrease of friction and wear occurs when the relative humidity increases to 30% and higher, where the friction coefficient becomes less than 0.4 and the wear coefficient reduces to the scale of 10<sup>-17</sup> m<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>. In addition, the TiAlVCN-3 coating shows extra-ordinarily high friction and wear. This was caused by the low hardness of the coating triggering severe deformation and abrasive wear. In comparison, the TiAlN/VN coating shows remarkable decrease of friction coefficient from 0.58 to 0.42 with increasing humidity. The wear coefficients of the TiAlN/VN coating are in the scale of 10<sup>-17</sup> m<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>, being comparable to previous experiment results.<sup>35</sup> TiAlCrYN exhibits high friction and wear whereas the variation of humidity shows marginal influence. In brief, the tribological experiments suggest that the

incorporation of carbon in the TiAlVCN coatings brings about pronounced environmental-dependence of friction and wear properties as compared to the carbon-free nitride coatings.

### Conventional structural characteristics and growth morphology

Fig. 2 shows XRD traces of the TiAlVCN and TiAlN/VN coatings. Considering the small coating thickness, the XRD scans were made using a fixed incident angle of  $\Omega = 3^\circ$  whereas the detector scanned over the pre-defined range of  $30\text{--}100^\circ$ . The XRD analysis suggests that the TiAlVCN coatings exhibit NaCl-type cubic crystalline structure, similar to TiAlN/VN. Precise measurements of residual stress and stress-free lattice constant were undertaken on the TiAlVCN coatings to compare with TiAlN/VN and results are shown in Table 2. The TiAlN/VN coating exhibits high compressive residual stress of  $-10.06$  GPa. In contrast, the residual stress values in the TiAlVCN coatings are lower and dependent on the  $\text{CH}_4 : \text{N}_2$  ratio, from  $-7.56$  GPa in TiAlVCN-1 to  $-1.34$  GPa in TiAlVCN-3. The stress-free lattice constant values of the TiAlVCN coatings, between  $0.4161$  and  $0.4168$  nm, are consistent to each other but slightly higher than the constant of TiAlN/VN ( $0.4107$  nm), which account for a difference of  $0.0057$  nm or a relative variation of  $1.39\%$ . Similar expansion of metal nitride caused by partition of carbon was reported in the literature<sup>21,22</sup> in a series of carbon-containing TiN coatings, in which the lattice parameter of the Ti(N,C) carbonitride was reported to be between the lattice constants of TiN ( $a_0 = 0.426$  nm) and TiC ( $a_0 = 0.432$  nm). Therefore, in the current study, the measured lattice expansion should be an indication of partial carbon partition in the TiAlVN nitride to form TiAlN(N,C) carbonitride.

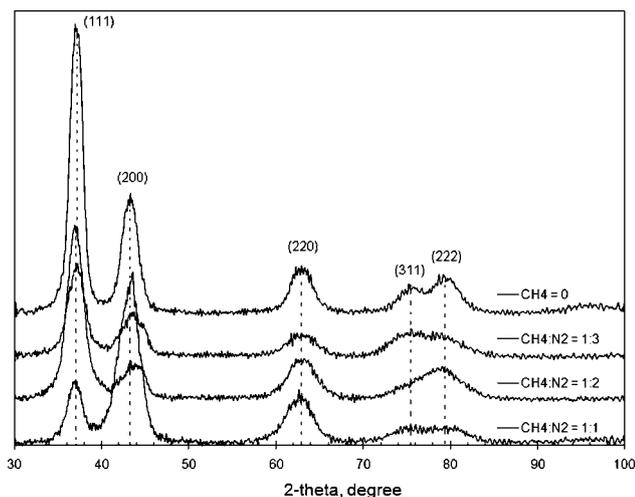
Typical high-resolution FEG-SEM images of the TiAlVCN coatings are shown in Fig. 3. The coatings exhibit nano-scale rough surfaces having cellular-like topography. According to previous cross-sectional TEM work,<sup>36</sup> each cellular cell corresponds to the top of a columnar grain. The carbon-free TiAlN/VN coating shows sub-micron scale surface grain size, Fig. 3a. The incorporation of carbon can be found to result in smaller grain sizes down to nano-scale, Fig. 3b–d. In addition, FEG-

**Table 2** Residual stress and the stress-free lattice constants

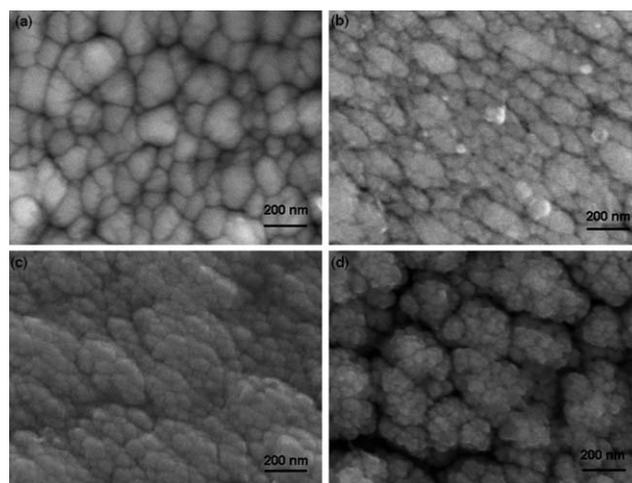
	Residual stress/GPa	Lattice parameter/nm
TiAlN/VN	$-10.06 \pm 2.61$	0.4107
TiAlVCN-1	$-7.56 \pm 0.31$	0.4168
TiAlVCN-2	$-5.48 \pm 0.75$	0.4161
TiAlVCN-3	$-1.34 \pm 0.40$	0.4163

SEM observations also reveal variation of coating morphology. Whereas the TiAlVCN-1 mainly exhibits reduced grain size as compared to the TiAlN/VN, the TiAlVCN-2 and TiAlVCN-3 coatings show sub-micron scale block cells and each block cell contains up to tens of sub-cells of identical nano-scale size. In particular, the boundaries of the block cells on the TiAlVCN-3 coating surface become valleys, suggesting the formation of a sub-dense coating structure. Statistic profiles of the cell diameters of the coatings are shown in Fig. 4, each having been determined by more than 150 measurements. The TiAlN/VN coating shows a broad range of grain size from  $50$  to  $160$  nm. Compared to the TiAlN/VN, all the TiAlVCN coatings exhibit reduced grain sizes depending on the  $\text{CH}_4 : \text{N}_2$  ratio, *i.e.* higher  $\text{CH}_4 : \text{N}_2$  ratio leading to smaller grain size. The extreme case was found in the TiAlVCN-3 sample in which the grain size is only about  $40$  nm.

