On the structure and oxidation mechanisms in nanoscale hard coatings

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Abstract. Thin-film structures consisting of alternating nanoscale multilayers show substantial hardness increases compared with monolithic coatings of the constituent materials. Coatings, such as TiAlN/VN are deposited using PVD with individual coating bi-layer thickness of ~3nm. Since TiAlN and VN are isostructural and mutually soluble, mixing of the two layers during deposition is expected, which will inevitably affect properties. Energy filtered TEM using a field emission gun source allowed important information on layer structure, but failed to reveal details <1nm. Spherical aberration corrected scanning transmission electron microscopy (STEM) allowed the composition of individual atomic columns to be probed, which yielded a good match between experiment and numerical models of the layer mixing. For high speed machining operations, the oxidation behaviour of coatings becomes an important consideration. Static oxidation of TiAlN/VN films was studied in the range 550-700°C, and characterised by high temperature in-situ XRD and STEM/EDX/EELS of selected surface cross-sections. Oxidation of the TiAlN/VN coating started at ≥550°C with the VN being the first component to oxidise. At temperatures >600°C, a duplex oxide structure was formed, with several phases observed, including V₂O₅, TiO₂ and AlVO₄, with V₂O₅ being the dominant oxide at the outer layer at 638°C. These coatings exhibit low friction in dry sliding which is believed to arise from the inherently low friction of V₂O₅. Focused ion beam studies of wear tests at 630°C confirmed that the contact surface comprised small (~50nm), equiaxed and largely agglomerated V₂O₅ crystals, confirming the hypothesis.

1. Introduction:
Multilayer thin film coatings have been developed for some years for high temperature wear resistance, for example in high speed machining without a coolant. The high hardness of the coatings originates from the nm scale of the multilayer structure, although the exact origin of the hardness is still a matter of debate (see Scripta Mater. Viewpoint set No. 34 (2004)). The hardness of the multilayer is a function of the layer thickness, for example the optimum is around 3-4nm for TiAlN/CrN [1].

The hardness of a multilayer coating is clearly dependent on the structure of the interface between each layer. Nitride multilayers such as the TiAlN/VN reported here, are isostructural and mutually miscible. In the industrial scale coating unit used, mixing of the constituents between layers is inevitable because of the absence of shutters, with the substrate rotated between 4 targets. The exact mixing profile will be further complicated by the 3-fold rotation of the substrate, which is essential to permit homogeneous coating of complex shaped substrates, such as cutting tools.

Irrespective of which mechanism is taken to explain the high hardness of nm scale coatings, it is clear that the degree of this interfacial mixing will have a strong effect on mechanical properties.
However, the size and isostructural nature of the layers and the similar lattice parameters places severe demands on the techniques to characterise the interface and degree of intermixing. Coherent high resolution imaging and energy filtered TEM, both using a FEG source and a high resolution pole piece, failed to provide adequate resolution to determine the interface structure [2]. Therefore, in this work, Cs corrected STEM was used to characterise the interface and degree of mixing between layers.

Along with wear resistance, oxidation resistance is an equally important attribute for such coatings. TiAlN has inherently good oxidation resistance, with significant oxidation initiating at around 750°C. The addition of VN reduces the temperature for the onset of oxidation to around 550°C. However, the products of oxidation are believed to be Magnéli phases (e.g. \( V_nO_{2n-1} \), \( V_nO_{3n-1} \) or \( V_nO_{3n-2} \) with the rutile structure), which are easily shearable and consequently promote low friction coefficients during contact between two surfaces. Wear testing of TiAlN/VN coatings yields significantly lower friction than similar coatings such as TiAlN/CrN, and some evidence of \( V_2O_5 \) has been found in wear debris by Raman spectroscopy. However, little is known about the oxidation sequence, and the relative importance of the oxidation of the TiAlN and the VN. This paper examines the oxidation sequence and therefore the likelihood of beneficial Magnéli phases being formed.

2. Experimental procedure:

TiAlN/VN superlattice coatings were grown on a stainless steel substrate by reactive unbalanced magnetron (UBM) sputtering in an industrial scale physical vapour deposition coating machine (HTC-1000 ABS, manufactured by Hauzer Techno Coating BV, Venlo, The Netherlands). In order to improve adhesion and control residual stresses, the surface was firstly metal ion etched, followed by the deposition of a ~250nm VN base layer by UBM sputtering. The main coating was then deposited using at substrate bias voltages of \( U_B = -75 \) V and \( U_B = -85 \) V, at 450 °C in a common Ar+N\(_2\) atmosphere at a total pressure of \( 4.5 \times 10^{-3} \) mbar. Samples for coating had 3-fold rotation throughout the deposition process.

