Investigating worn surfaces of nanoscale TiAlN/VN multilayer coating using FIB and TEM

ZHOU, Z., CALVERT, C.C., RAINFORTH, W.M., LUO, Quanshun <http://orcid.org/0000-0003-4102-2129>, CHENG, Lixin and HOVSEPIAN, Papken <http://orcid.org/0000-0002-1047-0407>

Institute of Physics Publishing
doi:10.1088/1742-6596/26/1/022

Journal of Physics: Conference Series **26** (2006) 95–98
EMAG–NANO 05: Imaging, Analysis and Fabrication on the Nanoscale

Investigating worn surfaces of nanoscale TiAlN/VN multilayer coating using FIB and TEM

Z. Zhou[1], C.C. Calvert[1], W.M. Rainforth[1*], Q.Luo[2], L.Chen[2], P.Eh. Hovsepian[2]

[1]Department of Engineering Materials, University of Sheffield, S1 3JD UK
[2]Materials Engineering Research Institute, Sheffield Hallam University, S1 1WB UK

*m.rainforth@shef.ac.uk

Abstract. TiAlN/VN multilayer coatings exhibit excellent dry sliding wear resistance and low friction coefficient, believed to be associated with the formation of tribo-films comprising Magnéli phases such as V_2O_5. In order to investigate this hypothesis, dry sliding wear of TiAlN/VN coatings was undertaken against Al_2O_3. Focused ion beam was used to generate site-specific TEM specimens. A thin (2-20nm) tribo-film was observed at the worn surface, with occasional 'roll-like' wear debris (ϕ 5-40nm). Both were amorphous and contained the same Ti, Al and V ratio as the coating, but with the nitrogen largely replaced by oxygen. No evidence of Magnéli phases was found.

1. Introduction

A tribological contact is believed to consist of two base materials and the contact region of a 'third body' – called the tribo-film [1]. It is proposed that this tribo-film is a compositional mixture of the two base materials and oxidation products. A thin tribo-film is believed to be associated with low wear rates (so-called mild wear) and is known to strongly affect the friction coefficient. Even though this model of wear has been largely accepted for many years, the structure and role of the tribo-film are not understood and no direct observations have been undertaken.

TiAlN/VN multilayers, with a bilayer period of ~3nm, exhibit a combination of excellent dry sliding wear resistance (1.26×10^{-17} $m^3N^{-1}m^{-1}$) and low friction coefficient (μ = 0.4 pin-on-disc test against Al_2O_3) in comparison to other commonly used wear protective coatings [2], e.g. TiAlN (μ = 0.7-0.9), and are therefore current candidates for coatings for dry high speed cutting applications. The coatings exhibit lower friction than competitor coatings, which has been attributed to the formation of vanadium based Magnéli phases, such as V_2O_5, but direct evidence is only available for very high temperature tests. Other studies on similar coatings, TiAlN/CrN and TiAlCrYN, have found direct evidence of tribo-film, but this resulted from strong interaction with the counterface[3]. This work used focused ion beam (FIB) microscopy to produce site specific TEM cross-sections from the dry sliding wear of TiAlN/VN to directly study the structure of the tribo-film under conditions where wear rate and friction coefficient were low.

2. Experimental

TiAlN/VN multilayer coatings were grown on stainless steel substrates in an industrial scale physical vapour deposition coating machine. Details of the deposition process are given elsewhere [2]. Dry sliding wear tests against an Al_2O_3 ball were undertaken at a 1N load, speed of 0.05m/s and 1,129m distance. A specific wear rate of 2×10^{-16} $m^3N^{-1}m^{-1}$and a friction coefficient of ~0.5 were obtained.