Cross-sectional TEM observations indicated that the TiAlVCN coatings have dense columnar structure with sub-dense column boundaries. A typical bright field (BF) TEM image is shown in Fig. 5. Selected area diffraction analysis, giving the pattern inserted in Fig. 5, shows strong diffraction arcs of the  $\{111\}$ ,  $\{200\}$  and  $\{220\}$  planes of NaCl-type cubic structure, with the  $\{220\}$  diffraction arc being perpendicular to the growth direction, indicating a strong (220) texture. These characteristics are identical to those of carbon-free TiAlN/VN grown under the same conditions. In previous research, we have found that these were related to the low substrate bias voltage of  $-75$  V in the UBM sputtering deposition.<sup>36</sup>



**Fig. 2** X-Ray diffraction curves of the TiAlVCN coatings, with  $\text{CH}_4 : \text{N}_2 = 1 : 3, 1 : 2$  and  $1 : 1$ , and the TiAlN/VN coating ( $\text{CH}_4 = 0$ ).



**Fig. 3** High-resolution SEM images of the TiAlVCN coating surfaces: (a) TiAlN/VN coating at  $\text{CH}_4 = 0$ ; (b) TiAlVCN-1 at  $\text{CH}_4 : \text{N}_2 = 1 : 3$ ; (c) TiAlVCN-2 at  $\text{CH}_4 : \text{N}_2 = 1 : 2$ ; and (d) TiAlVCN-3 at  $\text{CH}_4 : \text{N}_2 = 1 : 1$ .

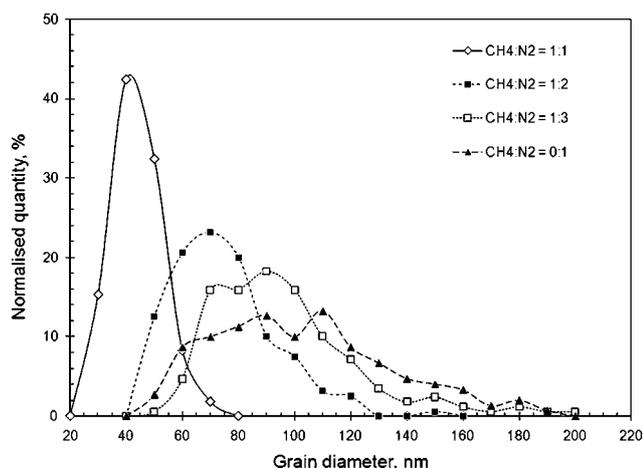


Fig. 4 Profile of grain sizes of the TiAlVCN and TiAlN/VN coatings.

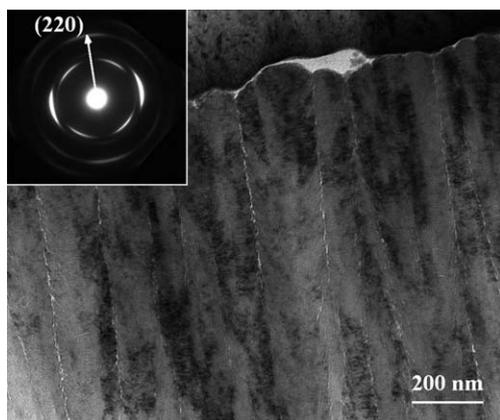


Fig. 5 Cross-section TEM BF image of the TiAlVCN-2 coating, showing dense columnar morphology. The inserted SAD pattern suggests its cubic crystalline structure and (220) texture.

However, while TiAlN/VN coatings showed nano-scale multilayer fringes in high magnification cross-sectional BF imaging,<sup>36</sup> such fringes were not observed in the TiAlVCN coatings. A comparison between the two types of coatings is shown in Fig. 6. The TiAlN/VN coating shows typical arch-like multilayer fringes in each column grain, representing mass-difference between the TiAlN (bright) and VN (dark) sub-layers.

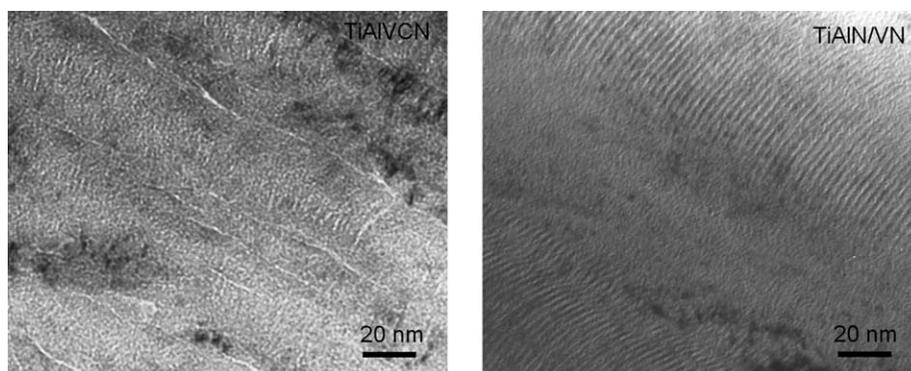


Fig. 6 Comparison of cross-sectional TEM BF micrographs of the TiAlVCN and TiAlN/VN coatings, showing different multilayer fringes.

In the TiAlVCN coating, the BF image shows irregular bright lines aligned perpendicular to the growth direction within each column and bright lines along the column boundaries. These bright features should be related to the low-mass regions of free-carbon domains, which has been confirmed in more comprehensive analyses using Raman spectroscopy, high-resolution TEM and TEM-EELS analysis.

#### Raman spectroscopy of carbon-related structural changes

Raman spectroscopic analysis has been carried out on the TiAlVCN coatings grown under various  $N_2 : CH_4$  ratios as well as on the carbon-free TiAlN/VN. Fig. 7 shows the overall spectra whereas Fig. 8 shows further details of the nitride optical bands and the carbon bands as a function of the  $CH_4 : N_2$  ratio.