Thermo-gravimetry (Cahn TG 131 microbalance) was used to define the oxidation kinetics and therefore the most appropriate temperature for study. Based on this isothermal heat treatment was undertaken a various temperatures between 550°C and 670°C, with the results at 600°C and 638°C tests reported here. This temperature was selected on the basis of XRD results (Philips MRD-Xpert) which indicated that \( V_2O_5 \) was a dominant oxide formed.

TEM cross-sections were prepared in the normal manner. Conventional high resolution TEM (HREM) was performed on a JEOL 2010F UHR (point resolution ~0.19nm) with a field emission gun at 200kV. The specimen was subsequently examined at the SuperSTEM Laboratory in Daresbury, UK, the full details of which are provided elsewhere [3]. HAADF images were acquired using a 0.1nm probe (although drift in the system may have led to a small increase in probe size with time), which yielded atomic resolution. The HAADF detector acceptance angle was 70 - 210 mrad. EEL spectra were acquired with the same probe size and with the detection angle roughly equal to the beam convergence angle (half angle 24mrad). The probe was moved 120 points along a line of 16nm (internally calibrated with the Si substrate) and held at each point with an exposure of 4 seconds to acquire the spectrum plus a fast letterbox-like HAADF scan of the area around. The effective scan trace was deduced from HAADF images recorded immediately before and after the EEL measurement. The additional letterbox scans were used to identify possible deviations from the assumed constant drift rate. Intensity profiles were then derived from net edge integration of the \( N K \), \( Ti L_{2,3} \) and \( V L_{2,3} \) ionisation edges, following background subtraction, with the background profile determined across the energy range. In order to obtain relative concentrations, the net edge intensities were normalized by inelastic Hartree-Slater cross sections and it was assumed that the stoichiometry was described by \( V_{1-x}Ti_{0.5x}Al_{0.5x}N \).

3. Results and discussion

Fig. 1a shows Fresnel contrast bright field image of the multilayer structure. Ti \( L_{2,3} \) and V \( L_{2,3} \) energy filtered maps (Fig.1b and c) suggested the complementary distribution of the layer structure.
Although the EFTEM spatial resolution of around 1nm was not sufficient to fully characterize the chemical distribution between the layers, it did clearly show a compositional modulation with a repeat of 4 layers. This was attributed to the 3rd fold rotation during deposition, details are given elsewhere [2]. Fig.1d and e give conventional high-resolution electron micrograph and HAADF image of the coating from around a position close to the base of the coating, acquired on the 2010F and SuperSTEM using a nominally 0.1nm beam respectively, taken from [3]. The conventional HREM image does not reveal the position of the layers, or the interface between layers because TiAlN and VN have the same structure and similar lattice parameter (0.418nm for TiAlN and 0.414nm for VN). However, for the HAADF image, if dynamical electron scattering is ignored, the signal in the image is \( \alpha Z^2 \). As noted in the introduction, TiAlN and VN are isostructural and intermixing of Ti and V is inevitable and therefore the atomic columns imaged probably consist of mixed Ti, Al and V (of course the N is not imaged because of the low scattering amplitude). However, the location of the VN and TiAlN layers can be seen, since the V-dominant columns have a higher average of the squared atomic number, giving brighter contrast. The image demonstrates that there is partial coherency between layers, as expected. The (200) planes are perpendicular to the layers and therefore the interface between layers is approximately along (220). However, the image also reveals the irregular nature of the interface, something that was not resolved by EFTEM or CTEM. Indeed, the layers appear to be irregular to the point that in some areas the VN layers may not be fully separated.

Fig. 1. a) Fresnel contrast bright field TEM micrograph of the multilayer structure b) Ti L\textsubscript{2,3} EFTEM image and c) V L\textsubscript{2,3} EFTEM image. d) Coherent HREM micrograph of the multilayer structure. e) HAADF image showing the multilayer structure (layers run top to bottom with the VN brighter than the TiAlN, see text). f) EEL line scan data (solid lines) along with numerical calculations of the intermixing (dotted lines). After Zhou et al. [2].

Fig. 1f gives experimental and calculated compositional profiles from a line scan from a region close to that shown in Fig. 1b. The experimental data was obtained by moving the nominally 0.1nm probe 120 points along a line of 16nm, holding at each point with an exposure of 4 seconds to acquire the EEL spectrum. The full details of the numerical calculation are given in [2]. The match between the experimental and calculated profiles is very good. Thus, the data and model both indicate an interface region between individual layers of ~1nm, and that V and Ti are present throughout the coating, such that no individual layer is pure VN or TiAlN. The intermixing of layers will have reduced the interfacial coherency strains and Koehler force arising from modulus mismatch.
The full details of the high temperature oxidation are reported elsewhere [4]. High temperature XRD showed that V$_2$O$_5$ was first detected at 597ºC, and the intensity increased to a peak at 638ºC, followed by a decrease to zero around ≥678ºC, consistent with the melting temperature of this phase. SEM showed that much of the outer oxide at 638ºC was V$_2$O$_5$. AlVO$_4$ was found at ≥608ºC and TiO$_2$ at 600ºC onwards.