Cross-sections of the worn surfaces were prepared for TEM observation using FIB. Carbon coating was deposited prior to FIB milling to protect the worn surface layer upon exposure to the ion beam. Subsequently, a Pt layer was deposited on top of the area of interest before Ga ion beam milling. TEM (JEOL JEM 2010F) in conjunction with energy dispersive x-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) was employed to analyse the worn surface layer. EDS composition data was obtained in EDS mode with 1 nm probe. EELS measurements were made in conventional TEM diffraction mode (image coupling to spectrometer) on ultra thin (<30nm) areas. Sample areas were chosen that were thin enough to avoid the need for spectral de-convolution. For each area CK, NK, Ti $L_{2,3}$, $VL_{2,3}$ and OK-edges and associated low loss spectra were collected with total integration times of 15 seconds. The 0.6mm EELS entrance aperture was used, giving a collection angle of 2 mrad at the cameral length used. The energy resolution was 1.2eV for all EELS measurements. Elemental maps were also obtained by energy filtered transmission electron microscopy (EFTEM) using a Gatan GIF2000. Jump ratio images were generated using the standard energy slit conditions.

3. Results and discussion

Fig.1a shows a typical scanning electron microscopy (SEM) plan-view of the worn surface. The wear track was smooth, around 100μm wide with wear debris piled up on either side. Within the wear track 'roll'-like debris was present, with the long axis of the roll perpendicular to the sliding direction on top the track. Similar rolls have been widely reported for the mild wear of hard materials, e.g. in the sliding wear of SiC-Al_2O_3 nanocomposites [4], but their structure and origin is still a matter of debate. Longitudinal TEM cross sections were extracted using FIB as indicated by the double arrowed bar, in order to study the worn surface, including these rolls. Fig.1b shows a zero loss filtered image of a cross section of worn surface. It comprises the multilayer coating, surface tribo-film, carbon and Pt deposition. The tribo-film is amorphous and between 2-20nm thick. A few roll-like wear debris particles were preserved at the coating surface in the FIB section. They are also amorphous, with a diameter between 5-40nm, attached to the surface tribo-film with loose amorphous material (Fig.1b). Table 1 gives the composition of the various positions as determined by EDS, which showed a similar ratio of Al, Ti and V for all the debris compared to the bulk. Loose wear debris was also picked up from the wear track for examination in the TEM (Fig. 1c). This included rolls and more irregular shaped particles. The composition of the loose wear debris exhibited a greater scatter than found at the worn surfaces in the FIB prepared TEM specimen. Due to overlapping of OK and VL lines in EDS, EELS was employed to analyse O and N in these areas.

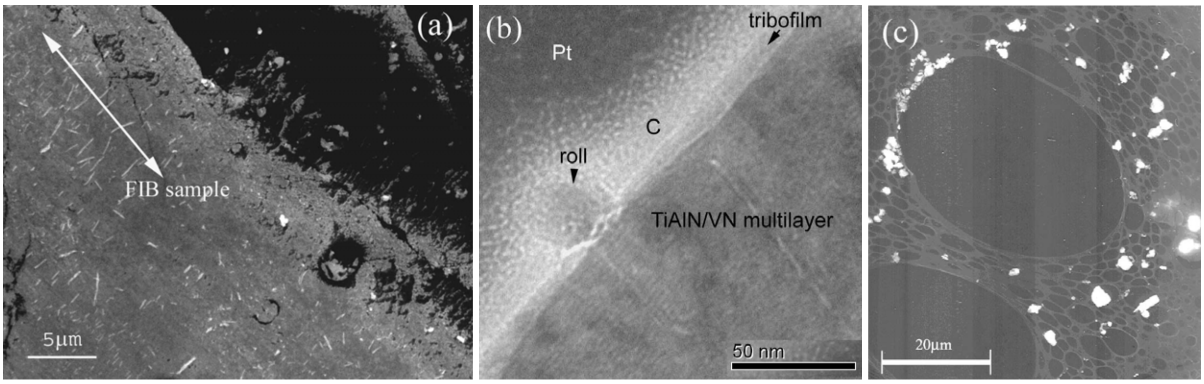

Figure 1. (a) SEM micrograph of the worn surface and roll-like wear debris. (b) Zero loss filtered image of a cross section of worn surfaces. (c) TEM micrograph of loose wear debris supported on a carbon film.