The TiAlN/VN coating shows both an acoustic band at  $200\text{--}400\text{ cm}^{-1}$  and an optical band at  $550\text{--}700\text{ cm}^{-1}$ . For transition metal nitrides, Raman spectroscopy detects distortions induced by vacancies, including an acoustic band induced by metal ions and an optical band by non-metal ions.<sup>37</sup> The TiAlVCN coatings also show acoustic and optical bands from their crystalline nitride components. In addition, the optical bands become broader with slightly lower intensity when the  $CH_4$  to  $N_2$  ratio was increased from 1 : 3 to 1 : 1, Fig. 8. As the optical band is induced by vacancies of non-metal ions, this change should be related to the filling-up of some nitrogen vacancies with carbon

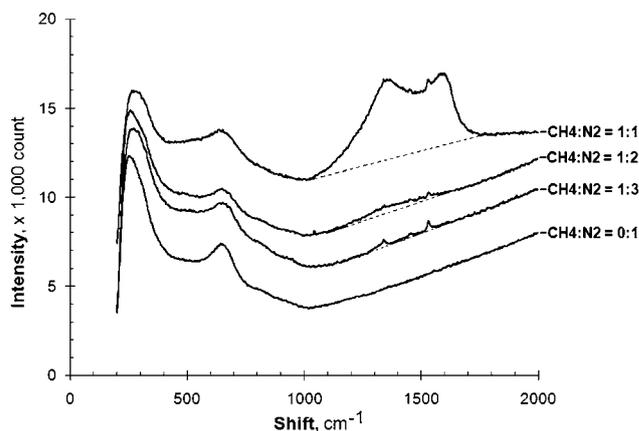
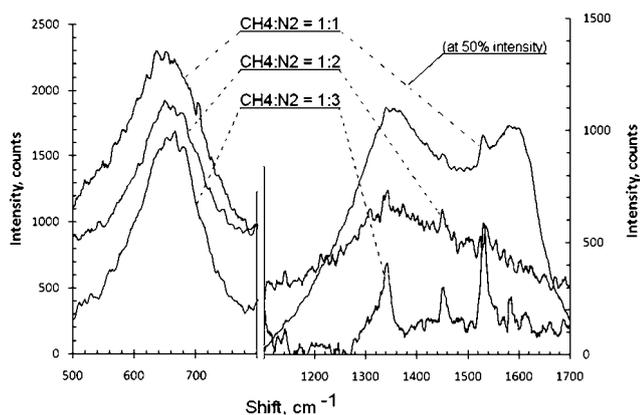


Fig. 7 Raman spectra of TiAlN/VN and TiAlVCN coatings.



**Fig. 8** The Raman optical band ( $500\text{--}800\text{ cm}^{-1}$ ) of nitride and the D and G bands ( $1100\text{--}1700\text{ cm}^{-1}$ ) of free-carbon compared among the TiAlVCN coatings.

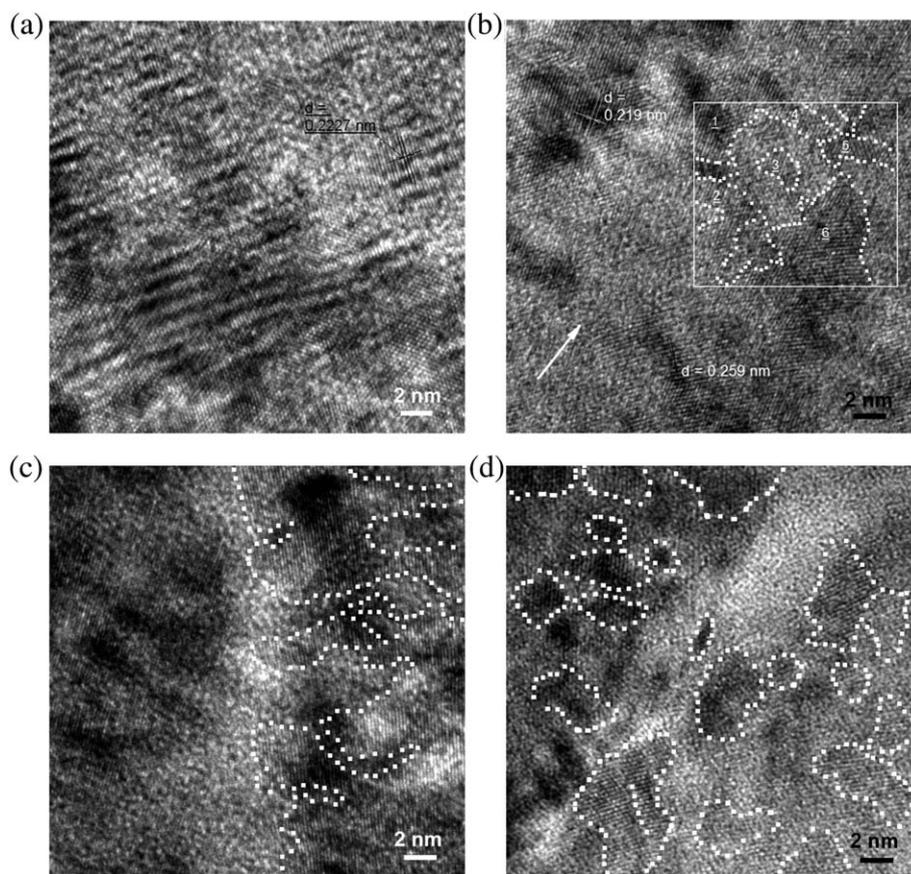
atoms, *i.e.* partial dissolution of carbon atoms in the nitride lattice.

Furthermore, the TiAlVCN coatings have a composite structure of carbon-containing nitride TiAlV(N,C) and amorphous condensed carbon. The coatings TiAlVCN-1 and TiAlVCN-2 also show two low and broad peaks in the spectra, namely the D (disordered) band at  $1346\text{ cm}^{-1}$  and G (graphite) band at  $1533\text{ cm}^{-1}$  respectively. The observed D/G bands evidence the

presence of free carbon domains. According to ref. 38 the D band arises from the breathing modes of  $\text{sp}^2$  atoms in clusters of six-fold aromatic rings, whereas it is forbidden in perfect graphite structure and is only active in disordered carbon. The G band arises from the in-plane bond-stretching motion of pairs of  $\text{sp}^2$  carbons of graphite. Thus, the D/G bands in Fig. 7 suggest disordered carbon instead of crystalline graphite. Moreover, the volume fraction of free-carbon would be very small for the TiAlVCN coatings grown at  $\text{CH}_4:\text{N}_2$  ratios of 1:3 and 1:2, which is suggested by comparing the intensities between the nitride optical band and the D/G bands. When the  $\text{CH}_4$  to  $\text{N}_2$  ratio was increased to 1:1, the D/G bands show two broad peaks and are more pronounced than the acoustic and optical bands of the nitride, implying that amorphous carbon became a major component of the coating.