Fig. 2 gives a bright field STEM image from a cross-section of the coating/oxide interface following oxidation at 600ºC for 30mins together with the electron diffraction evidence to identify the crystals in the top layer (arrowed) as AlVO$_4$ (left) and TiO$_2$ (right). The oxide shows a duplex structure. The inner region has a nanocrystalline structure, with extensive porosity, while the outer region exhibits a heterogeneous mix of larger crystals. Diffraction studies of the outer layer positively identified V$_2$O$_5$, TiO$_2$, and AlVO$_4$. The extreme outer layer contained a significant proportion of V$_2$O$_5$. Thus, small amounts of TiO$_2$ and AlVO$_4$ were present at 600ºC, although in insufficient quantities to be detected by XRD. The bottom of Fig.2 gives the EDX elemental maps together with the BF STEM image at the same scale. Al and V diffused outwards formed the AlVO$_4$, with TiO$_2$ dispersed between the outer layer and inner layer. STEM/EDX mapping displays the 2-D results for a relative large area, enabling the understanding of complex, multiphase specimen much easier than by using point/line analysis and EFTEM imaging.

Fig. 3a gives a higher magnification image of the interface between the coating and the oxide. The inner oxide layer was porous and nanocrystalline, but the phases present could not be uniquely identified. Occasional TiO$_2$ (rutile) particles and V$_2$O$_5$ needles were positively identified. Although no unique identification could be made because of the fine nature of the crystallites, it was believed to be made up of V$_2$O$_5$, VO$_2$, and Al$_2$TiO$_5$. The observation of V$_2$O$_5$ and VO$_2$ is consistent with Lugscheider et al [5]. Thus, the conclusion is that the inner oxide layer was made up predominantly of intermediate
vanadium oxides (a direct product of oxidation of the VN layer), TiO$_2$ and a phase most likely to be Al$_2$TiO$_5$, although not uniquely identified. The reactions were therefore summarised:

$$4\text{TiAlN} + 7\text{O}_2 \rightarrow 2\text{Al}_2\text{TiO}_5 + 2\text{TiO}_2 + 2\text{N}_2$$

and subsequently:

$$\text{Al}_2\text{TiO}_5 + \text{V}_2\text{O}_5 \rightarrow 2\text{AlVO}_4 + \text{TiO}_2.$$
dominated by V, with very little Al or Ti detected. This suggests that the surface layer was derived from the break-up of one of the large V$_2$O$_5$ crystals observed by SEM.

The observation of V$_2$O$_5$ on the contact surface is in-line with the hypotheses presented in the literature on the low friction properties of these coatings. However, while comparatively low and stable friction is promoted, the wear rates at this temperature are comparatively high, not surprising given that the bearing surface was a porous oxide aggregate.

4. Summary:
Extensive mixing of component atoms between the 3nm TiAlN/VN multilayers has been quantified and agrees well with numerically based models of the deposition process. Oxidation of the multilayer coatings led to a duplex oxide structure, with several phases observed, including V$_2$O$_5$, TiO$_2$, and AlVO$_4$, but other phases were also present. The low friction observed in the dry sliding of these coatings was confirmed to arise from an outer layer almost entirely of V$_2$O$_5$, produced by the attrition of large V$_2$O$_5$ crystals which formed at the outer surface during oxidation of the coating.

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References
[1] Munz, W –D, Lewis, DB, Hovsepian, P Eh, Schonjahn, C, Ehiasarian, A, and Smith, II, (2001). Surf. Eng., 17, 15.
[2] Zhou, Z, Rainforth, WM, Rother, B, Ehiasarian, A, Hovsepian, P. Eh, and Münn W-D, (2004). Surf. Coat. Technol., 183, 275.
[3] Zhou, Z, Rainforth, WM, Falke, U, Falke, M, Hovsepian, P. Eh, (2005) Philos. Mag. (in press)
[4] Zhou, Z, Rainforth, WM, Lewis, DB, Creasey, S, Forsyth, JJ, Clegg, F, Ehiasarian, A, Hovsepian, P.Eh Münnz, W-D, (2004) Surf. Coat. Technol. 177-178, 198.
[5] Lugscheider, E, Knotek, O, Bobzin, K., Barwulf, S, (2000) Surf. Coat. Technol., 133-134, 362.
[6] Zhou, Z, Rainforth, WM, Luo, Q, Chen L, and P Eh Hovsepian, Proc. EMAG 2005, this proceedings.