The sample prepared by FIB generally had a thickness t>0.5λ (λ, mean free path). However, the worn surfaces region was slightly thinner and were around t = 0.5λ. Fig.2 compares normalized and background subtracted EEL spectra from coating, worn surface, bond, rolls and loose debris. N K, Ti $L_{2,3}$, V $L_{2,3}$ and O K edges are all evident in these regions suggesting a form of $TiAlVN_xO_y$ (Al is not included in a spectrum here as the Al K is at 1560eV, but was present as determined by EDS). N intensity decreased in loose wear debris compared to the worn surface regions attached to a coating, in conjunction with a significant rise in O, but the Ti was constant. V L_2:L_3 changes ratio from the coating to the worn surface, in association with the appearance of the O K-edge, indicating progressive oxidation of V begins at the worn surface. The changing of $VL_{2,3}$ is also associated with the N K, indicating a variation in the degree of sub-stoichiometry, which is common in VN_x compounds [5]. However, further investigation of the near edge fine structure would require spectroscopy at superior energy resolution.

Table 1 EDS Composition ratio

	Al	Ti	V
loose debris	1.1	1	2.0
rolls	1.2	1	2.4
bond	1.3	1	2.3
tribo-film	1.3	1	2.4
coating	1.3	1	2.4

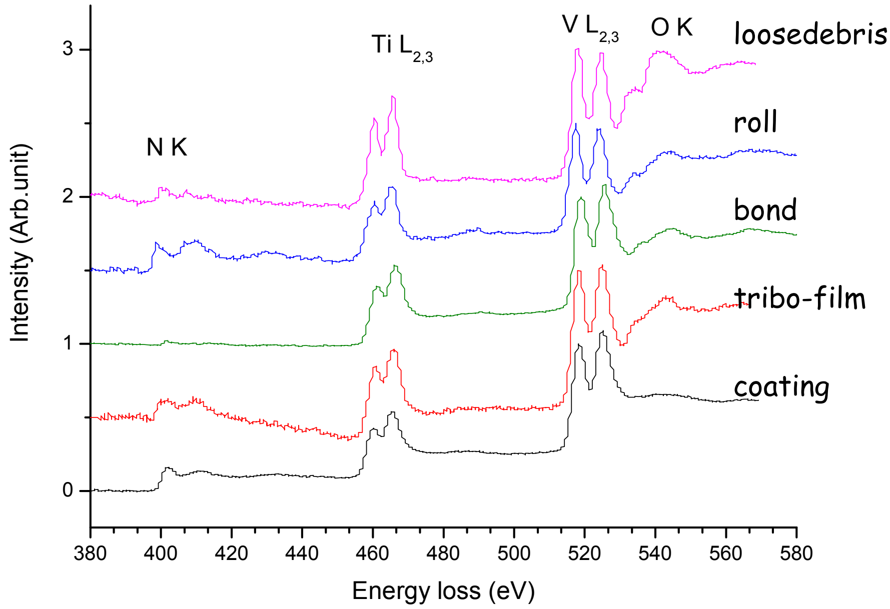

Fig.2 Experimental EEL Spectra from coating, worn surface, bond, roll-like and loose debris.

Fig.3 shows the EFTEM images of the roll-like debris separated from the worn surface by the thin amorphous tribo-film. Table 2 lists the energy windows and slit widths used to form these images. The thickness map in conjunction with the t/λ profile (position is highlighted in the thickness map) indicated that the area is too thick for the 3-window method and therefore jump ratio maps were obtained to minimize the effect of diffraction contrast/plural scattering. N K, O K and C K maps roughly indicated the location of the coating, the tribo-film and roll-like wear debris, the areas that had been oxidized, and the C protecting layer. However, note the O map includes overlapping information from the OK and V $L_{2,3}$, as shown by the apparent presence of O in the coating. In this respect, EEL data from individual point is more useful, Fig.2.

Irrespective of the errors associated with a thick specimen, it is clear that the tribo-film is essentially an amorphous phase comprising approximately the same elements as the coating, but with the nitrogen largely replaced by oxygen. Such tribo-films are known to be associated with low wear rates and friction coefficients, but this work is the first direct view of their structure. The inherent low friction is likely to be associated with the amorphous structure and uniform surface coverage. The rolls are believed to be associated with the periodic detachment of the tribo-film, followed by 'rolling-up' as a result of residual stresses [6]. Again, this work is the first to produce a direct section through the rolls, and we have found no evidence that they form from rolling up of a detached film, rather they have a constant structure throughout their core.