### High-resolution TEM of nano-crystalline structure

More details of the composite structure were observed using high-resolution TEM at phase contrast imaging. Selected results are shown in Fig. 9. In Fig. 9a, the TiAlN/VN coating exhibits typical polycrystalline structure with long-range lattices. The observation is similar to the previous high-resolution TEM of similar TiAlN/VN coatings.<sup>39,40</sup> The Moire fringes in Fig. 9a were caused by overlapping of sub-grains. In Fig. 9b–d, the TiAlVCN-1 and TiAlVCN-2 coatings show mixed structures containing



**Fig. 9** Cross-sectional high-resolution TEM micrographs: (a) the in-column structure of TiAlN/VN; (b) the in-column structure of TiAlVCN-1, where the coating growth direction is indicated by an arrow; (c) the column boundary area of TiAlVCN-1; and (d) the column boundary area of TiAlVCN-2. The white dots inserted in the images help identify the boundaries between ordered and disordered regions.

both ordered and disordered regions, which can be identified as crystalline TiAlV(N,C) and amorphous carbon, respectively. The amorphous carbon distributes preferentially along the column boundaries and inside the columnar grains. The amorphous carbon inside the columns occurs as nano-scale domains having multilayer-like profile. In Fig. 9b, the in-column structure of the TiAlVCN-1 coating comprises TiAlV(N,C) nanocrystallites separated by amorphous carbon. In Fig. 9c, the boundary area between two columns is completely disordered and exhibits brighter contrast, suggestive of segregated amorphous carbon. A similar structure was observed in the TiAlVCN-2 sample. In Fig. 9d, the two columns exhibit a mixture of crystallite islands separated by an amorphous medium. The column boundary area is also completely amorphous.

Thus, according to the definition described in the literature,<sup>9–15,19–22</sup> the TiAlVCN coatings can be termed as nanocomposites of nc-TiAlV(N,C)/a-C, namely nano-crystalline TiAlV(N,C) and amorphous carbon.

The high-resolution TEM observation also provides structural details about the nanocomposition formation. First, it is noted that most of the nano-crystalline domains within each columnar grain exhibit an identical lattice orientation. These nano-crystallites are more like sub-grains of a single columnar grain, instead of randomly oriented crystallites caused by re-nucleation in

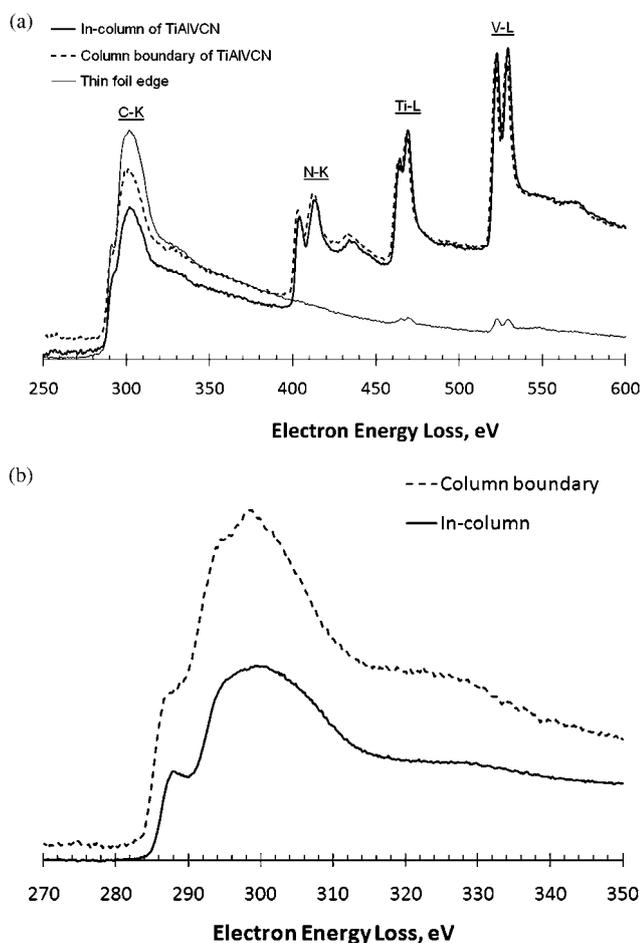
completely interrupted growth. This finding is important as it evidences that the precipitation of condensed carbon did not completely block the columnar crystalline growth. Instead, the growth might proceed continuously between the condensed carbon domains. Such growth agrees with the model suggested in the literature.<sup>28</sup> Secondly, the lattice fringes in the obtained high-resolution TEM images were measured to calculate the lattice parameters. Similar analyses have also been reported by other researchers.<sup>21,22,39,40</sup> The results show that the TiAlVCN-1 and TiAlVCN-2 coatings exhibit lattice constants of  $0.449 \pm 0.004$  and  $0.448 \pm 0.004$  respectively, in which each value was calculated from nine measurements. The TiAlN/VN coating shows a constant of  $0.444 \pm 0.004$  nm. Again the measured lattice constants of the TiAlVCN-1 and TiAlVCN-2 coatings are comparable to each other but larger than of TiAlN/VN by 0.96 or 1.17%. This result is consistent with the XRD measurement as shown in Table 2. Obviously, the lattice expansion implies partial substitution of nitrogen ions by the incorporated carbon. In addition, it may be argued that the  $a_0$  values obtained from TEM measurements are systematically higher than the XRD measurements (Tables 2 and 3). However, because identical TEM imaging conditions were applied to all the samples, this method is available to reveal the relative variation by comparing the obtained  $a_0$  values.

### TEM-EELS analysis

TEM-EELS analysis has been conducted on samples TiAlVCN-1 and TiAlVCN-2 to explore the structural and chemical characteristics. Spectra were acquired at several areas of the cross-section TEM foil: within a TiAlVCN column grain; at the column boundary region; and at the extremely thin edge with  $t/\lambda = 0.19$ , where  $t$  is the foil thickness and  $\lambda$  the mean free path of approximately 100 nm. Fig. 10a shows the acquired core loss spectra and Fig. 10b provides more details of the C-K edge. In Fig. 10a, the edges of C-K, N-K, Ti-L<sub>2,3</sub> and V-L<sub>2,3</sub> are well distinguished from each other. Each edge shows an ionization threshold followed by a well-shaped pattern. The characteristic energy loss values of the edges are summarised in Table 3.

The EELS analysis addresses several findings. In the first, the spectra exhibit almost identical N-K, Ti-L<sub>2,3</sub> and V-L<sub>2,3</sub> edges, in terms of energy positions and the edge shapes, as compared to the carbon-free TiAlN/VN coating.<sup>41</sup> In particular, the N-K edge follows the ionization threshold at 398.5 eV consists of two strong narrow peaks at 403.5 and 412.0 eV and a low broad peak at 431.0–438.5 eV, which are typical features of stoichiometric nitrides. It is known that the energy loss near edge structure (ELNES) can be used as ‘fingerprints’ to distinguish compounds of similar chemical compositions because it is sensitive to the changes in the local bonding characteristics, coordination and charge distributions of the ionized atoms.<sup>42</sup> Thus, The ELNES of N-K in Fig. 10a suggests that the nitride crystallites in the TiAlVCN coatings still retain the stoichiometric cubic structure. This conclusion is consistent with the Raman spectroscopy, XRD and TEM-SAD analyses.

Secondly, the EELS analysis reveals preferential distribution of carbon along the column boundaries. As column boundaries of the TiAlVCN coatings show brighter contrast, *e.g.* in Fig. 6a and 9c and d, segregation of light elements was suspected to exist there. The two spectra in Fig. 10a were acquired in the in-column



**Fig. 10** Electron energy loss spectra of TiAlVCN coating: (a) the core-loss spectra at 250–600 eV; (b) the C-K near edge structure.

**Table 3** Energy loss near-edge structure analysis of the TiAlVCN coating: (1) peak positions of the C, N, Ti and V EELS edges; and (2) a comparison of the normalised net peak integrations of the EEL spectra acquired in-column and at column boundary

	C-K	N-K	Ti-L <sub>2,3</sub>	V-L <sub>2,3</sub>
Energy loss edge/eV	285.5	398.5	458.8	516.5
Peak positions/eV	291.5, 301.5	403.5, 412.0, 431.0–438.5	464.0, 468.5	522.5, 529.0
Normalised integration (%)				
Integration window/eV	279.0–307.5	388.0–415.5	449.0–471.0	508.0–531.5
In TiAlVCN column	34	20	18	28
In column boundary	41	19	12	27

region and in the column boundary region, close to each other, and showed similar integrated intensities of the C, N, Ti and V edges, of  $1.14$  and  $1.25 \times 10^6$ , respectively. The similar intensities might indicate comparable sample thickness. Therefore, net peak integration has been made on the individual edges. The normalised intensities are shown in Table 3, which suggest that the column boundary contains more carbon and less titanium than the in-column region. However, the enrichment of carbon at the column boundaries is under-estimated because the focused electron beam would unavoidably have penetrated into the nc-TiAlV(N,C) column since that the column boundaries were non-flat and much narrower than the TEM foil thickness (*i.e.* 50–80 nm based on zero-loss EELS peak estimation). Nevertheless, the determined carbon enrichment along the column boundary agrees with the TEM BF and high-resolution imaging, especially for the fully amorphous column boundary.

Thirdly, the ELNES of the C-K edge suggests graphite-like structure of the amorphous carbon. In Fig. 10b, the C-K edge is featured by an ionization threshold at 285.5 eV and the following components of a broad band around 301.5 eV as well as a small pre-edge resonance at 291.5 eV. The small pre-edge shoulder should correspond to the  $1s-\pi^*$  transition owing to the weak bond of the  $\pi$  electrons. The broad band was attributed to the overlapping  $1s-\sigma^*$  transitions at the  $sp$ ,  $sp^2$  and  $sp^3$  sites. The presence of the  $1s-\pi^*$  transition indicates a  $sp^2$ -type graphite-like structure of the carbon. On the other hand, the main  $1s-\sigma^*$  transition peaks show featureless smooth shape, suggestive of an amorphous structure. These interpretations are in good consistence to the Raman spectroscopy and HR-TEM observation. More detailed interpretations of EELS C-K edges can be found in the literature.<sup>43–46</sup>

Finally, it is noticed that, the edge of the TEM foil exhibits only a strong C-K edge whereas other edges almost disappear. This phenomenon suggests that most of components other than carbon had been sputtered away owing to the difference in the sputtering yields. Sputtering yield is a parameter depending on the characteristics of the solid surface under sputtering and the energy, mass and incident angle of bombarding ions. It was reported that the sputtering yield of carbon accounts for only ~20% of the sputtering yields of Ti and V under Ar-ion bombardment.<sup>47</sup> Consequently, the different sputtering yields resulted in preferential sputtering removal of elements other than carbon during the ion beam milling, which thereafter left an almost pure carbon top layer on the surface of the foil.

## Discussion

By co-sputtering of TiAl and V targets in a reactive atmosphere of mixed  $N_2 + CH_4 + Ar$ , multicomponent coatings in the

Ti–Al–V–N–C system have been grown. In this paper, the influence of carbon incorporation on the formation of the nanocomposite structure has been revealed using sophisticated analytical techniques of SEM, XRD, TEM, EELS and Raman spectroscopy. The relationship between the amount of carbon incorporation and the resulting mechanical and tribological properties has also been established.

## Nanocomposite structure of the magnetron sputtered TiAlVCN coatings

The structure of the composite coatings can be described in terms of three aspects. In the first, the coatings exhibited dense columnar growth morphology, arch-like growth front, sub-dense column boundaries, NaCl-type cubic crystalline, and strong (220) texture (Fig. 5). Such characteristics are identical to the carbon-free TiAlN/VN coatings grown under the same sputtering conditions, except that the grain size decreased with increasing  $CH_4 : N_2$  ratio. Secondly, when carbon was introduced during the TiAlN/VN deposition, the majority of incorporated carbon atoms were found to condense as a separate phase of amorphous carbon, distributing either along the column boundaries or inside the columnar grains as nano-scale islands, which has been confirmed by Raman spectroscopic analysis (Fig. 4 and 5) and high-resolution TEM (Fig. 6). Thirdly, some carbon dissolved in the nitride lattice by occupying some of the octagonal vacancies and or partially replacing nitrogen atoms. The dissolved carbon, forming multicomponent carbonitride TiAlV(N,C), has been found to result in lattice expansion as determined by XRD and HR-TEM (Tables 2 and 3).