Table 2 Energy windows for EFTEM maps in Fig.3

	C-K (284eV)	N-K (401eV)	Ti-$L_{2,3}$ (456eV)	V-$L_{2,3}$ (513eV)	O-K (532eV)
Range pre-edge	252-282	369-399	426-456	489-509	489-509
Range Post-edge	284-314	402-432	457-487	510-530	535-555
Slit (eV)	30			20	

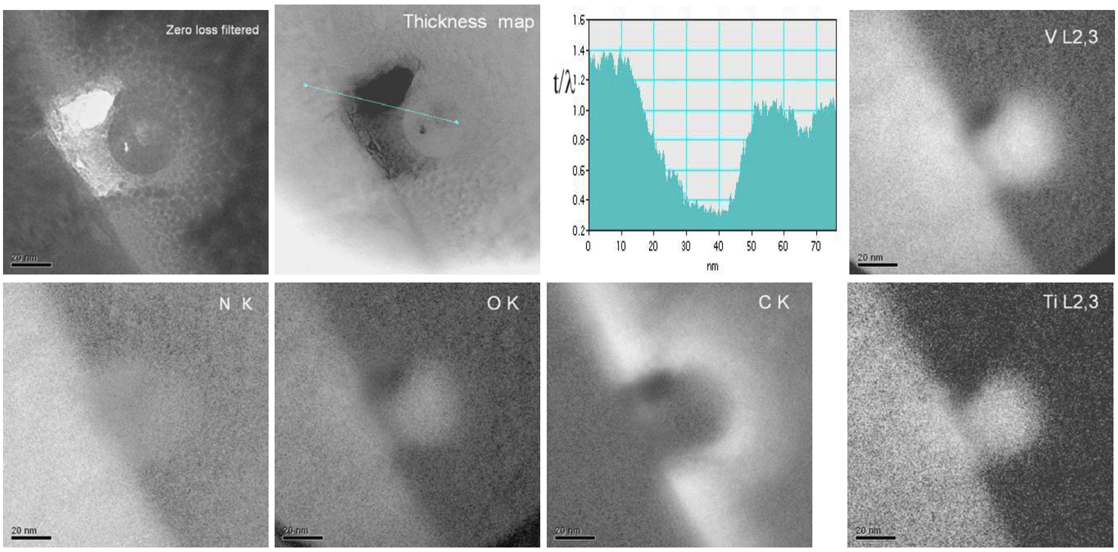

Figure 3. Zero loss energy filtered image of a roll-like particle (cross-section) attached to worn surface with loose amorphous material. Thickness map with t/λ ratio profile from the line highlighted in thickness map. EFTEM jump ratio images suggest that the roll was O-, V- and Ti-rich.

4. Summary

Worn surfaces and wear debris from the dry sliding of TiAlN/VN multilayer coatings against Al_2O_3 were examined. Detailed TEM examination of worn surfaces, in particular roll-like wear debris adhering to worn surfaces has been achieved the first time due to FIB prepared site specific cross section samples. A surface tribo-film of 2-20nm thick was observed, on top of which occasional rolls were found. All debris was amorphous and contained the same Al, Ti and V ratios as in the coating, but with the nitrogen replaced by oxygen. The amorphous phase is important in promoting low friction, but the mechanism of roll formation remains uncertain.

Acknowledgments – Thanks are due to EPSRC for funding.

References

[1] M. Godet, Wear 100 (1984) 437.
[2] P. Eh.Hovsepian, D.B. Lewis, W.D. Munz, Surf.& Coat Technol. 133-134 (2000) 166.
[3] Q. Luo, W.M Rainforth, W.D. Munz, Wear 225-229 (1999) 74.
[4] S. Bajwa, W.M. Rainforth, W.E. Lee, Wear 259(2005) 553.
[5] F. Hofer, P. Warbichler, A.Scott, R. Brydson, I. Galesic, and B. Kolbesen, J. Microscopy 204 (2001) 166.
[6] W. M. Rainforth, J.Mater.Sci. 39(2004) 6705.