Consequently, the TiAlVCN coatings exhibit a complex heterogeneous nano-structure: firstly each columnar grain is a nanocomposite mixture of TiAlV(N,C) nano-crystallites and nano-scale domains of amorphous carbon; secondly the columnar nanocomposite grains and the inter-column amorphous carbon form a three-dimensional 'columnar nano-structure'. Such columnar nano-structures were suggested in the literature.<sup>48</sup> While nanocomposite structures for carbon- and silicon-containing TMN coatings has been repeatedly reported, *e.g.* refs. 9–16 and 18–27, this is the first time that a complex heterogeneous composite structure is found in carbon-containing TMN coatings.

## Kinetics of nanocomposite structure formation

Before discussing the growth kinetics, it is necessary to clarify three concepts, namely the formation of the columnar

morphology, limited solubility of carbon in transition metal nitride, and the formation of amorphous carbon.

Current research suggests that the coatings grown by UBM sputtering exhibited dense columnar structure and rough surfaces. The growth model was predominantly governed by the low substrate bias voltage which resulted in limited mobility of species on the growth front.<sup>36</sup> The incorporation of carbon had been shown to influence the columnar growth by leading to smaller grain size. Moreover, this growth model resulted in preferential distribution of amorphous carbon along the column boundaries.

The limited carbon solubility in the lattice of metal nitrides facilitates accommodation and condensation of carbon atoms at the nitride growth front. In the lattice of transition-metal nitrides, nitrogen occupies the octagonal vacancies. It was reported in literature<sup>21,22</sup> that, in magnetron sputtered Ti–C–N coatings, increasing nitrogen partial pressure in the deposition of TiC coating led to complete replacing of carbon by nitrogen. On the other hand, however, increasing the power applied on the solid carbon (graphite) target during the deposition of Ti(N,C) only resulted in limited dissolution of carbon in the nitride. Instead, the increased carbon content triggered the formation of amorphous carbon. This phenomenon was attributed to the stronger binding of nitrogen relative to carbon, to metal ions. Furthermore, aluminium component in the Ti–Al–V–N–C system was also likely to promote precipitation of amorphous carbon. There are reports<sup>49,50</sup> that non-carbide-forming elements such as aluminium and nickel in the Ti–Al–C or Ti–Ni–C ternary systems tend to repel carbon atoms/ions out of the carbide lattices to promote condensation of free carbon. Such a repelling effect can be explained by the chemical inertness between carbon and these elements. For the same reason, the chemical inertness was claimed to promise good performance of carbon-coated tools in machining aluminium alloys for the prevention of aluminium adhesive built-up on the cutting edge.<sup>17</sup>

Finally, as an element of tetravalent bonding, carbon can form strong  $\sigma$ -bonds out of its four equivalent hybridized 2s- and 2p-orbitals. Depending on the degree of hybridization, carbon may form several structures of  $sp^1$  linear chains,  $sp^2$  planar structures, and  $sp^3$  three-dimensional tetrahedral networks.<sup>51</sup> In particular,  $sp^2$  bonded carbon is featured by strong two-dimensional (in-plane)  $\sigma$ -bonds and weak inter-plane  $\pi$ -bonds, which has been found not only in crystalline graphite, but also in carbon onion clusters, amorphous carbon, as well as in carbon nano-tubes. According to Raman spectroscopy and EELS analysis (Fig. 7, 8 and 10), the carbon clusters in the nc-TiAlV(N,C)/a-C nanocomposites exhibited  $sp^2$  amorphous structure with both strong  $\sigma$ -bonds and weak  $\pi$ -bonds.

The kinetics of the nc-TiAlV(N,C)/a-C nanocomposite formation can be described below.

Initial growth of TiAlV(N,C) crystallites repelled extra carbon atoms towards the growth front surface to result in a gradually thickened carbon-rich layer or clouds. Such a carbon-rich layer was dynamically movable under ion bombarding, and thereafter preferentially filled up the valleys between the cellular-like growing grains and condensed as amorphous carbon with  $sp^2$  hybridized structure. Carbon-rich layers also accumulated upon the growing column fronts as small islands of amorphous carbon. As a result, these islands partially blocked the

continuous growth of the TiAlV(N,C) crystallites. Further crystallization of incident Ti, Al, V and N ions/atoms might take place either by epitaxial growth rounding over the condensed carbon islands, or by forming new nuclei of TiAlV(N,C) upon these islands. It was more likely that the epitaxial growth mode dominated the TiAlV(N,C) nano-crystallite formation. Under such mode, the newly formed crystallites should have identical lattice orientation to the parent grains. Interestingly, this is supported both by TEM-SAD analysis and by HRTEM observations.

### The mechanical and tribological properties of TiAlVCN coatings

Carbon incorporation, through the formation of  $sp^2$  bonded amorphous structure, has shown significant influence on the mechanical properties and tribological behaviours of the TiAlVCN coatings.

It has been frequently reported that nanocomposite nitride coatings showed superhardness.<sup>9–15,25–27</sup> The plastic and elastic properties of composite coatings are determined by both the nano-crystallite nitride and the resin-like grain boundaries. As reported in the literature, an important condition of superhardness is that the interfacial phase has to show strong chemical bonds, such as covalent Si–N bonds, and be extremely thin, *e.g.* a single atomic layer or close.<sup>14</sup> Obviously the coatings investigated in this paper did not meet the condition by showing much thicker  $sp^2$  bonded a-C domains within the composite columns and, more importantly, the heterogeneous distribution of  $sp^2$  bonded a-C in column boundaries. The graphite-like  $sp^2$  chemical structure consists of strong  $\sigma$ -bonds and weak  $\pi$ -bonds. In particular, the weak  $\pi$ -bonding is responsible for low hardness and low elastic modulus. Similar hardness properties can be found in other a-C containing coatings.<sup>24,25</sup> For the TiAlVCN coatings grown under low  $CH_4$  flux, their hardness and *E* modulus were dominated by the major structural component, *i.e.* the nc-TiAlV(N,C). Importantly, the TiAlVCN coatings exhibit slightly lower hardness and elastic modulus than the carbon-free TiAlN/VN coating. The limited decrease of hardness and elastic modulus should be attributed to the two-dimensional network of amorphous carbon along the column boundaries. Interestingly, the lower elastic modulus is beneficial to the mechanical properties by substantial decrease of the residual compressive stress.

The nc-TiAlV(N,C)/a-C composite coatings show friction and wear properties strongly dependent on the microstructure and the test environment. Given that an alumina ball (estimated hardness 15 GPa) was employed as the sliding counterface, high hardness is an essential requirement for the coating to resist plastic deformation and abrasive wear. Therefore, the coatings grown at low  $CH_4$  to  $N_2$  ratios, which showed high hardness values, exhibited low wear rates, whereas that grown at high  $CH_4$  to  $N_2$  ratio showed much higher wear rate, Fig. 1. The strong dependence of friction and wear on the humidity can be explained by the incorporation of amorphous carbon in the coatings. Many carbon based coatings exhibit strongly environmental dependent friction and wear properties.<sup>52,53</sup> In the  $sp^2$  chemical bonding structure of amorphous carbon, the fourth orbital could make feasible self-adhesion of carbon clusters between themselves, or interactions with environmental species, such as [H–O] molecules in humid air, to weaken self-adhesion.

Consequently, a transition from high to low friction was found at RH ca. 30%. At higher humidity, the wear rate can be even lower than for carbon-free TiAlN/VN. In this research, extensive experimental investigations have been carried out on the friction and wear properties as well as the associated mechanisms. However, it is not the topic of this paper to report comprehensive studies of the friction and wear mechanisms, which will be to be published as a separate article.

## Conclusions

1. Multicomponent Ti–Al–V–N–C coatings grown by magnetron sputtering in a controlled mixture of N<sub>2</sub> and CH<sub>4</sub> exhibited columnar cross-sectional morphology, nano-scale rough surface, NaCl-type cubic polycrystalline structure and (220) texture. The structure of the coatings has been characterised to be a complex architecture of columnar grains of nc-TiAlV(N,C)/a-C nanocomposites and an inter-column network of amorphous carbon. For the phase constituents, the majority of carbon atoms/ions were found to condense as amorphous carbon with graphite-like sp<sup>2</sup> chemical bonding, whereas some carbon atoms/ions were dissolved in the TiAlV(N,C) carbonite. Segregation of carbon has been found to play a decisive role in the nanocomposite formation. In the columnar growth, some amorphous carbon condensed on the top of the columnar grains partially covering the front surface, resulting in a composite structure of TiAlV(N,C) nano-crystallites and nano-scale amorphous carbon domains, whereas the amorphous carbon segregated along the column boundaries, forming a two-dimensional network.

2. The coatings grown at low CH<sub>4</sub> : N<sub>2</sub> ratios of 1 : 3 and 1 : 2 were dominated by the nc-TiAlV(N,C) crystallites and therefore exhibited high hardness of 29 GPa, only slightly lower than the TiAlN/VN. Their Young's modulus and residual compressive stress were substantially lower than the latter. Their tribological properties were found to be strongly dependent on the environment. In dry air with RH < 30%, they exhibited high friction coefficient at 0.5–0.7 and high wear rate at the scale of 10<sup>-16</sup> m<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>; in humid air with RH > 30%, their friction coefficient decreased to 0.38–0.5 and the wear rate became extremely low, in the scale of 10<sup>-17</sup> m<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>. The coating grown at high CH<sub>4</sub> to N<sub>2</sub> ratio of 1 : 1 contained a large amount of amorphous carbon, resulting in much lower hardness and Young's modulus, and thereafter triggering higher wear rate by several orders of magnitude.

## Acknowledgements

Partial financial support from The European Commissions, through the research project (Grant No. GRD1-2001-40514), and from Engineering and Physical Sciences Research Council (EPSRC, UK, Grant No GR/N23998/01) is acknowledged.

## References

- W. D. Münz, *J. Vac. Sci. Technol., A*, 1986, **4**, 2717.
- S. Paldeys and S. C. Deevi, *Mater. Sci. Eng. A*, 2003, **342**, 58.
- P. H. Mayrhofer, A. Horling, L. Karlsson, J. Sjolen, T. Larsson, C. Mitterer and L. Hultman, *Appl. Phys. Lett.*, 2003, **83**, 2049.
- U. Helmersson, S. Todorova, S. A. Barnett, J. E. Sandgren, L. C. Markert and J. E. Greene, *J. Appl. Phys.*, 1987, **62**, 481.
- J. S. Koehler, *Phys. Rev. B: Solid State*, 1970, **2**, 547.
- X. Chu, M. S. Wong, W. D. Sproul and S. A. Barnett, *J. Mater. Res.*, 2011, **14**, 2500.
- W. D. Münz, L. A. Donohue and P. Eh. Hovsepian, *Surf. Coat. Technol.*, 2000, **125**, 269.
- P. Eh. Hovsepian, Q. Luo, G. Robinson, M. Pittman, M. Howarth, D. Doerwald, R. Tietema, W. M. Sim and M. R. Stalley, *Surf. Coat. Technol.*, 2006, **201**, 265.
- S. Veprek, S. Reiprich and S. Li, *Appl. Phys. Lett.*, 1995, **66**, 2640.
- M. Kong, W. Zhao, L. Wei and G. Li, *J. Phys. D: Appl. Phys.*, 2007, **40**, 2858.
- Q. M. Wang and K. H. Kim, *Acta Mater.*, 2009, **57**, 4974.
- J. Neidhardt, Z. Czigany, B. Satory, R. Tessadri, M. O'sullivan and C. Metterer, *Acta Mater.*, 2006, **54**, 4193.
- C. Lu, Y. W. Mai and Y. G. Shen, *J. Mater. Sci.*, 2006, **41**, 937.
- L. Hultman, J. Bareno, A. Flink, H. Soderberg, K. Larsson, V. Petrova, M. Oden, J. E. Greene and I. Petrov, *Phys. Rev. B*, 2007, **75**, 155437.
- R. F. Zhang, A. S. Argon and S. Veprek, *Phys. Rev. Lett.*, 2009, **102**, 015503.
- E. Konca, Y.-T. Cheng, A. M. Weiner, J. M. Dasch, A. Erdemir and A. T. Alpas, *Surf. Coat. Technol.*, 2005, **200**, 2260.
- M. Lahres, P. Muller-Hummel and O. Doerfel, *Surf. Coat. Technol.*, 1997, **91**, 116.
- Y. Cheng and Y. F. Zheng, *Surf. Coat. Technol.*, 2007, **201**, 4909.
- D. Martinez-Martinez, C. Lopez-Cartes, A. Justo, A. Fernandez and J. C. Sanchez-Lopez, *Solid State Sci.*, 2009, **11**, 660.
- M. Nose, T. Kawabata, S. Khamseh, K. Matsuda, K. Fujii, S. Ikeno and W. A. Chiou, *Mater. Trans.*, 2010, **51**, 282.
- Y. H. Lu, J. P. Wang and Y. G. Shen, *Appl. Surf. Sci.*, 2009, **255**, 7858.
- Y. H. Lu and Y. G. Shen, *Appl. Phys. Lett.*, 2007, **90**, 221913.
- X. Zhang, J. Jiang, J. Lin and J. J. Moore, *Surf. Coat. Technol.*, 2009, **203**, 3450.
- J. M. Lacker, W. Waldhauser, R. Ebner, R. J. Bakker, T. Schoberl and B. Major, *Thin Solid Films*, 2004, **468**, 125.
- H. K. Li, G. Q. Lin and C. Dong, *J. Inorg. Mater.*, 2010, **25**, 517.
- S. L. Ma, D. Y. Ma, Y. Guo, B. Xu, G. Z. Wu, K. W. Xu and P. K. Chu, *Acta Mater.*, 2007, **55**, 6350.
- R. H. Wei, *Surf. Coat. Technol.*, 2008, **203**, 538.
- P. B. Barna and M. Adamik, *Thin Solid Films*, 1998, **317**, 27.
- Q. Luo, P. Eh. Hovsepian, D. B. Lewis, W.-D. Münz, Y. N. Kok, J. Cockrem, M. Bolton and A. Farinotti, *Surf. Coat. Technol.*, 2005, **193**, 39.
- P. E. Hovsepian, A. P. Ehasarian, A. Deeming and C. Schimpt, *Vacuum*, 2008, **82**, 1312.
- Q. Luo, C. Schimpt, A. P. Ehasarian, L. Chen and P. Eh. Hovsepian, *Plasma Processes Polym.*, 2007, **4**, S916.
- A. R. Franco Jr, G. Pintaúde, A. Sinatora, C. E. Pinedo and A. P. Tschiptschin, *Mater. Res.*, 2004, **7**, 483.
- Q. Luo and A. H. Jones, *Surf. Coat. Technol.*, 2010, **205**, 1403.
- P. Eh. Hovsepian, D. B. Lewis, C. Constable, Q. Luo, Y. N. Kok and W. D. Münz, *Surf. Coat. Technol.*, 2003, **174–175**, 762.
- D. B. Lewis, S. Creasey, Z. Zhou, J. J. Forsyth, A. P. Ehasarian, P. Eh. Hovsepian, Q. Luo, W. M. Rainforth and W. D. Münz, *Surf. Coat. Technol.*, 2004, **177–178**, 252.
- Q. Luo, D. B. Lewis, P. Eh. Hovsepian and W. D. Münz, *J. Mater. Res.*, 2004, **19**, 1093.
- H. C. Barshilia and K. S. Rajam, *J. Mater. Res.*, 2004, **19**, 3196.
- J. C. Sanchez-Lopez, A. Erdemir, C. Donnet and T. C. Rojas, *Surf. Coat. Technol.*, 2003, **163–164**, 444.
- H. Meidia, A. G. Cullis, C. Schonjahn, W. D. Münz and J. M. Rodenburg, *Surf. Coat. Technol.*, 2002, **151–152**, 209.
- M. Kong, N. Shao, Y. Dong, J. Yue and G. Li, *Mater. Lett.*, 2006, **60**, 874.
- Q. Luo, Z. Zhou, W. M. Rainforth and P. Eh. Hovsepian, *Tribol. Lett.*, 2006, **24**, 171.
- F. Hofer, P. Warbichler, A. Scott, R. Brydson, I. Galesic and B. Kolbesen, *J. Microsc.*, 2002, **204**, 166.
- J. C. Sanchez-Lopez, A. Erdemir, C. Donnet and T. C. Rojas, *Surf. Coat. Technol.*, 2003, **163–164**, 444.
- A. P. Merkle, A. Erdemir, O. L. Eryilmaz, J. A. Johnson and L. D. Marks, *Carbon*, 2010, **48**, 587.
- L. Ponsonnet, C. Donnet, K. Varlot, J. M. Martin, A. Grill and V. Patel, *Thin Solid Films*, 1998, **319**, 97.

- 
- 46 A. Alexandrou, H.-J. Scheibe, C. J. Kiely, A. J. Papworth, G. A. J. Amaratunga and B. Schultrich, *Phys. Rev. B: Condens. Matter*, 1999, **60**, 10903.
- 47 S. L. Rohde, Sputtering Deposition, in ASM Handbooks on-line version, *Vol. 5: Surface Engineering*.
- 48 J. Musil, Physical and mechanical properties of hard nanocomposite films prepared by reactive magnetron sputtering, in *Nanostructured Hard Coatings*, ed. J. T. M. De Hosson and A. Cavaleiro, Springer Science + Business Media, LCC, New York, NY, USA, 2006, pp. 407–463.
- 49 M. Lindquist, O. Wilhelmsson, U. Jansson and U. Wiklund, *Wear*, 2009, **266**, 379.
- 50 E. Lewin, B. Andre, S. Urbonaite, U. Wiklund and U. Jansson, *J. Mater. Chem.*, 2010, **20**, 5950.
- 51 A. Krueger, *Carbon Materials and Nanotechnology*, Wiley-VCH, Weinheim, 2010, p. 6.
- 52 L. Xia and G. Li, *Wear*, 2008, **264**, 1077.
- 53 A. Erdemir and C. Donnet, *J. Phys. D: Appl. Phys.*, 2006, **39**, R311.